Diffusion of small molecules in amorphous SiO$_2$: effects on the properties of the material and on its point defects

Laura Nuccio

S.S.D. FIS/01

Palermo, Febbraio 2009

Supervisore: Prof. Roberto Boscaino
Coordinatore: Prof. Antonio Cupane
Acknowledgements

Three years are a time long enough to go through several different situations and sometimes troubles, and to realize that most of them would have been even more hard to overcome without people around you. For this reason there are many people that deserve my gratitude for their scientific or human contribution to the realization of this thesis.

I would like to thank Prof. R. Boscaino for sharing with me his large scientific experience and knowledge. But even more important, I thank him because he showed me how a true passion for science, an outstanding ability to direct and a constant attention to people around him can exist together. It is also a pleasure for me to express my gratitude to Dr. S. Agnello for all the time he spent with me performing experiments and talking about results. He was always helpful, but at the same time allowed me to develop my autonomy. I am also grateful to him for the great attention and respect he always paid to my work and my ideas. I sincerely acknowledge Prof. M. Cannas, Prof. F. Gelardi and Prof. M. Leone for the many stimulating discussions, that gave an important contribution to my understanding of these scientific problems. All these people had a fundamental role in the development of my idea of what scientific research should be.

Among the people who gave me their advices on scientific questions, a special role was played by my colleagues. The value of their suggestions and comments was in fact equal to the importance of their support. Their friendship allowed me to overcome even the hardest periods and made this PhD an important human experience. In particular I would like to thank Dr. G. Buscarino and Dr. F. Messina for sharing with me their enduring enthusiasm, as well as their deep understanding of Physics, and for all the time they spent discussing with me about my work.

I also want to thank all the scientists I had the pleasure to meet and whose valuable comments improved my understanding of my experimental results, especially Prof. V. A. Radzig, Dr. L. Skuja, Prof. A. N. Trukhin. Among them I wish to express my gratitude in particular to Prof. K. Kajihara, who carefully read my thesis and gave me useful suggestions and comments.

I am grateful to G. Napoli, G. Tricomi and F. Testaino for the technical assis-
tance during my experiments. I also thank E. Calderaro and A. Parlato of the Nuclear Engineering Department of the University of Palermo for taking care of the $\gamma$ irradiation in the IGS-3 irradiator, B. Brichard for the $\gamma$ irradiation at SCK-CEN Belgian Nuclear Research Center and R.M. Montereali and G. Messina for the $\beta$ irradiation at the Frascati Research Centre of the ENEA.
Contents

Preface 1

I Background 3

1 Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments 5
  1.1 Amorphous silicon dioxide: structure and point defects 5
  1.1.1 E'γ centre 7
  1.1.2 ODC(II) and H(I) centres 9
  1.1.3 Non Bridging Oxygen Hole Centre and Peroxy Radical 11
  1.1.4 Silanol group 16
  1.2 Radiation effects in silica 19
    1.2.1 Generation of ODC(II) upon irradiation: preliminary results 20
  1.3 Effects of thermal treatments on point defects in silica 22
    1.3.1 Effects of thermal treatments on the ODC(II): preliminary results 24

2 Diffusion and reaction of molecules in silica 27
  2.1 Diffusion in solids 27
    2.1.1 Diffusion 27
    2.1.2 Diffusion and reaction 31
    2.1.3 Water diffusion in silica 32
    2.1.4 Oxygen diffusion in silica 36
  2.2 Reaction kinetics 37

3 Experimental techniques: theoretical background 41
  3.1 Electron paramagnetic resonance 41
    3.1.1 Spin Hamiltonian 42
    3.1.2 Spin Hamiltonian: the Zeeman term 42
    3.1.3 Spin Hamiltonian: the Hyperfine term 44
6.4 Conclusions ................................................. 100

7 Annealing of point defects ................................... 101
  7.1 Introduction .............................................. 101
  7.2 Annealing processes of radiation induced oxygen deficient point defects 103
     7.2.1 Experiment ........................................... 103
     7.2.2 Results and discussion ............................... 104
  7.3 Annealing processes: evidence for a distribution of the reaction activation energies ........................................ 110
     7.3.1 Experiments and results ............................... 110
     7.3.2 Discussion ............................................ 114
  7.4 Quantitative analysis of the effects of thermal treatments on point defects ............................................... 118
     7.4.1 Experiments ........................................... 118
     7.4.2 Results and Discussion ............................... 119
  7.5 Conclusions .............................................. 130

Conclusions ................................................... 131

List of related papers ....................................... 135

Bibliography .................................................. 137
Preface

Amorphous silicon dioxide, or silica, has been the subject of a great interest and of intensive studies for several decades. One of the reasons for the attention devoted to this material is its widespread use in many fields of modern technologies, ranging from telecommunications to microelectronics. Moreover, due to its simple structure, silica has always been considered a model system for the study of the properties of amorphous materials. Notwithstanding the extensive studies carried out on the properties of silica, several aspects are still barely understood, so that the attention toward it has not faded out yet.

Many studies on silica actually deal with the properties of its point defects, that can be both native and radiation-induced, since they can significantly affect the properties of the material. In fact, point defects can act as charge traps, or change the refractive index, or give rise to Optical Absorption and Photoluminescence activities because of the presence of their energy levels in the band gap. The generation of point defects upon irradiation and their subsequent thermal annealing is influenced by several factors, as the kind and energy of the radiation, the characteristics of the material, and the nature and amount of impurities present in it. This latter point is particularly relevant because small interstitial molecules (as hydrogen, oxygen or water) are present even in so-called extremely pure silica since its production, can be produced during the irradiation, or can be absorbed from the atmosphere during thermal treatments. Moreover, some of these molecules, as for example hydrogen or fluorine, are ad hoc introduced in the material to improve specific features, as its radiation hardness. Finally, thermal treatments in oxygen or water vapour atmospheres have an important role in the thermal oxidation of silicon. A certain attention was paid to the effects of the presence of hydrogen, due to the large use of the hydrogen loading technique to improve the radiation hardness of optical fibres. Nevertheless, many aspects of the interaction of small molecules with silica and its point defects are still poorly understood.

An experimental study on the effects of the presence and diffusion of small molecules on the properties of silica and on its point defects is reported in this thesis. The idea on which this work was funded is that many phenomena and properties of
silica, apparently far from each other as the SiOH content and the annealing properties of point defects, are all strongly influenced by the presence and diffusion of small molecules. Under an experimental point of view, the samples were subjected to different treatments, including $\gamma$ and $\beta$ irradiations and thermal treatments both in normal and controlled atmospheres. The results were then obtained by combining several spectroscopic techniques, aimed at investigating different properties of silica and of its point defects. The interest was focused in particular on the effects of water and oxygen molecules, as they have a technological interest and because they can be produced during the irradiation of silica. Their effects on the radiation hardness and on the annealing properties of radiation induced point defects were studied. Moreover, an important effect of thermal treatments on the original properties of silica, that was hypothesized to be related to hydrogen diffusion, was also found.

The thesis is divided into two parts. In Part I a general overview on the literature about point defects (Chapter 1) and diffusion (Chapter 2) in silica, as well as a theoretical background for the experimental techniques used (Chapter 3) is given. The attention in this first part was focused on the information we considered useful for the understanding of the experimental results, and some preliminary experiment is also presented.

In Part II the experiments performed and the main results are reported. In particular in Chapter 4 the instruments are described, while in Chapters 5, 6 and 7 the experiments and results are discussed. Finally the main conclusions are resumed. Most of the results shown in this thesis, or on closely related topics, have been published as papers on scientific journals. References to these papers are reported in a List of related papers at the end of Part II.
Part I

Background
Chapter 1

Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

In this first Chapter a basic description of the structure of amorphous silicon dioxide and of some of its main point defects will be given. A review of the present knowledge about the effects of irradiation and thermal treatments on this system, that will be further investigated in Part II, will be also proposed.

1.1 Amorphous silicon dioxide: structure and point defects

The structure of the crystalline forms of silicon dioxide, the most common being \( \alpha \)-quartz, was extensively examined by X-ray and neutron diffraction studies. It was concluded that the basic structural unit of these crystalline solids, apart from Stishovite, is a SiO\(_4\) tetrahedron, having at the centre a silicon atom bonded to four oxygen atoms (See Figure 1.1) [1, 2]. In \( \alpha \)-quartz the bond length between silicon and oxygen can be 1.60\( \text{Å} \) or 1.62\( \text{Å} \), each tetrahedron having two short-bonds and two long-bonds, and the \( O - \hat{Si} - O \) bond angle takes the value 109.5\( ^\circ \). Tetrahedra are connected by sharing an oxygen atom, forming an angle \( Si - \hat{O} - Si = 144^\circ \) [1, 2].

Unlike the crystalline structures of silicon dioxide, that of amorphous SiO\(_2\), also called silica, is poorly understood. The most successful model in describing the structure of silica is the Continuous Random Network (CRN), based on X-ray and neutron scattering results [3, 4]. According to this model silica shares with \( \alpha \)-quartz the basic structural unit, and differs from the crystal because of a random orientation of the
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Figure 1.1: Model structure of SiO$_2$. Black and white circles represent silicon and oxygen atoms respectively.

The structure described by this model is amorphous as it lacks translational invariance, and as a consequence long range order. A good agreement between known properties of silica and the results of recent quantum calculations using this kind of model has been shown [6–11].

On the other hand, the fact that amorphous and crystalline forms of SiO$_2$ share the same short range order accounts for the similarities between some of their properties. In fact their covalent bonds guarantee good mechanical resistance, while the wide band gap ($\sim 9$eV) determines a high optical transparency from infrared to ultraviolet and a low electrical conductivity [2, 12]. These characteristics made silica one of the most used materials in many fields of the modern technologies, as optoelectronics and microelectronics, as well as in the production of devices as optical fibers, photonic crystal fibers and nanowires [1, 2, 12]. Moreover, due to its very simple chemical structure, silica is usually considered a model system for the study of the properties of amorphous materials. These facts have been holding the interest in a-SiO$_2$ for many years.

Particular attention has always been devoted to the study of the properties of point defects in silica, due to the fact that their presence, often associated with optical absorption (OA) and photoluminescence (PL) activities, can compromise the characteristic features of the material.

In the framework of an ideal "regular" structure for an amorphous system described
for example by the CRN, a point defect is defined as a deviation from such a structure whose typical dimensions are of the order of the interatomic distance. Point defects can be classified into two different categories: as intrinsic defects if they only include the atoms constituting the material (for example vacancies), or as extrinsic defects if they also involve different atoms (for example substitutional atoms, as germanium instead of silicon in a reticular site). Many point defects are induced in silica during its production, but many studies, and this thesis among them, are focused on radiation induced point defects. In fact many different radiation sources (UV, X, \(\gamma\) and \(\beta\) rays) are known to create point defects in silica, as will be better explained in Section 1.2.

Many different experimental techniques can be used to investigate the properties of point defects, depending on the specific features of each centre. As an example Electron Paramagnetic Resonance (EPR) can be used for the detection of paramagnetic point defects, allowing also to obtain detailed structural information about them, while OA and PL can be used to reveal the presence of diamagnetic optically active centres.

In the following Subsections the main spectral and structural features of the point defects studied in this thesis will be described.

### 1.1.1 E'\(\gamma\) centre

The name E' centres describes a class of radiation induced paramagnetic point defects, always present in irradiated silica \([1, 13, 14]\). These different centres share the fundamental structural property of having an unpaired electron localized in a \(sp^3\) hybrid orbital of a threefold coordinated silicon (See Figure 1.2) \([1, 13–17]\). For this reason the E' centre is also called sometimes silicon dangling bond *. The structures of these distinct defects differ in the surroundings of the \(\equiv Si^*\) moiety, where the symbol \(\equiv\) indicates three bonds with three different oxygen atoms and \(^*\) the unpaired electron. These differences reflect on different EPR signals, making it possible to distinguish them from each other. Their classification is mainly based, on an historical point of view, on these differences in their spectral features, while their structural models have been debated until recent years \([13, 18–23]\).

The generation of these defects was widely studied in literature, and a complex scenario depending on the material and on the irradiation was shown \([1, 18]\).

Among the many different kinds of E' centres in silica, the attention in this thesis will be focused on the most common of them, the E'\(\gamma\) centre \([1, 13–16, 19, 24, 25]\).

*One type of E' centre, the E'\(\delta\), has been recently established to consist in an unpaired electron delocalized over four \(sp^3\) orbitals of nearly equivalent Si atoms. As a consequence its inclusion within the category of the E' centres is funded on a wider interpretation of the above definition of E'.

---

1.1. Amorphous silicon dioxide: structure and point defects

---

7
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Figure 1.2: Model structure of the E' centre. Black and white circles represent silicon and oxygen atoms respectively. The arrow represents the unpaired electron in its orbital, schematically represented as the shadowed region.

Figure 1.3: Typical X-band EPR spectrum of E'$_\gamma$ centre as detected at room temperature in a silica sample $\gamma$-irradiated at 2000kGy.

It shows a characteristic EPR signal with principal g values $g_1=2.0018$, $g_2=2.0006$ and $g_3=2.0003$ (See Figure 1.3) [1]. The E'$_\gamma$ centre is also responsible for an OA band at 5.8 eV with FWHM 0.7eV [1, 18, 26–28]. It has been recently suggested that other kinds of E' centres contribute to this OA band too [29]. Many different models were proposed to describe the microscopic structure of the E'$_\gamma$ centre. The most accepted one describes this defect as an asymmetrically relaxed
1.1. Amorphous silicon dioxide: structure and point defects

positively charged oxygen vacancy (≡Si⁺ +Si≡), in which the silicon atom not owning the unpaired electron (Si⁺) relaxes backwards with respect to its basal oxygen atoms, forming a further bond with a rear oxygen atom [15]. This model was first determined for the E′₁ centre in α-quartz, and it was concluded that the E′γ centre in silica has an analogous structure basing on the similarities between their principal g values and hyperfine structures [1, 15]. Further studies, both experimental and theoretical, showed that in the E′γ centres in silica the Si atom owning the unpaired electron could relax through the plan of its basal oxygen atoms in a back projected configuration, giving rise to differences in the spectral properties [1, 24, 30, 31].

1.1.2 ODC(II) and H(I) centres

The ODC(II) belongs to the important class of the oxygen deficient centers (ODC) in silica. The relevance of these point defects is due to their OA bands in the UV and vacuum-UV spectral ranges and to their PL activities [1, 18]. They can also be precursors for other point defects, and play an important role in connection to the photosensitivity of silica [13, 18, 32]. For all these reasons they have aroused great interest since the mid-fifties and have been widely studied in recent years both experimentally and by simulation [30, 32–40].

The ODC(II) is one of the most debated among ODCs. It is diamagnetic and it is responsible for an OA band peaked at 5.02 eV (B₂α band), inside which two PL bands, peaked at 4.4 eV (α_I band) and at 2.7 eV (γ band), can be excited (See figure 1.4) [18, 37, 38].

The ODC(II) can be observed in oxygen deficient as-grown materials, and its concentration depends on the oxygen deficiency conditions during the growth process [36, 38, 41–43]. It is also known that γ irradiation gives rise to the growth of a PL band at 4.4 eV (α_R band), excited at 5.02 eV, showing small differences from the native α_I band [35]. These differences were related to slightly different environments surrounding the center, and the defect responsible for the PL band α_R was associated to a radiation induced ODC(II) [35].

Even if the optical features of the ODC(II) are well known, several aspects concerning this defect, as its structure and its generation and annealing mechanisms, are barely understood and are still subject of study [18, 34, 44]. Two different structural models were put forward for the point defect responsible for these spectral features, a neutral oxygen vacancy [34, 45, 46] and a two-fold coordinated silicon atom [38, 44, 47, 48]. The vacancy model for the ODC(II) is supported by the evidence of a correlation between the α_I intensity and the E′γ centres, of which the oxygen vacancy is believed to be a precursor [49, 50]. It was also observed a growth of the EPR signal of the E′γ centres simultaneously to the decay of the B₂α band upon UV irradiation.
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Figure 1.4: Typical PL spectrum at room temperature excited at 5eV of ODC(II) centre. The band at 5eV is the PLE band. Adapted from Reference [38].

This result was attributed either to the photoionization or to the trapping of a hole in an oxygen vacancy [45, 46]. However these correlations are still debated [42, 51–54], because of the existence of many other precursor sites for the E'\(\gamma\) centre that can cause deviation from the expected correlations, suggesting also that those observed were not significant [37].

The twofold coordinated silicon model for the ODC(II) was proposed on the basis of luminescence polarization data [38]. They are in fact in agreement with a C\(2_v\) symmetry, and as a consequence they do not support the vacancy model. Theoretical studies determined that the twofold coordinated silicon should have a singlet-singlet absorption transition at 5.1eV, and the triplet-singlet and singlet-singlet emission transitions at 2.6eV and 4.6eV respectively [47, 55, 56]. This optical transitions scheme is in good agreement with the experimental evidences for the ODC(II). For all these reasons the twofold coordinated silicon (See Figure 1.5(a)) is nowadays rather widely believed to be the correct model for the ODC(II).

The ODC(II) is believed to be the precursor site for another point defect, the H(I) centre [37, 39, 57]. The spectral fingerprint of the H(I) centre, that is a paramagnetic point defect, is a hyperfine EPR doublet split by \(\sim 7.4\)mT [15, 58, 59]. A typical EPR signal of the H(I) centre is shown in Figure 1.6. Isotope exchange experiments proved that this defect is hydrogen related [59, 60]. Nowadays it is commonly believed that
1.1. Amorphous silicon dioxide: structure and point defects

The microscopic structure of the H(I) centre is a silicon atom bonded to two oxygen atoms and one hydrogen atom, and with an unpaired electron in the sp³ hybrid orbital left. A schematic representation of the structure of the H(I) centre is shown in Figure 1.5(b) [18, 39, 60]. As anticipated the H(I) is believed to originate from the reaction of a twofold coordinated silicon with a hydrogen atom, according to the reaction

\[
\text{Si}^{\bullet} + H \rightarrow \text{Si}^{\bullet} - H
\]  

(1.1)

This latter hydrogen atom can be generated through several processes, as radiolysis or photolysis, from hydrogen containing groups in silica (as OH groups) [61], or through the breakage of a hydrogen molecule on another paramagnetic point defect as the Non Bridging Oxygen Hole Centre (See Subsection 1.1.3) [37].

1.1.3 Non Bridging Oxygen Hole Centre and Peroxy Radical

Non Bridging Oxygen Hole Centres (NBOHC) and Peroxy Radicals (POR) are, together with the E’ centres, among the main radiation induced paramagnetic point defects in silica. As well as the E’ centre, they belong to the class of the dangling bonds defects [44].

The NBOHC give important contributions to the OA of irradiated silica in the visible and ultraviolet spectral ranges. In fact they are responsible for OA bands at 2.0 eV, 4.8 eV and 6.8eV [18, 62, 63]. The assignment of the strong (oscillator strength \( f = 0.2 \)) absorption band at 4.8eV to NBOHC was controversial for a long time, due
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

![Typical X-band EPR spectrum of the H(I) centres as detected in a silica sample γ-irradiated at a dose of 5000kGy. The central part of the spectrum is not shown, as it shows the distorted resonance signal of the E'γ centres. In the inset the EPR resonance line of the E'γ centres, detected in not distorting conditions, is shown. Adapted from Ref. [57]

**Figure 1.6:** Typical X-band EPR spectrum of the H(I) centres as detected in a silica sample γ-irradiated at a dose of 5000kGy. The central part of the spectrum is not shown, as it shows the distorted resonance signal of the E’γ centres. In the inset the EPR resonance line of the E’γ centres, detected in not distorting conditions, is shown. Adapted from Ref. [57]

to its overlap with a nearly identical 4.8 eV OA of interstitial ozone molecule [64], and also because a part of NBOHC is *EPR silent* [65, 66]. A PL band at 1.9eV can be excited inside these absorption bands [18, 67, 68].

The spectral characterization of POR in bulk silica is instead more controversial. Their OA band on silica surfaces is found at ~5.4eV, with FWHM≈1.2eV and oscillator strength $f \approx 0.06$ [69]. The spectral parameters of this band are very close to those of surface NBOHC (peak position≈4.9eV, FWHM≈1.2eV and $f \approx 0.05$). This fact, together with the existence of interconversion processes between these two defects, made the identification of the spectral features of POR difficult. An OA band at 5.3eV with FWHM≈1.3eV and $f \approx 0.05$ is nowadays attributed to POR [44].

Both these centres were first identified by their EPR signals [13, 70, 71]. EPR studies also allowed to determine their microscopic structures, by analyzing their $^{29}$Si and $^{17}$O hyperfine structures in isotopically enriched materials and comparing their
1.1. Amorphous silicon dioxide: structure and point defects

Figure 1.7: Model structures of (a) Non-Bridging Oxygen Hole Centre (NBOHC) and (b) Peroxy Radical (POR). Black and white circles represent silicon and oxygen atoms respectively.

Table 1.1: EPR parameters for NBOHC and POR in silica, as obtained in Ref. [70].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NBOHC</th>
<th>POR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1$</td>
<td>2.0010</td>
<td>2.0014</td>
</tr>
<tr>
<td>$g_2$</td>
<td>2.0095</td>
<td>2.0074</td>
</tr>
<tr>
<td>$g_3$</td>
<td>2.078</td>
<td>2.067</td>
</tr>
</tbody>
</table>

principal $g$ values with the calculated ones [70, 72]. NBOHC was established to be an oxygen dangling bond, and the peroxy radical a dangling bond on a peroxy group (See Figure 1.7).

A typical EPR spectrum showing a mixture of the signals of the two centres is shown in Figure 1.8. The $g$ scale in Figure 1.8 was obtained by using the resonance line of $E'_\gamma$ centres as reference. The value $g = 2.0006$ was set in correspondence to the zero crossing point of the $E'_\gamma$ resonance line. The principal $g$ values attributed to NBOHC and POR from literature data, reported in Table 1.1, are indicated by lines in Figure 1.8 [70]. Although the signals of the two point defects overlap in the spectrum, it is possible to identify some spectral feature typical of each of them, thanks for example to the known principal $g$ values (See Table 1.1) and to computer simulations of their lineshapes. A computer simulation of the EPR spectra was in fact previously reported in literature and it is shown in Figure 1.9 [70]. Experimental evidences deriving from annealing experiments can also be taken into account in the attempt to identify specific spectral features of the two defects. In fact it is known that the
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Figure 1.8: Typical X-band EPR spectrum of NBOHC and POR at room temperature. Dash-dotted and dashed lines indicate the principal g values attributed to NBOHC and POR respectively.

typical annealing temperature of POR is much higher than that of NBOHC [72]. As a consequence by performing annealing experiments it is possible to destroy all the NBOHC and isolate some specific features of the spectrum of POR. The disappearance of the NBOHC can be univocally detected by their PL band at 1.9eV. These evidences together allow to conclude that POR are responsible for the positive peak at g=2.067 in Figure 1.8, while the one at g=2.0095 is mainly due to the NBOHC. The deep negative peak observable in the spectrum includes contributions from both of them.

Differently from other ordinary defects in silica, as the E’ centre, NBOHC and POR have not analogous in α-quartz. This is probably due to the lack of appropriate sites for these defects in the ordered structure of α-quartz. Several generation mechanisms have been proposed for both these defects, involving different precursors. NBOHC can be created by breaking strained Si-O bonds [73, 74]

\[
\equiv Si - O - Si \equiv \rightarrow \equiv Si - O^\bullet + \bullet Si \equiv
\]  

(1.2)
or an O-H bond in a silanol group

\[ \equiv Si - O - H \rightarrow \equiv Si - O^* + H \] (1.3)

This latter process is sometimes more efficient, for example under F\textsubscript{2} laser irradiation (7.9eV) \cite{44}. The peroxy linkage \( \equiv Si - O - O - Si \equiv (POL) \) can be a precursor for NBOHC too.

\[ \equiv Si - O - O - Si \equiv \rightarrow \equiv Si - O^* + \cdot O - Si \equiv \] (1.4)

POR can be created by reaction of interstitial oxygen molecules with an E’ centre \cite{13, 61}

\[ \equiv Si^* + O_2 \rightarrow \equiv Si - O - O^* \] (1.5)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{Typical EPR spectra at 100K and computer simulations (dots) of the (a) “dry” and (b) “wet” OHC (old names for POR and NBOHC respectively). Adapted from Reference [70].}
\end{figure}
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

or through the reaction of atomic oxygen with a NBOHC [75]

\[ \equiv Si - O^* + O \rightarrow \equiv Si - O - O^* \]  
(1.6)

They can also be generated through the breakage of a Si-O bond in a POL, with the simultaneous formation of an E' centre [12]

\[ \equiv Si - O - O - Si \equiv \rightarrow \equiv Si - O - O^* + ^*Si \equiv \]  
(1.7)

1.1.4 Silanol group

A silanol group is a hydroxyl (OH) group bonded to a Si atom of the silica network. They will be sometimes called simply OH groups hereafter. OH groups are one of the main impurities in silica glass, and their concentration has always been one of the main parameters, together with the manufacturing procedure (See Section 4.1), used in the characterization of amorphous silicon dioxide for many different reasons. Due to the great relevance of the effects of the presence of OH groups in many technological application of silica, great efforts were made to improve the production techniques, aiming to obtain OH-free materials. For this reason many works were published both about the spectral features of OH groups and their generation processes [76–86].

The presence of their optical absorption bands at 2.72 µm, 1.39 µm and 0.9 µm affects the optical transparency of the material in the middle and near infrared (IR), reducing the regions of possible application of silica in many fields of technological interest, as optical fibers and laser physics [12, 80, 87]. They also reduce the transmittance of silica in the vacuum-ultraviolet (v-UV) spectral range, as they absorb at energies higher than 7.3eV [76–79, 88]. OH groups are also important for what concerns the radiation resistance of silica, as they are known to be precursors for many important radiation induced point defects, as the E' centre and the NBOHC [44]. On the other hand they are known to relax the glass structure improving the radiation hardness of silica irradiated by light sources of energies lower than 7eV [89].

In this thesis silanol groups will be detected through their IR absorption band at \(~ 3670 cm\(^{-1}\)\), corresponding to a stretching vibration [90]. A typical absorption spectrum is shown in Figure 1.10. It is known that the shape of this band depends neither on the manufacturing procedure nor on the OH concentration, in a range from \(10^{-1}\) to \(10^3\) ppm \(^\dagger\) [80].

\(^\dagger\)The acronym ppm means parts per million by weight. For the OH groups in silica 1ppm \(~ 7.7 \cdot 10^{16} cm^{-3}\).
1.1. Amorphous silicon dioxide: structure and point defects

Figure 1.10: Typical Infrared Absorption spectrum of silanol groups as detected at room temperature in a silica sample containing ~800 ppm of OH groups.

