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Defect Related Luminescence in Silicon Dioxide Network: A Review

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1. Introduction

The discovery of strong luminescence at room temperature from silicon cluster has attracted an enormous attention in recent years due to its potential applications in Si-based optoelectronic devices, especially blue and UV luminescence devices. Several studies have addressed the question of augmentation and stabilization of luminescence emission with different treatments, such as electron irradiation, thermal treatments and ion implantations. Even though observed visible light can be explained by the quantum confinement (QC) effect, many experimental results obey to the QC model supported surface state. Theoretically, the effects of quantum confinement on band gap of silicon indicate that it should be possible to obtain a blue light or shorter wavelength photons from the porous silicon if the silicon crystal size can be reduced to a certain value, e.g. to the diameter of 2-5 nm. However, it is rather difficult in practice to obtain a blue/white luminescence even when nanocrystals with diameters smaller than 2.0 nm are present. Some authors attributed this difficulty to the formation of surface Si-O bonds, which lead to mid-band gap trapped electrons and hole exciton states and thereby remove the dependency of the luminescence on cluster size. But in this case a luminescence emission was obtained in the red and yellow regions. It was found that some post-treatments such as anodic oxidation and oxidation in air could reduce the effective size of the Si nanocrystallites, thus causing a blue shift of the luminescence spectrum. If the red-yellow emission of the PS could be combined with a blue/green emission by modification of the PS surface such as oxidation or metal coating, it would be possible to obtain white light. This would mean an economical route to silicon based LEDs. Silicon dioxide, SiO₂, is widely distributed in the environment, and is present in the form of sand on all beaches and deserts. It is the starting material for the production of silicate glasses and ceramics. It may occur in crystalline or amorphous form, and is found naturally in impure forms such as sandstone, silica sand or quartz. Its specific gravity and melting point depend on the crystalline structure. Silica is known to occur in many crystalline phases or modes (α -quartz, β -quartz, α -cristobalite, β -cristobalite, α -tridymite, β -tridymite, γ -tridymite, coesite, melanophlogopite, keatite, fassigite, stishovite, chalcedon, agate, moganite, and others) besides some amorphous phases (opal, hyalite, sintered pearl, lechateierite, natural silica glass) [Fanderlik 1991]. Silicon dioxide is not only one of the most abundant materials on earth as mentioned, but also a critical material component of considerable technological importance. Today's modern electronics greatly depends on silicon dioxide for the manufacture of semiconductors and microelectronic devices, besides

it is the basic material of which the most of common communication optical fibers are presently made. In its pure amorphous form, it is drawn into fibers for use in optical communications. Its high melting temperature (≈ 1700 °C) and its chemical stability make it an excellent thermal and electrical insulator and hence the principal dielectric in silicon electronic technology, particularly in metal-oxide-semiconductor (MOS) devices [Nicollian and Brews 2002], where it is used as a gate oxide. High quality SiO_2 films are obtained by thermal oxidation of silicon; thermally oxidized SiO_2 forms smooth and low-defect interfaces with Si.

From a fundamental point of view, silicon dioxide is equally useful as a model amorphous material because of its chemical simplicity. It is not surprising that much research effort has been expended to understand the properties of this material. Despite hundreds of publications available, only in a few cases have an unequivocal identification of the atomic structure of the defects and an explanation of their production mechanisms been attained [Griscom 1977, Skuja 1998]. Most of the available information comes from theoretical models and other experimental investigations of naturally or synthetically prepared specimens, but many questions still remain unsolved. Accordingly, many of the optical features characterizing the as-grown material (that is the material prior to any treatment) are not attributable to a specific defect having a known structure. Also, the identification of the precursor of radiation-induced defects and the exact mechanism of their generation are still debated. As the number of device components on a chip continues to increase, where the performance and reliability of these devices are controlled by electrically active defects, the precise control of oxidation and its understanding on an atomic scale of silica has been a subject of great interest and importance in the modern Si technologies, especially those related to thin oxidize layers with high quality. It has been observed that irradiation, mechanical stress, temperature change and the presence of impurities can effect the formation of defects and/or the transformation of existing defects to other defects in SiO_2 [Mitchell and Denure 1973, Trukhin et al. 1998, Fitting et al. 2004]. Irradiation of SiO_2 induces various types of structural defects, which cause degradation in SiO_2 -based electronic and optical devices. Charge trapping at these defect sites degrades the current/voltage performance of metal-oxide semiconductor (MOS) devices, for example, and ultimately leads to device failure when such a device is exposed to high-energy radiation in space-based applications. Such and other problems are caused or at least initiated by the creation or transformation of luminescent point defects. Therefore a physical understanding of the structure and formation mechanisms of these defects is becoming increasingly important. But because of the nature of the chemical bond in silicon dioxide, a reliable guess of the detailed structure of particular luminescent defects has not been possible until now. A point defect embedded in a solid matrix (crystal or amorphous) is strongly interacting with its neighboring atoms. Then the study of the electronic states of the luminescent defects is a many-body particles system problem.

A half century of spectroscopy examinations of point defects in crystalline and glassy silica have led to identification and characterization of about a dozen intrinsic defect types (those constructed of silicon and/or oxygen atoms or ions) and around ten times as many defect varieties involving the presence of impurities. Luminescent defects in SiO_2 could be electrically charged or uncharged, diamagnetic or paramagnetic. Many such defects have been associated with optical absorption or emission bands, which may pose problems for long-path-length optical systems (fiber optics). Luminescent defects in amorphous silicon dioxide ($a\text{-SiO}_2$) have been defect investigated by numerous spectroscopic techniques,

including optical absorption spectroscopy (OA), electron spin resonance (ESR) or the often so-called electron paramagnetic resonance (EPR), photoluminescence spectroscopy (PL), photoluminescence excitation spectroscopy (PLE), cathodoluminescence spectroscopy (CL), infrared spectroscopy (IR), Raman spectroscopy and many more. All of these experimental approaches have yielded valuable insights, but have not given an explicit model for defect types in silica network. ESR spectra have afforded some detailed atomic-scale structure characterizations, especially of two fundamental classes of defects: a dangling electron on Si atom denoted by E' -center and the oxygen deficient center (ODC). These defects have been known in α -SiO₂ since 1956 [Weeks 1956].

2. Structures, defects and properties of silicon dioxide

2.1 Structure of pure silicon dioxide

The basic structural unit of vitreous SiO₂ and silicate glasses is the SiO₄ tetrahedron [Mozzi and Warren 1969, Bell and Dean 1972, Gerber and Himmel 1986]. A tetrahedron is a polyhedron composed of four triangular faces, three of which meet at each vertex. A regular tetrahedron is one in which the four triangles are regular, or "equilateral," and is one of the platonic solids (convex polyhedron). There are four oxygen atoms, one located at each apex of a regular tetrahedron and a single silicon atom is located at the center of the tetrahedron, Fig. 2.1. This silicon atom has a valence charge of 4 in sp^3 orbitals, meaning that it is looking to acquire four electrons through sharing with other atoms to complete its outermost energy shell, known as the valence shell. An oxygen atom has two electrons in its outermost shell that are available to bond with the silicon atom. If four oxygen atoms surround one silicon atom, where each oxygen atom offers one electron, then the silicon atom's outermost shell will be complete and stable. The resulting arrangement comprises a silicate molecule. One electron remains, allowing those oxygen atoms to search for another silicon atom to share an electron and form another tetrahedron. Tetrahedrons are linked together through oxygen bonds and the arrangement of these links between the basic tetrahedral units determines the classification of the silicate. When the tetrahedra are not linked together, as each exists in isolation, the material is classified as a Nesosilicate. If groups of two tetrahedra are linked together, the material is then classified as a Sorosilicate. If all of the tetrahedra link back onto each other to form a closed ring, then the material becomes a Cyclosilicate.

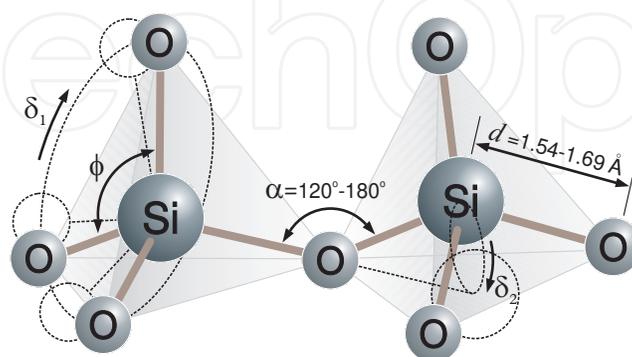


Fig. 2.1 Three-dimensional schematic of a pure fragment of the regular silica structure. The structure is defined by several parameters; the Si-O bond length (d), the tetrahedral angle (ϕ), the inter-tetrahedral bond angle (α), and the bond torsion angles (δ_1 , δ_2), [Henderson and Baker 2002].

The bonding in silicon dioxide is complex. The Si-O bond energy is very high (4.5 eV) compared to the Si-Si bond (2.3 eV) and has an approximately 50:50 ionic:covalent nature and lone-pair oxygen orbitals are present [Fanderlik 1991, Edwards et al. 2000]. The covalency favors tetrahedral coordination of Si by O and maintains the O-Si-O bond angle (φ) very close to the ideal tetrahedral angle of 109.5° . Some of the literature indicates that the Si-O bond length (d) in various modifications of silicates may vary in the range of 0.154 nm to 0.169 nm [Slater 1965, Weber and Cromer 1965], while the mean value specified for d is 0.162 ± 0.005 nm. In most cases one can treat the SiO_4 tetrahedra as rigid units, which can be linked together by their corners to form pairs, rings, chains, sheets, or frameworks. In this case the inter-tetrahedral Si-O-Si bond angle (α) can be defined. Measurements have been shown that the angle (α) varies with the different tetrahedra of the polyhedron, according to respective form of silicas (for vitreous SiO_2 from 120° to 180° and for quartz between 146° and 155°) [Fanderlik 1991, Nicholas et al. 1991].

Fig. 2.2 shows how the energy of a Si_2O_7 pair of tetrahedra varies as a function of Si-O bond length and the Si-O-Si bond angle [van Santen et al. 1991]. It is demonstrating that Si-O-Si bonds prefer to be linked rather than straight. However, the gently-sloping energy valley extending to 180° , which implies large variations in Si-O-Si bond angle (α) could occur in a structure with relatively slight energy penalty in order to accommodate changes in temperature, pressure, bulk composition, or local atomic environment. Silica does not produce any separate molecules ($\text{O}=\text{Si}=\text{O}$) because double bonds do not form. The parameters, such as the inter-tetrahedral bond angle (α) and the bond torsion angles (δ_1, δ_2), that define the way in which individual tetrahedra are linked together are highly variable [Mozzi and Warren 1969]. This variation in parameters distinguishes a glass from its corresponding crystalline analogue. To avoid the formation of a structural entity with an unsaturated electron cloud at the silicon atom in the case of a single bond, the $[\text{SiO}_4]^{4-}$ tetrahedra join to produce a polymer with various spatial arrangements. As a result of the alternative possibilities of structural arrangement, there exist a number of modifications of crystalline silica. In other words, the different types of silicate structure arise from the ways in which these tetrahedra are arranged. They may exist as separate unlinked entities, as linked finite arrays, as infinite one-dimensional chains, as infinite two-dimensional sheets or as infinite three-dimensional networks.

2.2 Intrinsic defects in silicon dioxide

The presence of defects in the silica matrix can dramatically change its structural, electrical, and optical properties. Many parameters, such as manufacturing processes, irradiation, mechanical stress, change of temperature, and the presence of impurities may cause the formation of defects and/or lead to the transformation of the existing defects to other types of defect. Commonly, defects can be grouped according to their structure and size as point defects, dislocations (linear defects), and plane defects [Stevens-Kalceff and Philips 1995, Kofstad 1988]. The following types of point defects can be considered as intrinsic or extrinsic. Intrinsic point defects involve atoms of the host matrix only, i.e. vacancies (the host atoms are missing, Schottky defects or Frenkel pairs) and self-interstitials (additional host atoms at an interstitial position). Extrinsic point defects involve atoms chemically different from the host crystal, such as those used for electrical doping. Defects in a perfect silica glass could include oxygen or silicon vacancies and their interstitials, Si-Si or O-O homobonds or under-coordinated silicons or oxygens.

