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Absorption edge in silica glass

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Vacuum ultraviolet absorption measurement was carried out in silica glass over a wide temperature range from 4 to 1900 K, and structure of the absorption edge and its origin have been elucidated. The main factor that determines the Urbach tail of silica glass is the thermal vibration rather than the structural disorder frozen-in at the glass transition temperature, resulting in a strong temperature dependence of the absorption edge far below the glass transition temperature. Furthermore, freezing process of the disorder from the viewpoint of electronic structure was observed.

I. INTRODUCTION

Structural disorder frozen in amorphous materials is an important factor to determine their physical properties. For example, structural disorder form localized states within the band tails of electronic states,[1] which cause changes of the optical and electric transport processes in amorphous materials. Therefore, the amount of the disorder is crucial to control physical properties of amorphous solids. It is useful for estimating the amount of disorder to examine shape and position of the absorption edge as a function of temperature and/or annealing temperature.[2] In amorphous semiconductors, especially in amorphous silicon,[2–6] such investigations have been carried out because of its importance as the active material of thin film solar cells.

On the other hand, studies in oxide glasses on structural disorder by investigating the absorption edge are scarce. Recently, however, the absorption edge of silica glass is becoming of great industrial interest, since this material is probably the only candidate as optical glass applicable for vacuum ultraviolet (VUV) light projection microlithography. Since the F_2 excimer laser with the wavelength of 157 nm is a promising light source in the next generation of microlithography, and silica glass has its absorption edge just around this wavelength, it is therefore very desirable to extend the transparent range to shorter wavelengths.

Careful analysis of how to determine the absorption edge in silica glass must be the most promising experimental starting point. For the analysis the following points are important; (1) separation of two kinds of the disorder, i.e., frozen-in structural disorder and thermal disorder, to determine the absorption edge, and (2) investigation of freezing process of the structural disorder. In this paper VUV absorption measurement in silica glass over a wide temperature range between liquid He temperature and 1900 K will be reported, and structure of the absorption edge and its origin will be discussed by analyzing in detail the temperature dependence of absorption spectra.

II. STRUCTURE OF OPTICAL ABSORPTION EDGE

Effects of the structural disorder on the electronic structure of amorphous solids are clearly recognized at the band edges,[2] as schematically illustrated in Fig. 1(a). Differences from the perfectly ordered system are (1) narrowing of band gap, and (2) formation of localized states within band tails. These effects on electric structure are reflected in the absorption edge of amorphous solids, which can be represented by two separate regions,[2] as shown in Fig. 1(b). One is generally termed the ‘‘Urbach region,’’ where absorption spectra $\alpha(E)$ can be represented by the exponential form

$$\alpha(E) \propto \exp(E/E_U), \tag{1}$$

where E_U is called the Urbach tail energy. This region is attributed to the optical electronic transition between a localized band tail and an extended band, as shown by arrows A in Fig. 1(a). The other is the ‘‘Tauc region,’’ which is attributed to a transition between the extended valence band and the conduction band, as shown by arrow B in Fig. 1(a). The absorption spectrum in this region can be approximated by the following:

$$\alpha(E) \propto (E-E_O)^2/E, \tag{2}$$

where E_O is termed the optical energy gap. E_O is normally used for defining the energy gap of amorphous semiconductors, but it usually does not coincide with the mobility edge related to photoconductivity. E_U and E_O are useful measures for describing structural disorder.

It should be noted that structural disorder in amorphous solids is caused not only by static disorder frozen in at the glass transition temperature T_g, but also by thermal vibration. We can divide these two contributions by fitting temperature dependences of E_U and E_O to the following equations:[3–6]

$$E_U(T) = \frac{1}{\sigma_0}\left(E_T(T) + \frac{X\hbar\omega_0}{2}\right), \tag{3}$$

$$E_O(T) = E_O^0 - L_0\left(E_T(T) + \frac{X\hbar\omega_0}{2}\right), \tag{4}$$

where $E_T(T)$ is the energy of thermal vibration and can be approximated by the Einstein model:

$$E_T(T) = \hbar\omega_0\left(\frac{1}{2} + \frac{1}{\exp(\hbar\omega_0/k_BT)-1}\right) = \hbar\omega_0 \coth\left(\frac{\hbar\omega_0}{2k_BT}\right), \tag{5}$$

where $\hbar\omega_0$ is the effective energy of an Einstein oscillator, E_O^0 is the optical gap of perfectly ordered system, and σ_0 and

L_0 are temperature-independent parameters related to the deformation potential. For convenience, the static structural discorder are represented by a dimensionless measure X of the ratio of its energy to the zero-point vibrational energy $\hbar\omega_0/2$. In amorphous silicon these equations have been well fitted to experimental results, resulting in a good separation of both contributions.[6] These equations indicate that as the temperature rises E_U and E_O change due to the thermal vibration, and the absorption edge becomes smoother and shifts to lower energies. The change can also be observed in crystalline solids, since in crystals, deviation from perfectly ordered system can also be generated by the thermal vibration.