- 3690±2 cm\(^{-1}\) free single OH groups, interacting neither with each other nor with regular network bonds (See Figure 1.11(a));
- 3660±4 cm\(^{-1}\) single OH groups slightly H-bound to bridging oxygen atoms (See Figure 1.11(b)) and couples of OH groups hydrogen bonded to each other in linear configuration (vibration of one of the OH groups, not participating in the hydrogen bond) (See Figure 1.11(c));
- 3630±6 cm\(^{-1}\) single OH groups bonded with regular network linkages and couples of OH groups hydrogen bonded to each other in linear configuration (vibration of one of the OH group, participating in the hydrogen bond)(See Figure 1.11(b) and (c));
- 3565±14 cm\(^{-1}\) couples of OH groups hydrogen bonded to each other in cyclic configuration (See Figure 1.11(d)).

OH groups can be generated during the synthesis procedure, and as a consequence be present in as-grown materials (See also Section 4.1). They can also be generated by subsequent treatments. We will focus now on these latter generation processes,
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Figure 1.11: Schematic representation of possible configurations of silanol groups according to Ref. [80].

as they will be relevant in the continuation of this thesis.

In many previous studies OH groups are generated as a consequence of reactions of silica with thermally loaded molecules that diffuse through the glass matrix.

In particular, the generation of OH groups was often observed as a consequence of several reactions between diffusing water molecules and the glass network or network-bound groups upon thermal treatment [81–83, 92, 93]. The Reaction

\[
\equiv Si - O - Si \equiv + H_2O \rightleftharpoons 2 \equiv SiOH
\]  

was proposed to generate OH groups in silica samples treated in water vapour atmosphere at temperatures ranging from about 200\(^\circ\)C to 1200\(^\circ\)C (See also next Chapter) [92]. A water molecule can also react, besides regular lattice sites, with an oxygen vacancy through the Reaction [93]

\[
\equiv Si - Si \equiv + H_2O \rightarrow \equiv SiOH + \equiv SiH
\]  

A reaction between network-bound chloride (SiCl groups) and water was also recently proposed to account for the generation of OH groups in Cl containing materials [81].

\[
\equiv SiCl + H_2O \rightarrow \equiv SiOH + HCl
\]  

This process was observed by treating samples in \(H_2O\) (partial pressure ~ 7bar) at 400\(^\circ\)C for 480h or at 800\(^\circ\)C for 24h [81].
1.2. Radiation effects in silica

The generation of OH groups was also observed after thermal treatments in hydrogen, instead than water, atmosphere at temperatures higher than 400°C [81, 84]. Direct reaction of hydrogen molecules with the silica network was put forward as generation mechanism for OH groups in hydrogen excess conditions [93]

\[
\equiv Si - O - Si \equiv +H_2 \rightarrow \equiv SiOH + \equiv SiH
\]  \hspace{1cm} (1.11)

Evidence for OH generation in low OH synthetic silica after exposure to an hydrogen atmosphere was given by Shelby in 1980 [81, 84]. In a first time this effect was attributed to the reaction of peroxy linkages (\(\equiv Si - O - O - Si \equiv\)) with hydrogen molecules [84, 85]

\[
\equiv Si - O - O - Si \equiv +H_2 \rightarrow 2 \equiv SiOH
\]  \hspace{1cm} (1.12)

This OH generation was also explained later as due to Reaction 1.8, in which water was previously formed through the reaction between the diffusing hydrogen and oxygen molecules loaded in the sample by previous thermal treatments or already present in materials produced in oxygen rich environments, according to the Reaction [81, 86]

\[
2H_2 + O_2 \rightarrow 2H_2O
\]  \hspace{1cm} (1.13)

1.2 Radiation effects in silica

The generation of point defects due to irradiation is an important subject of study, as radiation induced point defects can modify the macroscopic properties of the material, affecting the performances of silica based devices in high radiation environments. The seriousness of damage and the kind of processes determining it depend on several parameters, as the kind of irradiation, its energy, and the characteristics of the irradiated material [2].

The processes giving rise to radiation damage can be classified in two categories: knock-on and radiolysis processes [94]. During knock-on processes an impact makes an atom of the lattice move from its site to an interstitial position leaving a vacancy [94]. All the chemical bonds have to be broken and the atom has not to be recaptured by its vacancy for this process to be effective. The threshold energy for these processes in silica is \(\sim 10eV\) for an oxygen atom and \(\sim 20eV\) for a silicon atom [94]. In some cases, as neutron or ions irradiations, the displaced atoms can give rise to knock-on processes themselves, significantly enhancing the damage. In radiolysis processes electronic excitation or ionization are caused by radiation [94]. These
effects can later cause the generation of a point defect. The most of the generated electron-hole pairs gives rise to luminescence, due to their recombination, while others interact with the lattice and can also cause the breakage of chemical bonds or the displacement of an atom. Finally they can also be trapped in an impurity site or on a preexisting point defect.

As anticipated, a parameter that can influence the effectiveness of the generation of point defects upon irradiation is the presence of impurities or doping elements. In fact they can either act as precursors, or can play a protective role. As an example it is known that adding interstitial hydrogen molecules (hydrogen loading) enhances the radiation hardness of silica, as hydrogen reduces the generation of stable defects by saturating dangling Si or O bonds [95–98]. On the other hand OH groups are generated in these processes, leading to the previously mentioned loss of transparency in the IR and v-UV spectral ranges, and to the generation of transient NBOHC of which OH groups are precursors [95]. Furthermore, it was observed that the hydrogen loading enhances the generation of oxygen vacancies upon laser irradiation [44, 99].

1.2.1 Generation of ODC(II) upon irradiation: preliminary results

As anticipated, the kind and energy of radiation used can in general make great differences for what concerns the kind and concentration of generated defects. However for the kind of radiation used in this thesis (\( \gamma \) and \( \beta \) rays) and for the defects mainly treated (E'\( \gamma \) and ODC(II)) it was shown that the differences are negligible. In fact the effects of \( \gamma \) and \( \beta \) radiation on the generation of ODC(II) in a very wide range of doses were compared, and no significant changes in its spectral features, by changing both the nature of radiation and the dose, nor in the concentration at a given dose were observed (See Figure 1.12) [48]. As a consequence it was hypothesized that the structure of the point defect depends neither on the kind of radiation nor on the dose [48]. The same result had been previously obtained for the E'\( \gamma \) centre [73, 100].

The characteristics of the material can have a strong influence too, as the defects generation often occurs by modifying preexisting defects, usually called precursors. These precursor sites can be defects preexisting in the as-grown materials, or can be induced by irradiation. But it is important to note that they can also simply be strained Si-O bonds, that can exist in some reticular site due to the amorphous structure of silica. These strained bonds, even if they can not be considered point defects, would be weaker than regular ones and could be more easily damaged by irradiation. As an example the ODC(II) was suggested to be generated through the breakage of normal or strained Si-O bonds [35, 42, 50], based on the evidence of the
1.2. Radiation effects in silica

Figure 1.12: Amplitude of the PL band centred at 4.4 eV excited at 5.0 eV, associated to the ODC(II) centres, as a function of the irradiation dose, detected in natural dry silica samples. Filled symbols represent the $\gamma$ irradiated samples, and open symbols the $\beta$ irradiated ones. Adapted from reference [48].

growth of the $\alpha_R$ band (See Subsection 1.1.2) also in synthetic silica samples originally free of optically active defects. This defect is then an excellent sample system for the study of these generation processes in general. For this reason its dependence on dose was investigated in many different materials [48]. It was observed that two ranges of doses can be clearly distinguished, characterized by two different defect concentration growth rates for the ODC(II), the one observed at doses higher than $\sim 10^4$ kGy being less efficient than the one observed at doses below this value. An example of this behaviour is shown in Figure 1.12 [48]. In the low dose range the PL amplitude was observed to depend nonlinearly on the dose $D$, through power laws of the kind $D^\alpha$ with $\alpha < 1$, in many silica materials for more than two decades of dose [48].

This kind of dependence on the dose was often observed for the concentrations of radiation induced point defects in glasses, and various models have been put forward [73, 101, 102]. Galeener et al. proposed a phenomenological model describing the generation of point defects under irradiation as the superposition of a process
of formation from the matrix and one of activation of preexisting precursors [103].

According to Mashkov et al. [104] the radiation would create irreversibly defects from

the network, and reversibly from a set of precursor sites, the two processes following

respectively power law kinetics and Kohlrausch kinetics. A further model proposed
to explain the origin of the observed power law dependence considers the observed
curves to be composed by the contributions of a distribution of independent defect
subpopulations, each characterized by a different production rate constant [101].

Unfortunately, many of these different models lead to power law behaviours as those
actually observed, and are then successful in fitting the experimental results. As a
consequence a conclusive interpretation of these processes has not been achieved yet.

However it is important to note that in the high dose range the generation efficiency
becomes lower than in the previous one, but no saturation of the concentration of
ODC(II) is observed. As a consequence it can be hypothesized that different processes
take place in the two dose ranges. Moreover these findings suggest that ODCs(II)
can also be originated from Si-O bonds in the amorphous network, in agreement with
some features of the above cited models.

Notwithstanding the interest in radiation effects, also due to their technological
relevance, the exact generation mechanisms and the role eventually played by im-
purities in these processes for many point defects are still not clear. For this reason
they will be further investigated and discussed in Chapter 6.

1.3 Effects of thermal treatments on point defects

in silica

The interest toward thermal treatments is connected to both technological and
basic reasons. In fact, thermal treatments are often part of industrial manufacturing
procedures of many devices, as they can help to relax mechanical stresses. Moreover
they can be used to delete radiation effects. On the other hand, thermal treatments
can be a useful tool for the study of the properties of point defects. In fact, heating
an irradiated sample above specific threshold temperatures determines a change in
the concentrations of point defects. These threshold temperatures strongly depend
on the defect itself, the specific material and the treatment conditions.

An example of this behaviour is the E'\(_\gamma\) centre, whose thermal annealing was stud-
ied due to the importance of this defect and its ubiquitous presence in irradiated sil-
ica. However a complex scenario results from these previous studies [19, 70, 105, 106].

Isochronal annealing of E'\(_\gamma\), POR and NBOHC centres in dry silica were studied by
Stapelbroek and coworkers [70]. A decay of E'\(_\gamma\) and NBOHC was observed, together
1.3. Effects of thermal treatments on point defects in silica

Figure 1.13: Optical density and EPR intensity as a function of the treatment temperature in a synthetic dry, oxygen excess material. The samples were annealed 10 minutes at each temperature. "Wet OHC" and "dry OHC" are old nomenclatures for NBOHC and POR, respectively. Adapted from reference [70].

with a growth of POR (See Figure 1.13). They hypothesized that the precursor site of POR releases a free electron, and that the E'\(\gamma\) centre, that is thought to be a hole trapped in an oxygen vacancy, is annealed as a consequence.

The same result, basing on the simultaneous one-for-one growth of the peroxo radicals, was later reinterpreted in terms of the reaction of the E'\(\gamma\) centre with molecular oxygen diffusing in the SiO\(_2\) matrix, through the reaction [107]

\[
\equiv Si^* + O_2 \rightarrow \equiv Si - O - O^* \tag{1.14}
\]

The oxygen involved in this reaction can in fact be available due to radiolytic processes, as the energy of \(\gamma\) rays allows the displacement of bounded oxygen atoms, that can then dimerize to form O\(_2\) [107]. The annealing of the E'\(\gamma\) centre observed in high OH silica was instead attributed to the reaction with diffusing water, according to the reaction [19, 106]

\[
\equiv Si^* + H_2O \rightarrow \equiv SiOH + H \tag{1.15}
\]
1. Amorphous silicon dioxide: structure, effects of irradiation and thermal treatments

Water molecules were hypothesized to have a radiolytic origin too, created by the reaction between displaced oxygen atoms and radiolytic hydrogen [19, 106]. Finally, $E'_{\gamma}$ annealing was observed in oxygen-deficient low-OH samples too [19]. Due to the fact that the concentration of molecular species that can diffuse was very low, and that the annealing of the $E'_{\gamma}$ centre took place at temperatures higher than in other materials, the authors proposed that the $E'_{\gamma}$ annealing in these samples is due to thermal excitation of holes to the valence band or electrons to the conduction band [19].

1.3.1 Effects of thermal treatments on the ODC(II): preliminary results

For what concerns the annealing process of the ODC(II), a strong similarity was observed between its isochronal annealing curves and those of $E'_{\gamma}$ centre in many different materials, as can be observed in Figure 1.14 [108]. This result shows that even if the annealing kinetics is peculiar to a given material, ODC(II) and $E'_{\gamma}$ centres are affected in a similar way by thermal treatments. The experimental evidence of the close similarity between the behavior of the annealing curves of the ODC(II) and $E'_{\gamma}$ centres suggests that the microscopic process causing the annealing could be the same for both the defects. As stated above, diffusion-reaction processes involving molecular oxygen or water had already been established to be responsible for the
1.3. Effects of thermal treatments on point defects in silica

Annealing of the $E'_{\gamma}$ centre in the temperature range in which the ODC(II) annealing is also observed. As a consequence the annealing of the ODC(II) could be proposed to be due to its reactions with the same species responsible for the annealing of the $E'_{\gamma}$ centre. This suggestion is also supported by previous experimental evidences of reactions of the ODC(II) with molecular oxygen or water on activated silica surfaces, according to [109–111]:

$$= Si^{\bullet} + O_2 \rightarrow = Si\underset{O}{\overset{O}{\bigtriangleup}}$$

(1.16)

$$= Si^{\bullet} + H_2O \rightarrow = Si\underset{H}{\overset{OH}{\bigtriangleup}}$$

(1.17)

suggesting that similar centers could arise in bulk silica during the annealing.

Notwithstanding the great number of experimental observations of these annealing processes, at least for what concerns the $E'_{\gamma}$ centre, the general scheme for this annealing processes has not been clarified yet. Moreover some important aspects of these processes, as their being diffusion or reaction limited (See Section 2.2), and quantitative information on the processes and the effects of the disorder of the glass matrix on these diffusion-reaction processes, were not studied. They will be further investigated in Chapter 7.
Chapter 2

Diffusion and reaction of molecules in silica

As the leitmotif of this thesis is the presence and diffusion of small molecules inside silica, an introduction to the subject of diffusion in solids is due. In this Chapter a basic description of the general phenomenology of diffusion in solids, and of the reaction kinetics will be given. The Chapter will start with an overview on the ideal case of diffusion without reactions with the solid matrix, and then the issue of diffusion with simultaneous reaction will be discussed. A specific in-depth examination of the complex problem of the diffusion of water and oxygen in amorphous silicon dioxide will be also proposed by reviewing the present knowledge about these phenomena. In the second part of the Chapter bimolecular reactions, that will be used to model the annealing processes of point defects, and their reaction kinetics will be discussed.

2.1 Diffusion in solids

2.1.1 Diffusion

Diffusion is a transport phenomenon, consisting in the movement of molecules from a region to another one due to a gradient of chemical potential. In many cases of interest, as those treated in this thesis, this condition is equivalent to a gradient of concentration. In describing diffusion phenomena, a measure of the rate of flow is usually given by the quantity called flux, usually denoted by $J$, that is the amount of material flow through a unit area per unit time. A phenomenological relation between the flux and the gradient of concentration is
2. Diffusion and reaction of molecules in silica

![Figure 2.1: Diffusion of matter into a region.](image)

given by the Fick’s first law of diffusion [112–114]. If the change in concentration, and as a consequence diffusion, are in the x direction, Fick’s first law can be written

\[ J = -D \frac{\partial c}{\partial x} \quad (2.1) \]

where \( c \) is the concentration of diffusing particles. Equation 2.1 can be considered a definition of the quantity \( D \), called diffusion coefficient.

In order to describe the time dependence of a diffusion process, we refer to Figure 2.1. The rate of change in concentration inside the slab of volume \( A\Delta x \) between \( x \) and \( x + \Delta x \), can be written as

\[ \frac{\partial c(x,t)}{\partial t} = J(x,t)/\Delta x - J(x+\Delta x,t)/\Delta x \quad (2.2) \]

where the first term in the right side accounts for the increase in concentration in the slab due to the flux from the left, while the second term accounts for the decrease due to the efflux on the right. Using Fick’s first law (Equation 2.1) it is possible to write

\[ J(x,t) - J(x + \Delta x,t) = -D \frac{\partial c(x,t)}{\partial x} + D \frac{\partial c(x + \Delta x,t)}{\partial x} = \]

\[ = -D \frac{\partial c(x,t)}{\partial x} + D \frac{\partial}{\partial x} [c(x,t) + (\frac{\partial c(x,t)}{\partial x})\Delta x] = \]

\[ = D(\frac{\partial^2 c(x,t)}{\partial x^2})\Delta x \quad (2.3) \]
2.1. Diffusion in solids

and substituting back into Equation 2.2

$$\frac{\partial c(x, t)}{\partial t} = D \left( \frac{\partial^2 c(x, t)}{\partial x^2} \right)$$ (2.4)

The latter equation is also called Fick’s second law [112, 113].

It is empirically found that the temperature dependence of the diffusion coefficient $D$ can be expressed through an Arrhenius’ relation

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right)$$ (2.5)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and the pre-exponential factor $D_0$ and activation energy $E_a$ are parameters that depend on the diffusing molecule and on the composition of the solid, but are temperature-independent [92, 113, 114].

To explain the evidence that diffusion in solids is an activated process it is worth considering the diffusion process into the microscopic perspective. Atoms or molecules in a solid can jump from one site to another one thanks to the thermal vibrations of the atoms in the lattice, giving rise to diffusion. There are several possible diffusion mechanism. If the diffusing species jumps into a vacancy the species is said to diffuse by a vacancy mechanism. If instead it passes from an interstitial site to a neighbouring one without permanently displacing any of the matrix atom, it is said to diffuse by an interstitial mechanism [113]. The vacancy mechanism is mainly effective in metals and alloys, and in many ionic compounds, whereas the interstitial mechanism dominates in nonmetallic solids, as silica.

Going back to the physical meaning of the existence of an activation energy for diffusion, and referring to the interstitial mechanism for diffusion that is relevant in this thesis, the activation energy can be interpreted as the energy needed to jump from an interstitial site to another one [92, 113]. To do this, in fact, the diffusing molecule needs to overcome a potential barrier, corresponding to the necessary geometric re-arrangement of the surrounding lattice atoms.

In accordance to this model the activation energy can be considered equal to the energy needed to enlarge a spherical cavity from a radius $r_D$ to $r$ [92, 115, 116]. This activation energy can be written as [116]

$$Q = E_a = 8\pi G r_D (r - r_D)^2$$ (2.6)

where $G$ is the elastic shear modulus for the glass, $r_D$ represents the original radius of the interstitial cavity and $r$ the radius of the diffusing molecule. In silica a better
agreement with experimental data is obtained by changing the factor 8 to 4, probably because in an open structure as silica the strain energy for dilation is lower than in a liquid for which Equation 2.6 was derived [92, 115, 116]. The openness of silica matrix also accounts for the experimental evidence of the usually lower activation energy values observed for the diffusion of a given molecule in silica with respect to other solids. Equation 2.6 also indicates that the smaller the diffusing species, the lower the activation energy.

In the framework of this microscopic description of diffusion processes, pressure effects can play a role. In fact, keeping in mind the scheme of interstitial diffusion, it is quite obvious that strong structural changes due to pressure can lead to a variation in the size and number of interstitial sites and as a consequence in the diffusion efficiency. A detailed model of the solid structure and of the diffusion mechanisms, leading to an exact relationship between $D$ and the fraction of vacant interstitial sites and probabilities for a molecule to jump into a particular one, would be needed to obtain a quantitative estimation of the changes in $D$ due to pressure [113]. Unfortunately such relationships are usually available for simple systems as metal and binary alloys, but can be hardly obtained for a complex and disordered structure as silica [113]. As the maximum pressure applied to the samples in our experiments was of the order of 200bar, and it is known that permanent volume changes are not observed in silica for pressures lower than $\sim$ 12kbar [117], only transient and relatively small volume changes due to pressure could possibly take place during the experiments presented in the following chapters.

The diffusion parameters of some chemical species in silica are listed in Table 2.1, as reported in literature [106, 118–123].

**Table 2.1:** Diffusion parameters of chemical species in amorphous silicon dioxide. The pre-exponential factors and activation energies are listed together with the diffusion coefficient calculated at room temperature using Equation 2.5.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$D_0$ ($\text{cm}^2\text{s}^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>$D_{\text{room}}$ ($\text{cm}^2\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$1\cdot10^{-4}$</td>
<td>0.18</td>
<td>$9.5\cdot10^{-8}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$5.7\cdot10^{-4}$</td>
<td>0.45</td>
<td>$1.5\cdot10^{-11}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$1\cdot10^{-6}$</td>
<td>0.79</td>
<td>$5.3\cdot10^{-20}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>$2.9\cdot10^{-4}$</td>
<td>1.17</td>
<td>$5.9\cdot10^{-24}$</td>
</tr>
<tr>
<td>He</td>
<td>$3\cdot10^{-4}$</td>
<td>0.24</td>
<td>$2.8\cdot10^{-8}$</td>
</tr>
</tbody>
</table>
2.1.2 Diffusion and reaction

Up to now, we have described the phenomenon of diffusion without any interaction between the diffusing species and the lattice. This is of course an ideal approximation, as chemical reactions occurring during the diffusion of substances in solids are common. A typical example is hydrogen diffusion in silicon. In fact, the reaction

\[ H_2 + 2Si \rightarrow 2SiH \]  

(2.7)

takes place during this process [92]. Another example is the dissolution and diffusion of water vapour into oxides, as silica glass, and its reaction with the network [92]

\[ \equiv Si - O - Si \equiv + H_2O \rightleftharpoons 2 \equiv SiOH \]  

(2.8)

This process will be better discussed in the next paragraph, due to the importance of water diffusion in silica in this thesis.

As the rate of diffusion is influenced by removal or supply of reacting species, it is necessary to discuss the cases in which reactions between the network and the diffusing molecules take place [92]. Two different situations can be distinguished: the one in which the reaction goes to equilibrium at each place in the solid (called local equilibrium), and the one in which equilibrium between the dissolved molecules and the reaction product is not reached at every point (processes not at local equilibrium) [92].

We consider here only the case of local equilibrium, as the non-equilibrium one is not necessary for the continuation of this discussion. To illustrate the local equilibrium case we will use Reaction 2.8 as example. Referring to Figure 2.1, a differential equation for the case of diffusion plus reaction can be derived. In fact, besides the contribution of fluxes entering or leaving the slab already considered in deriving Equation 2.4, the removal or generation of diffusing species (H$_2$O in our example) in the slab has to be considered in this case too. If we call $r$ the concentration of reaction products (OH groups in our example), a term ($\partial r / \partial t$) has to be subtracted from the rate of change of flux in the slab represented by Equation 2.4. This latter Equation takes hence the form

\[ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right) - \frac{\partial r}{\partial t} \]  

(2.9)

To solve this equation it is necessary to know the relation linking $c$ and $r$. In some cases the simple linear dependence

\[ r = K_1 c \]  

(2.10)
applies, and from Equation 2.9 it follows

\[
\frac{\partial c}{\partial t} = \frac{D}{1 + K_1} \left( \frac{\partial^2 c}{\partial x^2} \right) \tag{2.11}
\]

This Equation has the same analytical aspect as Equation 2.4, but for an effective diffusion coefficient \( D_e = D/(1 + K_1) \). It is therefore evident, basing on Equation 2.10, that if \( K_1 \approx 0 \), i.e. if the concentration of dissolved species \( c \) is much greater than that of reacted groups \( r \), the diffusion process is not significantly influenced by the reaction \( (D_e \approx D) \). On the other hand a high concentration of reacted groups leads to a decrease of the effective diffusion coefficient. In many reactions the simple linear relation 2.10 does not hold. A more general relation between \( c \) and \( r \) is [92]

\[
r^n = K_nc \tag{2.12}
\]

In the case of our example (Reaction 2.8), and in other cases of interest [92], \( n = 2 \) and \( r >> c \), and the effective diffusion coefficient takes the form [92]

\[
D_e = \frac{2rD}{K_2} \tag{2.13}
\]

Then, in the case of \( n = 2 \), the effective diffusion coefficient \( D_e \) is directly proportional to the concentration of reacted groups \( r \).

Now two examples of diffusion in silica, that will be of fundamental interest in the following of this thesis, will be proposed.

### 2.1.3 Water diffusion in silica

The diffusion and reaction of water in silica have been widely studied. A brief review of these results as discussed in literature is presented in this Section.

As already mentioned, water is commonly believed to diffuse in silica, and to react with the glass matrix according to Reaction 2.8 [92].
At high temperatures (\( T > 600^\circ C \)) the reaction is fast compared to the diffusion process. In this conditions a local equilibrium is established, described by the equilibrium constant \( K_2 = r^2/c \), where \( r \) is the concentration of reacted OH groups, \( c \) that of molecular water and the subscript 2 in \( K_2 \) indicates that the reverse reaction is bimolecular [83, 92, 124]. It is experimentally observed that water is present in very low concentrations, often barely detectable, and OH groups, that are considered relatively immobile, are the main species present at high temperatures. Under these conditions the effective diffusion coefficient can be expressed according to Equation 2.13, where \( D \) is the actual diffusion coefficient of molecular water [83, 92, 124].
Diffusion experiments in this range of temperature were performed, as an example, by making water diffuse into unhydrated glass. The profiles of hydrogen were measured through infrared absorption and radioactive tritium. The agreement between the experimental hydrogen profile and that calculated using Equation 2.13 was very good [92, 125–128].

At lower temperatures the phenomenology appears more complex. Experiments on water diffusion in silica were performed at temperatures lower than \( \sim 600\,^\circ\text{C} \) by measuring the OH profiles through infrared absorption [83, 124]. The authors of these works observed that by plotting in an Arrhenius plot the effective diffusion coefficient data at temperatures lower than \( \sim 600\,^\circ\text{C} \) together with those at higher temperatures previously obtained by other authors, two different temperature ranges could be evidenced (See Figure 2.2) [83, 93, 124]. In fact, the effective diffusion coefficient at low temperatures results to be higher than the value that would be predicted by extrapolating data at higher temperatures. They also calculated the activation energies corresponding to the two different slopes, and found the activation energy for diffusion to be \( \sim 80\text{kJ/mol} \) (\( \sim 0.82\text{eV} \)) and \( \sim 40\text{kJ/mol} \) (\( \sim 0.41\text{eV} \)) at temperatures respectively higher and lower than \( \sim 600\,^\circ\text{C} \) [124]. For what concerns the diffusion at low temperatures, they also found out that the low temperature effective diffusion coefficient exhibited a time dependent behaviour. Moreover the diffusion profiles at these temperatures indicate that the diffusion coefficient does not depend on concentration, and as a consequence the above description, leading to the expression 2.13 for the diffusion coefficient, does not apply [83, 93, 124].

The authors proposed several explanations for these experimental results. They hypothesized that a non-equilibrium reaction between water and the glass matrix could account for the observed anomalies in the effective diffusion coefficient with respect to Equation 2.13 [83, 93, 124]. They based this hypothesis on a previous study on a thin SiO\(_2\) film on silicon, and on an analogous effect observed for hydrogen diffusion in silica [130, 131]. However they also hypothesized a change in the nature of the reaction at \( \sim 600\,^\circ\text{C} \), based on the different features of IR spectra at low and high temperature [83, 93, 124]. In fact, at high temperature free OH is predominating, while at low temperatures they also observed the presence of hydrogen bonded hydroxyls (See also Subsection 1.1.4 for more details about different kinds of OH groups) [83, 124].

