DEFECTS GENERATION AND THEIR ELECTRONIC STRUCTURE

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Abstract

The strong localization of electronic and vibrational excitations in the silica glass network causes the effective intrinsic defects or structural imperfections generation in this material. Single Si-O bond breaking initiates the defect generation process. Analysis of experimental results leads to the conclusion, that primary (elementary) intrinsic defects in silica are neutral threefold coordinated silicon atoms (E'-centers) and neutral nonbridging oxygen atoms. The reactions between these defects leads to the generation of aggregate defects (peroxy radicals, peroxy bridges, Si-Si bonds et.c.). The defects models are evaluated from the analysis of their generation and annihilation processes. The electronic structure of the defects comes from silica spectroscopic property changes when these defects are generated.

1. INTRODUCTION

The best optical waveguides with losses of only 0,1 dB/km have been obtained from fused silica. One of the basic demands upon such high quality optical materials is their resistance to external disturbances. The main reason of the physical properties changes of fused silica by external influences is the structural imperfection (intrinsic defect) generation in this material.

An increase of optical fiber drawing temperature and drawing speed, use of higher light intensities associated with lasers and a shift of the quantum energies to ultraviolet or vacuum ultraviolet (VUV) region raise the intrinsic defect generation effectivity in fused silica. This happens because the Si-O bond breaking takes place under the above influences, either directly or by the self-trapped exciton decay. Stabilization of the ends of the broken Si-O bond could be by direct restoring of the glass network or by secondary reactions.

The generation of intrinsic defects in fused silica as a result of the self-trapped exciton decay has been frequently observed experimentally (see e.g. [1-3]. Fiber drawing induces the same intrinsic defects as radiation capable to generate excitons (see [4] and references therein). It means that the single Si-O bond breaking is the first step in the intrinsic defect generation process. The change of density and other basic physical properties of silica under the influence of intensive light has been observed [5, 6]. The present paper deals with primary atomic processes leading to the generation of elementary intrinsic defects, as well as reactions due to secondary defect interaction leading to the changes both in glass structure and basic physical properties. The defect electronic structure is evaluated from fused silica spectroscopic property changes when these defects are generated.

2. ELEMENTARY DEFECT GENERATION

As it was shown in [7], breaking of a single Si-O bond can lead to the generation of stable elementary intrinsic defects only in glassy form of SiO_2. In this case to stabilize the ends of the broken Si-O bond, it is necessary to have an appropriate microcavity near the broken bond. The existence of such microcavities of the size around 5 A° and concentration approximately 10^{21} cm^{-3} in fused silica is proved in [8] by Raman spectroscopy investigations of hydrogen dissolved in fused silica. Furthermore, it has been noted [23] that the basic defects in fused silica - E' center, peroxide radical, nonbridging oxygen and twofold coordinated silicon("oxygen vacancy") - have very close spectroscopic properties both in the bulk and the surface of glass.

There are different hypotheses regarding the elementary defect generation micromechanisms and the nature of stabilized defects in fused silica. Experimental results [1,2,6,9] show that one type of the stable generated defects are E'-centers. Yet there are different models for these centers in fused silica. First, it was shown theoretically in [10] that the spectroscopic properties of E'-center can be explained by a model consisting of an oxygen vacancy in which there is a trapped hole. However, the experimental work [11] has shown also, that the main spectroscopic characteristics of E'-center are largely determined by the isolated threefold coordinated silicon atom.