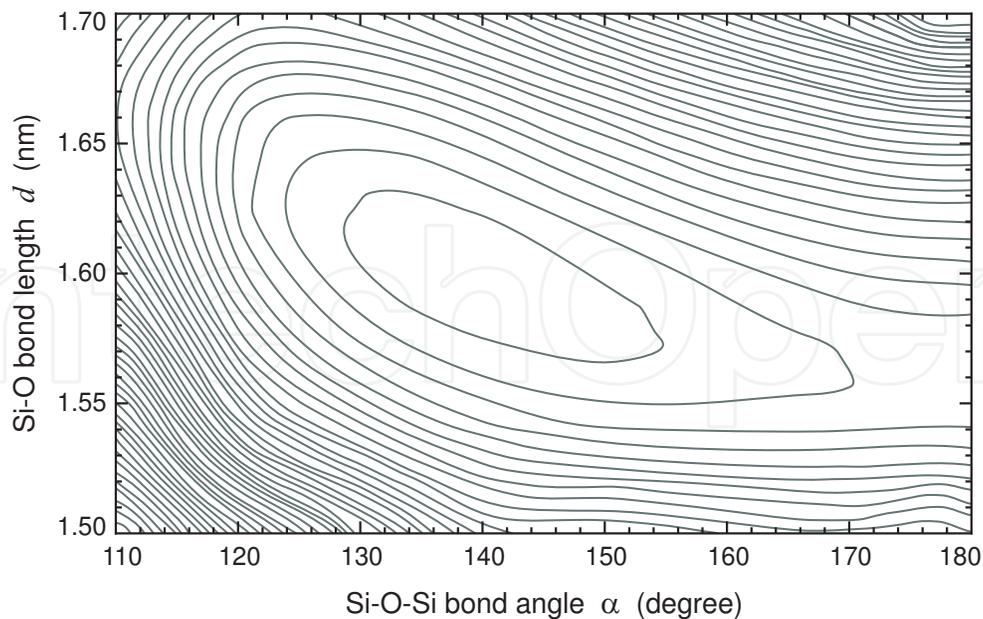


Fig. 2.2 Total energy as a function of Si–O bond length and Si–O–Si bond angle. Contour lines in units of kJ/mol, [van Santen et al. 1991].

Due to the high Si–O bond energy (4.5 eV), the crystalline quartz is resistant to chemical weathering (it is only soluble in hydrofluoric acid and in hot alkalis) and to corrosion [Lamkin et al. 1992, Lide 2004]. It is hard (Mohs' hardness 7), brittle, and has a very high melting point at around 1710°C [Lide 2004]. Due to its wide energy band gap of about 9 eV, it is optically transparent and shows low electrical conductivity [Fan et al. 1998].

Generally, a homobond is electrostatically neutral although both Si–Si and O–O bonds may become positively charged by trapping holes. Irrespective of their electrical charges, defects can be divided into two classes: diamagnetic and paramagnetic. As a general rule, all stable paramagnetic defects have optical absorption bands associated with them, since they represent half-occupied energy transitions to the valence band and electron transitions to the conduction band are both possible. Diamagnetic defects may have absorption bands associated with electron transitions to the conduction band. The confirmed examples of diamagnetic defects in α -SiO₂ have electron absorption bands in the ultraviolet or vacuum ultraviolet spectral regions, implying that the uppermost filled levels of these states lie below the middle of the 9 eV band gap [Griscom 1977].

A variety of defect structures are known to exist in silica materials and were one of the major subjects of extensive experimental and theoretical studies [Stevens-Kalceff 2000, Song et al. 2001, Lu et al. 2002]. Many aspects regarding the nature of the defects and their correlated properties are still controversial and not yet completely understood. Quite a lot of defect types have been discussed in the literature and many reproduction models have been proposed for each one. In this part we will review the main defects in the silica network but whether any of these models is correct remains an open question of considerable interest.

2.2.1 E' -center

Probably the best known paramagnetic defect in all forms of SiO₂ is the E' -center which was first detected in late fifties using electron paramagnetic resonance (EPR) spectroscopy [Weeks 1956, Weeks and Nelson 1960, Griscom et al. 1974, Gobsch et al. 1978]. It is

associated with the 5.85 eV absorption band in quartz and silica glass and no associated emission band has been observed where its nonradiative mechanism has been reported by some authors [Pacchioni et al. 1998a, Kajihara K. et al. 2003]. From studies of the hyperfine structure in the EPR spectrum it is known that E' -center can comprise an unpaired electron in a dangling tetrahedral (sp^3) orbital of a single silicon atom which is bonded to just three oxygens in the glass network [Griscom 1979a, Isoya et al. 1981]. This generic E' -center is shown in Fig. 2.3, which is often denoted by $\equiv\text{Si}\bullet$, where the three parallel lines represent three oxygen separate bonds to one silicon atom and the dot denotes the unpaired electron.

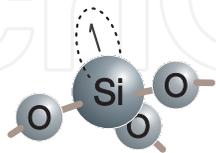


Fig. 2.3 Generic E' -center. The large atom is silicon, the smaller ones are oxygens

Previous EPR studies on irradiated α - SiO_2 have demonstrated that there are several distinguishable variants of the E' -center in terms of their g values but in common all have the structure $\equiv\text{Si}\bullet$ [Griscom 1990a]. These E' -center variants are also distinguished by virtue of different annealing kinetics depending on both the character of the irradiation and the water contents in dry or wet oxidized SiO_2 , as shown in Fig. 2.4 [Griscom et al. 1983, Griscom 1984, Griscom 1985].

Four main types of E' -centers, labeled E'_α , E'_β , E'_γ and E'_s have been identified in vitreous silica depending on their spectroscopic signatures [Skuja 1998]. Several models have been suggested based on different precursors for each of these defects where some of these types are associated with hydrogen atoms. Optically stimulated electron emission technique (OSEE) shows that each one of these types of E' -centers has a distinguishable absorption band in the range of 5.7 eV [Zatsepin et al. 2000], see Fig. 2.5.

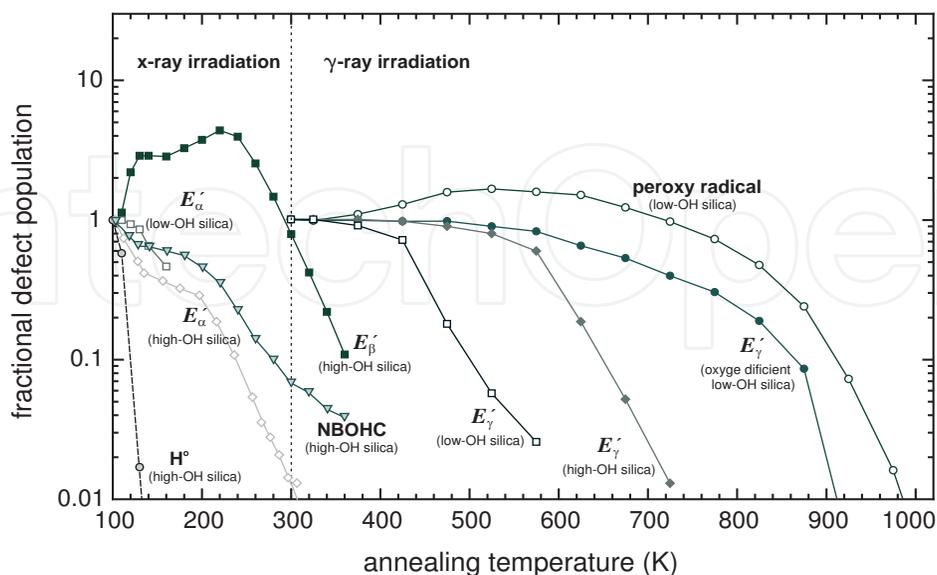


Fig. 2.4 Normalized isochronal anneal curves for radiation-induced defect centers (E' , NBOHC and peroxy radical) in high-purity silica (low-OH silica: <5 ppm OH and high-OH silica: 1200 ppm OH), [Griscom 1984].

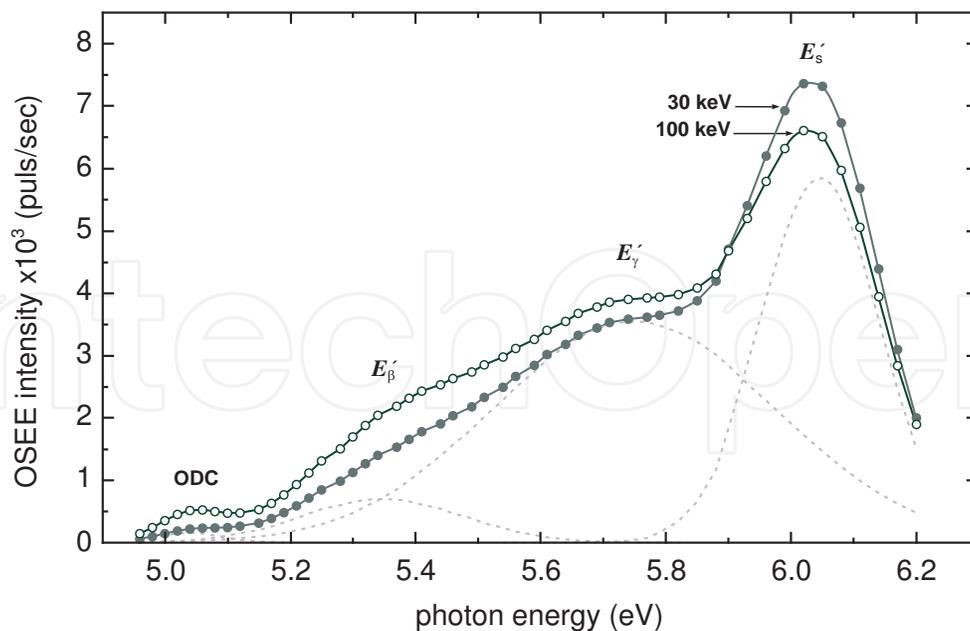


Fig. 2.5 OSEE spectra of glassy SiO_2 irradiated by Fe^+ ions of two different energies, 30 and 100 keV, the absorption bands of E'_β , E'_γ and E'_s -centers are detected, besides a very weak absorption band associated with oxygen deficient centers (ODC), [Zatsepin et al. 2000].

It was inferred that the E'_α variant in silica initially observed by Griscom [Griscom 1984], is a defect which tends to anneal in times on the order of minutes up to hours above 100 K. It was suggested that this center is created by a radiolytic process which moves an oxygen atom from an undisturbed network site $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ into a neighboring position which must be chemically bonded, since insufficient energy can be transferred from an X-ray generated Compton electron to result in a net breakage of bonds [Uchino et al. 2001]. Fig. 2.6 illustrates one of the conceivable ways in which such a process could come about. The oxygen-oxygen (peroxyl $\equiv\text{Si}-\text{O}-\text{O}$) bond suggested to be formed in Fig. 2.6 should be a relatively stable entity according to recent theoretical calculations [Griscom 1979a]. Still, less exotic mechanisms for E'_α production, not inconsistent with the data, might be the momentary rupture of strained oxygen bonds $\equiv\text{Si}\cdots\text{O}-\text{Si}\equiv$. Here $\bullet\text{O}-\text{Si}\equiv$ is the notation for the non-bridging oxygen hole center (NBOHC), and is in fact seen by electron spin resonance (ESR) in X-ray irradiated silicas in numbers comparable to the E'_α -center.

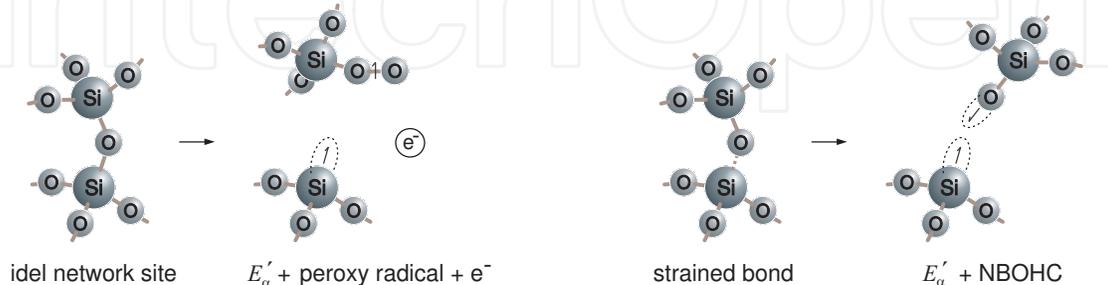


Fig. 2.6 Schematic models for the E'_α -center in pure $a\text{-SiO}_2$, the arrow denotes the unpaired spin and dashed balloons represent their orbital.

E'_β in silica network (E'_2 in quartz) features a proton trapped in the oxygen vacancy and the silicon atom containing the unpaired spin relaxed outwards [Griscom 1991, Weeks 1963], i.e.

the interaction of the unpaired spin associated with a long-bond silicon with the hydrogen atom is weak enough to not saturate each other. Two possible formation reactions of E'_β are shown in Fig. 2.7.

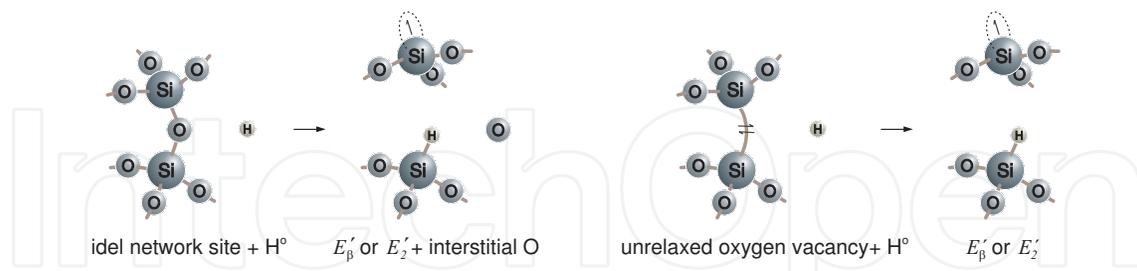


Fig. 2.7 Schematic models for the E'_β -center in pure α -SiO₂. The arrow denotes the unpaired spin and dashed balloons represent their orbital. The E'_β -center is considered to be the closest analog for E'_2 -center in quartz.