These data were afterwards reinterpreted in a different way by another author [92]. Doremus in fact proposed that the observed unexpectedly high and time dependent effective diffusion coefficient at low temperatures does not depend on a change in the mechanism, but it is instead an effect of the diffusion reaction mechanism [92]. In more details, he proposed that at high temperatures the OH groups pairs, even if they are almost immobile, can diffuse far enough to reach other SiOH groups pairs.
This fact makes the reverse reaction of 2.8 bimolecular, leading to the effectiveness of the expressions $K_2 = r^2/c$ and $D_e = 2rD/K_2$. At low temperatures instead an OH pair can not diffuse far enough to sample other pairs, and the two OH react only within themselves forming water. In this case hence the reverse reaction would be of the first order and the expressions $K_1 = r/c$ and $D_e = D/(1 + K_1)$ apply. Moreover, at temperatures lower than $\sim 500^\circ$C the first order reverse reaction is dominant, but it does not reaches equilibrium at short times. He supposed that at short treatment times residual defects or strains can be present, that can increase the rate of diffusion of OH groups, making the diffusion lengths of these groups large enough to maintain the reverse reaction bimolecular. The author also proposed that these conditions cause the apparent time dependence of the effective diffusion coefficient.
Finally, following this reasoning, he calculated the actual diffusion coefficient of water \( D \) from the \( D_e \) data of Wakabayashi and Tomozawa [124]. In Figure 2.3 (extracted from Reference [92]) data at higher temperatures calculated from References [125–128, 132–135] are plotted together with the data at lower temperatures from Reference [124]; the line is a linear regression with activation energy of 70kJ/mol. He found out hence that \( D \), differently from \( D_e \), does not depend on time, and that his result fits well with the trend extrapolated from diffusion data at higher temperatures [92].

The values for \( D_0 \) and \( E_a \) shown in Table 2.1 are effective values. This choice was made considering that these values will be used in Chapter 7 to analyze the annealing processes of point defects due to their reactions with diffusing water molecules. In this kind of process the important parameter is the effective diffusion coefficient, since eventual mechanisms slowing down the overall process, as reactions between water and the lattice, have to be taken into account.

**Figure 2.3:** Arrhenius plot of the diffusion coefficient of water into silica glass. Extracted from Reference [92]. Points are calculated from experimental results in References [125–128, 132, 133] (circles), References [134, 135] (triangles) and Reference [124] (squares). The straight line is a linear regression with activation energy of 70kJ/mol.
2. Diffusion and reaction of molecules in silica

2.1.4 Oxygen diffusion in silica

Diffusion of oxygen in oxides plays a fundamental role in many important phenomena, as corrosion and oxidation of metals and semiconductors. However, some important aspects of this phenomenon have been controversial for a long time. For example, transport of oxygen in silica glass mediated by the migration of several chemical species, such as \( \text{O}_2 \), water, or silicon monoxide, were proposed. Different diffusion mechanisms, for example, interstitial or vacancy diffusion were also put forward. In the following, a brief review on oxygen diffusion in silica will be proposed.

For what concerns the species by which oxygen transport takes place, in many papers no distinction was initially made, but more attention was paid to this aspect in recent years. Indeed, oxygen transport through silicon monoxide in silicates was tentatively proposed to account for processes above \( \sim 1300^{\circ}\text{C} \) [136]. Due to the still high uncertainty of this hypothesis and to the temperatures at which SiO diffusion should take place, much higher than the temperatures of interest in this thesis, it will not be further considered in the following. Furthermore, molecular water was sometimes considered an efficient way to transport oxygen inside silica, in a wider meaning of oxygen transport, also due to its widespread presence in many materials and its higher diffusivity with respect, for example, to molecular oxygen [92]. On the other hand, the fact that in oxygen diffusion experiments the diffusing species is molecular oxygen was proved by several experiments [86, 119, 137]. The oxygen permeation through silica shows a linear dependence on \( \text{O}_2 \) pressure, in accordance with Henry’s law [119]. The growth rates of silica thin films through silicon thermal oxidation predicted by using the value of the diffusion coefficient for molecular oxygen are in good agreement with experimental observations [138]. A good agreement between the diffusion parameters for molecular oxygen and measured quantities was also observed for diffusion in bulk silica [137]. Finally, the values of activation energy for \( \text{O}_2 \) diffusion derived from different experimental data [86, 119, 137] agrees well with the value calculated using formula 2.6 and the radius suggested by Doremus [86, 92]. All these evidences strongly support the idea that molecular oxygen diffuses in silica, and that its diffusion takes place without appreciable interactions with the matrix [119, 137].

As anticipated, another debated aspect is the mechanism of oxygen diffusion. The fact that the vacancy diffusion succeeds in modeling the diffusion mechanism in many solids could lead to hypothesize that it applies to oxygen diffusion in silica too, with oxygen ions jumping from one oxygen vacancy of the lattice to another one.

It is also worth to mention that diffusion of atomic oxygen through peroxy linkages (\( \equiv \text{Si} - \text{O} - \text{O} - \text{Si} \equiv \)) was also proposed, based on density functional calculations [139]. Some experimental results supporting this diffusion mechanism, involving atomic
rather than molecular oxygen, was also found [140]. However this result was obtained by treating samples directly in atomic oxygen atmospheres. Notwithstanding this variety of hypothesis on the mechanism of oxygen diffusion, there is now a general agreement about the idea that oxygen diffuses in silica as a molecule through an interstitial mechanism [119, 136, 137, 141].

The activation energy for $O_2$ diffusion was estimated through several experiments, both of gas transport and isotope exchange, and values ranging between 1.17 eV and 1.35 eV were found [92, 141].

In the following of this thesis oxygen diffusion will be discussed in connection to defects related processes, in which a strong distinction has always been made between $O_2$ and $H_2O$ related effects. For this reason the expression oxygen diffusion will be referred only to the diffusion of molecular oxygen in the following.

2.2 Reaction kinetics

In the previous Section of this Chapter we dealt with the diffusion of molecules in solid systems, and with the possible influence of reactions between the molecules themselves and the lattice. In this Section we will move forward, to tackle the issue of what happens when these diffusing molecules encounter a point defect and react with it. This phenomenon will be in fact of fundamental importance in the continuation of this thesis, as already anticipated in Section 1.3.

This process can be modeled as a bimolecular reaction, in which two species $A$ and $B$ combine to form the product $P$

$$ A + B \rightarrow P \quad (2.14) $$

the two reactants $A$ and $B$ being the point defect and the diffusing molecule in our system [112]. Here we are assuming the reverse process to be negligible. Nothing changes if there is more than one product.

We are interested in the reaction kinetics, i.e. the time dependence of the concentrations of reactants and products, here considered as global concentrations [112, 114]. In many cases of interest the rate of a reaction, i.e. the rate of change of any of the involved species, is proportional to the product of the concentrations of the two reactants, as expressed by the following rate law [112]

$$ rate = -\frac{dA}{dt} = -\frac{dB}{dt} = \frac{dP}{dt} = k[A][B] \quad (2.15) $$

where $k$ is a coefficient not depending on the concentrations called rate constant.

More in general the concentrations on the right side of equation 2.15 could be raised
to some power \[112\]. Different rate laws for reactions with the same stoichiometry could account for different mechanisms \[112\].

The rate constant \(k\) usually depends on temperature according to the Arrhenius’ expression

\[
k = A \exp\left(\frac{-E_a}{k_B T}\right)
\]  

(2.16)

where the parameters \(A\) (called pre-exponential factor) and \(E_a\) (activation energy) are almost temperature independent and can be determined by a linear fit of \(\ln k\) as a function of \(1/T\) \[112\].

The reaction kinetics can obviously be strongly influenced by the transport properties of reactants. In fact the molecule and the defect need to meet and to be within a certain distance \(r_0\) from each other to have the possibility to react. As a consequence two different time scales characterize the overall process, the diffusion time and the reaction time \[114\]. The diffusion time \(\tau_d\) is the typical time that an arbitrary diffusing molecule needs to meet an arbitrary point defect within the reaction-range distance \(r_0\), while the reaction time \(\tau_r\) is the typical time they need to react when they are held within \(r_0\) \[114\]. The diffusion-reaction processes are usually classified on the basis of the relation between these two different time scales.

If \(\tau_d << \tau_r\) the limiting step in the overall diffusion-reaction is the reaction, and the process is usually called reaction-limited. In this limit a diffusing molecule needs to approach a defect within a distance \(r_0\) several times before actually reacting.

If instead \(\tau_d >> \tau_r\), the diffusing molecule likely reacts with a point defect at their first encounter and the process is known as diffusion-limited \[114\]. Of course intermediate situations can exist.

Several models can be proposed to describe diffusion-limited processes. The Smoluchowski’s model is among the simplest ways to treat them \[114\], and it allows to derive an expression for the rate constant of a diffusion-limited reaction \[114, 142\].

The simple-minded Smoluchowski’s model consists of a single sphere \(A\) of radius \(r_0\) acting as a perfect immobile trap. It means that any other particle \(B\) that diffuses and hits the sphere \(A\) immediately reacts with it and is removed from the system (See Figure 2.4). This fact imposes a boundary condition, that describes the reaction process, for the diffusion equation.

The density of particles \(B\), \(\rho_B(\vec{r}, t)\), where \(|\vec{r}|\) is the distance from \(A\) and \(t\) the time, is considered uniform at great distances from the trap, its value being \(\rho_{B0}\). \(\rho_B\) evolves according to Fick’s second law (Equation 2.4)

\[
\frac{\partial \rho_B}{\partial t} = D \nabla^2 \rho_B
\]  

(2.17)
2.2. Reaction kinetics

Figure 2.4: Immobile perfect trap of radius \( r_0 \) (grey circle) surrounded by diffusing particles (white circles).

and the above mentioned boundary condition can be written as

\[
\rho_B(\mathbf{r}, t)_{r \leq r_0} = 0
\]

(2.18)

The number of particles \( B \) per unit time through a spherical surface of arbitrary radius \( r \) centred on \( A \) has to be independent of \( r \) in stationary conditions, and can be written, using first Fick’s law (Equation 2.1), as

\[
N = 4\pi r^2 J = -4\pi r^2 D \frac{\partial \rho_B}{\partial r} = \text{constant}
\]

(2.19)

where \( D \) is the diffusion coefficient of the particles \( B \). \( N \) represents the change per unit time in the total number of particles \( B \) due to trapping.

Equation 2.19 can be solved to find an expression for \( \rho_B(r) \) using the boundary condition 2.18. The result is

\[
\rho_B(r) = \frac{-N}{4\pi D} \left( \frac{1}{r_0} - \frac{1}{r} \right)
\]

(2.20)

By taking the limit for \( r \to \infty \), and considering that the value \( \rho_B(\infty) \) represents the global macroscopic concentration \([B]\) of particles \( B \), the following expression for \( N \)
2. Diffusion and reaction of molecules in silica

(i.e. the change per unit time in the number of particles B) is found

\[ N = -4\pi r_0 D[B] \quad (2.21) \]

The rate of change in the concentration of particles B can be found as

\[ \frac{d[B]}{dt} = \frac{N}{V} = -\frac{4\pi r_0 D[B]}{V} \quad (2.22) \]

where \( V \) is the sample volume. Finally, if we consider the more realistic case of more than one trap, and if we call \( N_A \) their number, Equation 2.22 has to be multiplied by \( N_A \), obtaining the following expression for the rate of the reaction

\[ \frac{d[B]}{dt} = \frac{N \cdot N_A}{V} = N[A] = -4\pi r_0 D[A][B] \quad (2.23) \]

Comparing this expression with Equation 2.15 the following important expression for the rate constant of a diffusion limited process is obtained

\[ k_d = 4\pi r_0 D \quad (2.24) \]

It is evident that this simple model involves many approximations, as it does not take into account, for example, the removal of the traps and the possibility that the traps diffuse too. Other more complex models for diffusion-limited reactions that take into account these effects have been proposed in literature, but we will not illustrate them here as they will not be applied in the following of this thesis.

The present knowledge on water and oxygen diffusion in silica described in the first Section of this Chapter will be the landscape of the experiments and results that will be described in the second part of this thesis. The models for reactions and the reaction kinetics described in the last part of this Chapter will be instead the theoretical background for the comprehension of the annealing processes of point defects in silica that will be studied in Chapter 7.
Chapter 3

Experimental techniques: theoretical background

The purpose of the present Chapter is to give the basic theoretical background necessary for the understanding of the experimental techniques used to perform the experiments presented in the following chapters.

3.1 Electron paramagnetic resonance

Electron Paramagnetic Resonance (EPR) spectroscopy can be used to study systems with non-zero electronic magnetic moments. For this reason it is a very useful tool for the study of radiation induced point defects in silica. In fact, defects with unpaired electrons, having non-zero magnetic moments, can be created by the breakage of molecular bonds due to radiation. Moreover EPR is a powerful technique to shed light on the microscopic structure of point defects. In fact most of the present knowledge on the structures of point defects in silica was obtained through EPR studies [1].

In a typical EPR experiment a sample experiences the interaction with two orthogonal magnetic fields. A static magnetic field $\mathbf{H}$ induces a splitting in the electronic ground state energy levels, as a consequence of its interaction with the electronic magnetic moment. The second magnetic field $\mathbf{H}_1$ oscillates at microwave frequency, and can induce electronic transitions between the energy levels split by $\mathbf{H}$. The EPR phenomenon is the resonant absorption of electromagnetic energy by the spin system, taking place when the frequency of the microwave radiation matches one of the characteristic transition energies of the system [143–147].
3.1.1 Spin Hamiltonian

When ions with partially filled shells and non zero magnetic moment are embedded in a solid, they cannot be treated as free ions. It is necessary to take into account their interaction with surrounding ions in the description of their energy levels. The energy associated to this interaction is usually in the range $10^2 \div 10^4 \text{cm}^{-1}$ [144, 145].

Two different approaches to the study of the magnetic properties of ions in solid systems exist [144, 145]. The first one is the Crystalline Field Theory. It assumes that each ion experiences an electric field generated by the surrounding ions. This field has the same symmetry as its sources, i.e. the lattice symmetry. The presence of this crystalline field determines a Stark splitting of the ion energy levels [144, 145]. An intrinsic implication of this method is that bonds are considered purely ionic. The second, more sophisticated approach allows to take into account covalent bonds, by considering the electronic wave function distributed over a group of atoms forming molecular orbitals of type $\sigma$ or $\pi$ [144]. Both these approaches lead to obtain groups of almost degenerate energy levels. The exact energy distribution of these levels depends on the symmetry of the ion orbitals and of its surrounding, and it can be obtained by the group theory method [144]. An important information is given by the Kramers theorem, that states that the lowest degeneracy of a system having an odd number of electrons, in absence of a magnetic field, is double [144, 145]. EPR measurements involve transitions between energy levels split apart by $\sim 0.3 \text{cm}^{-1}$. As a consequence, the only energy levels of interest are those which are degenerate (or nearly degenerate) in absence of an external magnetic field.

An useful tool to describe the effects of the external magnetic fields on the nearly degenerate group of levels of interest is the effective spin Hamiltonian (or simply spin Hamiltonian) [144, 145]. An effective spin operator $\hat{S}$ is defined. $\hat{S}$ is a fictitious angular momentum, such that the degeneracy of the group of levels chosen is $2\hat{S} + 1$ [144, 145]. In some cases the spin Hamiltonian can be theoretically derived from the true Hamiltonian, but it is usually introduced on the basis of empirical considerations, taking into account the paramagnetic centre symmetry. In the following we will use the spin Hamiltonian approach to describe the properties of the paramagnetic centres of interest in this thesis.

3.1.2 Spin Hamiltonian: the Zeeman term

The interaction between the paramagnetic system and the external static magnetic field $\mathbf{H}$ is described by the Zeeman operator [144, 146]

$$H_{\text{zeeman}} = -\mu \cdot \mathbf{H}$$

(3.1)
where $\mu$ is the magnetic moment of the paramagnetic center. If the magnetic moment is due only to the electronic spin angular momentum, that is the simplest and most common situation for point defects, the Zeeman interaction operator can be rewritten as follows

$$H_{\text{zeeman}} = g_e \mu_B \mathbf{H} \cdot \mathbf{S}$$  \hspace{1cm} (3.2)

where $g_e = 2.0023$ is the free electron splitting factor, $\mu_B = 9.27408 \times 10^{-24} \text{ J/T}$ is the Bohr magnetic moment and $\mathbf{S}$ is the spin operator in units of $\hbar$. The eigenvalues of $H_{\text{zeeman}}$, that represent the energy levels of the system, are

$$E_{\text{zeeman}} = g_e \mu_B m_S$$  \hspace{1cm} (3.3)

where $m_S$ is the eigenvalue of the component of $\mathbf{S}$ along the direction of $\mathbf{H}$. The Zeeman interaction between the paramagnetic system and the external magnetic field determines a removal of the degeneracy between states characterized by different values of $m_S$ (See Eq.3.3).

The magnetic field $\mathbf{H}_1$ oscillating at frequency $\omega$ induces transitions between these Zeeman sublevels, split by $\mathbf{H}$. The selection rule $\Delta m_S = \pm 1$ exists for these transitions. It means that only transitions between adjacent levels are allowed. As a consequence the resonance condition is

$$\hbar \omega = g_e \mu_B H$$  \hspace{1cm} (3.4)

An EPR spectrum is obtained by measuring the energy absorbed by the paramagnetic system from the microwave field as a function of the amplitude of the static magnetic field $\mathbf{H}$, with fixed amplitude and frequency for the oscillating magnetic field $\mathbf{H}_1$ [143–147].

If the paramagnetic centre under consideration is embedded in a solid matrix, a more sophisticated approach is necessary. In this case, in fact, the spin-orbit interaction leads to an anisotropy in the Zeeman interaction [144]. To account for this effect the $g_e$ factor needs to be substituted by a tensorial quantity $\hat{g}$. The principal values $g_1$, $g_2$ and $g_3$ are usually different from the free electron value $g_e$. As a consequence the spin Hamiltonian becomes

$$H_{\text{zeeman}} = \mu_B \mathbf{H} \cdot \hat{g} \cdot \mathbf{S}$$  \hspace{1cm} (3.5)

and the resonance condition can be rewritten as

$$H_z = \frac{\hbar \omega}{\mu_B \sqrt{g_1^2 \cos^2 \theta_1 + g_2^2 \cos^2 \theta_2 + g_3^2 \cos^2 \theta_3}} = \frac{\hbar \omega}{\mu_B g}$$  \hspace{1cm} (3.6)

where $\theta_i$ are the angles between the direction (z) of the static magnetic field and the principal axes of the $g$ tensor, that depend on the paramagnetic centre symmetry. The $g_i$ values can be obtained from the EPR spectrum, as they correspond to specific features of the latter, as described in Subsection 3.1.5.
3. Experimental techniques: theoretical background

3.1.3 Spin Hamiltonian: the Hyperfine term

When an atom with non zero nuclear magnetic moment $I$ is located near to the paramagnetic ion, a new term needs to be introduced in the spin Hamiltonian, accounting for the hyperfine interaction [144, 146–149]. This new term in the Hamiltonian has to take into account two contributions: an anisotropic one, deriving from the dipolar interaction between the magnetic moment of the electron and that of the nucleus, and an isotropic one due to the so called Fermi contact term [144, 147, 149]. This is accomplished by introducing a hyperfine tensor $\hat{A} = \mathbf{1} A_0 + \hat{T}$, where $\mathbf{1}$ is the unity matrix, $A_0$ is the isotropic hyperfine coupling constant and $\hat{T}$ introduces the anisotropy due to the dipolar interaction. The new hyperfine term in the spin Hamiltonian can be written as

$$H_{hf} = \hat{S} \cdot \hat{A} \cdot \mathbf{1} \quad (3.7)$$

The anisotropic component is usually negligible with respect to the contribution of the contact term, and the hyperfine interaction can be described, in first approximation, by a scalar, $A_0$. If the applied magnetic field is intense ($A_0 << g\mu_B H$), first order perturbation theory can be applied, by treating the Zeeman interaction first and then the hyperfine interaction. Following this procedure, if the principal axes of $\hat{A}$ and $\hat{g}$ coincide, the following expression for the energy contribution of the hyperfine interaction is obtained [144]

$$E_{hf} = A \cdot m_S \cdot m_I \quad (3.8)$$

where $m_S$ and $m_I$ are the electronic and nuclear magnetic quantum numbers, and $A^2 = g_1^2 \cos^2 \theta_1 A_1^2 + g_2^2 \cos^2 \theta_2 A_2^2 + g_3^2 \cos^2 \theta_3 A_3^2$, the parameters $A_i$ being the principal values of the $A$ tensor. If the principal axes of $\hat{A}$ and $\hat{g}$ do not coincide, an analogous result is obtained, but the out-diagonal terms of $\hat{A}$ appear in the expression for $A$ [144]. The new eigenvalues for the total Hamiltonian can then be written as

$$E = g\mu_B H m_S + A m_S m_I \quad (3.9)$$

The main transitions are those for which $\Delta m_S = \pm 1$ and $\Delta m_I = 0$, taking place for

$$\hbar \omega = g\mu_B H + A m_I \quad (3.10)$$

As a consequence each electronic transition splits into $2I+1$ equally spaced lines (hyperfine multiplet) corresponding to the different values of $m_I$, due to the hyperfine interaction [144]. Figure 3.1 shows the energy levels scheme for a system with $S=I=\frac{1}{2}$.
3.1. Electron paramagnetic resonance

Figure 3.1: Energy levels scheme for a system with S=1=\frac{1}{2}.

The k arrow indicates the only transition that would take place in the absence of hyperfine interaction, while the q and n arrows correspond to the transitions permitted when it is present. An estimation of the value of A can be obtained by measuring the magnetic field splitting between the two lines of the hyperfine doublet in an EPR spectrum.

3.1.4 Paramagnetic centres in solids

The systems of interest in this thesis are paramagnetic centres embedded in a solid matrix. For such systems it is necessary to take into account the interactions between different paramagnetic centres and between the latter and the lattice, in addition to the interaction with the external magnetic field [144, 146].

A phenomenological description of the behaviour of a spin system is given by Bloch’s Equations [145]. They are a set of equations describing the interaction of the components of the macroscopic magnetization $\mathbf{M}$ of a solid containing paramagnetic centres with a time-dependent magnetic field. Two phenomenological time constants, $T_1$ and $T_2$, are introduced to describe the spin-lattice and the spin-spin interactions. Bloch’s equations are

$$\frac{dM_x(t)}{dt} = \gamma [\mathbf{H}_T \times \mathbf{M}(t)]_x - \frac{M_x(t)}{T_2}$$

(3.11)
3. Experimental techniques: theoretical background

\[
\frac{dM_y(t)}{dt} = \gamma [\mathbf{H}_T \times \mathbf{M}(t)]_y - \frac{M_y(t)}{T_2}
\]  
(3.12)

\[
\frac{dM_z(t)}{dt} = \gamma [\mathbf{H}_T \times \mathbf{M}(t)]_z - \frac{M_z(t) - M_0}{T_1}
\]  
(3.13)

where \( \gamma = g_e \mu_\beta / \hbar \) is a constant, named gyromagnetic ratio, whose value depends on the system and for a free electron is \( \gamma = 1.76 \cdot 10^7 \text{s}^{-1} \text{G}^{-1} \). \( \mathbf{M} \) is the macroscopic magnetization, \( \mathbf{H}_T \) is the total magnetic field (sum of the static and oscillating fields), \( \omega \) is the microwave frequency, and \( M_0 \) is the equilibrium value of the z component of magnetization. It can be easily seen by looking at the Bloch equations 3.11, 3.12 and 3.13 that their solution strictly depends on the time dependence of the magnetic field. Specific solutions for equations 3.11, 3.12 and 3.13 are obtained for particular cases. The most important one for continuous wave oscillating field occurs when

\[
\frac{H_1}{d[H + H_m]} << \sqrt{T_1 T_2}
\]  
(3.14)

where \( H_1 \) is the microwave field amplitude, \( H \) the static magnetic field and \( H_m \) the modulation field. The latter is a slowly oscillating magnetic field parallel to the static magnetic field used in order to enhance resonance detection (See Chapter 4 for further details). Equation 3.14 is called slow passage condition, and it means that the rates of time change of \( H \) and \( H_m \) are slow with respect to the main relaxation rates of the paramagnetic centers [150]. From the Bloch’s equations, assuming the slow-passage condition valid, the power absorbed by the spin system per unit volume can be derived [145]

\[
P = \frac{\gamma \omega M_0 T_2}{1 + (\gamma H - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2 H_1^2}
\]  
(3.15)

For low intensity oscillating field, i.e. upon the condition \( \gamma^2 H_1^2 T_1 T_2 << 1 \), the absorption line has Lorentzian shape, its amplitude is proportional to \( H_1^2 \) and its half width at half maximum is equal to \( 2/\gamma T_2 \). In this case the area of the absorption line is proportional to the total number of spins. The physical meaning of this condition, called non saturation condition, is that the power of the incident field is low enough for the relaxation mechanisms to dissipate the absorbed energy. When the non saturation condition is not satisfied the absorbed power assumes a constant value proportional to \( M_0 \) and not depending on \( H_1 \) (saturation condition) [145, 147].
3.2. Optical spectroscopy: Absorption and Photoluminescence

3.1.5 Powder and amorphous lineshape

The lack of long range order has to be considered when dealing with powdered or amorphous paramagnetic substances. In this case the principal axes of the paramagnetic centres are randomly oriented with respect to the magnetic field, and the resonance fields (Equation 3.6) are distributed. As a consequence the spectrum is the superposition of many single centre lines, each one due to all the paramagnetic centres whose principal axes have a specific orientation with respect to the magnetic field [143, 147]. The observed resonance line is the envelope of many Lorentzian lines, one for each possible value of the random $\theta_i$. This gives rise to the so-called powder lineshape.

Moreover in an amorphous system bond angles and distances are statistically distributed. This fact implies that there are slight differences in the microscopic structure of defects, and hence in $\hat{g}$ and $\hat{A}$ tensors. Distributions of the principal values of these tensors have then to be considered for these systems, and a further inhomogeneous broadening of the absorption line of an amorphous with respect to that of a powder is obtained [143, 147]. Notwithstanding these difficulties, it is possible to obtain an experimental estimation of the principal values by measuring the field values corresponding to specific features of the absorption spectrum. For example for a paramagnetic system with orthorhombic symmetry the $\hat{g}$ principal values can be obtained by measuring the magnetic field corresponding to the first maximum, the zero crossing and the second minimum in the derivative spectrum.

3.2 Optical spectroscopy: Absorption and Photoluminescence

The optical properties of silica are affected by the presence of point defects, as the energy separation between their electronic states is lower than the intrinsic energy gap of silica. The electronic transitions between the energy levels of a point defect are fingerprint of a specific defect. For this reason optical spectroscopies, as absorption and photoluminescence, are of fundamental importance in this thesis for the individuation of the presence of defects.

