Optical properties of molecules trapped in silica glasses

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Silica glasses were prepared by the vapor-phase axial deposition (VAD) method with changing preparation conditions. O_2 molecules were found to be dissolved in the order of $10^{17}cm^{-3}$.

On the ArF excimer laser irradiation of the glasses having the absorption band above 7eV, the absorption band at 4.8eV was induced. The band was assigned to the Hartley bands of O_3 molecule. The reaction model was proposed to be

$$O_2\ (\text{trapped}) \xrightarrow{h\nu} 2O\ (h\nu \geq 5.1\text{eV})$$

and

$O + O_2 \rightarrow O_3$ (trapped).

On exciting the induced 4.8eV band, a photoluminescence at 1.9eV was observed. The reaction was proposed to be

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2 \quad (h\nu \geq 4.1\text{eV})$$

and

$$O(^1D) \rightarrow O(^3P) + 1.9\text{eV}.$$

INTRODUCTION

Silica glasses have potential applications to optical components in excimer laser lithography of ULSI (ultra large scale integral circuit) process. However, most of the glasses produced by a various of methods have optical absorption in vacuum ultra violet (VUV) region. On the excitation of the absorption bands may arise solarization and/or luminescence, which are serious problem of the process, because the former induces changes in refractive index and latter causes smearing of circuit patterns. Metallic impurities are not responsible for the optical absorption, because their concentration is reduced below ppb level in the synthetic silica glasses. The optical absorption and luminescence are related to the lack of stoichiometry and halogen impurities.

In the recent papers,[1-3] we proposed that oxygen deficient type defects (SiO_{2-x}) were originated from a thermal decomposition reaction which was symbolically expressed as; $SiO_2 \rightarrow SiO_{2-x} + x/2O_2$, under the high temperature process manufacturing high purity synthetic silica glasses. On the other hand, oxygen excess type defects (SiO_{2+x}) would be originated in the case of high O_2 partial pressure in the fabrication process of silica glasses. Therefore, most of the absorption bands are related to the nonstoichiometry; oxygen defficient and oxygen excess centers. For instance, 7.6eV,[4-6] 5.8eV,[7] 5.17eV,[1,8] 5.06eV[2,5,9,10] bands are attributed to oxygen deficient centers and 2.0eV[11-13] band to an oxygen excess center.

As for 4.8eV absorption bands, there have been several works reporting its generation and structural models. Skuja found the 4.8eV band in neutron irradiated Suprasil W and the band was correlated to the non-bridging oxygen hole center (NBOHC).[14] Stathis et al. reported that on the irradiation of Suprasil W with an F_2 excimer laser the grouth of 4.8eV absorption and 1.9eV luminescence was observed, the latter being excited with N_2 laser. They found a different tendency of growth rate between absorption coefficient at 4.8eV and the intensity of 1.9eV luminescence band.[15] Devine found that the absorption coefficient at 4.8eV changed in harmony with the concentration of NBOHC in Suprasil W under annealing.[16] Besides Suprasil W, 4.8eV band was generated in wet SiO_2 produced by a direct process, oxidation of $SiCl_4$ in H_2-O_2 flame. Nakamura et al. found 4.8eV band in wet SiO_2 glass irradiated with X-ray[17] and Tohmon et al. found the band in the SiO_2 glass fabricated with plasma technique irradiated with γ-ray.[18]

Notwithstanding many works on the optical properties of the synthetic SiO_2 glasses, the structural and reaction models responsible for the optical behavior are not conclusive. We think that this is partly due to the difference in the samples used by the different authers. In the course of the studies on oxygen defficient centeres,[1-3] we had a strong impression that dissolution of the gas molecules such as O_2, Cl_2 in the synthetic SiO_2 glasses may be a determining factor of photochemistry and optical properties in VUV-UV region.

EXPERIMENTAL PROCEDURE

A. Sample preparation

We prepared the silica glasses with the vapor phase axial deposition (VAD) technique.[19] The VAD soot rods with a large surface area ($\simeq$200cm^2/g) were sintering under different ambients, which were O_2/He=1/10, 3/10, 7/10 and 10/10 to fabricate the SiO_{2+x} type glasses. Such samples were named as VAD1, VAD3, VAD7 and VAD10, respectively.