The first model of the E'-center [10] is used by Itoh et al. [12] to interpret the transient optical absorption of self-trapped excitons. Their self-trapped exciton model consists of an oxygen vacancy and a peroxy bridge, which is formed when the oxygen links with a bridging oxygen connected to one of the two 3-fold coordinated silicons. It should be noted that an analogous situation occurs if the rotation of the silicon-oxygen tetrahedron with a non-bridging oxygen is discussed in details in accordance with the defect generation mechanism suggested in [7]. We must take into account that during the relaxation process the

state in which the tetrahedron has turned a little (for about 30^{o}) is being fixed and then the place of one bridging oxygen is occupied by two oxygens, i.c. a peroxy bridge forms there. Thus until the discussed stage of the self-trapped exciton decay into stable intrinsic intrinsic defects the models proposed in [7] and [12] lead to similar geometric configurations. Reasonable differences appear when the stable intrinsic defects in fused silica generated by the self-trapped exciton decay are considered. It is assumed in Refs.[2, 12] that peroxy radicals and E'-centers as oxygen vacancies are formed. On the other band the experimental results of Refs. [6, 7, 9] indicate another possibility: the self-trapped exciton decay in fused silica generates primary E'-centers as a neutral threefold coordinated silicon atoms and neutral non-bridging oxygen centers.

Since in the latter case neutral defects are generated, their concentrations are not mutually correlated by the charge compensation rule. Therefore taking into account the defect generation peculiarities (the possible elementary defect generation from the existing aggregate defects [13]) and the following interaction reactions, we may conclude that the generated non-bridging oxygen atom and the threefold coordinated silicon atom concentrations most likely will not be equal. However the mechanism proposed [2] for the stabilization of the broken Si-O bond components demands the equality of these concentrations to maintain the charge balance. It is necessary to mention that non-bridging oxygen atoms are always induced in pure fused SiO_2 by VUV light or fiber drawing [3, 4, 6, 9].

If as a result of the self-trapped exciton decay positively charged E'-centers as oxygen vacancies and neutral peroxy radicals are generated as it is assumed in [2, 12], then it is also necessary to identify the negatively charged defects the concentration of which in equal to the E'-center concentration in order to realize the charge compensation. However, up to now the negatively charged defects, generated as a result of broken Si-O bond end stabilization, have not been identified in SiO_2

glass. The existence of neutral peroxy radicals is usually found in glass by the ESR measurements [3, 4, 6]. It is possible that peroxy radicals appear as a result of interaction reactions between the generated non-bridging oxygen centers. Since the valent vibration of non-bridging oxygen in fused silica have a quasilocal nature, in the event of a repeated excitation it is easier to break its bond with silicon and form a free oxygen atom which can move to another non-bridging oxygen center and form the more stable peroxy radical center.

3. REACTIONS BETWEEN DEFECTS

It is natural to assume that the basic physical properties of fused silica are mainly changed by secondary reactions among primary intrinsic defects, because as discussed in Ref.5 the primary defects left after the influence of light (concentration about $10^{17}cm^{-3}$) cannot be responsible for the observed changes of physical properties (increase of the density from 2,2 to 3,0 g/cm^3 and the refractive index from 1,46 to 1,65). Let us discuss in detail the possible secondary reactions and the changes of physical properties they can arouse. As discussed in Section 2 the stabilization of the elementary intrinsic defects in the glass network takes place when it appears in the microcavity. At the large enough excitations the next elementary defect can appear in the microcavity and a chemical bond between it and the previously generated defect can be formed . In such a way "the darning" of the microcavity takes place and it leads to the increase of the local density in the material. If the opposite elementary defects (the threefold coordinated silicon and the non-bridging oxygen) meet in the microcavity, then the Si-O bond is restored. Whereas if equal defects meet in the microcavity, then weaker O-O and Si-Si bonds can be formed. Because of this, during the excitation more and more of the above mentioned weaker chemical bonds appear in the SiO_2 network leading to the decrease of the mechanical strength of the material. It should be noted that the concentration of weak bonds can exceed the primary concentration

of microcavities ($10^{21}cm^{-3}$), because after the fulfillment of the initial microcavity new microcavities appear nearby in which the induced elementary defects can meet again and form chemical bonds. In such a way a gradual diffusion of microcavities on the sample surface and the disappearance from the sample take place and this leads to the increase of both the glass density and the light refractive index.