According these equations, E_U and E_O change almost linearly against temperature at higher temperatures, if X is independent of temperature. However, X should increase in supercooled liquid states above T_g, where the frozen-in structural disorder becomes relaxational and the glass structure changes slowly. Looking at deviations of E_U and E_O from extrapolations of their variations below T_g, we can investigate the freezing process of structural disorder around T_g.

III. EXPERIMENTS

A. Experimental procedure and sample

VUV absorption spectra were measured by a spectrophotometer, which we developed ourselves[7] and is applicable to over a wide temperature range from liquid-He temperature to 2000 °C. The light source was a D_2 lamp with a power of 30 W. An optical system with double beams was adopted, resulting in measurements with an error of absorbance no more than $\pm 1\times 10^{-3}$ even in VUV region. A spectral linewidth of the instrumental function is 0.9 nm. The methods to reduce thermal radiation at high temperatures and to reduce the VUV damage of specimens by the D_2 lamp are described in detail in Ref. 7.

Samples were fused silica glasses manufactured by Nippon Silica Glass Co., Ltd. Since OH concentration was less than 10 wt ppm and Cl was not detectable in all specimen used, the Urbach edge could well be determined, unaffected by the OH and Cl absorption. Oxygen vacancies in the glass network generate absorption of $\sim$10 cm^{-1} around 7.6 eV, but it did not disturb measurements of the Urbach edge where absorption ranged from 10 to 5×10^3 cm^{-1}. Crystalline quartz was also used as a specimen for a comparison.

To exactly determine the Urbach edge, surface reflection must have been removed from the measured absorbance. At room temperature, we could calculate the surface reflection from the optical constants around the absorption edge measured by a VUV ellipsometer. However, this ellipsometer was not applicable to high temperature measurements. Therefore, we measured four samples with different thicknesses of 10, 30, 120, and 1000 μm to determine inner absorption coefficient α and reflectance R by the following relations:

$$\alpha = -\left(\ln\frac{t_1}{t_2}\right)\bigg/ d, \quad R = 1 - \sqrt{\frac{t_1}{\exp(-\alpha L)}},$$

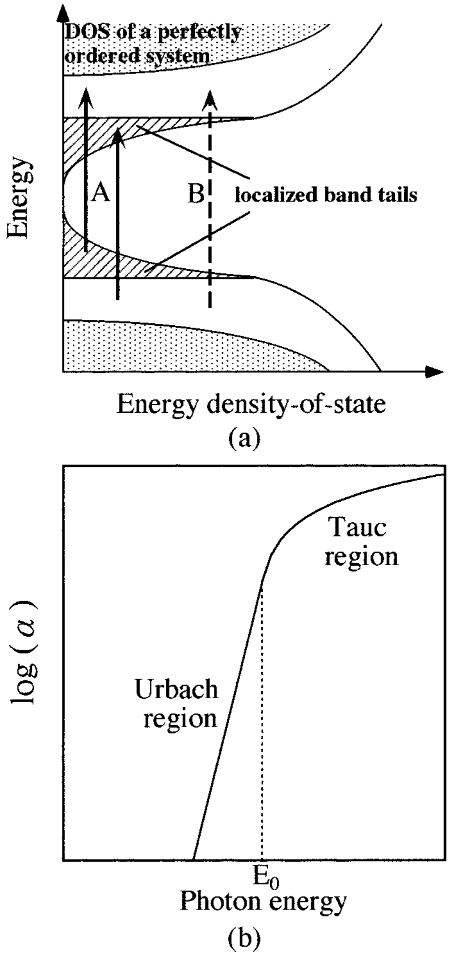

FIG. 1. Schematic representations of (a) the electronic structure and (b) the absorption edge in amorphous materials. Arrows *A* and *B* in (a) show the optical electronic transition in the Urbach and Tauc regions, respectively.

where t_1 and t_2 are the transmittance of the samples with L and $(L+d)$ thickness, respectively.