E'_γ -center is the closest analog of the E'_1 -center in α -quartz [Griscom 1980, Boero et al. 1997]. According to current theoretical calculations [Feigl et al. 1974, Yip and Fowler 1975, Mysovsky et al. 2004], E'_γ is suggested to consist of a positively charged single oxygen vacancy composed of a nearly planar $\equiv\text{Si}^+$ unit and a singly occupied dangling bond $\equiv\text{Si}\bullet$, namely, $\equiv\text{Si}^+ \bullet\text{Si}\equiv$ [Uchino et al. 2000b, Agnello et al. 2002]. An unrelaxed oxygen monovacancy ($\equiv\text{Si}\cdots\text{Si}\equiv$) or an unperturbed SiO₂ fragment ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) is assumed to be the precursor of this defect as shown in Fig. 2.8. There is no indication that hydrogen is involved in this defect [Feigl et al. 1974]. E'_γ is stable for years at room temperature [Griscom 1984].

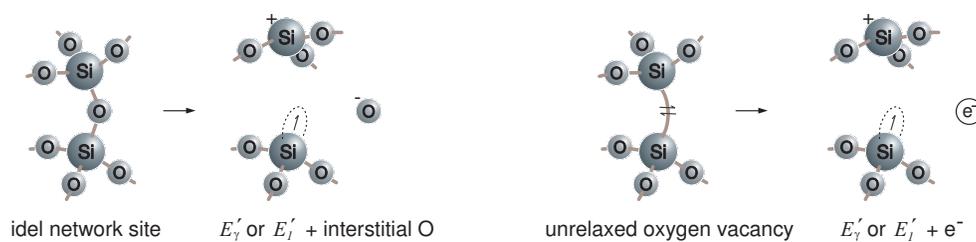


Fig. 2.8 Schematic models for the E'_γ -center in pure α -SiO₂. The arrow denotes the unpaired spin and dashed balloons represent their orbital. The E'_γ -center is considered to be the closest analog for E'_1 -center in quartz.

Relaxing of the Si atom with the unpaired spin towards oxygen vacancy results in the E'_4 -center. It is in fact the most reliably characterized of these defects depending on the experimental and theoretical analysis [Isoya et al. 1981]. E'_4 -center consists of a hydrogen substituting for an oxygen atom in α -quartz [Mysovsky et al. 2004]. This center, Fig. 2.9, is observed in crystalline silicon dioxide (α -quartz) but there is no evidence of existence of E'_4 -center in silica glass [Griscom and Friebele 1986]. Some other authors [Rudra et al. 1985, Majid and Miyagawa 1993, Snyder and Fowler 1993] suggested that the E'_2 and E'_4 are in fact the same defect, but with long-bond silicon relaxed through the plane of its three oxygen neighbors such that the unpaired spin points away from the vacancy. But this configuration is predicted to be slightly lower in energy than the E'_4 configuration. In surface center studies, several variants of surface E' -centers were found [Bobyshev and Radtsig 1988]. Two of them are depicted in Fig. 2.10, $E'_s(1)$ which seems like the normal E' -center but with a constant isotropic hyperfine splitting, and the second is $E'_s(2)$ which has a dangling silicon bond with a neighboring hydroxyl (OH) group [Skuja 1998].

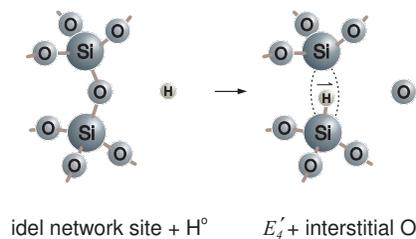


Fig. 2.9 Schematic model for E'_4 -center in crystalline SiO_2 . The arrow denotes the unpaired spin which interacts with a hydrogen atom to relax the oxygen vacancy by forming Si-Si bond.

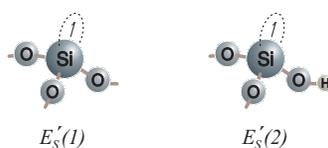


Fig. 2.10 Schematic models for surface E' -center (E'_s) in pure $a\text{-SiO}_2$. The arrow denotes the unpaired spin and dashed balloons present their orbital. Hydrogen saturates the dangling oxygen bond

2.2.2 Oxygen-deficiency center (ODC)

It should be mentioned first that all E' -center types are also considered as oxygen deficiency centers but in this subsection a review of a different (non-paramagnetic) kind of oxygen deficiency center will be given. This defect center is entitled simply by a neutral oxygen vacancy which is often denoted ODC and indicated generally as $\equiv\text{Si}-\text{Si}\equiv$.

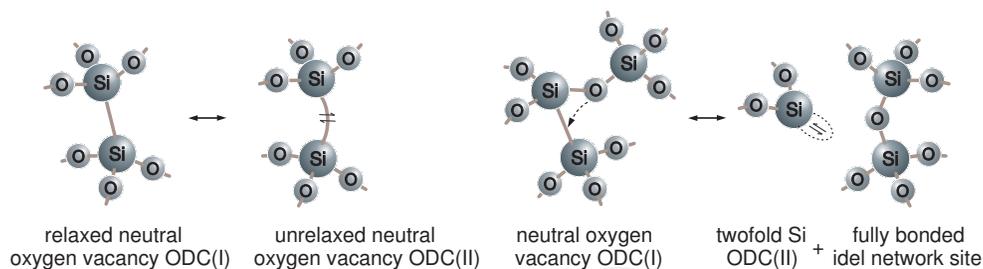


Fig. 2.11 Schematic illustration of the transformation between ODC(I) and ODC(II) visualizing two possible models for the ODC(II), the unrelaxed oxygen vacancy and the twofold coordinated silicon.

It is diamagnetic and can be directly investigated by photoluminescence (PL) or cathodoluminescence (CL) spectroscopy. The literature mostly describes two models for the ODCs: neutral oxygen vacancy ODC(I) and the twofold coordinated silicon ODC(II) denoted as $=\text{Si}\bullet\bullet$. The ODC(I) represents one of the essential defects in all silicon dioxide modifications in a form of simple oxygen vacancies; here two Si atoms could relax and make a silicon silicon bonding (relaxed oxygen vacancy $\equiv\text{Si}-\text{Si}\equiv$) or stay in unstable interaction condition and form an unrelaxed oxygen vacancy ($\equiv\text{Si}\cdots\text{Si}\equiv$) which each one of them could be a precursor for the other under some undeclared circumstances, see Fig. 2.11, and both are considered as a key role in many defect-type generations and transformations in the silica matrix, as shown in Figs. 2.7 and 2.8. The 7.6 eV absorption band in irradiated and as grown $a\text{-SiO}_2$ has been ascribed to the neutral oxygen vacancy ODC(I) [Imai et. al 1988,

Hosono et al. 1991]. The ODC(I) can also be converted to $\equiv\text{Si-H}$ groups in thermal reaction with hydrogen molecules according to the visualized reaction shown in Fig. 2.12.

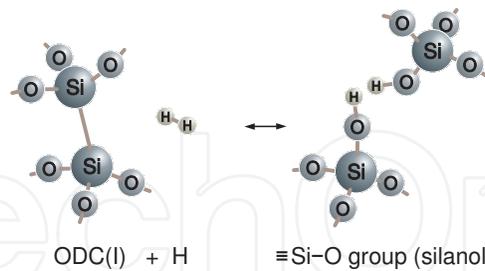


Fig. 2.12 Schematic illustration of the ODC(I) conversion to silanol groups in thermal reaction with hydrogen molecules.

In addition, two photoluminescence (PL) bands, 4.4 eV (decay constant $\tau=4$ ns) and 2.7 eV (decay constant $\tau=10.4$ ms) have been observed under excitation of the 5 eV, 6.9 eV or 7.6 eV bands, indicating the interaction of ODC(II) with ODC(I) [Nishikawa et al. 1994, Seol et al. 1996]. Based on their lifetimes, the 4.4 eV and 2.7 eV bands have been ascribed to singlet-singlet ($S_1 \rightarrow S_0$) and triplet-singlet ($T_1 \rightarrow S_0$) transitions at the site of oxygen-deficient type defects, respectively [Skuja 1998]. The interconversion between the ODC(I) and ODC(II) in an energy diagram is given in Fig. 2.13. The origin of ODC(II) associated with the optical absorption band at ~ 5 eV is one of the most controversial issues in the defect research field of a-SiO₂ [Skuja et al. 1984, Griscom 1991, Skuja 1992a, Skuja 1998]. The first model hypothesis suggested for ODC(II) was a neutral diamagnetic oxygen vacancy [Arnold 1973], later two other models have been proposed for ODC(II): twofold coordinated silicon [Skuja et al. 1984, Skuja 1992a] and the unrelaxed oxygen vacancy [Imai et al. 1988] as shown in Fig. 2.11. The oxygen vacancy model was further supported by the finding that two-photon photobleaching of SiODC(II) by KrF laser ($h\nu=5$ eV) generates E' -centers [Imai et al. 1988]. But the origin of the ODC(II) is still a matter of controversy.

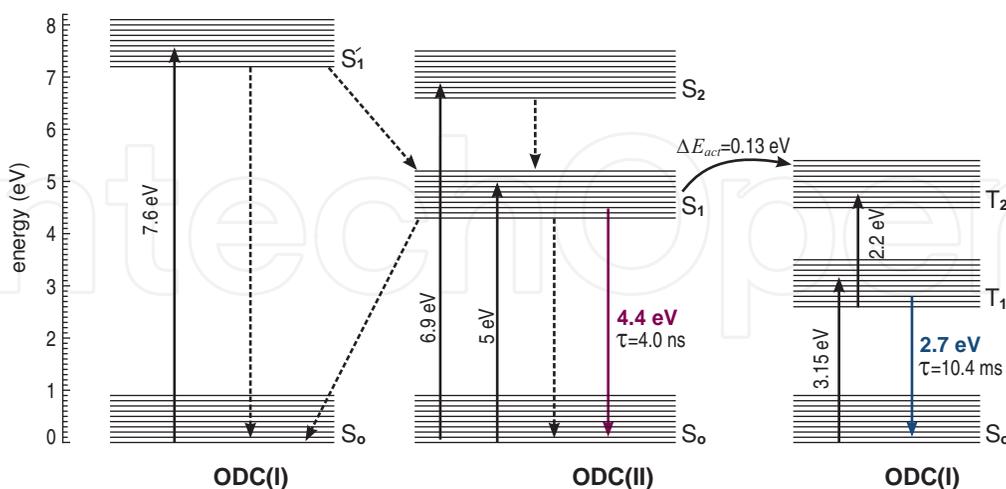


Fig. 2.13 Diagram of the energy levels proposed for the optical transitions at the site of two oxygen-deficient centers: ODC(I) and ODC(II). Transformation between the two states is assumed by the excitation at 7.6 eV. Solid and dotted arrows represent radiative and non-radiative electronic transitions, respectively. ΔE_{act} is the thermal activation energy for singlet-triplet conversion, τ are the radiative decay times, [Skuja 1998 and Nishikawa 2001].

2.2.3 The non-bridging oxygen hole center (NBOHC)

This center can be visualized as the oxygen part of a broken bond (Figs. 2.6 and 2.15). It is electrically neutral and paramagnetic and represents the simplest elementary oxygen-related intrinsic defect in silica. It is well characterized both by EPR and by optical spectroscopies like photoluminescence (PL) and cathodeluminescence (CL).

The main optical characteristics of NBOHC are shown in Fig. 2.14, it has an absorption band at 4.8 eV with FWHM=1.07 eV, oscillator strength $f=0.05$; an asymmetric absorption band at 1.97 eV, FWHM=0.17 eV, $f=1.5 \times 10^{-4}$; a photoluminescence band excited in these two absorption bands, at 1.91 eV, FWHM=0.17 eV, decay constant around 20 μs . Out of these three characteristics, the most unique fingerprint of this center is the 1.9 eV luminescent band in the red region of the visible light spectra.

It has been postulated that the NBOHC arises when hydrogen atoms are liberated radiolytically from one member of a pair of OH groups in wet silica (high OH group) according to Fig.2.15 [Stapelbrok et al. 1979].