As an another way of the appearance of peroxy radicals as a result of secondary reactions, we should analyze the situation when in the microcavity of than increased size appear two non-bridging oxygen atoms and it is not possible to form a O-O bond. It can be that under the further excitation one of the non-bridging oxygens is torn from the silicon and joins the nearest non-bridging oxygen thus forming a peroxy radical.

The generation of the twofold coordinated silicon atoms also is a secondary process. The simplest way is to break a Si-O bond near the threefold coordinated silicon atom (E'-center). Then the non-bridging oxygen atom and twofold coordinated silicon atom appear. Thermally the peroxy radicals and twofold coordinated silicon atoms are the most stable as their diffusion in the glass network is much more difficult than the diffusion of the threefold coordinated silicon and non-bridging oxygen atoms.

4. DEFECTS ELECTRONIC STRUCTURES

The electronic structures of the elementary defects of fused silica, which explains its optical properties, were developed in our previous works for non-bridging oxygen [14] and for threefold coordinated silicon [15] atoms. The electronic structure of non-bridging oxygen atom is still under development. But the highest interest now concerns the electronic structure of twofold coordinated silicon atoms.

The models for most of intrinsic defects in silica are still

under development. While a controversy over details of electronic structure of different defects remains, there exists a general agreement on atomic structures of E'-center, non-bridging oxygen and peroxide radical.

A notable exception is the defect, which gives rise to the 5,03 eV optical absorption band in oxygen - deficient silica - the "B_2" center. Being diamagnetic, this defect eludes identification by ESR and despite the amount of published papers it's atomic structure is still under discussion.

Given the occurrence of B_2 center in oxygen-deficient glasses Arnold [15] in 1973 advanced the oxygen vacancy model. Since the B_2-center is not ESR-active and no other structure - sensitive information on this defect was available, it has become a generally accepted tradition to attribute the B_2-center to oxygen vacancy. Apart from the correlation with oxygen deficiency the main argument here is the decrease of B_2 band under irradiation and a simultaneous growth of the E'-center concentration [16, 17].However, a simple "one-to-one" anticorrelation between the E' and B_2 centers does not exist. The radial distribution functions for concentrations of initial B_2 and radiation-induced E' centers in optical fiber preforms are different [18].

Another model, proposed for the B_2-center is a twofold-coordinated silicon (Si_2^o-center) [18]. It was based on the analysis of the polarization data of the two luminescence bands at 4,3 and 2,7 eV, associated with B_2-center However the association of both these luminescence bands with a single center has been later challenged in several papers [e.g.,19].

An often overlooked argument which, however, could help to solve the controversy between the oxygen vacancy and Si_2^o models is the mutual conversion between the B_2-centers and the ESR-active hydrogen associated "H(I)" centers exhibiting the characteristic 7.4 mT doublet. This conversion was reported in [20] and in line with the oxygen vacancy model was attributed to hydrogen atom trapped into the oxygen vacancy. However recently it was shown [21] that H(I) center is due to a variant of E'-center, where one

oxygen ligand is substituted by a hydrogen.

Similar model for H(I) centers on the surface of SiO_2 was advanced previously in [22]. It was suggested [22] that H(I) centers are formed by trapping of protons at the diamagnetic sides of twofold coordinated silicon atom. Therefore the data on H(I) center structure and its generation process in line with the luminescence polarization data [18] may provide structure sensitive information indicating that Si_2^o model should be preferred.

According to this model, the electronic transition, responsible for the B_2 absorption band and 4.4 eV luminescence band is between the ground $^1A_1$ and excited $^1B_1$ states (classification in terms of C_{2v} symmetry). This is an allowed transition with an oscillator strength larger than 0.13 [24]. The excited state consists mainly of the 3p "non-bonding" orbital of the twofold coordinated Si atom, perpendicular to the O-Si-O plane. A SiF_2 molecule which is isoelectronic to SiO_2^{2-} cluster has the first excited state $^1B_1$ at 5.45 eV [25].

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