B. Experimental results

Figure 2 shows VUV absorption spectra of a sample of 120 μm thickness before reflectance correction. Temperature ranged from 4 to 1873 K, where the temperature interval was 25 K between 23 and 1873 K. The absorption edge shows a strong temperature dependence; it becomes gentle and shifts to lower energies with increasing temperature.

Reflection correction was carried out at each temperature to exactly determine the Urbach edge. An example at 298 K is shown in Fig. 3, where open and solid circles represent data before and after the correction, respectively. The Urbach edge was determined by fitting the corrected data, as shown by a solid line in Fig. 3. At this temperature reflection correction could be also done by using the VUV ellipsometer data. A dotted line shows the result. Both lines almost coincide. E_U was determined by the derivative of these lines; E_U at 298 K was 0.075 ± 0.05 eV. E_O could not be directly determined from the data, since absorption coefficient in the Tauc region as large as 10^4–10^5 cm^{-1} could not be measured in bulk samples. Absorption coefficient at E_O was reported

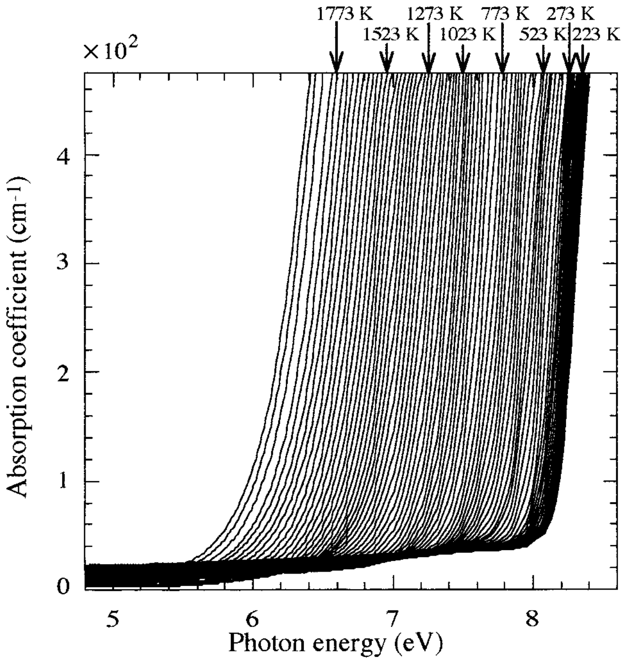

FIG. 2. VUV absorption spectra in silica glass before reflectance correction. The sample thickness was 120 μm. Temperature ranged between 4 and 1873 K, where the temperature interval was 25 K between 23 K and 1873 K. The absorption edge hardly changed below 223 K.

to be about $5\times10^3\ \mathrm{cm}^{-1}$ by several measurements using thin films and reflectance measurements.[8] Therefore, photon energy with $5\times10^3\ \mathrm{cm}^{-1}$ absorption coefficient was regarded as E_O; E_O is 8.52 ± 0.02 eV in Fig. 3.

Such correction was carried out at each temperature, and temperature dependences of E_U and E_O were deduced, as shown by solid circles in Figs. 4(a) and 4(b), respectively. They strongly depend on temperature even around room temperature. E_U and E_O of quartz at 298 K are given in the figures by the closed squares for comparison.

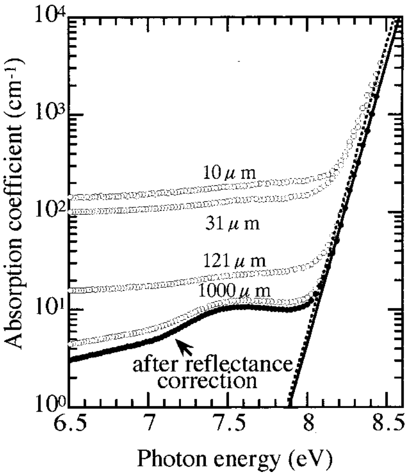

FIG. 3. Reflectance correction by using four samples with different thicknesses at 298 K. Open and solid circles represent data before and after the correction, respectively. Solid and dotted lines represent the Urbach edge determined by these corrected data and by VUV ellipsometer data, respectively.