B. Optical measurements

The optical absorption of silica glass was measured with a JASCO UVDEC-610C spectrometer (3-6eV) and a Seya-Namioka type spectrometer attached to the synchrotron orbital radiation (SOR) ring installed in Institute for Molecular Science, Okazaki, Japan (UVSOR, BL1B).

Photoluminescence was measured by using a spectrometer constructed in our laboratory consisting of Xe lamp (300W) as an excitation light source, 0.1m grating monochrometer (JASCO CT-10) for the excitation light, and 0.25m grating monochrometer (JASCO CT-25) with a photomultiplier detector (HTV-R446). All optical lenses used in the measurments are made from luminescence free and synthetic silica glass. Aqueous solutions of $NiSO_4$ and $CoSO_4$ were used as a filter for the excitation light to remove the lights with wavelength longer than 3.4eV. Wavelength depecdence of an overall sensitivity of the system was calibrated by using strong luminescence of Rhodamine 6G solution whose quantum efficiency as known to be 0.69-0.97.[20]

C. ESR measurements

Electron spin resonance (ESR) of glass samples before and after either an irradiation with an ArF excimer laser or annealing in H_2 gas was measured to examine effects of these treatments on the generation and elimination of paramagnetic centers and their concentration. X-band spectra were measured with JES-FE-2XG spectrometer at 77K. Power of microwave was 0.04mW or 20mW.

RESULTS & DISCUSSION

A. VUV absorption of as-prepared glasses

The Fig.1 shows VUV absorption spectra of the as-prepared glasses. For all the glass samples, a red shift of an absorption edge was pronounced from that of low OH silica glass.[21] This is a strong indication that some structural imperfections are present in the glass network. In a series of VAD samples, it is noticed that the optical absorption above 7eV region increases with an increase of O_2 partial pressure of sintering atmosphere.

B. Induced optical absorptions by irradiation with ArF excimer laser

Fig.2 show absorption spectra in UV-VUV region before and after ArF excimer laser irradiation. The spectra of samples obtained before the irradiation (dashed lines) are a continuous and monotonic extension of the VUV spectra shown in Fig.1.

On the irradiation of the ArF excimer laser, generation of optical absorptions was noticed. A distinct peak was generated at 4.8eV (255nm), whose full width at half maximum height (FWHM) was estimated to be 0.8eV. There was at least another induced band in VUV region, which was indicated as a rise in absorption at 6eV in Fig.2.

Additional but important observations for the spectra of the respective and irradiated samples are the following. The absorption intensity of the induced band at 4.8eV increased in the order of O_2 partial pressure of the sintering atmosphere.

C. 1.9eV luminescence

It was found that on exciting the induced 4.8eV absorption band a red luminescence with a peak energy of 1.9eV was recognized. Fig.3 shows a photoluminescence excitation spectrum (PLE), a dependence of the luminescence intensity on the excitation energy (solid line, open circle), the luminescence being monitored at 1.9eV (630nm). Unexpectedly the intensity maximum of the PLE spectrum was not at 4.8eV, where the peak maximum of the induced absorption band is located. One remarkable characteristic of the PLE spectrum is that there is a threshold wavelength at 3.9eV (320nm). Excitation efficiency was not zero at 5.5eV, this suggesting that the PLE spectrum still extends to VUV energy region. This observation is consistent with the one that the red luminescence is observable by eyes during the ArF excimer laser irradiation.

D. Structural and reaction model of the optical resposes

At the present stage, we discuss the origin of the optical absorptionsof the as-prepared and irradiated glasses and photoluminescence. In the succeeding subsections the experimental evidences supporting the model will be given.

Our tentative explanation of the observed phenomena is that

O_2 molecules unexpectedly dissolved in the glasses respond to the optical properties. Firstly, we reviewed very briefly photochemistry of O_2 molecules in the gas phase. It is well known that O_2 molecule in the gas phase[22] dissolved into oxygen atoms when irradiated with $h\nu \geq 5.1eV$,

$$O_2 \xrightarrow{h\nu} O \quad (h\nu \geq 5.1eV) \qquad (1).$$

The reaction between the generated oxygen atom and an O_2 molecule gives rise to ozone molecules as;