3.2.1 Electronic state of a point defect

When dealing with the study of the electronic structure of a point defect, it is necessary to take into account the coupling between the electronic and the vibrational degrees of freedom, and a many-body problem has to be solved.
The Hamiltonian of a system of N nuclei and n electrons can be written as \[148, 149\]

\[ H = T_e + T_N + V_{e-e} + V_{e-N} + V_{N-N} \]  

(3.16)

where \( T_e \) and \( T_N \) are the kinetic energies of the systems of electrons and nuclei, respectively, and \( V_{e-e}, V_{e-N} \) and \( V_{N-N} \) the potential energy terms associated to the electron-electron, electrons-nuclei and nucleus-nucleus interactions. In the framework of the Born-Oppenheimer and Franck-Condon approximations \( \dagger \) \[148, 149\] the state of the system can be described as the tensorial product of an electronic wave function \( \phi \) and a nuclear wave function \( \xi \)

\[ \psi(r, R) = \phi(r, R)\xi(R) \]  

(3.17)

where \( r \) and \( R \) are the electronic and nuclear coordinates respectively. The problem is then reduced to the solution of the two equations

\[ [T_e + V_e(r, R)]\phi(r, R) = \varepsilon(R)\phi(r, R) \]  

(3.18)

\[ [T_N + V_{N-N} + \varepsilon(R)]\xi(R) = E_{\nu}\xi(R) \]  

(3.19)

where \( \varepsilon(R) \) and \( E_{\nu} \) are the electronic and nuclear energy eigenvalues, and \( V_e(r, R) \) is the potential energy of interaction between electrons and nuclei and between the electrons themselves. This potential energy varies in varying the nuclei position \( R \), and as a consequence a parametric dependence on \( R \) is introduced for the eigenfunction and the energy eigenvalue of electrons. The total energy of the system is

\[ E_{TOT} = \varepsilon(R) + E_{\nu} \]  

(3.20)

By introducing the normal modes for the nuclear motion, the solution of Equation 3.19 can be written in terms of a product of harmonic oscillator eigenfunctions, one for each normal mode. The energy \( E_{\nu} \) is the sum of the energies of these harmonic oscillators. It can be then easily observed that a series of vibrational levels is associated to each electronic energy level \[151, 152\].

A typical energy level scheme, that describes well the spectral features of many defects, as for example the ODC(II), is shown in Figure 3.2 This scheme includes the

---

\( \dagger \) The Born-Oppenheimer approximation consists in separating the wave function of a molecule into a product of electronic, vibrational, and rotational functions. It is based on the idea that the electrons move much faster than nuclei, due to the great difference in their masses. The Franck-Condon principle states that the higher the overlap between the vibrational wavefunctions of the two states, the higher the probability of the transition.
3.2. Optical spectroscopy: Absorption and Photoluminescence

Figure 3.2: Typical energy levels scheme of a point defect. The absorption and decay transitions are also shown.

ground state $S_0$, that is supposed to be a spin singlet state, two singlet excited states, $S_1$ and $S_2$, and a triplet excited state $T_1$. Suppose now that the initial state of the system is its electronic and vibrational ground state $(0, 0)$, as expected at $T=0$. By a photon absorption the system can make a transition from the ground electronic state $S_0$ to one of the excited states $S_1$ or $S_2$. Suppose the transition is to $S_1$. An analogous transition to $T_1$ is forbidden by the spin selection rule. Due to the coupling between the electronic transition and the vibrational modes, the transition can connect the ground state $(0,0)$ to one of the vibronic levels of the excited electronic state $(1,n)$ (vibronic transitions). The optical absorption (OA) spectrum then appears as a single broad band, given by the envelope of many narrow subbands, each due to a given vibronic transition. When the system is in its excited state $S_1$, it relaxes to its vibrational ground state and the nuclei relax to their minimum energy configuration through non-radiative processes, before decaying to the ground state (See Figure 3.2 for typical timescales). The decay from $S_1$ to $S_0$ can take place through a radiative transition, called fluorescence, whose typical lifetime is $10^{-9} \div 10^{-8}$s. The emission energy is lower than the absorption energy (Stokes shift), due to the energy loss associated to the coupling with the vibrational modes. When the system is in the $S_1$ state it can also go to the $T_1$ state through a non-radiative transition (inter-system crossing). From $T_1$ the system can decay to $S_0$ through a radiative process called phosphorescence. Phosphorescence lifetimes are about $10^{-1} \div 10^{-5}$s, higher than fluorescence lifetimes, as this transition is forbidden by the spin selection rule.

In an amorphous material each point defect experiences different surroundings. The energies associated to an optical transition are therefore distributed, depending
on the environment [153]. As a consequence the optical bands exhibit an inhomogeneous broadening.

### 3.2.2 Optical absorption

The attenuation of a light beam propagating through an absorbing medium is described by the Lambert-Beer's law [1, 12, 152, 154]

\[
I(\omega, d) = I_0(\omega) e^{-\alpha(\omega)d} \tag{3.21}
\]

where \(\omega\) is the frequency of the incident radiation, \(I_0(\omega)\) its intensity, \(I(\omega, d)\) the transmitted intensity, \(d\) the path length inside the medium, and \(\alpha(\omega)\) is the absorption coefficient, that characterizes the absorption spectrum.

An absorption spectrophotometer usually measures a quantity proportional to \(\alpha(\omega)\), that is the optical density \(OD(\omega)\) (or absorbance) of the sample. It is defined by

\[
OD(\omega) = \log_{10} \frac{I_0(\omega)}{I(\omega, d)} \tag{3.22}
\]

The relationship between \(OD(\omega)\) and \(\alpha(\omega)\) is

\[
\alpha = \frac{1}{\log_{10} e} \frac{OD}{d} \tag{3.23}
\]

Let us now consider a sample containing a single absorbing species with concentration \(\rho\). The value of the absorption coefficient at a given frequency \(\alpha(\omega)\) is proportional to the concentration of absorbing species \(\rho\) through the absorption cross section \(\sigma(\omega)\) § [1, 12].

\[
\alpha(\omega) = \sigma(\omega) \rho \tag{3.24}
\]

The absorption profile \(\alpha(\omega)\) due to point defects is usually bell-shaped.

Another parameter often used to characterize the absorption properties of a given species is the so called oscillator strength. The oscillator strength \(f\) of an electric dipole transition at frequency \(\omega\) is defined by [1]

\[
f = \frac{2m\omega}{3\hbar e^2} |\langle \psi_1 | D | \psi_2 \rangle|^2 \tag{3.25}
\]

§In a different but equivalent approach the extinction coefficient \(\varepsilon\), that is proportional to the cross section, is used instead of the latter.
3.2. Optical spectroscopy: Absorption and Photoluminescence

where \( m \) and \( e \) are the mass and charge of electron, \( \psi_1 \) and \( \psi_2 \) are the initial and final states, and \( D \) is the electric dipole operator. The absorption cross section and the oscillator strength are equivalent ways to describe the efficiency of the absorption process due to a given concentration of species. The following relationship between the integral of the absorption band and the oscillator strength \( f \) can be demonstrated to be valid [1]

\[
\int \alpha(E) dE = \frac{\rho}{n} \left( \frac{E_e}{E_0} \right)^2 \frac{2\pi^2 e^2 \hbar}{mc} f
\]

(3.26)

where the \( \left( \frac{E_e}{E_0} \right) \) term, named effective field correction, takes into account the differences between the macroscopic electric field \( E_0 \) and the local microscopic field \( E_e \) acting at the position of the defect due to the polarization of the surrounding medium. From this relationship the Smakula’s equation, that will be used to determine the concentration of optically active point defects, can be derived (See Subsection 4.5.1).

3.2.3 Photoluminescence

A point defect that had reached its excited state by absorbing radiation at frequency \( \omega \) can decay to the ground state through a radiative process called photoluminescence (PL), by emitting a photon of frequency \( \omega_e < \omega \). Not all the defects having an OA band necessarily feature a PL activity. However, when it happens, PL offers important advantages with respect to OA. PL is in fact more selective, as the OA bands of different point defects often overlap, while the PL bands are usually isolated. Furthermore, PL time decay offers additional selective information useful in the characterization of the defects. These facts allows the identification of a specific point defect on the basis of its emission properties.

When a defect is excited by a source of constant intensity and decays by photoluminescence (stationary photoluminescence), the intensity of the emitted radiation can be expressed as [154]

\[
I_{PL} = \eta(\omega_e) \cdot I_0(\omega) \cdot (1 - e^{-\alpha(\omega) \cdot d})
\]

(3.27)

where \( \omega \) and \( \omega_e \) are the frequencies of incident and emitted radiation, and \( I_0(\omega) \cdot (1 - e^{-\alpha(\omega) \cdot d}) \) is the absorbed intensity, determined by using Equation 3.21. \( \eta(\omega_e) \) is a parameter, named luminescence quantum yield, that characterizes the efficiency of the luminescence process. \( \eta(\omega_e) \) is defined as the ratio between emitted photons and absorbed photons, and it is determined by the competition between radiative and non-radiative decay processes (See Subsection 3.2.1). In low absorption conditions \( (\alpha(\omega) \cdot d << 1) \) Equation 3.27 reduces to

\[
I_{PL} = \eta(\omega_e) \cdot I_0(\omega) \cdot \alpha(\omega) \cdot d
\]

(3.28)
In this case the intensity of the emitted radiation is proportional to the excitation intensity, and to the concentration of optically active defects through the absorption coefficient $\alpha$ (See also Section 4.5.1) [1].

3.3 Vibrational spectroscopy: IR absorption and Raman scattering

As a first approximation the energy of a molecule can be considered as resulting from the sum of three separate contributions, associated to the rotation of the molecule, to the vibrational motion of its atoms, and to that of electrons. This possibility follows from the large differences in the characteristic timescales of these motions and the Born-Oppenheimer approximation (See also Subsection 3.2.1). These three terms are characterized by great differences in the typical orders of magnitude of the energies involved.

In this paragraph we are mainly concerned with the transitions between vibrational levels, that are observed in infrared (IR) or Raman spectra. These transitions, that originate from vibrations of the nuclei constituting the molecule, usually are in the infrared range ($10^2 \div 10^4 cm^{-1}$), while rotational and electronic transitions occur instead in the microwaves ($1 \div 10^2 cm^{-1}$) and visible-ultraviolet ($10^4 \div 10^6 cm^{-1}$) regions, respectively [152, 155, 156].

Let's consider the vibration of a diatomic molecule. Through quantum mechanical considerations the vibrations of its nuclei can be described as the motion of a single particle, whose mass is the reduced mass of the system, and whose distance from equilibrium position equals the internuclear distance [157, 158]. A typical potential energy curve for a diatomic molecule is shown in Figure 3.3 (continuous line). For small deviation of the internuclear distance from the equilibrium this curve can be approximated by a parabolic potential (dashed line). In this case the system is a harmonic oscillator. In Figure 3.3 the energy levels of this harmonic oscillator are also shown.

In Figure 3.4 a schematic representation of the energy levels of a diatomic molecule is shown. As stated above, vibrational transitions of a molecule can be observed in both IR and Raman spectra. However, the physical origins of these two kinds of spectra are considerably different.

IR absorption spectra originate from the resonant absorption of a photon (at IR frequency) and the consequent transition between two vibrational levels of the electronic ground state (See Figure 3.4). The energy separation between the two

\[1 eV = 8065.6 cm^{-1}\]
3.3. Vibrational spectroscopy: IR absorption and Raman scattering

Figure 3.3: Potential energy curves for a diatomic molecule: actual potential (solid line), parabolic potential (dashed line), and cubic potential (dotted line). Adapted from Ref.[155].

Vibrational levels matches exactly the energy of incident radiation. An IR spectrum consists therefore in a measurement of the absorbed infrared light as a function of frequency. The intensity of absorption is described by Lambert-Beer’s law (Equation 3.21).

In acquiring Raman spectra, instead, the incident radiation is laser light in the IR or UV-vis regions, and the scattered light is measured. There are several contributions
3. Experimental techniques: theoretical background

to this scattered light, that can be easily obtained by the classical model described below [152, 155, 156].
The time dependence of the electric field of the incident laser light is

\[ E = E_0 \cos 2\pi \nu_0 t \] (3.29)

where \( E_0 \) is the amplitude, \( \nu_0 \) the frequency of the laser, and \( t \) the time. A dipole moment \( P \) is induced in a molecule irradiated by this laser

\[ P = \alpha E = \alpha E_0 \cos 2\pi \nu_0 t \] (3.30)

where \( \alpha \) is a constant called polarizability. If the molecules vibrates at frequency \( \nu_m \), the internuclear distance \( q \) depends on time through the relation

\[ q = q_0 \cos 2\pi \nu_m t \] (3.31)

where \( q_0 \) is the vibrational amplitude. For vibrations of small amplitude, as a first approximation, \( \alpha \) is a linear function of \( q \)

\[ \alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q \] (3.32)

where \( \alpha_0 \) is the polarizability at the equilibrium position, and \( \left( \frac{\partial \alpha}{\partial q} \right)_0 \) is the rate of change of \( \alpha \) with respect to the change of \( q \), evaluated at the equilibrium position.

By combining Equations 3.30, 3.31 and 3.32 we obtain

\[ P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos(2\pi(\nu_0 + \nu_m) t) + \cos(2\pi(\nu_0 - \nu_m) t) \right] \] (3.33)

The first term represents the scattered radiation at the same frequency of the incident light (Rayleigh scattering). The last two terms correspond to the Raman lines, that feature a shifted frequency with respect to the incident light. In particular this shift is equal to the vibrational frequency of the system \( \nu_m \). This shift can be towards lower frequencies (Stokes lines) or towards higher frequencies (anti-Stokes lines), as described by the terms at \( \nu_0 - \nu_m \) and \( \nu_0 + \nu_m \) respectively. Stokes lines are more intense than anti-Stokes lines, due to Boltzmann distribution of vibronic level population. Raman lines are very feeble, as their intensity is usually \( 10^5 \) times less intense than the incident beam.

It is evident, by looking at Equation 3.33, that if \( \left( \frac{\partial \alpha}{\partial q} \right)_0 = 0 \) the terms representing the Raman scattering vanish. This means that the vibration is not Raman active, unless its polarizability changes during the vibration. Moreover, as the vibration can be represented in terms of the motion of an harmonic oscillator, the selection rule for the quantum harmonic oscillator must be satisfied. As a consequence only
those transitions for which $\Delta \nu = \pm 1$ are allowed, where $\nu$ is the quantum number of vibration. This selection rule does not apply to an anharmonic oscillator. As a consequence the observation of overtones (i.e. absorption at frequencies multiple of the fundamental) is only possible because vibrations are anharmonic.

The transitions corresponding to Rayleigh and Raman scattering are represented in Figure 3.4. The system in its ground state is excited to a virtual level (dashed line) by the incident radiation. If it decays to the ground state again, the phenomenon of Rayleigh scattering originates. If instead it decays from the virtual level to the first electronic excited state the Stokes lines are observed. The system can also be excited to a virtual level from its first excited vibronic state, and then decay to the ground state, giving rise to the anti-Stokes lines.

In more complex systems, as polyatomic molecules or solids, the situation is much more complicated, as every nucleus performs its own vibration. A molecule constituted by $N$ atoms has $3N-6$ vibrational degrees of freedom. Any molecular vibration can be represented as the superposition of the $3N-6$ normal vibrations. The same phenomenology described for the diatomic molecule occurs, but with the multiplicity due to the presence of many vibrational degrees of freedom.
Part II

Experiments and results
Chapter 4

Materials, treatments and experimental setups

In the present chapter the materials on which the experiments were performed, the treatments they underwent, and the instruments used are discussed.

4.1 Materials

As anticipated in part I, the manufacturing technique has a great influence on the properties of a-SiO$_2$. It can influence the concentration of preexisting defects, that can act as precursors sites for other centres. The concentration of interstitial molecules as H$_2$, O$_2$ or H$_2$O also depends on the glass synthesis procedure. These molecules strongly affect the defects concentration during irradiation or thermal treatments by reacting with the centres themselves. For these reasons knowledge of the material manufacturing procedures is a relevant point for the understanding of point defects related processes.

In our experiments samples of commercial origin were employed, as the standardized industrial manufacturing procedures assures a high reproducibility. Commercial silica is usually classified in four different categories, described below [117, 159]:

**Natural dry (type I),** produced by melting quartz powders in an inert atmosphere at low pressure using an electric arc. The Si-OH content of these materials is low, usually less than 30ppm (parts per million by weight)\(^\text{1}\). Other impurities, the most common being Ge, Al or alkali elements, are present in the same amount as in the quartz powder, usually of the order of 10ppm.

**Natural wet (type II),** obtained by melting quartz powders in a H$_2$/O$_2$ flame.

\[^1\text{1ppm} \approx 7.7 \cdot 10^{10}\text{Si-OH groups/cm}^3\text{ in silica}\]
4. Materials, treatments and experimental setups

**Table 4.1**: Samples used in the experiments presented in this Thesis

<table>
<thead>
<tr>
<th>Material (nickname)</th>
<th>Type</th>
<th>Producer</th>
<th>[OH]ppm (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suprasil 300 (S300)</td>
<td>IV (synthetic dry)</td>
<td>Heraeus</td>
<td>&lt; 1 (7.7 · 10$^{16}$)</td>
</tr>
<tr>
<td>Suprasil F300 (F300)</td>
<td>IV (synthetic dry)</td>
<td>Heraeus</td>
<td>5 (3.8 · 10$^{17}$)</td>
</tr>
<tr>
<td>Infrasil 301 (I301)</td>
<td>I (natural dry)</td>
<td>Heraeus</td>
<td>7 (5.4 · 10$^{17}$)</td>
</tr>
<tr>
<td>Silica EQ906 (Q906)</td>
<td>I (natural dry)</td>
<td>Quartz &amp; Silice</td>
<td>20 (1.5 · 10$^{18}$)</td>
</tr>
<tr>
<td>ED-C (EDC)</td>
<td>VAD</td>
<td>Tosoh Quartz</td>
<td>&lt; 1 (7.7 · 10$^{16}$)</td>
</tr>
</tbody>
</table>

The Si-OH content of these materials is in the range 150÷1000ppm, but the impurities concentration is lower than in the powder as they are partially dispersed during the melting.

**Synthetic wet (type III)**, produced by hydrolysis of silicon compounds, as SiCl$_4$, in a H$_2$/O$_2$ flame. The Si-OH content of these materials is higher than 100ppm, and the other impurities are in much lower concentration than in the natural materials, due to the high purity of the reactants.

**Synthetic dry (type IV)**, produced by oxidation of SiCl$_4$ in a water free plasma. The Si-OH content of these materials is very low, usually less than 1ppm, but the Cl content is relevant (usually higher than 100ppm).

Another important technology for the production of silica glass, mainly used for the manufacturing of optical fibers, is the so called **Vapor Axial Deposition** (VAD). In the VAD technology, silica nanoparticles adhere to a rotating silica rod. During this process it is possible to control several properties, as temperature, doping or homogeneity.

In the following, dry materials will be used, because of the necessity to measure changes in the absorption of water related species. In fact OH or H$_2$O related processes will have a great importance in this thesis, and the detection of small changes in their concentrations would be prevented by the intense absorption of wet materials. The samples used, their type, producer, nicknames and OH content are listed in Table 4.1. Samples of size 5 × 5 × 1mm$^3$ were cut from slabs of size 50 × 5 × 1mm$^3$, having the widest surfaces optically polished. Only the Suprasil F300 samples are discs 2mm thick, cut from a cylinder of diameter 6.5mm and length ~ 10cm, and then optically polished.
4.2 Irradiations and thermal treatments

In this section the ionizing radiations used to generate many of the defects studied and the thermal treatments employed to anneal them are described. The latter were performed using two different systems, one of which optimized during this work to carry out treatments at high pressure and temperature in a controlled atmosphere.

4.2.1 $\gamma$ and $\beta$ irradiation

The $\gamma$ radiation emitted by a $^{60}$Co source and $\beta$ rays were used in this thesis to induce point defects in silica samples. The $\gamma$ irradiation were performed in the IGS-3 irradiator of the Department of Nuclear Engineering of the University of Palermo, and at the Kirsten facility of the SCK-CEN Belgian Nuclear Reserch Center. The energies of the $\gamma$ rays emitted by $^{60}$Co are 1.17MeV and 1.33MeV (mean energy 1.25MeV) and the dose rates of the two sources employed were $\sim 3\text{kGy/h}$ and $\sim 60\text{kGy/h}$, respectively.

The $\beta$ irradiation were performed in a LINAC accelerator at the Frascati Research Centre of the ENEA. The energy of the electrons was 3MeV, and the dose rate $\sim 430\text{kGy/h}$. The irradiations were performed at room temperature and in normal atmosphere, at doses up to 10000kGy.

4.2.2 Thermal treatments in normal atmosphere

Thermal treatments were performed to investigate the thermally activated annealing processes involving oxygen deficient point defects in silica. The thermal treatments in normal atmosphere were performed in an electric furnace with maximum operating temperature of about 1100°C, equipped with an internal thermometer and an electronic feedback circuit that allows the temperature to be set within $\pm 3^\circ \text{C}$. The samples experienced isothermal treatments, i.e. a sequence of thermal steps at fixed temperature and of progressively increasing duration. At each step the sample is rapidly ($<5\text{s}$) put on the oven floor, already heated at the preset temperature, and at the end it is extracted from the oven and left to cool to room temperature to perform the measurements. The temperature variation of the system due to the insertion of the sample is of the order of $5^\circ \text{C}$ and it is rapidly compensated within three minutes. Actually, this measured temperature variation of the order of $5^\circ \text{C}$, is mainly due to the rapid income of cold air in the oven when it is opened; this air flow makes the measured temperature appear immediately lower. This does not mean that the temperature of the walls and floor of the oven diminishes of $5^\circ \text{C}$ in the very short time during which the oven is opened ($<5\text{s}$). In fact, due to the very high
4. Materials, treatments and experimental setups

4. Materials, treatments and experimental setups

heat capacity of the material of the walls of the oven, a reasonable assumption is that the temperature of the walls remains almost unperturbed, and that the sample, that is in contact with the floor, reaches equilibrium at the floors temperature. In this scheme the time the sample needs to reach the treatment temperature is not the time in which the measured temperature goes back to the right value, as this measurement is affected by the air flow and the time appears longer. It is instead the time that the sample, with its typical specific heat (\(\sim 0.7 \text{kJ kg}^{-1}\text{K}^{-1}\)) and small mass, needs to reach thermal equilibrium with the floor of the oven with which is in contact. This time can be estimated to be less than 60s.

4.2.3 Thermal treatments in controlled atmosphere: the Parr reactor

The Parr reactor described in this subsection [160], was used to carry out the thermal treatments in controlled atmosphere and the loading experiments. This system was optimized on the occasion of this thesis. The scheme of the instrument is shown in Figure 4.1. The main part of this high temperature and pressure system is a steel cylindrical vessel of volume 240ml in which the samples are placed. A steel cover head equipped with gas charge and discharge pipes, an analogical pressure gauge and a digital pressure transducer to measure the internal pressure close the vessel. The cover head includes also a blind sink used to allocate a thermocouple that measures the temperature inside the vessel (this allocation enables a good result in reading the temperature of the atmosphere inside the vessel). Coned pressure fittings are used for the pipes connections. The vessel is equipped with a split ring cover clamp by which the head of the vessel is clamped to the cylinder through hardened steel bolts. The two sections of the split ring slide into place from the sides without interfering with any fittings attached to the head. The closing force is developed by simply tightening the set of compression bolts in the ring sections with a torque wrench; the torque value correlates to the working pressure of the vessel. The split ring is further tightened by an outer retaining ring. The cylinder and head are sealed by a flexible graphite gasket and a nickel high temperature grease, assuring no gas leakage. After closing the vessel, it is put inside a heater, on the wall of which a second thermocouple is placed. The digital pressure transducer and the thermocouples are connected to a digital controller. The latter is equipped with a feedback system for the heating, assuring the correct temperature reaching. The typical heating time is about two hours, while about six hours are necessary for the reactor to cool to room temperature. The maximum operating temperature and pressure are 500°C and 350bar.

For what concerns the treatments in oxygen and helium, the charging of the gas
4.2. Irradiations and thermal treatments

![Diagram of the Parr reactor]

**Figure 4.1:** Schematic representation of the Parr reactor. (1) sample chamber (2) flexible graphite gasket (3) charge pipe (4) discharge pipe (5) thermocouple sink (6) analogical pressure gauge (7) digital pressure transducer.

is performed at room temperature by connecting a bomb to the charge pipe. High purity He and O\textsubscript{2} were used, the main impurity being water with a concentration lower than 3ppm-mol. At the beginning gas fluxes through the sample chamber for some minutes, then the discharge pipe is closed. The initial pressure of the gas in the chamber at room temperature is set at a value such to obtain the target pressure at the end of the heating, according to the perfect gas law. Water vapour was instead generated during the treatments by putting liquid high purity deionized water (resistivity $\sim 18.2\text{M}\Omega/\text{cm}$) inside the sample chamber. The amount of water was calculated in such a way to assure the reaching of the maximum pressure at a given temperature, and at the same time to guarantee security conditions.
4. Materials, treatments and experimental setups

The samples can be placed in the sample chamber in two different ways. The simplest one consists in locating the sample on the chamber floor. This procedure was followed in every experiment not involving water. When the treatments are performed in water vapour atmosphere, a sample holder has to be used to avoid the sample getting in contact with liquid water. It is known, in fact, that silica is strongly damaged in these conditions [83, 161]. For this reason we built a stainless steel sample holder able to keep the sample in contact with the atmosphere but not with the liquid. In both cases the fact that the reactor floor and the sample holder are made of conducting materials guarantees a good thermal contact.

4.3 EPR spectrometer

In an EPR experiment a sample is placed in a microwave resonant cavity, located between the polar expansions of an electromagnet. The homogenous and uniform static magnetic field \( H \) created by the electromagnet determines a Zeeman splitting of the electronic energy levels. A microwave magnetic field \( H_1 \), normal to \( H \), is fed inside the cavity through a waveguide. When the \( H \) value satisfies the resonance condition (See Section 3.1)

\[
\hbar \omega = g \cdot \mu_B \cdot H
\]  

(4.1)

the oscillating field \( H_1 \) induces electronic transitions between the Zeeman sublevels. The microwave radiation that is not absorbed by the sample is reflected to the detection system.

A magnetic field \( H_m \) (modulation field) oscillating at low frequency (\(~100\)kHz) and parallel to \( H \) is generated by a couple of coils placed on the two sides of the cavity, and superimposes to \( H \). This modulation field allows an improvement in the signal to noise ratio, through the lock-in detection system described in Subsection 4.3.3. A detector generates a current proportional to the square root of the reflected microwave power. This current reaches a group of electronic devices, that optimize the signal to noise ratio and isolate the signal related to the sample absorption. The measurement of the microwave power absorbed by the sample as a function of the magnetic field \( H \) amplitude gives the EPR spectrum [143–147].

A scheme of the Bruker EMX spectrometer used to carry out the measurements presented in this thesis is shown in Figure 4.2 The system components are described in more details in the following subsections.
4.3. EPR spectrometer

Figure 4.2: Schematic representation of the EPR spectrometer.