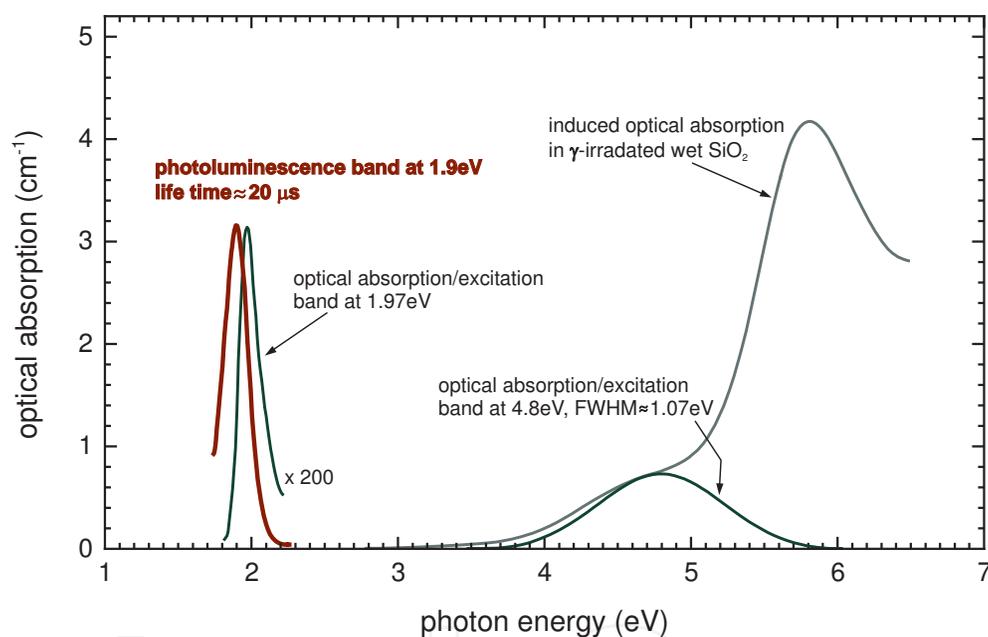


Fig. 2.14 Optical absorption and luminescence spectra of γ -irradiated wet silica illustrating the main optical properties of NBOHC: the absorption/excitation bands at 4.8 eV and 1.97 eV, and the photoluminescence band at 1.9 eV, [Pacchioni et al. 2000].

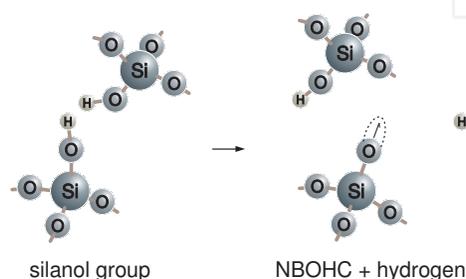


Fig. 2.15 A model of atomic structure of the non-bridging oxygen hole center (NBOHC) showing the possible generating processes of NBOHC in wet silica.

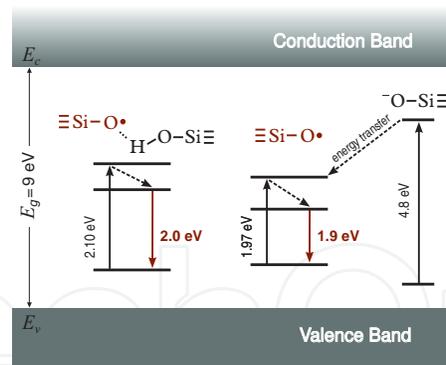


Fig. 2.16 Energy band diagram of different NBOHC energy states, [Munekuni et al. 1990].

However this reaction is not the only way of creating NBOHC. Oxygen dangling bonds may be created as well in wet and in dry silica (negligible amounts of OH groups) by rupturing of the strained Si–O bonds ($\equiv\text{Si}\cdots\text{O}-\text{Si}\equiv$) in the silica network (Fig. 2.6). Particularly there are no spectroscopic distinctions which have been established between the centers formed by these two precursors, but on the other hand some authors [Munekuni et al. 1990] proposed some differences in their emission energies, see Fig. 2.16.

If softer irradiation (X-ray) was used, the centers were created only in groups of Si–O–R (R: alkali ion). This behavior provides evidence that the centers are created in reactions similar to that visualized in Fig. 2.15, and they were attributed to NBOHC [Skuja 1994a, Skuja et al. 2006]. On silica surfaces, the same red luminescence band can be created by adding O atoms to surface E' -centers [Streletsky et al. 1982]. Another generic oxygen hole center is the self-trapped hole (STH), which exists in two different variants. STH_1 comprises a hole trapped on a normal bridging oxygen in the network ($\equiv\text{Si}-\overset{\cdot}{\text{O}}-\text{Si}\equiv$), while the STH_2 is suggested to consist of a hole delocalized over two bridging oxygens [Griscom 1991, Griscom 2000].

2.2.4 Peroxy bridge (POL)

In oxygen-excess silica, some of the excess oxygen is expected to form "wrong" oxygen-oxygen bonds, called peroxy bridges or peroxy linkages ($\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$). Calculations of atomic oxygen diffusion in SiO_2 suggested that POL structure is the lowest energy configuration for an oxygen interstitial [O'Reilly and Robertson 1983]. However, a definitive spectroscopic confirmation of their presence in silica is still absent. The experimental evidence is only indirect, but it is thought to be responsible for the exclusive (without the accompanying Si–H groups) generation of Si–OH groups during H_2 treatment of oxygen rich silica [Imai et al. 1987], as shown in Fig. 2.17. This reaction is accompanied by an increase of VUV optical absorption for $h\nu > 7$ eV indicating that the POL could possibly absorb in this region. POL was initially suggested to be the main precursor of peroxy radical defects, Fig. 2.18, as we will show in the following subsection [Friebele et al. 1979]. The calculation put the energy of the POL absorption band at around 6.4–6.8 eV with a small oscillator strength, $f=2\times 10^{-4}$ [Pacchioni and Ierano 1998b], such absorption would be hard to detect against the background of other bands in vacuum UV.

2.2.5 Peroxy radical (POR)

The Peroxy radical (POR) in silica is a paramagnetic defect with a hole delocalized over anti-bonding π -type orbitals of the O–O bond in the structure illustrated in Figs. 2.17 and 2.18. EPR spectroscopy shows that the POR is the best characterized oxygen excess defect in silica

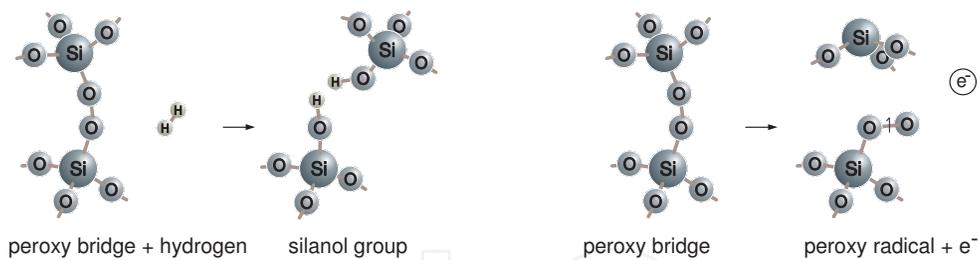


Fig. 2.17 Models presenting the suggested atomic structure of a peroxy bridge (POL) and its role in producing other possible defects in silica matrix.

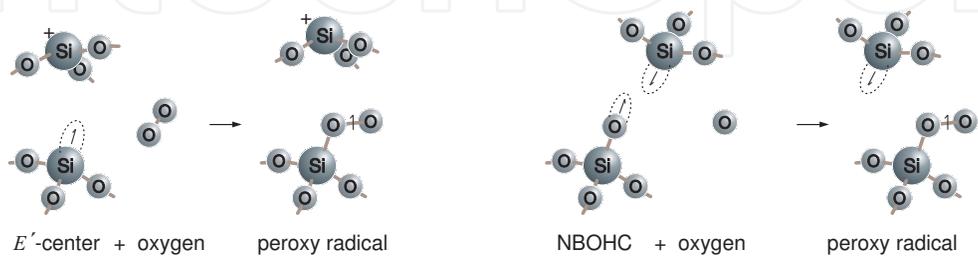


Fig. 2.18 Models presenting some possible generation modes for the peroxy radical (POR) structure in the silica matrix.

[Griscom 1991, Friebele et al. 1979]. However, the optical properties of POR in bulk silica are not accurately known. Good correlations between the isochronal annealing curves of EPR signals of POR and of the optical absorption band at 7.7 eV were reported in γ -irradiated dry silica [Stapelbroek et al. 1979]. The optical absorption spectrum observed for peroxy radicals on the surface of SiO₂ by the diffuse reflectance technique in the region around 5.4 eV with FWHM 1.3 eV and oscillator strength $f \approx 0.067$ was calculated [Bobyshev and Radtsig 1988].

2.2.6 The self-trapped exciton (STE)

The electronic excitation of solids produces mainly electrons, holes and excitons. Transient (short living) defects can be created through the combination of the electronic excitation energy of electron-hole pairs and electron-phonon interaction. The conversion of excitation to defects is initiated by self-trapping of excitons, by the trapping of electrons by self-trapped holes or by the consecutive trapping of an electron and hole by a defect. These transient defects can produce either radiative or non-radiative electronic transition, while non-luminescent transient defects disappear by recombination of defect pairs. Self-trapping is a widespread phenomenon in insulators [Hayes and Stoneham 1985, Song and Williams 1993].

The existence of the self-trapped excitons in crystalline SiO₂ is supported by experimental measurements of the optically detected magnetic resonance and transient volume change [Itoh et al. 1988]. The luminescence bands between 2 and 3 eV in the silica spectrum have been ascribed to the STE. Some authors suggested that the STE is the source of the characteristic blue luminescence in crystalline SiO₂, but it has been observed that this luminescence band is removed in quartz by intense electron irradiation (15 keV) at room temperature due to the electron hole recombination as shown in Fig. 2.19 [Griscom 1979b, Trukhin 1978, Trukhin 1980, Barfels 2001]. Almost the same luminescence band can be detected in the emission spectra of amorphous SiO₂ but with much lower intensities than the

other characteristic bands. STE perturbed by small distortions due to a structural defect give emissions in the same energy range. For example, Ge implanted quartz exhibits a luminescence band at 2.5 eV close to 2.8 eV in non-implanted quartz [Hayes and Jenkin 1988]. The excitation spectra for STE luminescence in α -quartz show a peak at 8.7 eV, which is ascribed to the first exciton peak. The absorption edge has been determined as 9.3 eV [Itoh et al. 1989], so the exciton binding energy is about 0.6 eV for α -quartz [Bosio and Czaja 1993]. The large energy difference between the band edge absorption (about 9 eV) and luminescence (2.8 eV) points to strong electron-photon coupling. The optical absorption spectra and the excitation spectra for fused silica are similar to those of α -quartz but exhibit modifications due to the amorphous structure [Trukhin 1992].

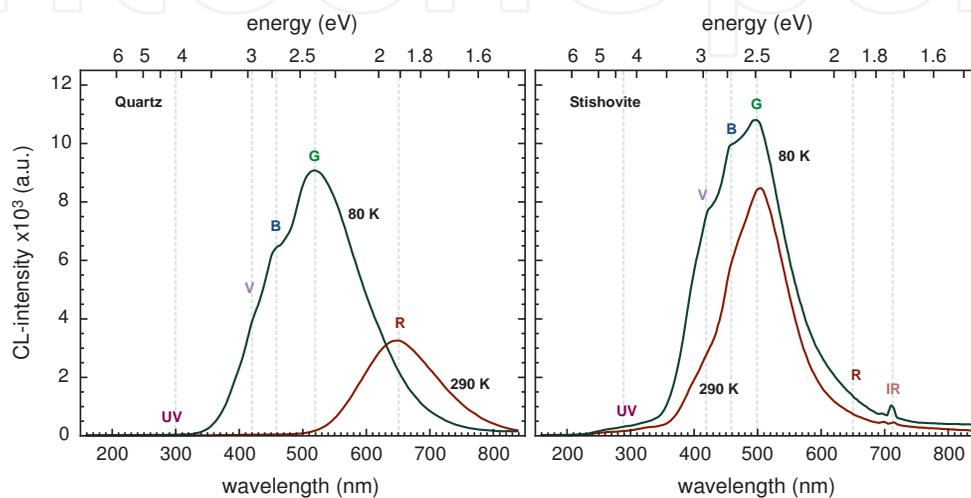


Fig. 2.19 CL-spectra of some crystalline SiO_2 (Quartz and Stishovite) at 290 K and 80 K, [Barfels 2001].

Meanwhile, several models have been proposed implying to clarify the STE. One of the first models considering that an oxygen atom will be removed to a peroxy bridge position [Griscom 1979a, Griscom 1979b] and other models are based on the proposition that a threefold coordinated silicon explains the transient absorption at 5.2 eV (E' -center) [Trukhin 1992, Trukhin 1994], see Fig. 2.20. All of these suggested models are based on the idea that the silicon-oxygen bond (Si-O) gets ruptured and forms an oxygen-oxygen bond ($-\text{O}-\text{O}-$) based on the fact that different local structures of the SiO_2 network provide different distances for oxygen-oxygen bonding. Each oxygen atom bonded to two silicon atoms by two types of Si-O bond, one by long bond $\approx 1.612 \text{ \AA}$ and another by short bond $\approx 1.607 \text{ \AA}$, as shown in Fig. 2.20 by dashed and solid bond connections [Hayes et al. 1984, Trukhin 1994]. These models explain different STE luminescence properties of different structures.

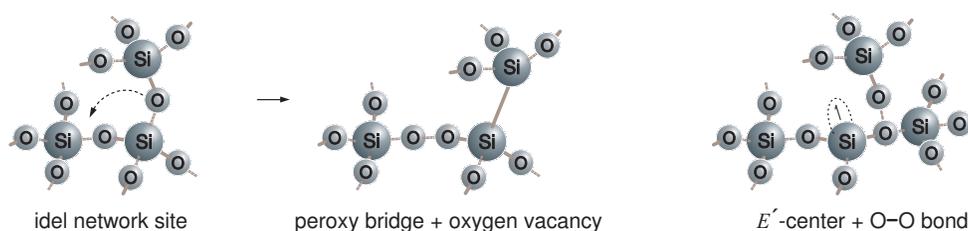


Fig. 2.20 Models of self-trapped exciton (STE) showing a creation of oxygen vacancy, E' -center and peroxy bridge due to the decay of a STE associated with an excited Si-O bond in crystalline SiO_2 .