$$O + O_2 \rightarrow O_3 \qquad (2).$$

Taking into account the above mentioned photochemistry of O_2 molecule, we examine validity of the proposed model. O_2 molecule itself has a characteristic absorption band above 7eV, namely Schumann-Runge bands.[22, 23] Therefore, our model requires a corresponding absorption above 7eV in the as-prepared glass samples. In Fig.4 open circle shows the difference spectrum between VAD10 and VAD1 in VUV region and open square denotes the spectrum of Schumann-Runge bands of O_2 molecule whose concentration is assumed to be $10^{17}cm^{-3}$. Both spectra superimpose each other. Therefore, O_2 molecule model satisfies the first requirement, VUV absorption of the as-prepared glasses. We can estimate concentration of O_2 molecules trapped in the glass network by using the known molar absorption coefficient of the O_2

at 7eV. However, there is the effect of other overlapping absorption in this energy region, for OH group. We confined ourselves to state that the difference in O_2 concentration between VAD1 and VAD10 is $1.0\times10^{17}cm^{-3}$ as shown in Table. The absolute concentration were given from IR measurements and will be discussed in the succeeding subsection E. The second requirement is that the model must given an explanation of the induced absorption at 4.8eV by an ArF excimer laser irradiation. If O_2 molecule dissolved in the glass network, it is expected to react according to eq.(1) and (2) on the irradiation, resulting in the formation of O_3. Ozone molecule has an absorption band peaking at 4.8eV whose full width at half maximum is 0.8eV, namele the Hartly bands.[24] The characteristics of the induced band, peak energy and width, coinside with those of HArtly bands. The concentration of O_3 molecule induced by ArF excimer laser irradiation was also estimated from molar absorption coefficient of the 4.8eV band seen in the irradiated silica glasses. These values are also shown in Table and in the order of $10^{16}cm^{-3}$.

The third observation which should be explained is the appearence of 1.9eV luminescence after the irradiation. We explain the optical response referring to the photochemistry of O_3 molecule in the gas phase; O_3 molecule is known to decompose to an oxygen atom of excited state and O_2 molecule. The excited oxygen of excited state and O_2 molecule. The excited oxygen relaxes by emitting light peaking at 1.9eV as shown in the reaction (3);

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2 \rightarrow O(^3P) + O_2 + 1.9eV \quad (h\nu \geq 4.1eV) \qquad (3)$$

We, therefore, propose that the same chain reactions are occuring in the silica glass containing O_2 molecule. This view is further supported by taking into accounts the photon energy dependence of photlysis of ozone molecule. In Fig.3 dotted line and closed circles show the quantum yield of $O(^1D)$ in the photolysis of O_3 at-40°C as a function of incident wavelength measured by Lin and DeMore.[25] Decomposition of O_3 has a threshold wavelength of the quantum yield of $O(^1D)$ are very close to those of excitation efficiency of 1.9eV luminescence induced in the silica glass by ArF excimer laser. It is likely that 4.8eV absorption band is attributed to ozone in the silica glasses and 1.9eV photoluminescence band is assigned to the radiative relaxation, $O(^1D)$ $O(^3P)$ + 1.9eV.

E. Changes in IR spectrum with heated H_2 treatment

In the previous subsection D, we proposed that O_2 molecules are dissolved in the silica glasses specially treated and they respond to the optical absorption above 7eV, the induced absorption at 4.8eV by ArF excimer laser irradiation and 1.9eV photoluminescence. In the present and succeding sections (E and F), we further confirm the model by examine the effect of chemical reactions of O_2 with hydrogen on the optical properties.

Fig.5 shows the difference spectra in IR region before and after the H_2 annealing at 800°C for 15hr for VAD1, 3, 7, and 10 samples. No detectable absorption was seen before the treatment for all the samples. No detectable absorption was seen before the treatment for all the samples. Growth of absorption peaks attributable to OH species is clearly noted and it showed the saturation within 15hr treatment. Absorption peak at $3630cm^{-1}$ which is attributed to gem-type OH clealy increased in the order of the O_2 partial pressure.[26] It is additionally seen in the figure that the broad absorption around $2900cm^{-1}$ which is attributed to hydrogen bonded OH[27] also incresed with increasing the partial pressure of O_2. These observations suggest that O_2 molecules trapped in the silica network reacts with H_2 molecule as $O_2 + 2H_2 \rightarrow 2H_2O$. It is unspecified that the H_2O formed in the reaction remains as the molecule or react with SiO_2 to form SiOH groups. The presence of hydrogen groups is an indication of the closely interacting OH groups, but it does not give a conclusive information which differentiates H_2O from SiOH. This point will be discussed in the succeeding subsection. By assuming the above reaction, concentration of O_2 molecules trapped in the silica network was estimated referring to the absorption coefficient of OH.[28] The O_2 concentration found in VAD1, VAD3, VAD7 and VAD10 are $2.2\times10^{17}cm^{-3}$, $2.4\times10^{17}cm^{-3}$, $2.9\times10^{17}cm^{-3}$ and $3.2\times10^{17}cm^{-3}$, respectively.