4.3.1 Resonant cavity

The resonant cavity is a metallic box with high conductivity walls, in which the microwave energy is stored [143–147]. Its dimensions are comparable to the microwave wavelength. The resonance frequency of the spectrometer used is \( \approx 9.8\,\text{GHz} \) (X band), the cavity employed has rectangular shape (See Figure 4.3(a)) and is placed at the centre of the polar expansions of the electromagnet.

Each normal mode of the cavity is characterized by a specific distribution of electric and magnetic fields. The normal mode we considered is named TE\(_{102}\), and its electric and magnetic fields distributions are represented in Figure 4.3(b) and (c).

The sample location inside the cavity is such that at this position the oscillating magnetic field has the maximum amplitude and the electric field is the lowest. This avoids dielectric losses. The coupling between the waveguide and the resonant cavity is obtained through a small hole in the cavity wall, called iris. A tunable screw allows the coupling optimization [147].

A quality factor \( Q \), that measures the efficiency of the cavity in storing energy,
4. Materials, treatments and experimental setups

**Figure 4.3:** (a) Resonant cavity of rectangular shape. The arrow indicates the iris, which connects the resonant cavity to the wave guide. Electric field lines in the YZ plan (b) and magnetic field lines in the XZ plan (c) for the TE\(_{102}\) mode. Adapted from Ref.[147]

is defined as [143]

\[
Q = \frac{2\pi \text{(Stored energy)}}{\text{Dissipated energy per cycle}} \tag{4.2}
\]

If the only dissipation were the one due to the resistivity of the cavity walls, the quality factor would be named \(Q_u\). However, in real cavities, there are holes for the insertion of the sample and for the coupling of the cavity with the waveguides. The radiative losses through these holes give a contribution to \(Q\), named \(Q_r\). A further contribution is associated to dielectric losses, and it is called \(Q_\varepsilon\). Finally, the absorption of the sample when the resonance condition is verified makes the quality factor diminish, and this fact can be described by a contribution \(Q_\chi\) to the quality factor. The total quality factor can then be expressed as

\[
\frac{1}{Q_{TOT}} = \frac{1}{Q_u} + \frac{1}{Q_r} + \frac{1}{Q_\varepsilon} + \frac{1}{Q_\chi} \tag{4.3}
\]

A growth of \(Q_{TOT}\) implies an enhancement in the signal to noise ratio and in the spectrometer sensitivity [143].
4.3.2 Microwave source and electromagnet

The microwave source used in our spectrometer is a Gunn diode. A Gunn diode is a GaAs device that generates microwave radiation when subjected to a direct voltage of about 10V [147, 162]. The power of the radiation generated by the Gunn diode practically does not depend on the frequency, in the frequency range of operation of the device.

The microwave power arriving from the source on the sample is adjusted by a variable attenuator (See Figure 4.2). The power attenuation with respect to a reference power, that is equal to 200mW for the Bruker EMX spectrometer, rather than the power itself is usually measured, according to the expression

$$\text{Att(dB)} = -10 \cdot \log_{10} \frac{\text{power transmitted to the cavity}}{\text{maximum power emitted by the source}}$$

(4.4)

When the static magnetic field \(H\), during the acquisition of a spectrum, assumes the resonance value, the resonance frequency of the cavity can change. As a consequence the detected EPR signal is not proportional to the absorbed power only due to transitions between Zeeman levels. To avoid this effect the microwave frequency of the source needs to be instantaneously fixed to the cavity resonance frequency. EPR spectrometers are then equipped with an automatic frequency control system (AFC) [143, 147]. In the EMX spectrometer the AFC system modulates the microwave signal at 76.8kHz. A part of this signal, opportunely corrected in amplitude and phase, is superimposed to the signal reflected from the cavity. When the frequency of the source is the same as that of the cavity the 76.8kHz component in the signal is zero. When this does not happen, a feedback error signal corrects the frequency of the Gunn diode, so that it has the same value as the resonance frequency of the cavity [143, 147].

The electromagnet needs to generate a constant and homogeneous magnetic field over the sample volume. The electromagnet used in these experiments generates a magnetic field of maximum amplitude of \(\sim 1T\), with a homogeneity of \(10^{-3}\) mT on a volume \(\Delta X \times \Delta Y \times \Delta Z = 22 \times 10 \times 5\) mm\(^3\) located at the centre of the gap between the poles of the electromagnet. The magnetic field amplitude value is measured by a Hall probe, that generates a voltage proportional to the magnetic field perpendicular to the probe itself, with a precision of \(8 \cdot 10^{-2}\) mT. A feedback circuit compares the voltage measured by the Hall probe with a reference value, and sends an error signal to the electromagnet to stabilize the correct value for the magnetic field. As a consequence of the experimental uncertainty on the Hall probe measurements, the absolute position of a resonance line is undetermined by the same amount.
### 4.3.3 Detection system, modulation system and output circuit

A Schottky diode is used as detector in the Bruker EMX spectrometer. It converts the microwave power reflected from the cavity into an electrical current. The better sensitivity is obtained by making the diode work in linear region, in which the current generated by the diode is proportional to the square root of the incident microwave power. This condition is obtained for incident microwave power greater than 1mW. A further signal, named *bias* is sent to the diode to make this condition satisfied. This signal, opportunely corrected in amplitude and phase (See Figure 4.2), superimposes to the one reflected from the cavity, ensuring that the incident power is sufficient for the diode to work properly.

A *lock-in* detection system is used to enhance the sensitivity of the EPR spectrometer. As already stated at the beginning of this paragraph, a modulation field, of variable amplitude and frequency, is applied parallel to $\mathbf{H}$. This field is generated by two coils powered by an alternate current generator. In this way a modulation in the paramagnetic system response is introduced. In fact, corresponding to the oscillations between the total magnetic field values $H_a$ and $H_b$, the power absorbed by the sample and that reflected oscillate too. As a consequence the detector current oscillates between the values $i_a$ and $i_b$ at the same frequency (See Figure 4.4). This signal reaches a *lock-in* amplifier, that amplifies and rectifies the signal components at the modulation frequency and with the right phase alone. The amplifier output is a voltage signal. The reference signal for the *lock-in* amplifier is taken from the modulation source, and corrected in phase to account for the different paths. This technique allows to enhance the signal to noise ratio [143, 147].

An intrinsic consequence of this modulation system is that the detected signal is proportional to the first derivative of the absorption curve. In fact the oscillation amplitude of the detector current, $|i_b - i_a|$, is detected. This quantity is proportional to the slope of the absorption curve in the midpoint of the interval between $H_a$ and $H_b$ (See Figure 4.4). It is also proportional to the modulation field amplitude for opportune values of this amplitude. To avoid distortion in the EPR lineshape, and to make the signal proportional to the first derivative of the absorption curve, the modulation field amplitude needs to be opportunely set. It has to be significantly lower than the absorption line width.

The *lock-in* amplifier output signal can be raised by changing the amplifier gain and is filtered by a low pass RC circuit, characterized by a time constant $T_{\text{const}}$ that can be varied between 0.01ms and 5.24s. This filter cuts the noise components at frequencies higher than $1/T_{\text{const}}$, and allows an improvement in the signal to noise ratio. Finally the signal reaches an integrator, that integrates it for a time, named
conversion time $T_{\text{conv}}$, that can be varied between 0.32ms and 2.62s. The integrated signal is converted to a digital signal and transmitted to a computer.

### 4.3.4 Concentration measurements of paramagnetic defects

As discussed in details in Section 3.1.4, in non saturation conditions the area of the absorption line is proportional to the number of spins. All the EPR measurements reported in the following were performed in non-saturation conditions. The concentration of paramagnetic point defects in this thesis was hence determined by comparing the double integral of the unsaturated EPR line to that of a reference sample with known spin concentration [143, 147]. The latter is a $\gamma$-irradiated silica sample whose $E'_\gamma$ concentration was determined by spin echo experiments [163]. The double integral normalized by the square root of the incident radiation power, the modulation field amplitude, the conversion time, the receiver gain and the sample volume is proportional to the concentration through the relation

$$\text{Concentration} = (\text{Normalized double integral}) \cdot 2.4 \cdot 10^{16} \text{centres/cm}^3 \quad (4.5)$$
4. Materials, treatments and experimental setups

We have estimated an absolute accuracy of 20% in this procedure; the relative concentrations are affected by a 5% error.

4.4 Spectrophotometer

The optical absorption measurements in the UV spectral range were carried out using a Jasco V-560 spectrophotometer. The scheme of this instrument is shown in Figure 4.5. The light emitted by a deuterium discharge lamp, operating in the wavelength range between 400nm and 190nm, is made monochromatic by a double monochromator employing a Czerny-Turner plane grating (600 lines/mm). The possible bandwidth values range from 0.1nm to 10nm. A beam splitter separates the monochromatic light in two beams, one of which goes through the sample, while the other one is used as reference. A photomultiplier measures the light at the end of these two paths, and gives a measurements of the sample absorbance (Abs). Even if the measurements presented in the following are performed between 190 and 400nm, the allowed wavelength range extends up to 900nm, a tungsten lamp being used between 400nm and 900nm instead than the deuterium lamp. The wavelength accuracy is ±0.3nm (at a spectral bandwidth of 0.5nm) The photometric range extends up to 5Abs, with an accuracy of ±0.002Abs.

Figure 4.5: Schematic representation of the Spectrophotometer Jasco V-560.
4.5 Spectrofluorometer

Steady state photoluminescence (PL) measurements were carried out by a Jasco FP-6500 spectrofluorometer. The scheme of the instrument is shown in Figure 4.6. The excitation light is emitted by a 150W Xenon discharge lamp. It is dispersed by a monochromator (Mono1), based on a grating with 1800 lines/mm, that permits to select an excitation wavelength $\lambda_{\text{exc}}$ between 220nm and 750nm, with a bandwidth $\Delta\lambda_{\text{exc}}$ varying between 1nm and 20nm. The monochromatic light is separated in two beams by a beamsplitter. One of the beams is directed on the sample, that is placed in a standard 45° backscattering configuration (reflected light is directed away from the detector). The emitted light is collected by a monochromator (Mono2) that selects an emission wavelength $\lambda_{\text{em}}$ with a selectable bandwidth $\Delta\lambda_{\text{em}}$, and finally it is detected by a photomultiplier (PMT1). The other part of the beam goes to a second photomultiplier (PMT2) that measures its intensity. This measurement is used to correct the measurements performed by PMT1 with respect to the temporal fluctuations of the Xenon lamp intensity.

The presence of two monochromators allows to perform two different kinds of measurements. In the first kind of acquisition, named emission spectrum, the excitation wavelength $\lambda_{\text{exc}}$ is fixed and the emitted light is detected as a function of the emission wavelength $\lambda_{\text{em}}$; this kind of detection measures the amplitude and spectral shape of the emission band due to the decay of the point defect from the excited to the ground electronic state (See Section 3.2). In the other one, named excitation...
4. Materials, treatments and experimental setups

spectrum, the emission at a fixed wavelength $\lambda_{em}$ is detected as a function of the excitation wavelength $\lambda_{exc}$, and it represents the efficiency of the emission process as a function of the excitation wavelength. All the PL emission measurements reported in the following and aiming to detect ODC(II) centres are performed by exciting with 248nm light and detecting the light emitted between 250nm and 500nm with bandwidths $\Delta \lambda_{em} = 3\text{nm}$ and $\Delta \lambda_{exc} = 5\text{nm}$. PL spectra are corrected for the spectral response of the monochromators and of the detection system. The precision in the estimation of the luminescence intensity is 10%.

4.5.1 Concentration measurements of optically active defects

The concentration of optically active defects in silica can be evaluated from optical absorption measurements by using the Smakula’s equation [1]

$$Nf = n \left( \frac{E_0}{E_{eff}} \right)^2 \alpha_{max} \Gamma \Delta \cdot 9.111 \cdot 10^{15} \text{eV}^{-1} \text{cm}^{-2} \quad (4.6)$$

where $N$ is the concentration of absorbing defects, $f$ the oscillator strength, $n$ the refractive index, $E_0$ the electric field of the incident light, $E_{eff}$ the effective electric field acting on the defect (larger than $E_0$ due to the polarization of the medium surrounding the defect), $\alpha_{max}$ and $\Delta$ the amplitude and full width at half maximum (FWHM) of the absorption band $^{**}$, and $\Gamma$ a numeric coefficient depending on the bandshape $^{††}$.

The effective field term $n(E_0/E_{eff})^2$ for silica is close to unity from the near IR to UV spectral range. As a consequence Equation 4.6 can be rewritten [1]

$$Nf = \alpha_{max} \Gamma \Delta \cdot 9.111 \cdot 10^{15} \text{eV}^{-1} \text{cm}^{-2} \quad (4.7)$$

One of the optically active defects studied in this thesis, the ODC(II) centre, is induced by irradiation together with other optically active defects. The absorption band of the ODC(II) centre (B$_{2\alpha}$ band centred at 5.02eV) is located in the same spectral region as the much more intense band of the E’ centres (centred at 5.8eV) [18]. This fact prevents the direct valuation of the ODC(II) concentration from their absorption band using the Smakula’s formula. As a consequence an alternative procedure, described in the following, was adopted. Unlike the absorption band, the

$^{**}$For the absorption band B$_{2\alpha}$ centred at 5.02eV attributed to the ODC(II) centres $f=0.15$ and $\Delta=0.3$eV. For the band at 5.8eV of the E’ centres $f=0.4$ and $\Delta=0.8$eV and for the 4.8eV OA band of the NBOHC $f=0.2$ and $\Delta=1.05$eV. [18]

$^{††}$For a Gaussian shape $\Gamma \approx 1.0645$ [1]
photoluminescence band at 4.4eV of the ODC(II) centres, excited at 5eV, is isolated and clearly detectable in all the samples examined. Moreover in low absorption conditions the intensity of emission is proportional to the absorption coefficient, according to Equation 3.28. The intensity of luminescence is corrected by a factor \( \frac{\alpha d}{1 - e^{-\alpha d}} \), where \( \alpha \) is the absorption coefficient at the excitation frequency, to account for the absorption of the sample. This expression was derived by using expression 3.28 for the intensity of luminescence, and considering that every infinitesimal slab of the sample is excited by light whose intensity can be determined through Lambert-Beer's law (Equation 3.21). The ODC(II) concentration was then evaluated by comparing the corrected PL intensity at 4.4eV of the samples under examination with that of a reference sample in which the absorption band at 5.02eV was clearly visible and isolated.

4.6 Raman measurements

Raman measurements were performed using a Bruker RAMII Fourier Transform Raman spectrometer, employing a 500mW Nd:YAG laser (1064nm) as light source and a InGaAs diode as detector. The laser beam is focused on the sample, whose geometric position can be adjusted to make the detection of the diffused light more efficient. The diffused light is collected in the same direction as the incident beam (back scattering geometry), filtered to cut the dominant Rayleigh elastic scattering, and directed to a Michelson interferometer. The scheme of the interferometer is shown in Figure 4.7. The beam splitter separates the incident light in two beams, one of which goes to a fixed mirror, while the other one to a moving mirror. The reflected beams superimpose at the beamsplitter on their way back from the mirrors. If the two mirrors are at the same distance from the beam splitter the reflected signals are in phase, otherwise they experience a phase difference proportional to the path difference. The reflected beams are then directed to the detector, that measures the signal intensity as a function of the path difference, also called interferogram. The interferogram depends on the spectral composition of the incident beam, and for each relative position of the mirrors specific wavelengths give maxima or minima at the detector. The Raman spectrum is obtained by making the Fourier transform (DFT) of the interferogram.

The sampling frequency of the spectrometer is fixed, as a consequence the lower the speed of the moving mirror the higher the density of points in the interferogram. Moreover the position of the moving mirror is detected by a laser pointing system, guaranteeing a high precision in determining the sampling interval (\( \delta x \)) of the interferogram. This fact implies that the spectral uncertainty is lower than in
4. Materials, treatments and experimental setups

Figure 4.7: Schematic representation of a Michelson interferometer.

other spectroscopic techniques. The signal to noise ratio is improved by taking for each point in the interferogram the average value of several samplings. The spectra presented in the following chapters were acquired accumulating 500 samplings, with a spectral resolution of 5 cm$^{-1}$.

Raman measurements will be used in the following to estimate the O$_2$ content of the samples. In fact, an O$_2$ photoluminescence band at 1272.2 nm excited at 1064 nm (Nd-YAG laser) superimposes to the SiO$_2$ Raman spectrum [164–166]. This band is due to the forbidden transition $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ [164–166]. The intensity of this PL band is calibrated against the neighbouring intrinsic Raman scattering bands of SiO$_2$ at $\sim$1060 cm$^{-1}$ and $\sim$1200 cm$^{-1}$, in accordance with literature data [164–166]. This choice was made as they are well defined in all the spectra and the closest to the PL band. This latter characteristic minimizes the influence of eventual uneven spectral sensitivity of the instrument on the intensity ratio. In this way the O$_2$ content of samples having an O$_2$ concentration higher than $\sim$5·10$^{16}$ molecules/cm$^3$ is estimated, with an uncertainty of $\sim$20%.

4.7 InfraRed absorption measurements

IR absorption spectra were obtained by using a Bruker Vertex 70 Fourier transform IR single-beam absorption spectrometer, mounting a MIR globar (i.e. an U-shaped silicon carbide piece) light source and a DLaTGS detector operating at room temperature and covering a spectral range from 4000 cm$^{-1}$ to 400 cm$^{-1}$. This instru-
4.7. InfraRed absorption measurements

The measurement employs the same interferometer as the Raman spectrometer described in the previous paragraph. Spectra were acquired with a spectral resolution of $1\text{cm}^{-1}$. The absorption spectrum of the empty beamline suitably normalized was subtracted from every spectrum to suppress the effects of water vapour. The precision of the band amplitude values is 1%.
Chapter 5

Intrinsic generation of OH groups in dry silica upon thermal treatments

Starting from this chapter, the experiments performed and the results obtained will be discussed. In this work the interest has been focused on the relevance of the presence and diffusion of small reactive molecules (H₂O, O₂, H₂) in silica, as they can strongly affect the properties of this material. Both the effects on unirradiated silica and its radiation hardness, and the effects on radiation induced oxygen deficient point defects will be discussed in the following chapters. Evidences on the influence of the intrinsic disorder of silica on some of these processes will be also reported and discussed.

In this chapter the effects of thermal treatments on unirradiated synthetic dry silica are discussed. A change in the OH content of this kind of materials is observed, and it is explained in terms of reactions between hydrogen and reticular sites.

5.1 Introduction

As discussed in detail in the introductory chapters, silanol groups (SiOH) concentration is a very important parameter in the characterization of silica materials. In fact OH groups are one of the main impurities in silica glass, and their optical absorption bands affect the transparency of silica in the IR and v-UV spectral ranges. On the other hand they are believed to improve the radiation hardness of silica irradiated by light sources of energies lower than 7eV by relaxing the glass structure [89]. For these reasons great efforts were made to improve the production techniques, and a huge number of works concerning both the spectral features of OH groups and
their generation processes were published, aiming to obtain OH-free materials. In these studies OH generation is usually observed as a consequence of reactions of silica with thermally uploaded molecules (See Section 1.1.4).

In this chapter we will show that OH groups are generated in originally dry silica upon thermal treatments in inert (helium) atmosphere. The observation of such effect upon treatments in helium atmosphere will lead to the conclusion that the observed effect is intrinsic, i.e. only due to molecules already present in the material since its synthesis.

This first experimental evidence of an intrinsic generation of OH groups in originally dry materials demonstrates that the important material property of being OH-free is not permanent, and can change upon thermal treatments. This fact has a fundamental importance for all those applications in which dry materials are needed.

5.2 Experiments and results

The experiments presented in the following were performed on two kinds of synthetic dry silica materials, S300 and EDC, both with $[\text{OH}] < 8 \cdot 10^{16} \text{cm}^{-3}$. Raman measurements were performed to detect the eventual presence of interstitial $\text{O}_2$. In this kind of measurements, performed using a Nd-YAG laser (1064 nm) as light source, the $\text{O}_2$ photoluminescence band at 1272.2 nm in fact superimposes to the SiO$_2$ Raman spectrum of samples having an $\text{O}_2$ concentration higher than the detection limit of $5 \cdot 10^{16}$ molecules/cm$^3$ [164–166]. The Raman spectra of both the S300 and EDC are shown in Figure 5.1. The 1272.2 nm PL band (Raman shift 1538 cm$^{-1}$) was not observed in these samples, establishing an upper limit for the $\text{O}_2$ concentration.

Two samples, one for each of the two materials, were contemporaneously thermally treated in Helium atmosphere at 390°C for 164h at the pressures of 2.7bar or 180bar. High purity Helium was used. Water is the main impurity possibly present, with a concentration lower than 3ppm. This treatments were performed in the Parr reactor described in Paragraph 4.2.3. The nicknames and treatments of the samples are listed in Table 5.1.

The infrared (IR) absorption spectra of the samples were measured before and after the treatments, to detect the OH absorption band at 3670 cm$^{-1}$. The concentration of OH groups was estimated using the Lambert Beer law [167]

$$ A = \epsilon C d $$

(5.1)

where $A$ is the absorbance at the band maximum, $\epsilon$ is the extinction coefficient [167], $C$ is the concentration of absorbing species, and $d$ is the path length of light in the sample.
Figure 5.1: Raman spectra of pristine S300 (continuous line) and EDC (dashed line) samples, called S300/0 and EDC/0 respectively.

Table 5.1: Nicknames of the samples and details of the treatments in helium atmosphere. Concentration of OH groups in the samples after the thermal treatments.

<table>
<thead>
<tr>
<th>nickname</th>
<th>He Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Treatment Time (h)</th>
<th>generated [OH] (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDC/He/2.7</td>
<td>2.7</td>
<td>390</td>
<td>164</td>
<td>1.9 · 10¹⁸</td>
</tr>
<tr>
<td>S300/He/2.7</td>
<td>2.7</td>
<td>390</td>
<td>164</td>
<td>1.2 · 10¹⁸</td>
</tr>
<tr>
<td>EDC/He/180</td>
<td>180</td>
<td>390</td>
<td>164</td>
<td>7.3 · 10¹⁸</td>
</tr>
<tr>
<td>S300/He/180</td>
<td>180</td>
<td>390</td>
<td>164</td>
<td>5.4 · 10¹⁸</td>
</tr>
</tbody>
</table>
5. Intrinsic generation of OH groups in dry silica upon thermal treatments

Figure 5.2: Infrared absorption spectra of the pristine material, sample S300/0 (dash-dotted line), and of the samples S300/He/2.7 (dashed line) and EDC/He/2.7 (continuous line) thermally treated at 390°C in He atmosphere at 2.7bar.

In Fig.5.2 the IR spectra of one of the samples before the treatments, named S300/0, and of the two samples treated in He at 2.7bar are shown. The ED-C and S300 samples had undistinguishable IR spectra before the treatments, and the IR absorption band at 3670 cm\(^{-1}\) of the SiOH groups was not observed (see dash-dotted line in Fig.5.2).

The IR absorption band at 3670 cm\(^{-1}\) was instead observed in all the samples after the treatments, the order of magnitude of the band amplitude being comparable in all the samples. In Fig.5.2 it can be observed that, even if this band is clearly detectable in both the samples treated in He at 2.7bar, its intensity is higher in the EDC/He/2.7 than in the S300/He/2.7. The same relationship between the intensities of this band in the two different materials was observed in the samples treated at 180bar, the EDC/He/180 band being more intense than the S300/He/180 band, as can be observed in Figure 5.3.

This comparison can also be quantitatively made by looking at the OH concentrations reported in Table 5.1. It can be observed that the OH concentration ratio between the S300/He/180 and EDC/He/180 samples (~1.4) is almost comparable to that between the S300/He/2.7 and EDC/He/2.7 samples (~1.6).

A further experiment showed that thermal treatments in O\(_2\) generate OH too. In
5.2. Experiments and results

Figure 5.3: Infrared absorption spectra of the pristine material, sample S300/0 (dash-dotted line), and of the samples S300/He/180 (dashed line) and EDC/He/180 (continuous line) thermally treated at 390\(^\circ\)C in He atmosphere at 180bar.

In this experiment another couple of samples, named S300/O2/180 and EDC/O2/180, was thermally treated in Oxygen atmosphere at 390\(^\circ\)C for 164h at 180bar, following the same procedure as the helium treatments. The maximum water content in the oxygen gas was the same as in the helium gas (<3ppm). The nicknames and treatments of the samples are listed in Table 5.2.

The growth of the above mentioned PL band of O\(_2\) peaked at 1272.2nm (Raman shift 1538cm\(^{-1}\)) is observed after the O\(_2\) treatment, accounting for the effectiveness of oxygen loading, as can be observed in Figure 5.4.

Table 5.2: Nicknames of the samples and details of the treatments in oxygen atmosphere. Concentration of OH groups in the samples after the thermal treatments.

<table>
<thead>
<tr>
<th>nickname</th>
<th>O(_2) Pressure (bar)</th>
<th>Temperature ((^\circ)C)</th>
<th>Treatment Time (h)</th>
<th>generated [OH] (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDC/O2/180</td>
<td>180</td>
<td>390</td>
<td>164</td>
<td>2.0 \cdot 10^{18}</td>
</tr>
<tr>
<td>S300/O2/180</td>
<td>180</td>
<td>390</td>
<td>164</td>
<td>1.3 \cdot 10^{18}</td>
</tr>
</tbody>
</table>
5. Intrinsic generation of OH groups in dry silica upon thermal treatments

**Figure 5.4:** Raman spectra of the pristine S300 (dashed line) and of the sample S300/O2/180 (continuous line) thermally treated at 390°C in O2 atmosphere at 180bar. The PL band of interstitial O2 at 1538 cm\(^{-1}\) excited by the NdYAG laser is also observed in the Raman spectrum of the O2 treated sample.

The IR absorption spectra of the two samples treated in O2 are shown in Figure 5.5. It can be observed in this Figure and in Table 5.2 that the OH concentration ratio between the S300/O2/180 and EDC/O2/180 samples (~1.5) is comparable to those between the helium treated samples (~1.4 ÷ 1.6), whereas the absolute efficiency of OH generation is lower in samples treated in O2 than in He at the same pressure.

In Figure 5.6 a comparison between the EDC/He/180 band shape and a typical OH absorption band (as detected in a Suprasil 1 sample supplied by Heraeus, with [OH]~ 7 \(\cdot\) 10\(^{19}\) cm\(^{-3}\)) is shown. The other samples subjected to treatments in controlled atmosphere reported in this Section show a comparable band shape as the EDC/He/180.

As regards the reference sample, it is known that the band shape of native OH groups is the same for every high purity silica glass, not depending either on the manufacturing method or on the OH concentration [80] (See Subsection 1.1.4). As a consequence the band shape of the Suprasil 1 sample shown here is representative of every native OH band.

It can be observed that the band shape of induced OH groups (continuous line)
Figure 5.5: Infrared absorption spectra of the pristine material, sample S300/0 (dash-dotted line), and of the samples S300/O2/180 (dashed line) and EDC/O2/180 (continuous line) thermally treated at 390°C in O2 atmosphere at 180bar.

differs from the usual shape of native OH (dashed line) at low wavenumbers.