2.2.7 Interstitial oxygen

Mostly all variants of manufactured high-purity dry SiO₂ contain natural interstitial oxygen atoms and an additional amount can be generated by ejecting oxygen atoms from their normal sites in the SiO₂ network during the irradiation. Another important point that has to be considered is the molecular oxygen. Principally O₂ molecules can be formed in irradiation processes from the already present oxygen atoms [Morimoto et al. 1992]. The first spectroscopic observation of O₂ molecules in silica was performed by Raman spectroscopy in optical fibers [Carvalho et al. 1985]. O₂ was detected by O–O stretching vibration at wavenumber 1549 cm⁻¹. Using this method the O₂ molecule concentration is found to be in the range of 10¹⁴–10¹⁸ molecules per cm³ in dry silicon dioxide [Skuja et al. 1998a].

In gas phase, oxygen molecules (O₂) dissolved to two atomic oxygen (2O) for $h\nu > 5.1$ eV ($\lambda < 242$ nm); the same can be expected to occur in silica glass following the photolytic reaction shown in Fig. 2.21. The atomic oxygens appearing as a result of this reaction might be expected to be relatively mobile in silica even at room temperature; then they interact with other oxygen molecules to form ozone (O₃) just as it occurs in the earth's atmosphere [Baulch et al. 1980, Finlayson-Pitts and Pitts 1986]. There are indications that the atomic oxygen becomes mobile at around 400 °C as detected by formation of the interstitial oxygen molecules at this temperature [Skuja et al. 2002, Kajihara et al. 2004]. Depending on the quantum yield for the gas-phase reaction of ozone dissociation, it is believed that O₃ molecules are responsible for both the 4.8 eV absorption and 1.9 eV luminescence in certain oxygen-rich silicas [Awazu and Kawazoe 1990, Griscom 1991, Skuja et al. 1995], which usually are attributed to the NBOHC by many authors [Kajihara et al. 2001, Cannas and Gelardi 2004, Bakos et al. 2004b]. The 1.9 eV luminescence band shifts between 1.8 and 2 eV depending on the excitation wavelength within the 2 eV absorption band [Skuja et al. 1995]. Other bands of possibly related origin have been observed in the 2.0–2.5 eV regions [Munekuni et al. 1990, Skuja 1994a]. O₂⁻ and O₃⁻ can be other candidates for the 1.8 eV band but the only truly unanimously agreed point is that the 1.8 eV luminescence band is related to excess oxygen in silica [Skuja et al. 1995].

Although the amount of interstitial O, O₂ and O₃ can be negligible in comparison with the whole oxygen content in a silica network, the presence of these interstitial atoms or fragments has to be considered when analyzing a large amount of accumulated defects in the silica matrix.

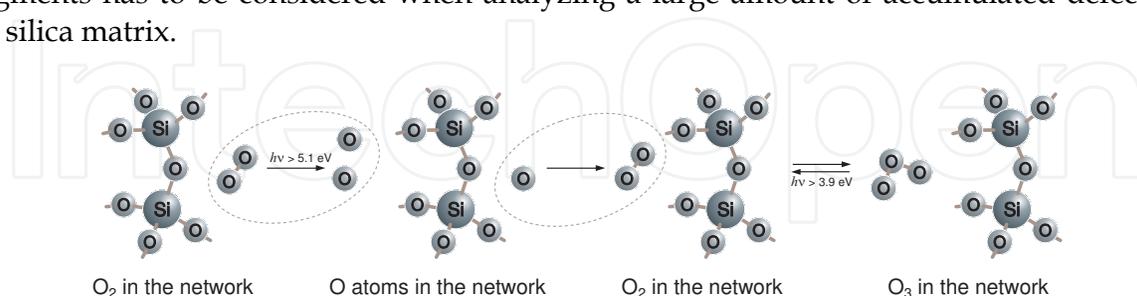


Fig. 2.21 Main interstitial atomic and molecular oxygen as well as ozone model in SiO₂.

2.2.8 Hydrogen-related defects and the state of water in SiO₂

Hydrogen in the form of steam has been used intentionally during thermal oxidation to increase oxidation rates. Very often it is also incorporated unintentionally into SiO₂ layers. Hydrogen is proposed to passivate the silicon or oxygen dangling bonds in SiO₂ network [Cartier et al. 1993, Fair 1997]. This passivation also decreases the number of non-bridging

oxygens which in turn reduces the viscosity of the silica layers substantially [Rafferty 1989]. Some authors considered hydrogen to be an intrinsic defect since it is commonly found in silicon dioxide. Hydrogen and water are ubiquitous impurities in SiO_2 . The energy levels of silanol ($\equiv\text{Si}-\text{O}-\text{H}$) and hydride ($\equiv\text{Si}-\text{H}$) groups have been calculated by tight-binding calculation [Robertson 1988]. The hydride groups seem to produce a filled s state just below the valence band (VB) and an empty σ^* state in the gap just below the conduction band (CB). This group is probably both an electron and a hole trap.

Hydride groups are expected in thermally grown silica, particularly near the interface due to the interaction of interstitial H_2 molecules with $\text{Si}-\text{O}-\text{Si}$ bridges. The H_2 is a byproduct of the fast oxidation of Si by any ambient water.

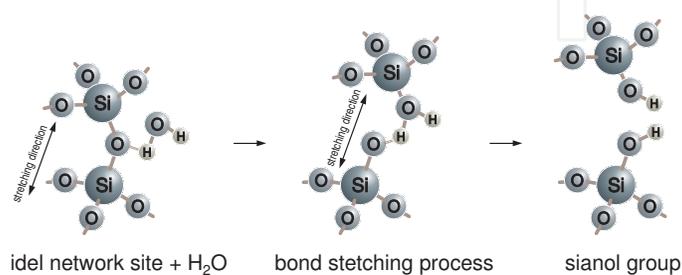


Fig. 2.22 A model of the structural state of water in SiO_2 network and its transformation to silanol groups, [Brunner et al. 1961, Bakos et al. 2004a].

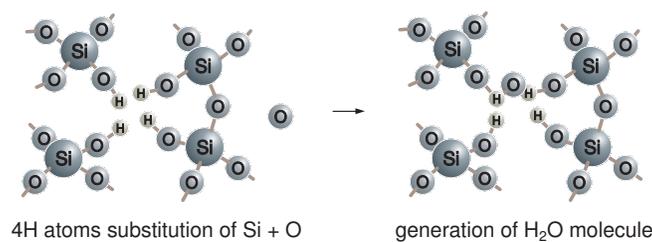


Fig. 2.23 A model of the structural state of water in SiO_2 lattice and its formation, [Nuttall and Weil 1980, McLaren et al. 1983].

It is proposed that water can be incorporated into the SiO_2 lattice according to the reaction illustrated in Fig. 2.22 [Brunner et al. 1961, Bakos et al. 2004a]. This is a preferred stress-induced mechanism and referred to "as hydrolytic weakening" [Griggs and Blacic 1965, Griggs 1967]. Calculations of total energy indicate that this reaction which uses an energy of ~ 0.1 eV is spontaneous for a $\text{Si}-\text{O}$ bond stretched beyond 4% of its normal bond length [Heggie 1992]. It has also been suggested that the solubility of water in the quartz lattice depends on the aluminum content [Kronenberg et al. 1986].

Another possible configuration shown in Fig. 2.23, assumes that hydrogen is incorporated in the quartz structure by means of $(4\text{H})\text{Si}$ defects where 4H^+ substitutes for Si^{4+} [Nuttall and Weil 1980, McLaren et al. 1983].

3. Fundamental of cathodoluminescence

3.1 Electron beam interaction with matter

When an electron hits a solid surface, it penetrates into the microstructure of the solid and interacts with its atoms. The resulting effects allow the extraction of analytical information

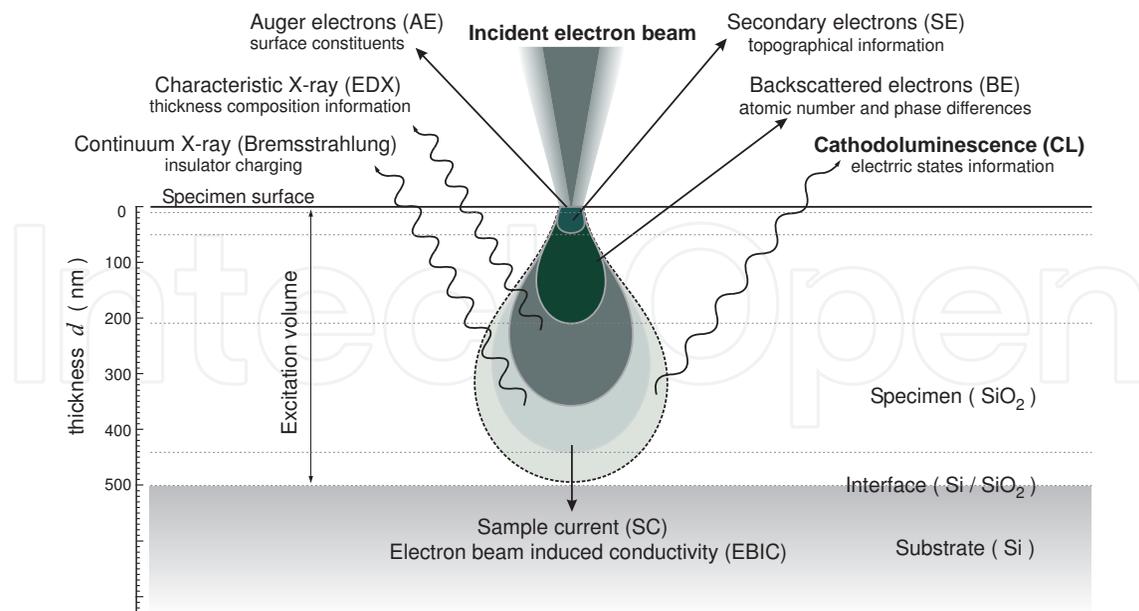


Fig. 3.1 Schematic representation of processes resulting from electron bombardment (modified after Reimer 1998). Note that the emissions come from different depths, e.g. CL and X-rays are emitted from deeper section levels than the secondary electrons.

on various properties of the material. The elementary interaction process involves collision of the electron with an atom, either with the positive atomic nucleus or with the electrons. Since the colliding particles are charged, the interaction is governed essentially by electrostatic Coulomb force. In an electron-nucleus collision, the atomic nucleus hardly changes its position since it is much heavier than the electron. The electron is therefore deflected at the nucleus without significant energy loss (elastic scattering). If the electron collides with the electrons of the atomic shells, then energy is transferred due to the equal masses of the colliding particles (inelastic interaction). Both scattering processes operate simultaneously side by side and provide a wide variety of useful signals. As a consequence of these different scattering events, an electron probe which originally was sharply focused in vacuum spreads over a greater volume after penetrating the solid. The shape and size of this scattering volume depends upon the material as well as the energy and angle of incidence of the probe electrons [Reimer 1998].

The elastic interactions between electrons and atoms or between electrons and the crystal lattice gives rise to a number of effects; the emission of secondary electrons (SE), backscattering of electrons (BE), Auger electrons (AE), characteristic X-ray (EDX) and cathodoluminescence emission (CL) but mainly most of the electron beam's energy will be absorbed (sample current) and converted into heat (phonons) [Ozawa 1990]. AEs and more generally SEs can only escape from the first few nanometers of the surface. This means that these signals originate from the top of the interaction volume, the lateral size of which is determined by the electron probe size which in turn defines the spatial resolution in AES and SEM. Backscattered electrons are higher in energy and can escape from deeper areas below the surface where the interaction volume is wider laterally, this results in a degraded image resolution for backscattered electron imaging in the SEM relative to that of secondary electron imaging [Reimer 1998]. Analyzing these signals may provide valuable information about the surface and atomic structure of the investigated substance. Two of these signals

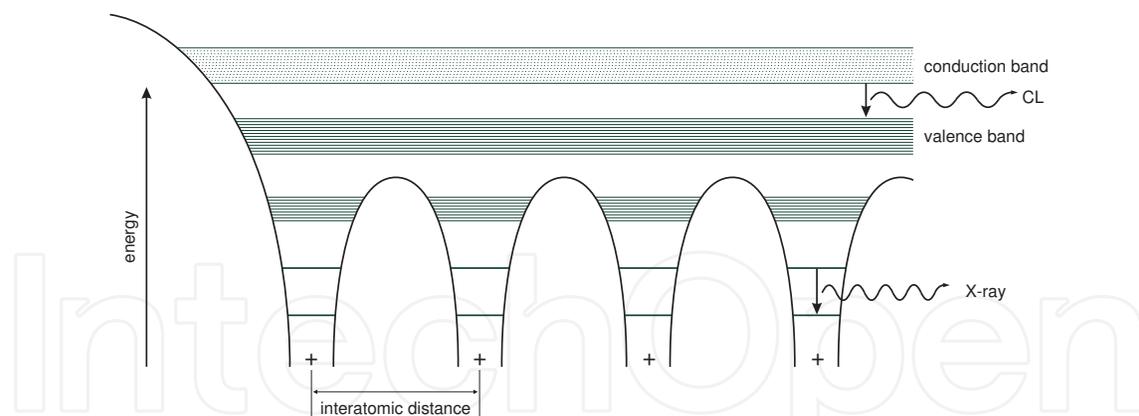


Fig. 3.2 Energy band diagram of one-dimensional lattice, [Yacobi and Holt 1990].

were among our main interest in this study, CL for luminescence defects investigation and EDX used for the atomic element component analysis. Fig. 3.1 illustrates schematically these effects and their major common applications.