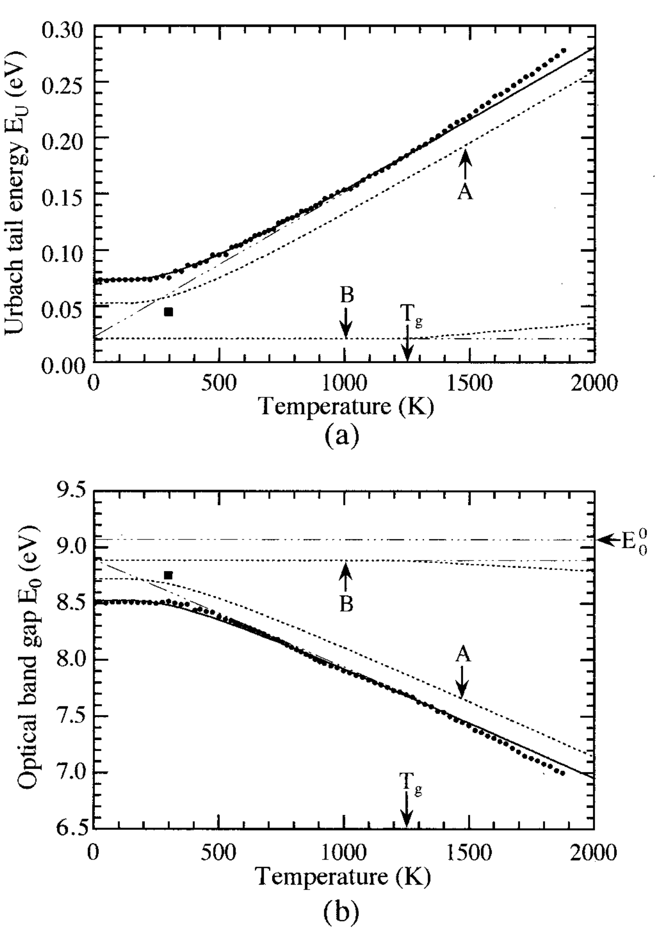

FIG. 4. Temperature dependencies of (a) the Urbach tail energy E_U and (b) the optical band gap E_O in silica glass, represented by solid circles. Data below 1200 K ($<T_g$) were fitted to Eqs. (3) and (4), and the fitting line is shown by solid lines. Dotted lines *A* and *B* represent contributions of thermal vibration and structural disorder besides thermal vibration, respectively. Other lines are guides for eyes. Solid squares indicate E_U and E_O of quartz at 298 K.

IV. DISCUSSION

E_U and E_O have been found to depend on temperature strongly. To separate contributions of the thermal vibration and the frozen-in structural disorder, data below 1200 K ($<T_g$) were fitted to Eqs. (3) and (4). The results are shown by solid lines in Figs. 4(a) and 4(b), and contributions of thermal vibration and of the frozen-in structural disorder are represented by dotted lines *A* and *B*, respectively. The fitting parameters determined in E_U were used for fitting E_O, as E_O could not be directly determined by the present measurements. The parameters are tabulated in Table I, where parameters reported in amorphous silicon[6] are also shown for comparison.

It was found that the contributions of thermal vibrations to E_U and E_O are larger than that of frozen-in structural disorder. The value of X in this silica glass is approximately 0.3 below T_g, and is much smaller than 8 as has been reported in amorphous silicon.[6] This fact is contrary to the common sense that the absorption edge in glass structure is mainly determined by the static disorder. From the viewpoint of the electronic structure, silica glass is not so very different from crystalline SiO_2. This conclusion is supported by the

TABLE I. Fitting parameters of the absorption edge, and E_O and E_U extrapolated to 0 K.

	Fitting parameters					
	X	$\hbar\omega_0$ (eV)	L_0	σ_0	E_O at 0 K (eV)	E_U at 0 K (eV)
Silica glass (Present work)	0.33 ± 0.03	0.079 ± 0.008	10.3 ± 0.06	0.66 ± 0.05	8.52 ± 0.04	0.073 ± 0.002
a-Si:H (Ref. 6)	8	0.026	7	2.5	1.83	0.048

fact that the corresponding values in quartz at room temperature are very close to the thermal terms in silica glass, as shown by squares in the same figures.

Above T_g, estimated to be about 1250 K, E_U and E_O deviate from the extrapolated lines. This means that the contribution of structural disorder besides thermal vibrations increases above T_g, as shows by change in the slope of curve B at T_g. Freezing process of structural disorder at T_g can be observed in this change. This result indicates that structural relaxation in silica glass is important for controlling the absorption edge.

V. CONCLUSIONS

Understanding the absorption edge of silica glass by VUV absorption measurements and theoretical considerations has been achieved.

(1) The main factor that determines the Urbach tail of silica glass is the thermal vibrations rather than the frozen-in structural disorder. This causes strong temperature dependencies of E_U and E_O far below T_g. Silica glass is very similar to quartz from the viewpoint of the electronic structure.

(2) To our knowledge, the first observation of the disorder freezing process has been achieved from the viewpoint of the electronic structure.

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