5.3 Discussion

The data presented in the previous paragraph clearly show that thermal treatments create OH groups in originally dry silica. Treatments in inert atmosphere were carried out to limit the possibility of reactive molecular species to be absorbed and to influence the reaction processes taking place in the materials.

In many studies the generation of silanol groups was in fact attributed to reactions involving water, as for example the reaction of water with the glass network [82, 83, 92]

$$\equiv Si - O - Si \equiv +H_2O \rightleftharpoons 2 \equiv SiOH$$  \hspace{1cm} (5.2)

or with an oxygen vacancy

$$\equiv Si - Si \equiv +H_2O \rightarrow \equiv SiOH+ \equiv SiH$$  \hspace{1cm} (5.3)
5. Intrinsic generation of OH groups in dry silica upon thermal treatments

**Figure 5.6:** Normalized infrared absorption spectra of the sample EDC/He/180 (continuous line) and of a reference sample (Suprasil 1, see text) with a typical band shape for the 3670 cm$^{-1}$ absorption band (dashed line).

The reaction
\[
\equiv \text{SiCl} + H_2O \rightarrow \equiv \text{SiOH} + HCl
\]  
was also recently observed in silica glass containing SiCl [81] (For more details on these Reactions see Subsection 1.1.4).

Other studies [81, 84] gave evidence of the generation of OH groups in low OH synthetic silica after exposure to a hydrogen atmosphere at temperatures higher than 400°C. Some authors proposed the reaction
\[
2H_2 + O_2 \rightarrow 2H_2O
\]  
between the diffusing hydrogen and oxygen molecules uploaded in the sample by previous thermal treatments or already present in materials produced in oxygen rich environments [81, 86]. This Reaction creates water, that could then participate to one of the above mentioned Reactions 5.2, 5.3 or 5.4. The reactions of $H_2$ with regular
network \[93\]

\[\equiv Si - O - Si \equiv +H_2 \rightarrow \equiv SiOH + \equiv SiH \]  
(5.6)

or peroxy linkages \[84, 85\]

\[\equiv Si - O - O - Si \equiv +H_2 \rightarrow 2 \equiv SiOH \]  
(5.7)

were also proposed.

To evaluate the possibility that the generation of OH groups is due to reactions with residual H\(_2\)O in the helium gas, we estimated the maximum amount of water possibly introduced in the sample chamber together with helium, basing on the nominal H\(_2\)O content in the helium bomb used. We calculated that the maximum number of H\(_2\)O molecules in the whole chamber for the 2.7bar treatment is \(< 2 \cdot 10^{16}\). This number is lower than the number of molecules needed to account for the overall observed OH content of the two samples \(\simeq 8 \cdot 10^{16}\).

Moreover, for both the 180 bar and 2.7 bar treatments the two samples of Suprasil 300 and ED-C were treated at the same time experiencing exactly the same atmosphere, pressure and temperature conditions. As a consequence, if the generation of OH groups were due to reactions with residual H\(_2\)O in the Helium gas, the effect should be the same in the two materials, in contrast with the observed systematic higher OH generation efficiency in the ED-C samples with respect to Suprasil 300. The comparable OH concentration ratios between the two materials, independent from the treatment, suggests hence that the OH generation is related to some intrinsic characteristics of the materials, as their impurity content.

Finally we can also observe that a small difference, only a factor \(\sim 4\), is observed by varying the pressure, and as a consequence the residual H\(_2\)O content in the atmosphere, of almost two orders of magnitude. This is in contrast with what expected for the absorption of molecules from the atmosphere. In fact, as long as Henry’s law is valid for molecular dissolution, the molecule concentration inside the sample should be proportional to pressure \[92, 112\]. These facts let us exclude that in this experiment the observed OH groups were the product of the reaction of the matrix with residual H\(_2\)O in the treatment atmosphere.

The possibility to exclude contribution of residual H\(_2\)O in the treatment atmosphere leads to conclude that the OH generation can take place as an intrinsic process, completely due to reactions between network sites, either normal or not, and hydrogen related chemical species that are already present in the material since its production. The fact that the OH generation efficiency slightly grows on increasing pressure (See Table 4.1) could be ascribed to changes in the diffusion parameters.
Once it was established that the generation of OH groups observed here is intrinsic, we will now discuss some possible reaction paths leading to such generation. We will consider the reactions observed in the past to be responsible for OH generation and we will hypothesize that they can also take place involving molecules already present in the materials. This latter hypothesis makes sense as the cited diffusing molecules are hydrogen, water and oxygen, that are known to be present in some kinds of silica.

The silanol generation through Reactions involving water (5.2, 5.3 or 5.4) can be excluded as no significant change in the IR absorption of $\text{H}_2\text{O}$ was observed (See the $3000 \div 3500\text{cm}^{-1}$ region [90] in Figures 5.2 and 5.3). The sequence of Reaction 5.5 followed by Reactions 5.2, 5.3 or 5.4 can not be responsible for the OH generation too. In fact the concentration of $\text{O}_2$ in these samples is lower than $5 \cdot 10^{16}$ molecules/cm$^3$, and this oxygen amount is not sufficient to produce the quantity of water necessary to generate the observed OH concentration ($\sim 10^{18}$ molecules/cm$^3$). Moreover, if Reaction 5.5 were effective, a change in the water content of the samples could be expected, and it was not observed.

As a consequence the silanol generation process during thermal treatments in inert atmosphere is probably due to reactions of $\text{H}_2$ with regular network (Reaction 5.6) or peroxy linkages (Reaction 5.7).

It can be shown that these reactions are both effective. By comparing the spectra shown in Figure 5.6 it was observed that the band shape of induced OH groups (continuous line) differs from the usual shape of native OH (dashed line) in the low wavenumbers region of the absorption band. It is accepted that hydrogen bonded pairs of OH groups contribute to the absorption band in this spectral region, while free single OH groups contribute to the high wavenumbers region of the absorption band [80]. Reaction 5.6 creates a single OH group, contributing to the high wavenumber part of the absorption band. Reaction 5.7 would create two OH groups in the same network site, leading to the enhancement of the bonded OH contribution to the band shape. As a consequence it can be guessed that both Reactions 5.7 and 5.6 contribute to OH generation, and that the difference in the band shape is due to a different ratio between the efficiencies of these reactions in this kind of treatments with respect to the OH generation during the glass synthesis.

The lower OH generation efficiency upon thermal treatments in oxygen atmosphere with respect to helium atmosphere could be ascribed to the possible reaction of hydrogen with excess oxygen, according to Equation 5.5, reducing the available hydrogen. However it remains an open problem that requires further investigation, because of the lack of direct experimental evidences. We acknowledge that it is not
an easy issue, and that more experiments are needed to solve it. However, it is worth noticing that the simple model proposed allows to point out that the OH generation mechanism is intrinsic, and involves hydrogen molecules already present in the material.

5.4 Conclusions

In summary we demonstrated that an intrinsic generation mechanism of OH groups exists in synthetic, nominally dry, silica. Differently from previous observed growths of the OH concentration due to reactions between reticular sites and molecules absorbed from the atmosphere, the one observed here is related to reactions with diffusing molecules already present in the material. The OH generation process observed is suggested to consist in the reaction of $\text{H}_2$, already present inside the samples, with peroxy linkages and regular network sites. As a consequence, originally dry materials can lose this property when thermally treated. This OH generation process is effective even at relatively low temperatures, as 390°C, and in inert atmosphere. For these reasons it should be taken into account in those applications for which OH free materials are needed.
Chapter 6

High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

In this chapter the effects of oxygen loading on the radiation hardness of silica is discussed. Strong changes are induced in the concentrations of many radiation induced point defects, and as a consequence on the optical and magnetic properties of a-SiO$_2$. These changes are suggested to arise either from the direct effect of the presence of oxygen or, in some cases, from high temperature and pressure effects. In both cases the differences observed will be attributed to modifications of the number of precursor sites for the defects.

6.1 Introduction

As reported in Chapter 1, technological impurities as hydrogen, oxygen, chlorine or fluorine are introduced even in so-called "extremely pure" silica during the glass synthesis or by subsequent treatments [137], and are ubiquitous over the network, either bonded or dissolved as molecular species in the interstitial sites of the matrix. In the previous chapter we showed that the original properties of amorphous silicon dioxide, as its OH content, can be altered due to thermally activated reactions with molecules contained in amorphous SiO$_2$.

These impurities are also known to strongly affect the nature and concentration of radiation induced point defects [43]. As mentioned in Section 1.2 for example, hydrogen loading was widely studied and it is known to increase radiation toughness by
6. High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

saturating dangling bonds [95, 96]. However, the H$_2$ loading enhances the generation of oxygen vacancies under irradiation by ArF or F$_2$ lasers [99].

It is known that the presence of molecular oxygen has a great influence on the concentration of point defects too. In fact it causes the thermal annealing of oxygen vacancies (also known as ODC(I)) [168] and of radiation induced E' centres, by converting them to peroxy radicals (POR) through a process that is reversible under irradiation [169]. Wide interest in the study of the effects of the presence of O$_2$ in silica was also due to its role in the silicon oxidation process [170]. For this reason the most of the past work was focused on the reactions taking place at the Si-SiO$_2$ interface, the understanding of the microscopic aspects of the interactions of O$_2$ in bulk silica and its influence on the radiation sensitivity remaining limited.

In this chapter we investigate the effects of oxygen loading of amorphous SiO$_2$ on its interaction with radiation. We compare the generation efficiency of several point defects under gamma irradiation in loaded and unloaded materials. We also compare the effects of the oxygen treatments to those of identical treatments in helium atmosphere, with the aim of distinguishing between the effects strictly due to the presence of oxygen and those due to eventual modifications induced by temperature and pressure.

6.2 Experiments

Samples of the synthetic dry silica Suprasil 300 were used. Five samples were treated in He atmosphere and five in O$_2$ atmosphere at 400°C and 180 bar for about 170 h, using the Parr reactor described in Subsection 4.2.3. The effects of the thermal treatment in controlled atmosphere were evaluated by observing the Raman and IR spectra of the samples. In Figure 6.1(a), the IR spectrum of the pristine material (dashed line) is compared to the spectrum of one of the He treated samples (dash-dotted line) and one of the O$_2$ treated samples (continuous line). As discussed in detail in the previous chapter, the IR band of the silanol groups, absent in the pristine material, is instead clearly present in the treated ones. SiOH concentration is lower in the O$_2$ treated than in the He treated samples as already observed. It is easy to note that, even if the sample used in this experiment were subjected to a treatment comparable to the one at high pressure in the previous chapter, a lower OH concentration is induced. The estimated OH concentration is in fact $\sim 1.8 \cdot 10^{18}$ cm$^{-3}$ for the helium treated samples and $\sim 1.2 \cdot 10^{18}$ cm$^{-3}$ for the oxygen treated ones. This can be easily explained in the framework of the mechanism hypothesized for this OH generation. In fact we concluded that this is an intrinsic mechanism, due to hydrogen present as impurity in the material. As a consequence a different impurity
content, that could exist between different slabs, as the ones used in this experiment and in the experiment reported in the previous Chapter, due to slight differences in the sample preparation, can account for the different generation efficiency.

As shown in Figure 6.1(b), the PL signal of molecular oxygen at 1272nm, excited at 1064nm, can be observed in the sample treated in O\textsubscript{2} atmosphere, superimposed to the Raman spectrum due to SiO\textsubscript{2} vibrations [166]. The estimated O\textsubscript{2} concentration is $\sim 5 \cdot 10^{17}$ cm\textsuperscript{-3}. An experimental test was also made to obtain an approximate estimation of the penetration depth of oxygen. In fact, basing on literature values for the diffusion coefficient, a small average penetration depth is expected. For this reason we treated a sample in oxygen atmosphere at 400°C and 180 bar and then performed a Raman measurement. A slab of $\sim 0.1$mm was mechanically removed from each side of the sample. By performing a new Raman measurement after the reduction of the sample thickness, the O\textsubscript{2} signal was observed to decrease of $\sim 60\%$. It was concluded that, even if the penetration is not uniform, oxygen molecules succeed in reaching a considerable portion of the bulk sample. No differences between the Raman spectra of the He treated and untreated materials were observed, the PL band at 1272nm being undetectable in both of them, as can be observed in Figure 6.1(b) where the two spectra result superimposed.

No changes in the other spectral features of the material are observed after these treatments.

These samples, after the high pressure thermal treatment, were $\gamma$-irradiated together with samples that had not undergone any previous treatment. The irradiation took place in a $^{60}$Co source (SCK-CEN, Belgium) having a dose rate of 60kGy/h, at doses ranging from 500 to 10000 kGy. IR, Raman, EPR, OA and PL measurements were carried out at room temperature on the pristine material, after the thermal treatment and after the irradiation.

### 6.3 Results and discussion

Differences between loaded and unloaded samples, depending also on the treatment atmosphere (He or O\textsubscript{2}), are observed for many point defects populations after irradiation. In this Paragraph these differences are discussed, with the aim of determining how the presence of oxygen molecules or the high pressure thermal treatments can cause these effects.

In Figure 6.2 the EPR spectra of NBOHC and POR in pristine (dashed line), He treated (dash-dotted line) and O\textsubscript{2} treated (continuous line) samples $\gamma$ irradiated at 5000 kGy are shown. As can be observed, the generation efficiency of NBOHC and POR is strongly enhanced in the O\textsubscript{2} treated samples, with respect to He treated and
6. High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

Figure 6.1: (a) IR absorption and (b) Raman spectra of pristine material (dashed line), He treated (dash-dotted line) and O₂ treated (continuous line) samples. The PL band of interstitial O₂ at 1538 cm⁻¹ excited by the NdYAG laser is also observed in the Raman spectrum of the O₂ treated samples.

The NBOHC centers were also detected by their PL band at 1.9 eV excited at 2 eV [18], and these data confirmed the EPR results. It can be in fact observed in Figure 6.3, in which the PL spectra of NBOHC in the unloaded (dashed line), He treated (dash-dotted line) and O₂ treated (continuous line) samples γ irradiated at 5000 kGy are shown, that the PL intensity at 1.9 eV in the oxygen treated sample is about two times more intense than in the other two samples. The NBOHC concentration was estimated by the PL measurements, and their concentration in the samples studied here varied between \( \sim 1 \cdot 10^{16} \text{ cm}^{-3} \) and \( \sim 2 \cdot 10^{17} \text{ cm}^{-3} \), growing on increasing the dose.

The main generation mechanisms usually put forward for the NBOHC formation upon irradiation involve the rupture of a Si-O bond in a regular lattice site, with the simultaneous formation of an E' centre [73, 74]

\[
\equiv Si - O - Si \rightarrow \equiv Si - O^* + ^{•}Si \equiv
\]

or the SiOH precursor site

\[
\equiv Si - O - H \rightarrow \equiv Si - O^* + H
\]
or the peroxo linkage (POL)

\[
\equiv Si - O - O - Si \equiv \rightarrow \equiv Si - O^\bullet + \bullet O - Si \equiv
\]

(6.3)

The effects of O\(_2\) and He treatments on the E’ centres generation need to be checked to evaluate reliability of Reaction 6.1 as generation mechanism for NBOHC in these experiments.

In Figure 6.4 the concentration of E’ centers as a function of dose is shown. It is evident that the E’ concentration at a given dose does not substantially depend on the sample treatment. As a consequence, as no differences are observed in the generation efficiency of E’ centres, Reaction 6.1 can be easily ruled out.

Process 6.2 can be ruled out too, by considering that the same amount of NBOHC and POR is observed in the He treated samples, that contain a measurable amount of SiOH groups, and in the untreated samples, that have no detectable IR absorption band of OH groups.

Then, our results support process 6.3 as generation mechanism of NBOHC. Moreover, \textit{ab initio} calculations suggested that O\(_2\) in silica creates POL by reacting with regular lattice sites [139].

In summary, the effect of preliminary O\(_2\) loading is to increase the number of POL, and as a consequence the efficiency of NBOHC generation through process 6.3.

\textbf{Figure 6.2:} EPR spectra of NBOHC and POR in the unloaded (dashed line), He treated (dash-dotted line) and O\(_2\) treated (continuous line) samples \(\gamma\) irradiated at 5000 kGy. The spectra were acquired at room temperature using a modulation amplitude of 0.3mT.
6. High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

Figure 6.3: PL spectra excited at 2eV of NBOHC in the unloaded (dashed line), He treated (dash-dotted line) and O$_2$ treated (continuous line) samples $\gamma$ irradiated at 5000 kGy.

The increased number of POL also accounts for the increased generation efficiency of POR. In fact, the possible mechanisms of POR generation are the reaction of O$_2$ with an E’ centre [70, 75]

$$\equiv Si^* + O_2 \rightarrow \equiv Si - O - O^*$$  \hspace{1cm} (6.4)

the reaction of atomic oxygen with a NBOHC

$$\equiv Si - O^* + O \rightarrow \equiv Si - O - O^*$$  \hspace{1cm} (6.5)

and the breakage of a Si-O bond in a POL, with the simultaneous formation of an E’ centre

$$\equiv Si - O - O - Si \equiv \rightarrow \equiv Si - O - O^* + ^* Si \equiv$$  \hspace{1cm} (6.6)

Processes 6.4 and 6.6 can be ruled out on the basis of the lack of any difference in the E’ concentration. As a consequence POR can be generated from NBOHC through process 6.5.

So exceeding oxygen, by reacting with the lattice, can create precursor sites for oxygen excess related defects, as NBOHC and POR.
6.3. Results and discussion

Figure 6.4: $E'_\gamma$ centre concentration as a function of the irradiation dose in He treated (squares), $O_2$ treated (triangles) and untreated samples (circles).

In Figure 6.5 the concentration of ODC(II) as a function of dose is shown. ODC(II) generation efficiency is reduced by both the He and $O_2$ treatments. The analogy between the two treatments leads to conclude that the most of this effect is not due to an eventual action of excess molecular oxygen in limiting the generation of oxygen deficient point defects by passivating them, even if a small contribution of this process can be guessed basing on the slightly lower generation efficiency in oxygen treated samples with respect to the helium treated ones. The negligible passivating effect of the excess oxygen is not surprising, since most reactions between molecules and point defects in silica are thermally activated, as already stated in Chapter 1, and they can not take place during these irradiation experiments at room temperature.

This analogy between the two treatments suggests instead that the precursors sites of ODC(II) are modified by the high temperature and pressure, and that the specific atmosphere plays only a minor, if any, role. This hypothesis seems reliable, as it is commonly thought that ODC(II) are generated by breakage of two Si-O bonds in a lattice site. The latter process is obviously more probable in stressed sites, that can be present in silica due to its amorphous structure, whose strained bonds can easily relax because of high temperature and pressure.
6. High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

Besides NBOHC, POR and ODC(II), the generation of another paramagnetic point defect, the H(I) center, is considerably affected by the pre-irradiation treatments. As shown in Figure 6.6 the H(I) concentration is lower in the He treated samples with respect to the untreated ones and it falls under the detection limit in the O\(_2\) treated samples. The H(I) was proposed to be generated by the reaction between an ODC(II) and a hydrogen atom, activated by the \(\gamma\)-induced breaking of an OH bond [57]. The lower H(I) concentration in the He treated samples with respect to untreated ones can be explained considering that its precursor site, the ODC(II), has a lower concentration in the former. However, since both the ODC(II) and SiOH concentrations are of the same order of magnitude in He and O\(_2\) treated samples, a comparable concentration of H(I) centers should be expected in these samples, in contrast with the results reported in Figure 6.6. As a consequence either the SiOH groups are not the hydrogen source for this process, or it should be hypothesized that the presence of oxygen inhibits its reaction with ODC(II), by activating other reaction paths for hydrogen. Supporting this latter hypothesis, studies on H\(_2\) loading in O\(_2\)-rich materials suggested that the most probable reaction in this case is the reaction between two H\(_2\) and one O\(_2\) molecules generating two H\(_2\)O molecules [171].

**Figure 6.5:** ODC(II) concentration as a function of the irradiation dose in He treated (squares), O\(_2\) treated (triangles) and untreated samples (circles).
6.3. Results and discussion

Figure 6.6: H(I) concentration as a function of the irradiation dose in He treated (squares) and untreated samples (circles). O<sub>2</sub> treated samples (triangles) don’t show the presence of H(I) centres.

Finally, the O<sub>2</sub> treatment strongly affects also the OA spectra of irradiated samples in the UV range. In Figure 6.7, as an example, the OA spectra of untreated (dashed line), He treated (dash-dotted line) and O<sub>2</sub> treated (continuous line) samples γ irradiated at 5000kGy are shown. It is clearly evident that pristine and He treated samples show similar behaviours, while the O<sub>2</sub> treated sample shows a higher absorption.

Several bands contribute to the absorption of irradiated silica in the UV spectral region [18, 44]. The spectrum is dominated by the intense E′,γ absorption band at 5.8eV, that is clearly visible in all the spectra in Figure 6.7 [13, 18, 26]. ODC(II), NBOHC and POR are all known to absorb in the region around 5eV, in particular at 5.0eV, 4.8eV and 5.3eV respectively [18, 44]. In Figure 6.8 a deconvolution of the optical absorption spectrum of the oxygen treated sample γ irradiated at 5000kGy is shown. The bands of the E′,γ, NBOHC and ODC(II) were considered in the fitting procedure. Literature values for the peak positions and FWHM of these bands were used [18]. A band at 6.25eV was also used to account for the tail of the absorption contributions at higher energies. The POR contribution was neglected due to its very low oscillator strength [18]. The parameters of the bands shown in Figure 6.8 are reported in Table 6.1. It can be observed that the above mentioned bands allow
to satisfactorily describe the observed absorption profile. This result remains valid in all the other samples, the bands amplitudes varying in accordance with the different concentrations of defects.

The observed differences in the spectrum of the oxygen treated samples with respect to the others can not be ascribed to the band of the $E'$ centres, as their concentration is almost the same in the three samples (See Figure 6.4).

These differences are then rather due to contributions at lower energy. The ODC(II) contribution can be excluded, as their concentration in $O_2$ treated samples is lower than in untreated ones. So the enhancement in the absorption of $O_2$ treated samples

![Figure 6.7: Optical Absorption spectra of the unloaded (dashed line), He treated (dash-dotted line) and $O_2$ treated (continuous line) samples $\gamma$ irradiated at 5000kGy.](image)

**Table 6.1:** Parameters of the bands shown in Figure 6.8.

<table>
<thead>
<tr>
<th>Peak position (eV)</th>
<th>FWHM (eV)</th>
<th>Amplitude (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.80</td>
<td>1.05</td>
<td>2.9</td>
</tr>
<tr>
<td>5.02</td>
<td>0.36</td>
<td>0.2</td>
</tr>
<tr>
<td>5.73</td>
<td>0.80</td>
<td>6.7</td>
</tr>
<tr>
<td>6.25</td>
<td>0.59</td>
<td>3.6</td>
</tr>
</tbody>
</table>
6.3. Results and discussion

Figure 6.8: Optical Absorption spectra of the O\textsubscript{2} treated (continuous line) sample γ irradiated at 5000 kGy (black line). Result of a fitting procedure (red line) performed using the four bands drawn in grey (See text).

due to point defects has to be attributed to their higher number of NBOHC. Actually, another band needs to be taken into account for the absorption in this spectral range, the one at 4.8 eV due to interstitial ozone molecules (O\textsubscript{3}) that almost coincides with that of NBOHC [44, 64]. In fact ozone molecules are known to be present in irradiated oxygen-reach silica [44]. The relevance of the O\textsubscript{3} contribution to the OA spectrum can be evaluated by comparing the amplitude of the band at 4.8eV obtained through the fitting procedure to the amplitude of the PL band of NBOHC (See Figure 6.3). The ratio between the amplitudes of the bands at 4.8eV of the oxygen and helium treated samples obtained through the fitting procedure illustrated above (2.9 and 1.3 cm\textsuperscript{-1} respectively) is comparable to the value of the ratio between the amplitudes of the PL bands at 1.9eV in the same samples (See Figure 6.3). This evidence is confirmed by the fact that a comparable result is obtained by estimating the NBOHC concentration from the PL and the OA spectrum. As an example, both using the amplitude of the component at 4.8eV in Figure 6.8 and from the PL spectrum of the same sample, a concentration of \( \sim 1.5 \times 10^{17} \) cm\textsuperscript{-3} is obtained. As a consequence the contribution of the ozone molecules to the OA spectrum of these samples can be neglected.

In summary the higher optical transparency loss of irradiated O\textsubscript{2} treated silica is due
6. High pressure thermal treatments effects on the radiation hardness of silica: Oxygen and Helium atmospheres

to the enhanced NBOHC generation efficiency, already discussed at the beginning of this paragraph.

6.4 Conclusions

A complex scenario originates from the comparison between the radiation effects in He treated, O$_2$ treated and untreated samples. The effects of the thermal treatments on the generation efficiency of point defects strongly depends on the defect examined. However all the effects observed here can be explained in terms of changes in the number of precursor sites.
We pointed out that the reduction of the ODC(II) generation efficiency can be ascribed to the high temperature and pressure modifications induced in the precursor sites of this defect. The increase in the generation efficiency of NBOHC and POR is instead due to the specific action of O$_2$, that induces the formation of oxygen excess sites as the peroxy linkages, precursors for these defects. The presence of dissolved oxygen also inhibits some hydrogen related processes, as the generation of H(I) centers.
On the basis of the observed effects, specific treatments could be set up to enhance the radiation resistance of the materials with respect to spectral features of interest, even if this could imply loss of performances in other ranges. Moreover all these effects have to be taken into account in the optimization of materials to be used in radiative environments.
Chapter 7
Annealing of point defects

In this last chapter the annealing processes of radiation induced oxygen deficient point defects in silica will be discussed. This subject finds its place in the framework of this thesis since these processes are attributed to the reactions of the defects with diffusing molecules. The microscopic processes responsible for the annealing of two radiation induced oxygen deficient point defects, the E', and the ODC(II), will be at first identified. Then the influence of the disorder characteristic of the amorphous matrix on these annealing processes will be clarified, and finally quantitative information on the activation energy distributions and on the character of the processes will be obtained.

7.1 Introduction

An always increasing attention is nowadays paid to the effect of thermal treatments on silica and on its point defects. Indeed, this kind of procedure can influence the properties of the material and as a consequence it is widely employed in the production of devices. Furthermore this procedure is used to anneal point defects induced by irradiation, and in some cases can also be a way to obtain information on the properties of defects [1, 106]. In fact the concentration of a point defect can change by heating the sample above a threshold temperature. This threshold temperature depends on the specific defect, the material, the irradiation conditions and previous treatments (See also Section 1.3).

The annealing of point defects following a thermal treatment of the sample can be attributed to different microscopic processes. Today it is commonly believed that the main process giving rise to such effects is the reaction of the defects with molecules diffusing through the matrix, as hydrogen, oxygen or water [25, 75, 106, 108, 118, 170, 172].
This kind of process is generally described as the result of the concurrence of two distinct phenomena, the diffusion of the molecule and its reaction with the defect. So the observed rate for the annealing process of a point defect is determined by the characteristic timescales of both these phenomena, even if in some cases one of them can be predominating (See Section 2.2).