The term cathodoluminescence (CL) designates the luminescence induced by energetic electron bombardment. Cathodoluminescence is excited from the region near the surface of the specimen and up to deeper than X-rays excitation volume, see Fig. 3.1. Therefore, the energy of the incident electron beam can be rather low (1-5 keV) to excite significant cathodoluminescence signals of use for the various applications. The CL signal is formed by detecting photons of the ultraviolet (UV), visible and near-infrared (IR) regions of the spectrum. These photons are emitted as the result of electronic transitions between the conduction and valence bands in semiconductors, and transitions between energy levels lying in the band gap of materials with wide band gap (insulators), Fig. 3.2. Many useful signals in these cases are due to transitions that involve impurities and a variety of defects.

X-ray spectrometry is based on the emission of X-rays from the atoms of a solid when struck by particles or waves of sufficiently high energy (electron beam in our case), followed by the relaxation of the atoms to the ground state after ionization. The X-ray spectrum produced by electron excitation consists of two parts, a continuous spectrum of deceleration radiation, known as "bremsstrahlung", and a line spectrum of the characteristic radiation. Characteristic X-rays will only be excited in the volume in which the electron energy exceeds the ionization energy of the inner shell involved. The general concept of X-ray emission-region and emission-process are shown in Figs. 3.1 and 3.2. The electron beam energy is typically in the range 10-20 keV and the energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 1-4 μm in depth, thus EDX is not a surface science technique, but it is a method used for providing sample composition information besides charging properties of insulators. Both CL and EDX techniques are commonly used in combination with a scanning electron microscope (SEM).

3.2 Process of luminescence excitation

Luminescence is produced by electron transitions between different energy levels. It may be produced by a band-band transition, transitions from band to localized state, or even between two localized states in a defect molecule, see Figs. 3.3 and 3.4. Luminescence is considered to form mainly in three steps. First, absorption of the excitation energy and stimulation of the atoms into an excited state, then transformation and transfer of the

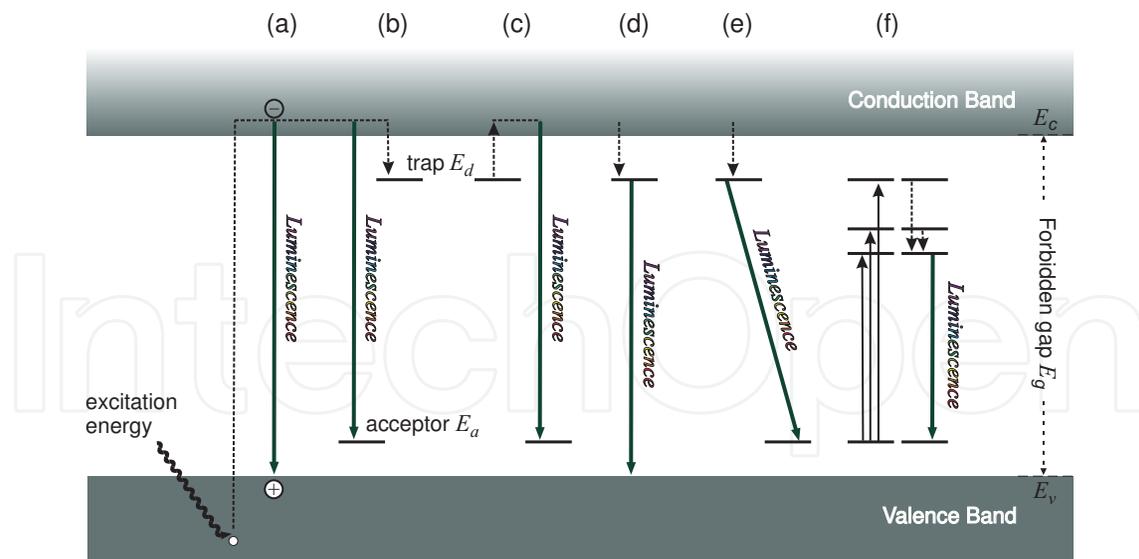


Fig. 3.3 Mechanisms of cathodoluminescence due to recombination processes in semiconductors or insulators: (a) recombination by direct band-to-band transition leads to intrinsic cathodoluminescence; (b-e) recombination via localized states in the forbidden gap results in extrinsic cathodoluminescence; (f) excitation and recombination within the defect energy levels. E_a =acceptor level, E_d =donor level, modified after Krbetschek et al. 1997.

excitation energy, and finally emission of light and relaxation to a non-excited state [Yacobi and Holt 1990]. The first two steps mainly depend on the mode of excitation, whereas the third step depends on the character of specific luminescence centers.

In crystals, complex interaction between atoms leads to the broadening of the energy levels into bands. In insulators like silica, a broad gap, called the forbidden gap, exists between the valence band and the conduction band. A precondition for cathodoluminescence is the existence of activators (impurity ions, lattice defects), which cause and occupy discrete energy levels in this forbidden zone. Luminescence centers can be differentiated by their energy position within the forbidden gap and divided into electron traps near the conduction band (donor level) and recombination sites in the vicinity of the valence band (acceptor level).

CL involves electron radiation induced excitation of an electron from the ground state to an excited state. Recombination of an electron from the conduction band with a hole in the valence band is possible in variety of ways: it may take place by a band-to-band transition or step by step via localized energy states within the forbidden gap. In a band-to-band transition shown in Fig. 3.3a, light is emitted with a photon energy $h\nu = E_g = E_c - E_v$; this type of CL is called intrinsic luminescence. Intrinsic CL is only likely to occur in semiconductors (GaAs and ZnS) in which recombination can take place directly, i.e. without changes in momentum. In indirect semiconductors (Si, Ge, and GaP) the special band structure requires a photon to take part in the recombination process so that momentum is conserved.

The extrinsic CL is a recombination that takes place via localized energy states within the forbidden gap. Excitation results in the trapping of an electron or in the recombination with a luminescent or a non-luminescent center (Fig. 3.3b). In the case of a luminescent transition, a photon is emitted. If the atom or the ion is placed in a crystal lattice, non-luminescent transitions are possible due to absorption or emission of lattice vibrations. A trapped

electron can be excited again, transits into the conduction band and may recombine with an activator element level resulting in emission of a photon (Fig. 3.3c), or a trapped electron may relax to the valence band and emit a photon (Fig. 3.7d). In the case of a small energy difference between electron trap and activator level, a direct luminescent transition of the electron to the recombination centre is possible (Fig. 3.3e). A More complex process is the excitation of several energy states lying deeper inside the forbidden gap and the subsequent relaxation and luminescence emission of a single activator is also possible (Fig. 3.3f). Such states can be due to point defects (impurities or lattice defects) and act as traps for electrons or holes. The variety of possible transitions and the thermally induced broadening of the energy states make the CL spectra very difficult to interpret.

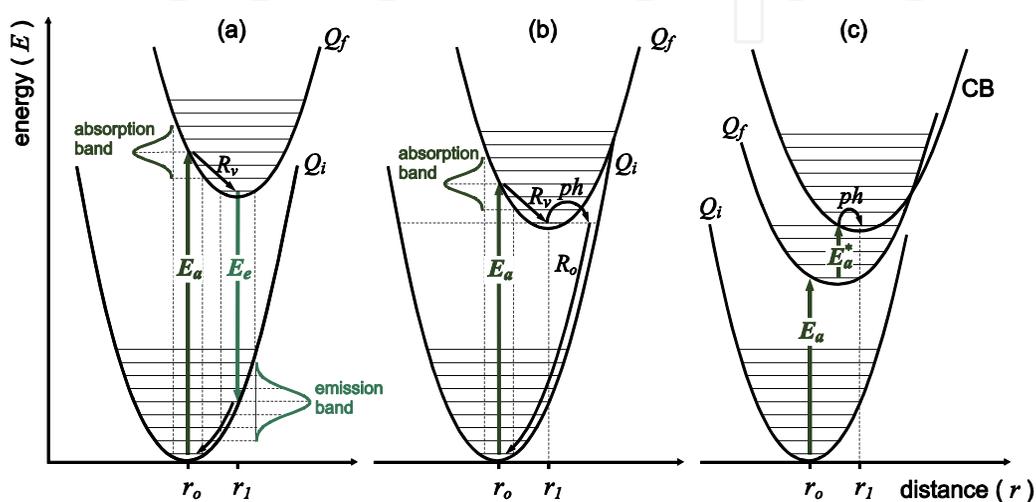


Fig. 3.4 Possible processes of excitation of a luminescence center explained in depending on configuration coordinate diagram assuming (a) radiative transition , (b) non-radiative transition , and (c) thermally assisted excitation into the conduction band, [Krbetschek et al. 1997].

The process of excitation and emission of an individual luminescence center can be described using a configuration coordinate diagram. It shows the potential energy curve of the absorbing center as a function of the relative distance (r) of the nucleus to the equilibrium position (electron in the ground state). Fig. 3.4 shows excitation of a defect atom/molecule from the ground state (Q_i) to excited state (Q_j) combined with radiative (Fig. 3.4a) and nonradiative (Fig. 3.4b) relaxation. As a particular case of excitation, thermally assisted excitation (Fig. 3.4c) into the conduction band and the relationship between the configurational coordinate and the band model are also shown.

In optical absorption (E_a) the center is promoted from the ground state to a higher vibration level of the excited state. After relaxation (R) to the zero vibration level of the excited state the electron returns with luminescence emission (E_e) or via a nonradiative transition with the emission of photons (ρ) and relaxes to the zero vibrational level (R_o). Since the electron transitions are faster than lattice relaxation, the absorption occurs adiabatically as a vertical transition (the Frank-Condon principle). The energy difference between absorption and emission is called Stokes shift. A special case of the excitation is thermally assisted ionization (Fig. 3.4c). After excitation to a higher energy level, the electron can escape to the conduction band (CB) by phonon absorption and recombine with other activators. This process may form the basis of infrared stimulated luminescence in feldspars [Hütt et al.

1988]. More complex processes may result from charge transfer. The electron is excited by high energy excitation into the charge transfer band and stored in a trap. After a second excitation with lower energy (e.g. thermal, infrared radiation) the electron escapes from the trap to an activator by a radiative or nonradiative transition. The life time τ of the trapped state depends on the depth (energy level) of the trap and the temperature, and can be determined using the Boltzmann relation $\tau = s^{-1} \exp(E/K_B T)$, where s is frequency factor, τ the absolute temperature and E the activation energy, i.e. the energetic depth of the trap.

3.3 Luminescence emission bands in silicon dioxide

The real structure of silica materials significantly influences their luminescence behavior. Moreover, defect contents and implanted elements dramatically changes the cathodoluminescence (CL) properties of silicas. The luminescence of silica is generally weak at room temperature, but it is highly variable depending on the specific conditions of silica formation. Crystalline SiO_2 modifications and amorphous silica show similar main luminescence bands. This is due to the fact that short-range order defects in silicate structure are determined mainly by silicon-silicon and silicon-oxygen interaction rather than by interactions between oxygen atoms [Berry and Vaughan 1985]. Since a strict correlation between the intensities of CL bands and concentrations of specific defects or trace elements does not exist, the interpretation of the origin of luminescence of silica materials is difficult. Furthermore, the band positions of the luminescence emissions can vary depending on the particular SiO_2 structure and the experimental conditions. The CL spectra of silica consist mainly of several emission bands in the blue up to the red spectral region. Investigation of natural and synthetic silica specimens show various emission bands which are ascribed to different intrinsic and extrinsic defects. The CL spectra of silica materials are generally consist of some different broad emission bands (defect's optical bands) instead of sharp spectral lines. Overlapped bands are commonly expected too, and it seems to be difficult to resolve these bands to their real components. Two reasons for the broadening of these transitions have been suggested: the first is due to the different static local environments (inhomogeneities) of defects in disordered glass called inhomogeneous broadening, and the second is due to the coupling of electronic transition to phonons called homogeneous broadening. The homogeneous broadening is the same for all related defect sites throughout the sample and occurs even for defects in otherwise ideal crystal. The main contribution to the defect's optical bands broadening (FWHM) in amorphous SiO_2 which is our main interest in this study, is usually from homogeneous broadening (0.2-1 eV) while the magnitude of inhomogeneous broadening is of the order 0.1 eV [Skujala 2000]. Table 3.1 summarizes the main PL and CL emission bands previously reported for $\alpha\text{-SiO}_2$ and $a\text{-SiO}_2$ and their proposed associations. Further on, cathodoluminescence can be divided into two categories: intrinsic CL, which is characteristic of the host lattice, and extrinsic CL which results from impurities. Larger defects such as dislocations and clusters may also have an effect on the CL signal. Intrinsic luminescence is enhanced by non-stoichiometry (vacancies), structural imperfections (poor ordering, radiation damage, shock damage), and impurities (non-activators), which distort the crystal lattice. The CL properties are mostly the result of luminescence-activating ions such as transition metals, rare-earth elements or actinides. Changes of the crystal field properties i.e., field strength, site symmetry, and coordination number, cause differences in the magnitude of the energy levels of the activator elements and also the splitting of closely spaced levels.

Table 3.1 (a): Reported CL and PL luminiscent bands in amorphous silicon dioxide (α -SiO₂) and crystalline quartz (α -SiO₂) and their proposed associations in IR-Green region.

wave length (nm)	energy (eV)	CL, PL emission band (eV)	Specimen	Association	References
1240	1.00	0.97	α -SiO ₂ & α -SiO ₂	O ₂ , O ₂ ⁻	Skuja et al. 1998b, Stevens-Kalceff 2000
1181	1.05	1.3 - 1.75	C & Si doped α -SiO ₂	Si & C nanocluster	Chae et al 1999, Rebohle et al. 2001a, Takagahara & Takeda 1992, Shimizu-Zunger & Wang 1996, Kim et al 2000, Wilkinson & Elliman 2004, Imakita et al. 2002, Yi et al. 2002, Zacharias et al. 1998, Zacharias et al. 2002, Lau et al. 2005.
1127	1.10		α -SiO ₂ and α -SiO ₂	Si-nanocluster	
1078	1.15				
1033	1.20				
992	1.25				
954	1.30		SiO _x	Si-nanocluster (d=5nm)	
918	1.35		α -SiO & α -SiO ₂	Si-nanocluster (d=4-2nm at 1.3-1.6eV)	
886	1.40		SiO _x	Si-nanocluster (d=10-25nm at 1.4-1.5eV)	
855	1.45	1.80	SiO _x	Si nanocluster	Cheylan et al. 2001, Sakurai 2003. Sakurai et al. 1999. Hinic et al. 1999, Hinic et al. 2003.
827	1.50		α -SiO ₂	ODC, Si nanocluster	
800	1.55		silica xerogel	NBOHC	
775	1.60	1.85 - 1.95	silica fiber	NBOHC	Munekuni et al. 1990. Skuja 1992b, Cannas & Gelardi 2004. Yu et al. 2004.
751	1.65		α -SiO ₂ & α -SiO ₂	NBOHC	
729	1.70		SiO _x	NBOHC	
708	1.75		α -SiO ₂	NBOHC	
689	1.80		α -SiO ₂	O ₂ ⁻ , O ₃ ⁻	Skuja et al. 1995.
671	1.85		α -SiO ₂	O ₂ , O ₃	Skuja et al. 2000a, Skuja et al.2000b.
653	1.90	2.0 - 2.2	α -SiO ₂ & silica gel	hydrogen defects (OH, SiH or SiH ₂)	Friebele et al. 1985, Hinic et al. 2003. Morimoto et al. 1996. Mitchell & Denure 1973, Ludwig et al. Kim et al 2000a, Ledoux et al. 2002, Y Shimizu-Iwayama et al. 1997, Im et al Perez-Rodriguez et al. 2003. Itoh et al. 1990.
636	1.95		ion doped α -SiO ₂ & α -SiO ₂	H & He implantation + annealing	
620	2.00		α -SiO ₂	trivalent Si center	
605	2.05		α -SiO ₂	Si nanocluster (d=3nm)	
591	2.10		α -SiO ₂	Si implantation, Si nanocluster	
577	2.15		ion doped α -SiO ₂	Si & C implantation + annealing	
564	2.20		α -SiO ₂	STE	
551	2.25	2.2-2.5	α -SiO ₂ & α -SiO ₂	STE	Trukhin 1992, Trukhin 1993, Stevens-Kalceff 1999, Itoh et al. 1988, Luff & Townsend 1990, Kim et al. 2000c. Zacharias et al. 2003. Hinic et al. 2003. Glinka 2000, Glinka et al. 1999. Yu et al. 2004.
551	2.25		Ge doped α -SiO ₂	STE associated with Ge	
539	2.30		Si doped α -SiO ₂	Si implantation + annealing	
528	2.35		α -SiO & α -SiO ₂	Si-nanocluster	
517	2.40		silica xerogel	organic components or E' center	
506	2.45		powder silica	H-related defect, surface Si-H species	
496	2.50		SiO _x	H-related defect	

Table 3.1 (b): Reported CL and PL luminescent bands in amorphous silicon dioxide ($a\text{-SiO}_2$) and crystalline quartz ($\alpha\text{-SiO}_2$) and their proposed associations in Blue-UV region.

Wavelength (nm)	Wavelength (eV)	Region	Material	Defect/Transition	Association	References	
477	2.60	Blue	ion doped $a\text{-SiO}_2$	$\text{Sn}^+, \text{Si}^+, \text{Ge}^+, \text{C}^+, \text{Cu}^+$ implantation	2.40 - 3.00	Calestani et al.2005,Perey-Rodriguez	
468	2.65		C doped $a\text{-SiO}_2$	crystalline SiC nonoclusters		Rebohle et al. 2001a, Rebohle et al. 2001b	
460	2.70		$\alpha\text{-SiO}_2$	$a\text{-SiO}_2$	STE	2.60 - 2.80	Trukhin & Plaudis 1979,Griscom 1985
451	2.75						Hayes et al. 1984, Stevens-Kalceff 1984
443	2.80		Violet	sol-gel SiO_2	ODC, Triplet-Singlet transition of Si	2.7 - 2.75	Griscom 1985, Paleari 2005.
428	2.90			ion doped $a\text{-SiO}_2$	ODC, Si implantation		Griscom 1990a, Skuja 1992a, Kuzuu
421	2.95			Si doped SiO_x	neutral oxygen vacancy	Yu et al. 2004.	
414	3.00			ion doped $a\text{-SiO}_2$	O implantaition, O-related center	Hagni 1987, Chiodini et al. 2000, Ane	
407	3.05			$a\text{-SiO}_2$ & $\alpha\text{-SiO}_2$	O_2^-	Stevens-Kalceff 2000.	
400	3.10			$a\text{-SiO}_2, \alpha\text{-SiO}_2$ & SiO_x	E' center	White et al. 2002.	
394	3.15	UV		$a\text{-SiO}_2$	STE's associated with Ge, Al & H	2.9 - 3.10	Khanlary et al. 1993, Yang et al. 1994
388	3.20			ion doped $a\text{-SiO}_2$ & $\alpha\text{-SiO}_2$	Al, C, & Ge implantation		Koyama 1980, Stevens-Kaceff 1998
382	3.25			$a\text{-SiO}_2$	-O-O- defects	Nishikawa et al. 1992.	
376	3.30			fused SiO_2 , $a\text{-SiO}_2$	O_2^-	Guzzi et al. 1987, Skuja & Trukhin 1992	
370	3.50		ion doped $a\text{-SiO}_2$	ODC	Anedda et al. 2003a.		
365	3.40		$\alpha\text{-SiO}_2$	Intrinsic defect	Alonso et al. 1983, Stevens-Kaceff & 1984		
344	3.60		UV	ion doped $a\text{-SiO}_2$ & $\alpha\text{-SiO}_2$	$\text{Al}^+, \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+ & \text{Ge}^+$ implantation	3.10 - 3.30	Qin et al. 1996, Tong et al. 1997, Truk
342	3.65			$a\text{-SiO}_2$	ODC or $\text{Al}^{3+}\text{-H}$ center		Stevens-Kalceff & Wong 2005.
335	3.70			$\alpha\text{-SiO}_2$, $a\text{-SiO}_2$	impurity incorporation during growth or Ge	Skuja & Trukhin 1989, Luff & Townse	
361	3.75			Ge doped $a\text{-SiO}_2$	oxygen vacancy related defect	Rebohle et al. 2002a, Rebohle et al. 2002b	
295	4.20	$a\text{-SiO}_2$		Triplet-Singlet emission of Ge	Hosono et al. 1992, Skuja 1998, Truk		
292	4.25	SiO		oxygen-related defect, Si nanocluster	Yang et al 2005.		
289	4.30	UV		ion doped $a\text{-SiO}_2$	twofold coordinated Sn, Ge	3.70	Skuja 1992a.
285	4.35			sol-gel $a\text{-SiO}_2$	E' -like surface center		Chiodini et al. 2000.
282	4.40			sol-gel silica	isolated silanol groups	Yao et al. 2001, Paleari et al. 2005.	
279	4.45			sol-gel silica	OH-related center	Anedda et al. 2003b.	
276	4.50		UV	ion doped $a\text{-SiO}_2$	Si excess defect	4.20 - 4.40	Weeks et al. 2005.
272	4.55			$a\text{-SiO}_2$	ODC, Singlet-Singlet transition		Griscom 1985, Griscom 1991, Skuja
270	4.60			sol-gel $a\text{-SiO}_2$	ODC, Singlet-Singlet transition of Si	Chiodini et al. 2000, Paleari et al. 2000	
267	4.65			$\alpha\text{-SiO}_2$ & $a\text{-SiO}_2$	divalent Ge defect	Hosono et al. 1992, Skuja 1998, Truk	
264	4.70			$a\text{-SiO}_2$	Si implantation	Magruder et al. 2003.	
261	4.75			Ge doped sol-gel $a\text{-SiO}_2$	GODC, Singlet-Singlet transition of Ge	Agnello et al. 2003, Trukhin et al.2003	
258	4.80						

Therefore the CL spectrum is not a characteristic property of the activator but a property of the mineral. The cathodoluminescence intensity generally increases with the concentration of the activator to a maximum and then decreases. This decrease is referred to as concentration quenching (self-quenching). It can be explained by the transfer of a part of the excitation energy to other activator ions which is more effective than luminescence emission. Some ions (quenchers) show broad and intense charge transfer bands in the absorption spectrum and cause quenching of the luminescence of activators with interfering emission bands.

The quenching by ions with intense charge transfer bands especially influences the visible and the near ultraviolet (UV) spectral ranges, whereas luminescence emissions in the infrared (IR) are more or less unaffected. Apparently, the quenchers cause new closely-spaced energy levels so that the electron can easily return to the ground state with the emission of low-energy photons (IR) or by losing heat energy [Marshall, 1988].

Quenching due to lattice defects may occur if the crystal structure is damaged by mechanical processes, radiation, growth defects or impurities. These lattice defects create new energy levels between the conduction and the valence bands resulting in absorption of the excitation energy, non-luminescent energy transfer or low frequency emission. Another process which may be responsible for lowering the luminescence intensity is thermal quenching. Principally, heating of a sample results in the release of electrons and accordingly in the excitation of thermoluminescence. During irradiation of a sample with high-energy particles (e.g., electrons, ions) a part of the energy can be transformed into heat which influences the energy transfer and non-luminescent transitions. As a consequence, the luminescence intensity decreases during electron bombardment and then stabilizes.

3.4 Cathodoluminescence spectroscopy (CL)

Conventionally, there are several kinds of cathodoluminescence devices that can be installed in SEM. One of them is a spectrometer-type device, which incorporates a parabolic mirror mounted on the spectrometer port designed for high efficiency of light collection, as used in this study. This specially designed mirror is used for collecting the CL. Despite the high generation factors for the electron-hole pairs, the external photon yield is small. Furthermore, the intensity generated inside the specimen is considerably reduced by absorption in the specimen and by the total reflection at the specimen surface.

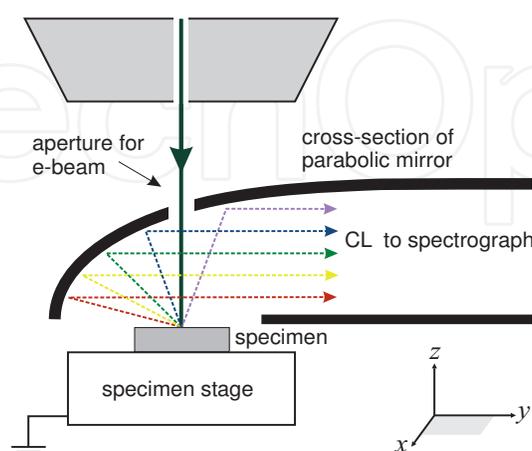


Fig. 3.5 Schematic diagram of the CL collection optics within the SEM (not to scale). The CL photons emitted by the electron-irradiated specimen are collected by a parabolic mirror and directed into the spectrograph by an optical guide.

One of the fundamental problems in CL measuring technique is therefore how to collect the emitted radiation over the largest possible solid angle with high efficiency. Fig. 3.5 shows a configuration using a parabolic mirror in which the primary electrons (PE) impact on the specimen through a hole in the parabolic mirror. Light quanta emitted into a solid angle π can be detected, where the specimen is located almost inside the mirror during the CL measurement for better CL signal collection. A silica fiber optic transmits the CL light to the entrance slit of grating spectrograph of type Spex-270M and it is registered in a single shot technique by a liquid nitrogen cooled charge coupled device CCD camera (Princeton Instruments, EEV 1024×256) with a spectral resolution of about 4 nm.