In this chapter the attention will be focused on the thermal annealing of two of the most diffused radiation induced oxygen deficient point defects, the E’γ centre and the ODC(II). As anticipated and discussed in more details in Section 1.3, the effects of heat treatments on these defects were studied and some microscopic models of reaction were put forward [19, 106, 108, 173–175].

The annealing of the E’γ centre was observed after irradiating samples at temperatures higher than about -70°C, and up to room temperature [176]. This process is known to be due to reactions with molecular hydrogen [120, 173–175], and it was widely studied, also because of the ubiquitous presence of this impurity in silica [19, 173, 177]. It was established that the reaction of an E’γ centre with H₂ in silica is not a diffusion limited process [173]. It was also established that the activation energy for H₂ diffusion in silica is distributed, as a consequence of the amorphous nature of the material [19, 177–179].

A few studies at higher temperatures were also carried out, and the annealing of the E’γ centre was attributed to reactions with other small molecules diffusing through the matrix [19, 106]. In low OH concentration silica the annealing of the E’γ centre observed at temperatures higher than 150°C was attributed to the reaction with oxygen [107]

\[
\equiv Si^* + O_2 \rightarrow \equiv Si - O - O^*
\]  

(7.1)

The annealing of the E’γ centre observed in high OH silica at temperatures higher than 300°C was instead attributed to the reaction with water [106]

\[
\equiv Si^* + H_2O \rightarrow \equiv SiOH + H
\]  

(7.2)

Based on the observation of a strong similarity between the isochronal anneal curves of the two defects, the annealing of ODC(II) was tentatively ascribed to reactions with the same molecules involved in the E’γ centre annealing, according to the reactions [108–111]

\[
\equiv Si^* + O_2 \rightarrow \equiv Si \; O
\]  

(7.3)
7.2. Annealing processes of radiation induced oxygen deficient point defects

Notwithstanding the increasing number of works about the diffusion of small molecules, different from hydrogen, in silica and their interaction with point defects at temperatures higher than 100°C [75, 170, 180], a general scheme for the annealing processes of these point defects has not been definitively established yet. Moreover some important aspects of these processes, as their being diffusion or reaction limited and the effects of the disorder of the glass matrix on these diffusion-reaction processes, were not studied.

In the present Chapter we will show the results of an extensive and articulated set of experiments, aiming to give a description of the thermal annealing process of E’γ and ODC(II) centres.

7.2 Annealing processes of radiation induced oxygen deficient point defects

Aim of the experiment presented in this Section is to shed light on the microscopic processes responsible for the annealing of E’γ centre and ODC(II), distinguishing among the reactions with different diffusing molecules proposed in literature.

7.2.1 Experiment

Three samples of the synthetic dry material Suprasil F300 were used. Preliminary to the experiment described in the following, they were γ irradiated at room temperature (60Co source, dose rate ~ 3kGy/h), up to a total dose of 1500kGy. The concentrations of defects were approximately the same in all the samples. In particular, the E’γ centre concentration was \((6.7 \pm 1) \cdot 10^{16}\) centres/cm\(^3\) and that of ODC(II) \((1.5 \pm 0.5) \cdot 10^{15}\) centres/cm\(^3\).

The three samples, that will be called F300/H\(_2\)O, F300/He and F300/O\(_2\) hereafter, were then subjected to isothermal heat treatments at 250°C and ~35bar in water, helium or oxygen atmospheres, respectively. The steps that constitute this experiment are schematically shown in Figure 7.1. These treatments were performed in the Parr reactor, mounting the samples on the steel sample holder. The treatments in oxygen and helium atmosphere were performed using the same steel sample holder as for the treatments in water vapour, to make the experimental conditions as comparable.
7. Annealing of point defects

Figure 7.1: Scheme of the experiment reported in Section 7.2.

as possible. The only difference between these three treatments was the treatment atmosphere.
It is worth noting that the heating and cooling rates do not play a relevant role in this experiment, as the conclusion are drawn by comparing the effects on the three samples, that experienced the same heating and cooling conditions. However, due to their not negligible duration, these conditions could influence eventual quantitative estimations of the annealing rates. For this reason these data were not used to obtain quantitative results about parameters like the activation energy for the annealing process. A different experiment that will be described in Section 7.4, carried out using a different system, was performed to this aim.

7.2.2 Results and discussion

The isothermal annealing curves of $E'_\gamma$ at a given temperature, that represent the defect concentration as a function of the treatment duration, were obtained. In
7.2. Annealing processes of radiation induced oxygen deficient point defects

Figure 7.2: $E'_{\gamma}$ centres concentration as a function of the treatment time at 250°C in the samples F300/H2O (squares), F300/He (circles) and F300/O2 (triangles). Initial concentrations are represented by continuous line (F300/H2O), dashed line (F300/He) and dash-dotted line (F300/O2).

Figure 7.2 a comparison between these curves for the three samples is shown. The initial concentrations of $E'_{\gamma}$ centres, indicated by lines, are comparable in the three samples. It can be easily observed that almost comparable results are obtained by treating the samples in helium and oxygen atmospheres (circles and triangles in Figure 7.2). The annealing rate of $E'_{\gamma}$ centres is instead considerably higher in the water vapour treated sample.

This experimental evidence leads directly to the conclusion that water molecules are responsible for the $E'_{\gamma}$ annealing. In fact the rate of a bimolecular reaction increases on increasing the concentrations of reactants. As a consequence, as the $E'_{\gamma}$ concentration is the same in the three samples, a strong increase in the rate should be observed when increasing the concentration of the molecule responsible for the $E'_{\gamma}$ annealing by saturating the treatment atmosphere with it. This effect is indeed observed by treating the sample in water vapour atmosphere, and let us identify water molecules as the agent that, efficiently reacting with the $E'_{\gamma}$ centres, mainly causes their thermal annealing in this experiment.

It could be guessed that this conclusion applies only to this specific material at this temperature. It will be shown instead in Section 7.4 that this is a general result, valid
7. Annealing of point defects

in a wide temperature range.

In this framework, the E_γ annealing observed in samples treated in different atmospheres can be attributed to the water molecules already present in the material due to production technique or irradiation or, for thermal treatments performed in air, also absorbed from the atmosphere.

The slightly higher efficiency of E_γ annealing in F300/O2 with respect to F300/He deserves to be commented. A first reason for this behaviour could be the initial slightly lower E_γ concentration in the F300/O2 with respect to F300/He, that can reflect on the following annealing.

However another reason could be put forward to explain the observed small differences between F300/O2 and F300/He. The above reported experimental evidence of water being the main responsible for the E_γ annealing does not exclude a small contribution of the previously suggested reaction of E_γ with oxygen [169]. The latter could in fact be entirely negligible in normal or water excess treatment conditions, but can give a small detectable contribution when the treatment atmosphere is saturated by oxygen. In this latter case, in fact, the rate of annealing due to oxygen could be enhanced due to its greater concentration; as a consequence this process could become detectable. This could be the case for the sample F300/O2, in which oxygen loading takes place during the thermal treatment. Indeed a concentration of the order of 10^{17} O_2 molecules/cm^3 was measured in the treated sample at the end of the treatment. Nevertheless, if the reaction with oxygen gave a strong contribution to the E_γ annealing, an increased number of POR should be observed.

In Figure 7.3 the EPR spectra of the three samples after 122h treatments are compared to that of an untreated sample (red line). The spectra at other treatment times show the same features. It can be observed by looking at the peak around 335mT (indicated by an arrow in Figure 7.3. See Subsection 1.1.3) that no growth of POR concentration is observed in any of the samples after thermal treatment, proving that the reaction with oxygen does not constitute a significant contribution to the E_γ annealing, even in oxygen excess treatment conditions.

It can be concluded that, unless very special conditions of high oxygen excess apply, the E_γ annealing can be attributed to reactions only with water molecules, and every other contribution can be neglected.

Even if it was not the aim of this experiment, it is worth noticing that information on the POR and NBOHC annealing processes can be also obtained by looking at Figure 7.3. It can be observed that the above mentioned reduction of POR and NBOHC concentration with respect to the value before the thermal treatments is much more evident in the F300/H2O sample than in F300/O2 or F300/He. This evidence, analogous to the one for E_γ centres, suggests a contribution of water to the thermal annealing of these point defects in this temperature range.
7.2. Annealing processes of radiation induced oxygen deficient point defects

Once proved that the annealing of \( \text{E'}_\gamma \) centres is mainly due to their reaction with water molecules, the OH concentration should be expected to feature an increase corresponding to the decrease in \( \text{E'}_\gamma \) concentration according to Reaction 7.2. In Figure 7.4 the IR absorption spectra of the three samples after 22h treatments are shown, compared to the spectrum of a sample before the thermal treatments (red line). The spectra at the other treatment times show the same behaviour. It can be observed that the intensity of the OH absorption band at 3670\( \text{cm}^{-1} \) in F300/He and F300/O2 is of the same order of magnitude, even if it is slightly lower in the F300/O2. These intensities are much lower than in the F300/H2O. The F300/H2O also shows a different spectrum profile. In fact the presence of interstitial molecular water, that in this case is absorbed from the atmosphere, is evident in the intense broad band around 3400\( \text{cm}^{-1} \). Moreover a shoulder on the low wavenumber side of the OH absorption band (around 3600\( \text{cm}^{-1} \)) is clearly recognizable. This contribution is attributed to hydrogen bonded OH groups (See Subsection 1.1.4).

The OH concentration can be estimated by using Lambert-Beer’s law (Equation 5.1). The lowest induced OH concentration, those in F300/He and F300/O2, are \( 2 \cdot 10^{17}\text{cm}^{-3} \) and \( 5 \cdot 10^{16}\text{cm}^{-3} \) respectively. These OH concentrations are higher than

---

**Figure 7.3:** Room temperature EPR spectra of NBOHC and POR in the F300/H2O (continuous line), F300/He (dashed line) and F300/O2 (dash-dotted line) after 122h treatments at 250° C. The red line is the spectrum of one of these samples before the thermal treatment.
7. Annealing of point defects

![Infrared absorption spectra](image)

**Figure 7.4:** Infrared absorption spectra of the samples F300/H2O (continuous line), F300/He (dashed line) and F300/O2 (dash-dotted line) after 22h treatments at 250°C. The red line is the spectrum of one of these samples before the thermal treatment.

The E’γ concentration decrease in these two samples, that are \( \sim 2 \cdot 10^{16} \text{cm}^{-3} \) and \( \sim 2.4 \cdot 10^{16} \text{cm}^{-3} \) respectively (See Figure 7.2). These data are compatible with the proposed Reaction 7.2, but a direct correlation between the generated SiOH groups and the annealed E’γ centers can not be found, because of the existence of other, already known, phenomena that generate SiOH too. In particular these facts can be simply explained by taking into account the results obtained in Chapter 5. The induced absorption in the F300/He and F300/O2 can be explained in terms of the generation of silanol groups in dry silica upon thermal treatments, probably due to reactions with hydrogen molecules, discussed in Chapter 5. The intense OH absorption in the F300/H2O sample can be instead explained by a main contribution due to OH groups generated through reaction of the silica matrix with the absorbed water molecules. It can be concluded that the observed OH generation is compatible with Reaction 7.2, but the possibility to observe a direct correlation between the annealed E’γ and the induced OH is prevented by other overriding contributions to the OH generation.

Finally, the isothermal annealing curves of ODC(II) were also obtained, to distinguish between its different proposed annealing mechanisms, as already done for the E’γ centre. In Figure 7.5 a comparison between these curves in the three samples
7.3. Annealing processes: evidence for a distribution of the reaction activation energies

![Graph showing ODC(II) concentration as a function of treatment time at 250°C for samples F300/H2O, F300/He, and F300/O2.](image)

Figure 7.5: ODC(II) concentration as a function of the treatment time at 250°C in the samples F300/H2O (squares), F300/He (circles) and F300/O2 (triangles). Initial concentrations are represented by continuous line (F300/H2O), dashed line (F300/He) and dash-dotted line (F300/O2).

is shown. It can be observed that the F300/H2O shows a higher annealing rate of ODC(II) than the F300/O2, as already observed for the E'\(_\gamma\) centre. So the annealing process of ODC(II) can be attributed to reaction with water too. This result is in accordance with what already suggested in a previous work on the basis of the observed analogy between the isochronal annealing curves of these two point defects [108]. For what concerns the lack of possibility of directly observing a correlation between the annealed ODC(II) and the generated OH, the same considerations as for the E'\(_\gamma\) centre apply.

Concluding, we individuated the microscopic mechanisms for the annealing of the E'\(_\gamma\) and ODC(II) centres at 250°C among those proposed in literature. Both these defects are annealed by reacting with water molecules, according to Reactions 7.2 and 7.4.
7.3 Annealing processes: evidence for a distribution of the reaction activation energies

Aim of the experiments presented in this Section is to study the influence of the amorphous structure of silica on the annealing processes of the \( \text{E}'_\gamma \) centre and ODC(II). Data on this subject are only available for processes related to hydrogen, at temperatures equal or lower than room temperature, for which a distribution of the activation energy of diffusion was assumed \([120, 177]\). However data at higher temperatures, at which reactions of point defects with different molecules occur, and evidences of the influence of the disorder on the activation energies for reaction are not exhaustive \([19, 120]\).

7.3.1 Experiments and results

Two different experiments are presented hereafter. In the former, three samples of the same natural dry material, Infrasil 301, referred to as I301/A, I301/B and I301/C, were used. Preliminary to every experiment described in the following, they were \( \beta \) irradiated at room temperature in a linear accelerator, up to a total dose of 2000 kGy, so that the concentrations of a given defect before the thermal treatments were approximately the same in all the samples. In particular, the \( \text{E}'_\gamma \) centre concentration has been estimated to be about \( 4.5 \cdot 10^{17} \) centres/cm\(^3\) and that of ODC(II) varied between \( 3.5 \cdot 10^{15} \) and \( 5.7 \cdot 10^{15} \) centres/cm\(^3\).

The samples were then subjected to different sequences of isothermal heat treatments at 200, 300 and 450°C in air using the furnace described in Subsection 4.2.2. The steps that constitute this experiment are schematically shown in Figure 7.6. The sample I301/A was thermally treated at 200°C for 100000 s. After this preliminary treatment this sample and the I301/B were subjected to the same isothermal treatment at 300°C. In figure 7.7(a) the isothermal anneal curves at 300°C for the \( \text{E}'_\gamma \) centres in the samples I301/A and I301/B are shown. The lines indicate the concentration of \( \text{E}'_\gamma \) centres before the beginning of the thermal treatment at 300°C in the samples I301/A and I301/B respectively. The overall duration of the thermal treatment was chosen in such a way that the annealing processes had practically reached a stationary state.

Figure 7.7(b) shows the analogous comparison for a treatment at 450°C. The sample I301/A is the one of the previous treatment at 300°C (so it had been subjected to thermal treatments at 200°C and 300°C), while the sample I301/C had not undergone any thermal treatment before the one at 450°C. The lines indicate the concentration of \( \text{E}'_\gamma \) centres before the beginning of the thermal treatment at 450°C in the samples
7.3. Annealing processes: evidence for a distribution of the reaction activation energies

Figure 7.6: Scheme of the first experiment reported in Section 7.3.

I301/A (solid line) and I301/C (dashed line).

From these figures we observe that the concentration of $E'_\gamma$ centres at the beginning of each thermal treatment is different in the two samples, due to the fact that in the pretreated samples it decreased during the preliminary thermal treatments. It can be easily observed that, notwithstanding this difference, the annealing curves of the two samples, at each temperature, tend to the same value.

A quantitative comparison between the effects of the different sequences of thermal treatments can also be made. In table 7.1 the variations of the concentration of $E'_\gamma$ centre after the overall treatment at each temperature are listed.

It can be observed that the $E'_\gamma$ concentration change following the thermal treatment at 300°C of the sample I301/B is equal to the sum of the analogous variations observed in the sample I301/A after the treatments at 200°C and 300°C. In the same way the $E'_\gamma$ concentration change following the thermal treatment at 450°C of the sample I301/C is equal to the sum of the analogous variations observed in the sample I301/A after the treatments at 200°C, 300°C and 450°C. This result means that the total number of point defects annealed at a given temperature does not depend on the sequence of thermal treatments leading to such temperature, but only on the final temperature value. In other words the concentration of $E'_\gamma$ centres tends to a value that is function of the temperature alone, and that does not depend on the sequence of thermal treatments the sample underwent. Moreover, another noteworthy
7. Annealing of point defects

Figure 7.7: (a) Concentration of E'_\gamma centres as a function of the treatment time at 300°C, as detected in the samples I301/A, previously treated at 200°C (filled symbols), and I301/B, not previously treated (open symbols). Solid and dashed lines represent the concentration of E'_\gamma centres respectively in the samples I301/A and I301/B before the beginning of the treatment at 300°C. (b) Concentration of E'_\gamma centres as a function of the treatment time at 450°C, as detected in the samples I301/A, previously treated at 200°C and 300°C (filled symbols), and I301/C, not previously treated (open symbols). Solid and dashed lines represent the concentration of E'_\gamma centres respectively in the samples I301/A and I301/C before the beginning of the treatment at 450°C.

Evidence is that the rate of the annealing process of the E'_\gamma centres is smaller in the pretreated sample at both temperatures, as can be easily observed in Figure 7.7. The same comparison was carried out for the ODC(II) centre, and the results are shown in figure 7.8. No significant change in the ODC(II) concentration is observed at 300°C, while such concentration tends to the same value in both samples at 450°C, as already observed for the E'_\gamma centres. So an asymptotic value for the concentration of a given defect exists, that is function of the annealing temperature alone.

The different annealing behaviour of E'_\gamma and ODC(II) centres can be explained on the basis of their being substantially different under a structural point of view. It is hence obvious that they can have different reaction properties.

In the second experiment two samples of the natural dry material Silica EQ906, named Q906/A and Q906/B, were \gamma irradiated at two different doses: 2500 kGy and 10000 kGy, respectively, so that the ODC(II) concentration in the second sample (2.4 \cdot 10^{15} centres/cm^3) was higher than in the first one (1\cdot 10^{15} centres/cm^3). The E'_\gamma
7.3. Annealing processes: evidence for a distribution of the reaction activation energies

Table 7.1: Variations of the concentration of $E'_{\gamma}$ centres observed in the experiment on the I301 samples described in Section 7.3 at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta[E'_{\gamma}]$ at 200°C</th>
<th>$\Delta[E'_{\gamma}]$ at 300°C</th>
<th>$\Delta[E'_{\gamma}]$ at 450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I301/A</td>
<td>$8 \times 10^{16}$ centres/cm$^3$</td>
<td>$8 \times 10^{16}$ centres/cm$^3$</td>
<td>$1.9 \times 10^{17}$ centres/cm$^3$</td>
</tr>
<tr>
<td>I301/B</td>
<td>$1.5 \times 10^{17}$ centres/cm$^3$</td>
<td>$1.9 \times 10^{17}$ centres/cm$^3$</td>
<td>$3.5 \times 10^{17}$ centres/cm$^3$</td>
</tr>
<tr>
<td>I301/C</td>
<td>$1.9 \times 10^{17}$ centres/cm$^3$</td>
<td>$1.9 \times 10^{17}$ centres/cm$^3$</td>
<td>$3.5 \times 10^{17}$ centres/cm$^3$</td>
</tr>
</tbody>
</table>

Figure 7.8: (a) Concentration of ODC(II) as a function of the treatment time at 300°C, as detected in the samples I301/A, previously treated at 200°C (filled symbols), and I301/B, not previously treated (open symbols). Solid and dashed lines represent the concentration of ODC(II) respectively in the samples I301/A and I301/B before the beginning of the treatment at 300°C. (b) Concentration of ODC(II) as a function of the treatment time at 450°C, as detected in the samples I301/A, previously treated at 200°C and 300°C (filled symbols), and I301/C, not previously treated (open symbols). Solid and dashed lines represent the concentration of ODC(II) respectively in the samples I301/A and I301/C before the beginning of the treatment at 450°C.

The concentration was instead about $1 \times 10^{17}$ centres/cm$^3$ in both the samples. The sample Q906/B was then subjected to a thermal treatment at 470°C aimed at making the concentration of ODC(II) equal to the one in the Q906/A sample. At the end of this treatment the concentration of ODC(II) in the sample Q906/B is $9 \times 10^{14}$ centres/cm$^3$. 

113
very close to that in the Q906/A (1 · 10^{15} \text{ centres/cm}^3). From this moment on, the two samples were subjected to the same isothermal treatment at 450°C, that is a temperature lower than that of the pretreatment of the sample Q906/B. The steps that constitute this experiment are schematically shown in Figure 7.9. It is worth noticing that this procedure is substantially different from that followed in the previous experiment, as in that case the pretreatment of the samples was done at a lower temperature than that of the final annealing; a further difference with respect to the previous experiment is that in this second case the pre-treatment at 470°C lasted the time needed to make the ODC(II) concentration in the Q906/B sample equal to the one in the Q906/A, and so the concentration at the end of this pre-treatment is not the asymptotic concentration relative to the temperature T=470°C. In figure 7.10 the isothermal annealing curves at 450°C for the ODC(II) and E_γ\gamma centres in the samples Q906/A and Q906/B are shown. It can be observed that the dependence on time of the defects concentration for the thermal treatment at 450°C is rather different in the two samples; in particular the effect of the annealing process is much smaller in the sample Q906/B, that had been pretreated at 470°C. In this sample in fact the annealing rates of both the defects studied are sensibly smaller than the analogous rates in the Q906/A sample.

### 7.3.2 Discussion

The aim of the two performed experiments was to investigate the dependence of the thermal sensitivity of oxygen deficient point defects on the thermal history of
7.3. Annealing processes: evidence for a distribution of the reaction activation energies

Figure 7.10: Concentration of (a) ODC(II) and (b) E', centres as a function of the treatment time at 450°C, as detected in the samples Q906/A (filled symbols), and Q906/B, previously treated at 470°C (open symbols).

As reported in the previous subsection, it was observed that at long treatments time the defect concentration has a stationary value depending only on the temperature. Moreover, it was observed that the annealing rate of both the defects at a given temperature $T_1$ is much lower in a sample pretreated at a temperature $T_2 > T_1$, higher than the one of the treatment under examination. Both these experimental results can be explained in the framework of the existence of a statistical distribution of the activation energy of the diffusion-reaction process. Similar hypothesis had been put forward previously [106], but many aspects have not been fully clarified. In a simple way of looking at the problem, one can imagine that each defect has its own characteristic activation energy value, which is statistically distributed within

the sample, and the possible influence of the amorphous structure of the material on such property.

The possible microscopic models for these annealing processes in the temperature range from 200°C up to 450°C were discussed in the introductory section; diffusion-reaction mechanisms involving molecular oxygen and water were put forward [19, 106]. In Section 7.2 it was demonstrated that the reactive molecule mainly responsible for these annealing processes is water.
the population of defects. The existence of this distribution of the activation energy implies that only a certain part of the total number of defects can react at a given temperature: those with activation energy values equal or lower than an appropriate one. Furthermore, the existence of a distribution of activation energies also implies a distribution of reaction rates, as to smaller activation energies correspond higher rates (See Section 2.2). As a consequence, in the first experiment (the one on Infrasil 301) the final concentration of defects at a given temperature after a long treatment time depends only on the temperature itself and not on previous thermal treatments at lower temperatures to which the sample has been subjected; the reason for this behaviour is that the final amount of defects annealed is the total number of defects whose annealing activation energy is low enough to let the reaction take place at the treatment temperature. This idea can be more easily understood looking at the schematic picture of the hypothesized distribution of activation energies reported in Figure 7.11. The light grey part of the distribution represents the defects with activation energies such that they can react at temperatures $T < T_1$, while the dark grey part represents those defects that can react at temperatures $T_1 < T < T_2$. When a thermal treatment at the temperature $T_2$ is performed, all the defects, the light and dark grey, are removed at the same time. When instead a sequence of two treatments at the temperatures $T_1$ and $T_2$ ($T_2 > T_1$) is performed, during the first one the light grey defects are removed, whereas during the second one the dark grey centres are annealed. The light grey defects, having smaller activation energies than

Figure 7.11: Schematic picture representing a distribution of the activation energies of the annealing process of the defects.
the dark grey centres, also have higher reaction rates, and this fact also explains the differences in rates observed. In conclusion, whatever the sequence of thermal treatments, at the end of the treatment at $T_2$ both the light and dark grey defects are removed, so the total number of defects annealed depends only on the temperature $T_2$, as observed.

In the same way the second experiment shows that the annealing rate at a temperature $T_1$ is much smaller in a sample pretreated at a temperature $T_2 > T_1$. It is possible to guess that this happens because the portion of defects able to react at the temperature $T_1$ has already been significantly annealed during the pretreatment at $T_2 > T_1$. In other words this second experiment gives evidence that the pre-treatment has significantly changed the distribution of the activation energies of the annealing process, affecting the thermal sensitivity of the defects.

All these considerations lead to the conclusion that a statistical distribution of the activation energies of the diffusion-reaction process exists. The existence of this distribution is also the origin of the dependence of the thermal properties of point defects on the thermal history of the sample, as different histories can give rise to differences in the distributions.

The existence of this distribution of activation energies can easily be physically interpreted referring to the fact that these processes take place inside an amorphous structure. In general two distinct contributions can be associated to the observed activation energy, deriving from the diffusion phenomenon and from the reaction process, although in some cases one of them can be overriding (See also Section 2.2). The former is a thermally activated process, as the motion of a molecule from one interstitial site to another one needs to overcome a potential barrier due to the geometrical arrangements of the lattice atoms; in an amorphous structure each lattice site is different, and this leads to a distribution of these potential barriers and consequently of the associated activation energy for the diffusion process. Concerning the activation energy for reaction, we observe that it is well known that the slightly different environments surrounding the defects have influence on the optical properties of the centre itself, determining a broadening of the absorption lines due to the existence of a distribution of the transition energies [153]. In the same way as the electronic transition energies are distributed, it can be guessed that the energies required for a reaction process to happen are distributed too, as a consequence of the differences in the defects environments. It can be concluded that, it does not matter which one of the above mentioned phenomena, diffusion or reaction, is the preponderating contribution to the activation energy of the overall diffusion-reaction process, this activation energy is distributed as a consequence of the disorder characteristic of the amorphous system in which the phenomenon takes place.

Nevertheless, in the experiments shown in this Section, all the comparisons were
made between samples undergoing the same treatment at the same temperature, and differing only for their previous thermal history. Moreover no modification in the Raman spectra, and consequently in the structure of the glass matrix on which the diffusion properties of a given molecule depend, was observed after the pretreatments of the samples. As a consequence it can be stated that the diffusion properties should be the same in the couples of samples compared, and the differences observed are due to differences in the activation energy distribution for the reaction process, that therefore is the limiting one here. However this latter conclusion will be better supported on a quantitative basis in the next Section.