The CL was excited using a continuous stationary electron beam with energy $E_0=10$ keV and stable current of ≈ 0.6 μA with focused beam diameter of ≈ 1 μm in TV scanning mode both at room temperature (RT) and liquid nitrogen temperature (LNT), working distance fixed at 14 mm where the electron beam was focused on a small area ($\approx 100 \times 100$ μm^2) of the specimen surface. The CL excitation and recording use the same parameters (experimental conditions) in order to get comparable spectra collected from different silicon dioxide samples.

The visible light spectrum over the wavelengths 200-800 nm collected by the CL mirror is composed of the real luminescence light and the background light produced by the electron beam. The background spectra is registered separately and subtracted from the measured CL signal to eliminate disturbing light radiation from the thermionic cathode and other sources. The background elimination was done periodically by switching the primary electron beam on and off (beam blinking) in each start of new CL measurement.

The whole experiment was performed in high vacuum. In order to achieve a good high vacuum, some special procedures were needed. Initially, the vacuum chamber was pumped down to 10^{-2} mbar using a rotary pump. Then the chamber was pumped down to about 10^{-6} mbar using a turbomolecular pump. After 24 hours of pumping, the pressure got down to around 10^{-7} mbar and the chamber achieved the HV operation conditions, which is good enough to perform both CL and EDX measurements.

3.5 Energy dispersive X-ray spectroscopy (EDX)

X-ray spectrometry is based on the emission of X-rays from the atoms of a solid when struck by particles or waves of sufficiently high energy (electron beam in our case), followed by the relaxation of the atoms to the ground state after ionization. The X-ray spectrum produced by electron excitation consists of two parts, a continuous spectrum of deceleration radiation, known as "bremsstrahlung", and a line spectrum of the characteristic radiation. The electron beam energy is typically in the range 10-20 keV and the energy of the X-rays emitted depends on the material under examination.

X-ray data are obtained with a wavelength dispersive spectrometer. The X-ray energy dispersive system component is a semiconductor crystal which acts simultaneously as a detector and analyzer [Fuchs et al. 1990]. In a similar way as in a proportional counter tube, X-ray quanta which penetrate the semiconductor detector generate pairs of charge carriers whose number is proportional to the energy of the incident quanta. The spectrum is obtained by evaluating the pulses (current) generated and amplified in the detector system according to their height and sorting them. This takes place in a multichannel analyzer. Each channel corresponds to a specific pulse height and to a specific energy after suitable calibration. The amount of the current pulse t generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.

The semiconductor detector is a special silicon diode called a lithium drifted silicon detector Si(Li), which is accommodated in a vacuum chamber and kept at a temperature of about 100 K by means of a cold finger. A beryllium window (about 10 μm thick) closes the evacuated chamber containing the detector and preamplifier. The window protects the detector from condensation and contamination as well as from scattered electrons and light. The entire system can be adjusted both horizontally and vertically.

Elements of low atomic number are difficult to detect by EDX. In all Si(Li) detectors, The absorption of the soft X-rays by the Beryllium window precludes the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced.

3.6 Fourier transform infrared spectroscopy (FTIR)

One of the most common methods of analyzing crystalline silica is based on the absorption of infrared light. Infrared radiation spans a part of the electromagnetic spectrum having wavelengths from 0.78 to 1000 μm . It is bounded by the red end of the visible region at high frequencies (≈ 300 THz) and the microwave region at low frequencies (≈ 300 GHz). At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed at the molecule, the molecule absorbs the radiation.

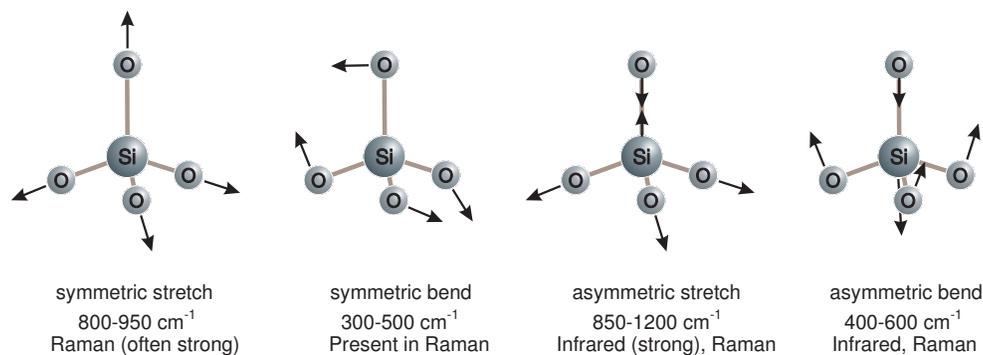


Fig. 3.6 Major vibrational modes for a nonlinear group, [Silverstein et al. 1981].

Different functional groups absorb characteristic frequencies of IR radiation. Thus, IR spectroscopy is an important and popular tool for structural clarification and compound identification in the sample and is even a common spectroscopic technique used for quantitative determination of compounds in mixtures. Infrared radiation is absorbed and the associated energy is converted into different types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the middle IR region. The major types of molecular vibrations are stretching and bending. The various types of vibrations for SiO_2 are illustrated in Fig. 3.6. IR spectra are obtained by detecting changes in transmittance (T) or absorption (A) intensity as a function of frequency. Transmittance is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I_0). Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance (T), $A = \log(T^{-1}) = -\log(I/I_0)$, The transmittance spectra provide better contrast between intensities

of strong and weak bands because transmittance ranges from 0 to 100% T whereas absorbance ranges from infinity to zero.

In this study we will focus on the most frequently considered portion of the middle IR region, between 400 and 4000 cm^{-1} (25 to 2.5 μm). The total number of observed absorption bands is generally different from the total number of fundamental vibrations. It is reduced because some modes are not IR active and a single frequency can cause more than one mode of motion to occur.

Absorption bands in the region of 2500-4000 cm^{-1} usually come from stretching vibrations between hydrogen and some other atoms with a mass of 19 or less. The O-H and N-H stretching frequencies fall in the 2500-3700 cm^{-1} region, with various intensities. Hydrogen bonding has a significant influence on the peak shape and intensity, generally causing peak broadening and shifts in absorption to lower frequencies. The C-H stretching bands occur in the region of 2700-3300 cm^{-1} [Settle 1997]. The bands 2000-2300 cm^{-1} and 935-1000 cm^{-1} are associated with Si-H bond-stretching band and Si-O bond-bending type mode, respectively. Another peak at 3675 cm^{-1} corresponds to the Si-OH bond [Hosono et al. 1999]. The absorption bands at the 1850-2700 cm^{-1} region usually come only from triple bonds and other limited types of functional groups, such as C \equiv C at 2100-2260 cm^{-1} , C \equiv N at 2220-2260 cm^{-1} , allenes C=C=C at 1900 to 2000 cm^{-1} , S-H at 2550 to 2600 cm^{-1} , P-H at 2275 to 2440 cm^{-1} [Settle 1997, Trukhin et al. 1999], Si-C at 800 cm^{-1} , Si-O at 500 cm^{-1} [Prado et al 2003].

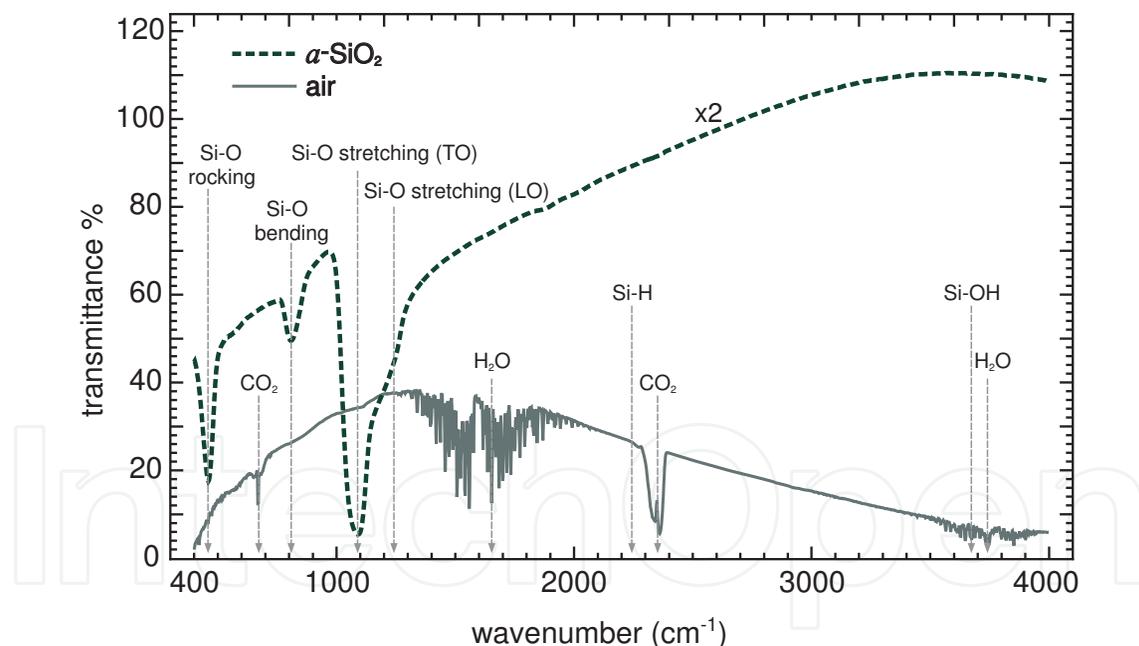


Fig. 3.7 A single-beam IR spectrum of $\alpha\text{-SiO}_2$ and air (background), showing different Si-O vibration modes and the contribution of the ambient water and carbon dioxide CO_2 .

Moreover, the transmission spectra show peaks at 890-1062 cm^{-1} and 2260 cm^{-1} , corresponding to the Si-O stretching frequency [Tsu et al. 1989, Saito and Ikushima 2002, Suzuki et al. 2003, Prado et al 2003], at 945 cm^{-1} assigned to Si-OH mode, and at 1650 cm^{-1} associated with H-O-H (H_2O) [Gendron-Badou et al. 2003]. Typical FTIR spectra in the range 400-4000 cm^{-1} of air and pure $\alpha\text{-SiO}_2$ layer are shown in Fig. 3.7, where some vibrational modes of Si-O and hydrogen incorporated molecules are pointed. Commonly

the transmission peaks at 1100, 471 cm^{-1} are attributed respectively to triply degenerated stretching and bending vibration modes of the tetrahedron, but 800 cm^{-1} corresponds to an inter-tetrahedral Si–O–Si bending vibration mode [Gendron-Badou et al. 2003].

Most commercial instruments to separate and measure IR radiation use dispersive spectrometers or Fourier transform spectrometers. Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. An IR spectrometer consists of three basic components: radiation source, interferometer (monochromator in dispersive IR system), and detector. Infrared transmittance measurements were performed using a FTIR spectrometer (Nicolet Magna IR 550) in the spectral range 400–4000 cm^{-1} . The spectral resolution was fixed to 4 cm^{-1} and the spectra were recorded at room temperature (RT) by means of non-polarized light under normal incidence. Most benchtop FTIR spectrometers are single-beam instruments. Unlike double-beam grating spectrometers, single-beam FTIR does not obtain transmittance or absorbance IR spectra in real time. A typical operating procedure is described as follows: A background spectrum (Fig. 3.7) is first obtained by collecting an interferogram (raw data), followed by processing the data by Fourier transform conversion. This is a response curve of the spectrometer and takes account of the combined performance of source, interferometer, and detector. The background spectrum (air) also includes the contribution from any ambient water (two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1}) and carbon dioxide (doublet at 2360 cm^{-1} and sharp spike at 667 cm^{-1} present in the optical bench. Next, a single-beam sample spectrum is collected, it contains absorption bands from the sample and the background (air). The background spectra have been eliminated in order to get the real vibrational response of the sample. Reference samples of the silicon substrate have also been used for background division.

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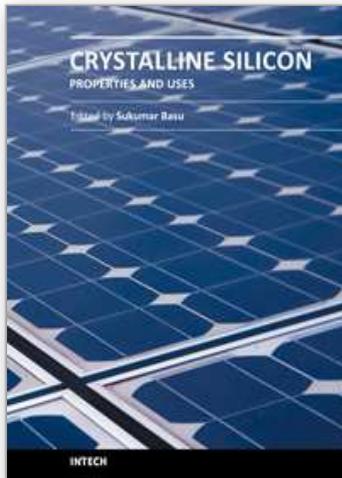
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The exciting world of crystalline silicon is the source of the spectacular advancement of discrete electronic devices and solar cells. The exploitation of ever changing properties of crystalline silicon with dimensional transformation may indicate more innovative silicon based technologies in near future. For example, the discovery of nanocrystalline silicon has largely overcome the obstacles of using silicon as optoelectronic material. The further research and development is necessary to find out the treasures hidden within this material. The book presents different forms of silicon material, their preparation and properties. The modern techniques to study the surface and interface defect states, dislocations, and so on, in different crystalline forms have been highlighted in this book. This book presents basic and applied aspects of different crystalline forms of silicon in wide range of information from materials to devices.

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