7.4 Quantitative analysis of the effects of thermal treatments on point defects

In the previous Sections of this Chapter important results on the annealing processes of the E\(^{\gamma}\) centre and ODC(II) were achieved. In particular it was concluded that water molecules are responsible for the thermal annealing of both the defects at 250°C, and that the activation energy for reaction is distributed. In this section a new set of experimental data will be presented and they will be analysed, together with already presented results, to obtain quantitative information on these annealing processes. Information on the activation energy distributions and on the character of the processes will be obtained, and it will be concluded that the microscopic mechanisms responsible for these annealings are the same, overall the whole temperature range examined.

7.4.1 Experiments

In this Section several sets of data will be used. The annealing data on Infrasil 301 of Section 7.3 will be used together with a new experiment presented hereafter. A sample of the synthetic dry material Suprasil 300 (referred to as S300/An in the following), was used. Preliminary to every annealing experiment, it was \(\gamma\) irradiated at room temperature up to a total dose of 4000kGy. In particular, the E\(^{\gamma}\) centre concentration was estimated to be about 7.5 \(\cdot\) 10\(^{16}\) centres/cm\(^3\) and that of ODC(II) 1.6 \(\cdot\) 10\(^{15}\) centres/cm\(^3\). The sample was then subjected to a sequence of isothermal heat treatments at 80, 150, 300 and 550°C in the furnace described in Subsection 4.2.2. The steps that constitute this experiment are schematically shown in Figure 7.12.

The heating and cooling conditions for this experiment have been chosen to minimize the time that the sample spends at temperatures different from the target
7.4. Quantitative analysis of the effects of thermal treatments on point defects

7.4.2 Results and Discussion

The overall treatment at 80°C lasted 12600s and induced no significant changes in the concentrations of defects. The annealing curves for the $E'_\gamma$ and the ODC(II) centres in the sample S300/An at the other temperatures are shown in Figure 7.13. Filled circles in the left panels ((a), (c) and (e)) represent the concentration of $E'_\gamma$ centres as a function of the treatment time at the three different temperatures, while the open squares in the right panels ((b), (d) and (f)) indicate the ODC(II) concentration during the same treatments as the $E'_\gamma$ centres. For both the defects the annealing process becomes more efficient on increasing the temperature. Lines are numerical solutions of a system of rate equations used to model the reactions that we are going to describe.

Reactions 7.2 and 7.4 were established to be responsible for the annealing of the $E'_\gamma$ and ODC(II) centres in the experiments presented in Section 7.2. We will assume them valid at the other temperatures too, and we will *a posteriori* verify the validity of this assumption. It is evident that further reactions are required, accounting for the fate of the hydrogen atom generated by Reaction 7.2. According to literature data, its dimerization forming $H_2$ and the reactions of both $H$ and $H_2$ with the $E'_\gamma$ have to be taken into account [179, 181]. Reactions of hydrogenous species with ODC(II) are not considered. In fact such reactions should produce H(I) centres, that are detectable by EPR and whose signal was not observed. Moreover, if the reaction of ODC(II)
Figure 7.13: Concentration of E$_\gamma$ (filled symbols) and ODC(II) (open symbols) as a function of the treatment time at (a) and (b) 150°C, (c) and (d) 300°C and (e) and (f) 550°C as detected in the sample S300/An. Lines are numerical solutions of the rate equations 7.16 (See text).
with the hydrogen produced through Reaction 7.2 were effective, it would be difficult to explain an effect like the one observed in the experiment on I301 described in the previous Section. In that experiment, in fact, the \( E'_\gamma \) were annealed at 450°C, and atomic hydrogen was produced according to Reaction 7.2, but no annealing of the ODC(II) was observed.

The system of reactions obtained taking into account all these processes is

\[
\begin{align*}
E'_\gamma + H_2O & \xrightarrow{k_1} SiOH + H && (a) \\
ODC(II) + H_2O & \xrightarrow{k_2} Si(OH)(H) && (b) \\
E'_\gamma + H & \xrightarrow{k_3} SiH && (c) \\
H + H & \xrightarrow{k_4} H_2 && (d) \\
E'_\gamma + H_2 & \xrightarrow{k_5} SiH + H && (e)
\end{align*}
\]

(7.5)

From these reactions a rate equations system can be derived

\[
\frac{d[E']}{dt} = -k_1[E'][H_2O] - k_3[E'][H] - k_5[E'][H_2] 
\] (7.6)

\[
\frac{d[ODC(II)]}{dt} = -k_2[ODC(II)][H_2O] 
\] (7.7)

\[
\frac{d[H_2O]}{dt} = -k_1[E'][H_2O] - k_2[ODC(II)][H_2O] 
\] (7.8)

\[
\frac{d[H]}{dt} = k_1[E'][H_2O] - k_3[E'][H] - k_4[H]^2 + k_5[E'][H_2] 
\] (7.9)

\[
\frac{d[H_2]}{dt} = k_4[H]^2 - k_5[E'][H_2] 
\] (7.10)

where \( k_1, k_2, k_3, k_4, k_5 \) are the rate constants relative to Reactions 7.5. Some careful hypothesis can be proposed to discuss the solution of these equations.
The order of magnitude of the rate constants of processes 7.5 can be estimated. Reactions 7.5(c) and (d) are limited by the diffusion of atomic hydrogen, and the values of $k_3$ and $k_4$, calculated at room temperature using Equation 2.16 and the values in table 2.1, is $k_3 \approx k_4 \approx 6 \cdot 10^{-14}\text{cm}^3\text{s}^{-1}$. Reaction 7.5(e) is reaction limited, and the values of preexponential factor and activation energy are known by literature data [176]. As a consequence $k_5$ at room temperature can be calculated, and the value obtained is $k_5 \approx 1 \cdot 10^{-20}\text{cm}^3\text{s}^{-1}$. Finally the character of Reactions 7.5(a) and (b) is not known a priori. They can be hypothesized to be diffusion limited. In this case the values of $k_1$ and $k_2$ could be calculated using Equation 2.16 and the values in table 2.1, and at room temperature they are $k_1 \approx k_2 \approx 2 \cdot 10^{-26}\text{cm}^3\text{s}^{-1}$. As a consequence it can be concluded that $k_1, k_2 << k_3, k_4, k_5$, and $k_5 << k_3 \approx k_4$. It is worth to notice that, even if the hypothesis of Reactions 7.5(a) and (b) being diffusion limited does not apply, these relations between the $k_i$ remains valid. In fact, if Reactions 7.5(a) and (b) were reaction limited, the values of $k_1$ and $k_2$ would be even smaller, confirming the above reported relations.

Let us suppose that at the beginning of the process $E'_\gamma$ and $\text{H}_2\text{O}$ are present in a comparable amount inside the sample. ODC(II) is also present, but with a lower concentration. Then their concentrations start to decrease, due to Reactions 7.5(a) and 7.5(b). H and $\text{H}_2$ are instead transient products. In fact, they are created through Reactions 7.5(a), 7.5(d), 7.5(e), and then consumed in Reactions 7.5(c), 7.5(d) and 7.5(e).

It is possible to further analyze these considerations to discuss Equation 7.9. Atomic hydrogen is slowly (rate constant $k_1$) produced by Reaction 7.5(a), and rapidly (rate constants $k_3$ and $k_4$) consumed by Reactions 7.5(c) and 7.5(d). Even if it is present in a higher initial concentration, H will be consumed by Reactions 7.5(c) and 7.5(d) in a time depending on $k_3$ and $k_4$, during which the much slower Reactions 7.5(a) and 7.5(b) are almost frozen. Apart from this possible fast transient, that could influence the process at short times but not the overall kinetics, H concentration is always much smaller than those of $E'_\gamma$ and $\text{H}_2\text{O}$ ($[\text{H}] << [E'_\gamma], [\text{H}_2\text{O}]$). Moreover the dependence on time of its concentration follows the slow changes of $[E'_\gamma]$ and $[\text{H}_2\text{O}]$, but with the before mentioned lower concentration.

These considerations lead to the possibility to apply the so called steady state approximation [112, 120]

$$\frac{d[H]}{dt} = k_1[E'][\text{H}_2\text{O}] - k_3[E'][H] - k_4[H]^2 + k_5[E'][\text{H}_2] \sim 0 \quad (7.11)$$

Identical considerations can be applied to H$_2$, whose diffusion is rather faster than that of H$_2$O, and the steady state approximation can be applied to it too

$$\frac{d[H_2]}{dt} = k_4[H]^2 - k_5[E'][\text{H}_2] \sim 0 \quad (7.12)$$
7.4. Quantitative analysis of the effects of thermal treatments on point defects

From Equation 7.12 it follows that

\[
[H_2] \simeq \frac{k_4[H]^2}{k_3[E']}
\] (7.13)

As \(k_3 \sim k_4\) and \([H] < [E']\), the term \(k_4[H]^2\) can be neglected with respect to \(k_3[E'][H]\). Applying this approximation and substituting Equation 7.13, Equation 7.11 becomes

\[
\frac{d[H]}{dt} = k_1[E'][H_2O] - k_3[E'][H] \sim 0
\] (7.14)

From this equation the following expression for the hydrogen concentration can be derived

\[
[H] \simeq \frac{k_1[H_2O]}{k_3}
\] (7.15)

Concluding, by using the above reported approximations, the rate equations system reduces to

\[
\begin{align*}
\frac{d[E']}{dt} &= -2k_1[E'][H_2O] \\
\frac{d[ODC(II)]}{dt} &= -k_2[ODC(II)][H_2O] \\
\frac{d[H_2O]}{dt} &= -k_1[E'][H_2O] - k_2[ODC(II)][H_2O]
\end{align*}
\] (7.16)

The numerical solutions of this rate equations system will be now compared to the experimental data to verify their capability of accounting for the observed time dependence of the defects concentrations. Before doing it, we remember that the rate constants usually show a dependence on temperature described by an Arrhenius law, that can be written, for the two rate constants \(k_1\) and \(k_2\) that appear in the final rate equations system, as

\[
k_1 = A_1 \exp\left(-\frac{E_{a1}}{k_BT}\right)
\] (7.17)

\[
k_2 = A_2 \exp\left(-\frac{E_{a2}}{k_BT}\right)
\] (7.18)

where \(A_i\) and \(E_{ai}\) are the pre-exponential factor and activation energy for the \(i^{th}\) reaction, \(k_B\) is the Boltzmann’s constant and \(T\) the absolute temperature at which
the reactions take place. In the special case of diffusion-limited reactions (See Chapter 2) the pre-exponential factor \( A_i \) takes the form

\[
A_i = 4\pi r_0 i D_0
\]

\( \text{(7.19)} \)

where \( r_0 i \) is the capture radius and \( D_0 \) the pre-exponential factor for water diffusion. \( r_0 i \) represents a distance under which the reaction is supposed to immediately take place, and it is usually considered \( \approx 5 \cdot 10^{-8} \text{cm} \) for reactions between point defects and small molecules in silica [106]. \( D = D_0 \exp (-E_a/(k_B T)) \) is the diffusion constant of \( \text{H}_2\text{O} \) in silica.

According to the results discussed in Section 7.3 it is necessary to introduce a statistical distribution of the activation energies \( E_{a1} \) and \( E_{a2} \) to account for the glassy disorder. A first attempt to describe this disorder effect by means of a Gaussian distribution was made, but the resulting solutions of the rate equations did not satisfactorily describe the experimental data. As a consequence asymmetric distributions were introduced. They were described as the matching of two half Gaussians, having the same mean value \( E_{ai} \) and different widths. A half Gaussian describes the distribution at energies lower than \( E_{ai} \), and the other one the part at energies higher than \( E_{ai} \). So, for each \( E_{ai} \) distribution, two \( \sigma \) were introduced. They were called \( \sigma_{i1} \) and \( \sigma_{i2} \) and describe the width on the lower and higher sides, respectively, of \( E_{ai} \). A typical shape for a distribution built in the above illustrated way is shown in Figure 7.14.

A comparison between the experimental annealing curves of \( \text{E}'_\gamma \) and ODC(II) centres in the S300/An sample and the numerical solutions of the rate equations is shown in Figure 7.13. As anticipated, in this Figure filled and open symbols represents \( \text{E}'_\gamma \) and ODC(II) respectively. Their concentrations are plotted as a function of the treatment time at 150°C ((a) and (b)), 300°C ((c) and (d)) and 550°C ((e) and (f)). Lines are the result of a fitting procedure performed by introducing the asymmetrical statistical distribution for the activation energy mentioned above.

The initial values of \( [\text{E}'_\gamma] \) and \( [\text{ODC(II)}] \) were the ones measured before the beginning of each treatment. The water concentration at the beginning of the treatment at 150°C was set equal to the total amount of water necessary to account for the overall (from 150°C to 550°C) annealing of \( \text{E}'_\gamma \) and ODC(II) centres. At each following temperature step (300°C and 550°C) this initial \( [\text{H}_2\text{O}] \) value was decreased of a quantity equal to the number of water molecules consumed in the previous ones. The preexponential factor for water diffusion \( D_0 \) and the capture radius \( r_0 \) were set equal to literature values, \( D_0=1\cdot10^{-6}\text{cm}^2\text{s}^{-1} \) and \( r_0=5\cdot10^{-8}\text{cm} \) [106], and were used to calculate \( A_i \) for both the defects. The activation energies and the widths of their distributions were determined through the fitting procedure. The uncertainties on the activation energy values and on the widths are \( \pm 0.01 \text{eV} \) and \( \pm 0.02 \text{eV} \), respec-
7.4. Quantitative analysis of the effects of thermal treatments on point defects

It can be easily observed that the solutions of the rate equations are in satisfactory agreement with the experimental data. The rate constants calculated using the above mentioned $D_0$ and $r_0$ values and the mean $E_a$ values obtained through the fitting are reported in Table 7.2, together with the widths of their distributions corresponding to the solutions plotted in Figure 7.13.

An analogous comparison was made for the thermal treatments on the sample I301/A (See Section 7.3) for comparison, and the parameters obtained are reported in Table 7.3. No values for the annealing of ODC(II) at 300°C are reported as no changes in their concentration are observed at this temperature.

The reason for reporting $k_i$ instead than $E_{ai}$ is that single temperature experiments do not allow to obtain the true values for the activation energy and the pre-exponential factor, as the $E_{ai}$ value at a fixed temperature depends on the specific values of $D_0$ and $r_0$ used to calculate $A_i$. Only the widths and $k$ have a direct physical meaning.

The true values of $E_{ai}$ and $A_i$ can only be found by comparing data at different temperatures. Our data allow such an analysis. In Figure 7.15(a) the Arrhenius plot relative to process 7.5(a) is shown. The ln(k), calculated using the k values in Ta-
7. Annealing of point defects

**Table 7.2:** Rate constant values for the annealing of $E'_\gamma$ ($k_1$) and ODC(II) ($k_2$) and widths of the distributions of the activation energies in the sample S300/An treated at 150°C, 300°C and 550°C.

<table>
<thead>
<tr>
<th></th>
<th>150°C</th>
<th>300°C</th>
<th>550°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'_\gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td>$1.0 \cdot 10^{-27} cm^3s^{-1}$</td>
<td>$7.8 \cdot 10^{-23} cm^3s^{-1}$</td>
<td>$1.6 \cdot 10^{-20} cm^3s^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{11}$</td>
<td>0.45eV</td>
<td>0.28eV</td>
<td>0.25eV</td>
</tr>
<tr>
<td>$\sigma_{12}$</td>
<td>0.4eV</td>
<td>0.4eV</td>
<td>0.25eV</td>
</tr>
<tr>
<td>ODC(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$</td>
<td>$1.4 \cdot 10^{-27} cm^3s^{-1}$</td>
<td>$9.5 \cdot 10^{-24} cm^3s^{-1}$</td>
<td>$5.7 \cdot 10^{-20} cm^3s^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{21}$</td>
<td>0.35eV</td>
<td>0.25eV</td>
<td>0.1eV</td>
</tr>
<tr>
<td>$\sigma_{22}$</td>
<td>0.28eV</td>
<td>0.28eV</td>
<td>0.28eV</td>
</tr>
</tbody>
</table>

**Table 7.3:** Rate constant values for the annealing of $E'_\gamma$ ($k_1$) and ODC(II) ($k_2$) and widths of the distributions of the activation energies in the sample I301/A treated at 300°C and 450°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>300°C</th>
<th>450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'_\gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td></td>
<td>$7.8 \cdot 10^{-24} cm^3s^{-1}$</td>
<td>$1.2 \cdot 10^{-21} cm^3s^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{11}$</td>
<td></td>
<td>0.4eV</td>
<td>0.25eV</td>
</tr>
<tr>
<td>$\sigma_{12}$</td>
<td></td>
<td>0.4eV</td>
<td>0.35eV</td>
</tr>
<tr>
<td>ODC(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$</td>
<td></td>
<td></td>
<td>$6.4 \cdot 10^{-22} cm^3s^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{21}$</td>
<td></td>
<td></td>
<td>0.1eV</td>
</tr>
<tr>
<td>$\sigma_{22}$</td>
<td></td>
<td></td>
<td>0.35eV</td>
</tr>
</tbody>
</table>
7.4. Quantitative analysis of the effects of thermal treatments on point defects

Figure 7.15: Arrhenius plots relative to the annealing of (a) the $E'_\gamma$ and (b) the ODC(II) centres.

Variables 7.2 and 7.3, is plotted as a function of the inverse of the absolute temperature. Different symbols correspond to values of $k$ in different samples. The straight line is a linear fit of the data according to the Arrhenius law. The true values $E_{a1}=1.23\,\text{eV}$ and $A_1=6.8\times10^{-13}\,\text{cm}^3\text{s}^{-1}$ are found from the linear fit.

The same analysis on the ODC(II) centres was carried out (See Figure 7.15(b)), $E_{a2}=1.25\,\text{eV}$ and $A_2=1.09\times10^{-12}\,\text{cm}^3\text{s}^{-1}$ were obtained.

The fact that all the data can be fit by a single Arrhenius law proves that in all the cases examined the microscopic process is the same. So Reaction 7.5(a), with its secondary Reactions 7.5(c) and (e), is responsible for the annealing of $E'_\gamma$ and Reaction 7.5(b) for the annealing of ODC(II) in the whole temperature range examined, depending neither on the sample nor on the treatment. This result about Reactions 7.5(a) and 7.5(b) being responsible for the annealing of $E'_\gamma$ and ODC(II) in a wide temperature range and not only for the experiment discussed in Section 7.2 had been anticipated there.

The same analysis was performed by putting in the Arrhenius plot the mean values of the activation energies weighted over the statistical distribution, instead than the peak values, and a comparable result was obtained.

The activation energies distributions found deserve attention. A complete description of these distributions was obtained. In Figures 7.16 and 7.17 the distributions
7. Annealing of point defects

Figure 7.16: Distributions of $E_{a1}$ and $E_{a2}$, based on the parameters in Table 7.2 for the S300/An sample. Continuous line represents the distribution at 150°C, dashed line at 300°C, and dotted line at 550°C.

of $E_{a1}$ and $E_{a2}$ in the sample S300/An, based on the parameters in Table 7.2, are shown. Continuous line represents the distribution at 150°C, dashed line at 300°C, and dash-dotted line at 550°C. It can be observed that the widths of the distributions asymmetrically decrease by progressively increasing the treatment temperature. These results strongly confirm the idea that thermal treatments modify the activation energies distributions for the annealing of point defects, already put forward on a qualitative basis in Section 7.3. It is found in fact that thermal treatments erode those processes having lower activation energy, evidencing the inhomogeneity of the process.

Finally the rate constants for processes 7.5(a) and 7.5(b) can be calculated using the values of $E_a$ and $A$ found. These experimental rate constants, calculated at 300K, are $k_1=1.4\times10^{-33}$cm$^3$s$^{-1}$ and $k_2=1.1\times10^{-33}$cm$^3$s$^{-1}$. The value expected for diffusion-limited processes, calculated considering the literature data of $E_a$ and $D_0$ for water diffusion, is $k=2.3\times10^{-26}$cm$^3$s$^{-1}$, much higher than the experimental values $k_1$ and $k_2$. This comparison between the experimental values and the value expected for diffusion-limited processes makes immediately evident that the theory of diffusion-limited processes is not adequate to account for the experimental data. In fact the observed processes are slower than expected for a diffusion-limited process. This ev-
Conclusions

Figure 7.17: Distributions of $E_{a2}$, based on the parameters in Table 7.2 for the S300/An sample. Continuous line represents the distribution at 150$^\circ$C, dashed line at 300$^\circ$C, and dotted line at 550$^\circ$C.

Evidence indicates that both Reactions 7.5(a) and 7.5(b) are reaction-limited. This fact also means that the distributions of activation energies introduced basing on the results of Section 7.3 are relative to the activation energy for reaction. This latter fact was already guessed before, as in the experiment shown in Section 7.3, all the comparisons were made between samples undergoing the same treatment at the same temperature, and differing only for their previous thermal history. Moreover, no modification in the Raman spectra, and consequently in the structure of the glass matrix on which the diffusion properties of a given molecule depend, was observed after the pretreatments of the samples in that experiment. As a consequence, it was stated that the diffusion properties were the same in the couples of samples compared, and the differences observed were due to differences in the activation energy distribution for the reaction process, that therefore could be hypothesized to be the limiting one.

However the quantitative analysis shown in this Section allows to unambiguously state this conclusion about the character of reactions 7.5(a) and 7.5(b).
7. Annealing of point defects

7.5 Conclusions

In this Chapter a characterization of the annealing processes of $E', \gamma$ and ODC(II) centres was given. In the first Section the microscopic processes were unambiguously identified among those proposed in literature. Reactions with diffusing water molecules are responsible for the thermal annealing of both the defects. In the second Section it was given for the first time a direct experimental evidence that the activation energies of the reaction processes responsible for the annealing of point defects in amorphous silicon dioxide are distributed. As such a distribution of activation energies is intimately related to the intrinsic disorder of the amorphous lattice, it can be thought to be a general feature of point defects in disordered solids. Finally the annealing data were compared to the solutions of the rate equations system describing these processes. The values of activation energies and the shapes of their distributions were obtained. It was also concluded that these annealing processes are reaction-limited. A quantitative estimation of the changes induced in the activation energies distributions by thermal treatments was obtained too, evidencing that an asymmetric shrinkage occurs.
Conclusions

In this Thesis an experimental study on the effects of the presence of small diffusing molecules in amorphous silicon dioxide subjected to thermal annealing was reported. The interest toward this subject is mainly due to the widespread presence of impurities, and in particular small molecules as hydrogen, oxygen or water, even in nominally high purity silica, and to the extensive use of thermal treatments in the industrial production procedures of many devices.

Annealing experiments, both in normal and controlled atmospheres, were performed and their effects on either as-grown either irradiated samples were studied. This investigation was carried out by using several spectroscopic techniques, aiming to probe different features of the material. The great relevance of these processes related to diffusing molecules was evidenced. In the following the main results obtained are summarized.

At first we investigated the effects of thermal treatments on the intrinsic properties of silica. The OH content, that is an important property usually used to characterize different silica types, was observed to change upon thermal treatment. OH groups were in fact generated in synthetic, originally dry, silica annealed in helium or oxygen atmospheres at \( \sim 400^\circ\text{C} \). This effect was observed in previous works as a consequence of the reaction of the network with molecules, for example water, absorbed from the treatment atmosphere. We showed instead for the first time, by performing treatments in inert atmosphere, that it can exist also as an intrinsic process. The OH generation process observed is suggested to consist in the reaction of H\(_2\), already present in the material, with peroxy linkages and regular network sites. As a consequence, originally dry materials can lose this property when thermally treated. This is an important effect that should be taken into account in all those applications for which OH free materials are needed.

We also dealt with the effects of thermal treatments and of the presence of small molecules on the interaction of radiation with silica. Hydrogen loading is nowadays commonly used to improve the performances of silica in applications as, for example, the production of optical fibers. For this reason it was studied in the past and a satisfactory description of the basic phenomena related to the improvement in the
radiation toughness of silica due to the presence of hydrogen was obtained. We focused instead on the effects of the presence of oxygen molecules, as a wide class of radiation induced point defects of great technological interest is related to oxygen deficiency, while some others to oxygen excess. Moreover, oxygen treatments play an important role in the thermal oxidation of silicon. We also checked the eventual effects of high temperature and pressure, not depending on the oxygen excess. To this purpose we compared the radiation effects in O$_2$ treated, He treated, and untreated samples. A complex scenario originates from this comparison. The effects of the thermal treatments on the generation efficiency of point defects strongly depend on the defect examined. However all the observed effects were explained in terms of changes in the number of precursor sites. In particular we observed that the generation efficiency of the ODC(II) centre was reduced both in helium and oxygen treated samples. As a consequence this effect was ascribed to high temperature and pressure modifications induced in the precursor sites of this defect. An increase in the generation efficiency of NBOHC and POR was instead observed in the O$_2$ treated samples. It was attributed to the specific action of O$_2$, that determines the formation of oxygen excess sites as the peroxy linkages, precursors for these defects. Oxygen excess could also lead to the formation of ozone molecules upon irradiation, that could contribute to the OA of silica in the UV spectral range, but this contribution to the OA spectrum seems negligible. Finally, the presence of dissolved oxygen also inhibits some hydrogen related processes, as the generation of H(I) centers. A full understanding of these effects could allow to set up specific treatments to enhance the radiation resistance of the materials with respect to spectral features of interest, even if this could imply loss of performances in other ranges. Moreover, as for the changes in the OH content mentioned above, all these effects have to be taken into account in the optimization of materials to be used in radiative environments.

Finally the effects of the thermally activated diffusion of small molecules on two radiation induced oxygen deficient point defects, the E’$_\gamma$ and ODC(II) centres, were studied. Data about the thermal annealing of these centres, usually attributed to their reaction with diffusing molecules, are reported in literature. However, many aspects of these processes, as the details of the microscopic mechanisms, their character, and quantitative information about their activation energies were still unknown or needed to be clarified.

We unambiguously identified the microscopic processes responsible for these annealings by comparing the efficiency of the processes in samples treated in different atmospheres of water, oxygen or helium. Reactions with diffusing water molecules were established to cause the thermal annealing of both the defects. We also gave, for the first time, a direct experimental evidence that the activation energies of the processes responsible for the annealing of point defects in amorphous
Conclusions

Silicon dioxide are distributed. Since such a distribution of activation energies can be hypothesized to be intimately related to the intrinsic disorder of the amorphous lattice, it can be thought to be a general feature of point defects in disordered solids. Finally we compared the solutions of the rate equations system describing these processes to the annealing data, to obtain quantitative information on the character of the processes, the activation energies and their distributions. It was concluded that these annealing processes are reaction-limited. The values of activation energies and the widths of their distributions were obtained. A quantitative estimation of the changes induced in the activation energies distributions by thermal treatments was obtained too.

We think that these results constitute an important progress in the understanding of the processes related to the presence and diffusion of small molecules in silica. We proved that they play a primary role in many phenomena of both basic and technological interest. As a consequence they have to be deeply understood, and taken into account to improve the production techniques of materials and devices.
List of related papers


- L. Nuccio, S. Agnello, R. Boscaino *Role of H₂O in the thermal annealing of the E’γ in amorphous silicon dioxide*, submitted to Physical Review B.
Bibliography


[151] M.Leone, S.Agnello, R.Boscaino, M.Cannas, and F.M.Gelardi. In *Silicon-based ma-