F. Effect of annealing under H_2 ambient on optical absorptions

Formation of OH species (H_2O or SiOH) during H_2 annealing was estimated by using IR absorption in the previous subsection E. We examined the effect of chemical reactions of the glasses with heated H_2 gas on the optical absorptions above 7eV. Fig.6 show changes in the optical absorption of the glasses with H_2 treatment at 600°C. We measured the samples of 2mm thick to accelerate diffusion of H_2 molecules.

As seen in Fig.6, the absorption intensity of the initial spectra of VAD10 above 7eV drastically decreased during the H_2 annealing The decrease in the intensity was almost proportional to $t^{1/2}$ up to 4hr, where t is a time of the treatment, this is suggesting that the reaction responsible for the decrease of the absorption intensity was diffusion controlled in the initial stage up to several hours and tends to saturate within about

10hr. The spectrum obained after 10hr treatment seems to approach to the initial spectrum of VADO (Fig.1), which was synthesized by sintering under He atmosphere. The change in the spectra in longer wavelength region was not clear because of the low absorption intensity due primarily to thin sample thickness.[21]

The decrease in the absorption intensity at 7eV due to the trapped O_2 molecules is assumed to be originated from the reaction;

$1/2O_2 + H_2 \rightarrow H_2O$ (trapped) (4)

or

$1/2O_2 + H_2 + \equiv Si{-}O{-}Si\equiv \rightarrow \equiv SiOH$ (5)

Two question may arise here above the reaction models. The first is if the products, H_2O or $\equiv SiOH$, give an absorption band in the same energy region with O_2 molecule. The second one is which mechanism is preferable between the above two. An appropriate method to approach to the solution intensity of the products.

Imai et al. found the linear relationship between OH concentration and VUV optical loss around 7-8eV,[5] for the silica glasseswhose OH concentration is 30-1500ppm. The estimated absorption cross section for OH groups in silica glass is $1.8\times10^{-20}cm^2$ at 7.5eV and $11\times10^{-20}cm^2$ at 7.8eV. On the other hand, the absorption cross sections for the Schumann-Runge bands of O_2 molecules in the gas phase are reported as $2\times10^{-20}cm^2$ at 7.5eV and $4\times10^{-20}cm^2$ at 7.8eV.[22,23] According to the eq.(5), one mole of O_2 gives 4 moles of SiOH. This gives rise to the decrease in absorption due to the elimination of O_2 molecule one order of magnetude larger than the increase due to the formation of ≡SiOH groups evaluated at 7.5eV. Therefore strong absorption above 7eV by Schumann-Runge bands of O_2 molecule turns into for weak OH absorption band in the reaction model of eq.(4), one mole of O_2 generates two moles of H_2O. The absorption cross section of H_2O in the gas phase is reported as $1\times10^{-18}cm^2$ at 7.5eV and $2\times10^{-18}cm^2$ at 7.8eV. Therefore absorption intensity at 7.5eV should remain unchanged during the reaction (eq.(4)). It is, therefore, likely that the H_2O molecule formed according to eq.(4) react further with glass network giving SiOH.

G. Results of ESR measurements

Fig.7 shows ESR spectrum of VAD1 sample irradiated with ArF excimer laser at room temperature and recorded at 77K. Before the irradiation, no signal was detected. After the irradiation, two signals appeared. One signal which could be detected with low microwave power (0.04mW) is assigned to E′ center (≡Si•) and another measured with high micro power (20mW) is to NBOHC (≡SiO•). As for the other samples except VAD0 and WET1, the same defects of a comparative concentration were detected. Therefore we can conclude that the samples which showed 4.8eV absorption band after the irradiation have simultaneously generated the NBOHC. Explanation of generation of the NBOHC and the E′ center on the irradiation is not conclusive. Our tentative interpretation is that the E′ center generated by the irradiation reacts with O atom decomposed from O_2 and O_3 photochemistry; $\equiv Si\cdot$ (E′ center) + O → $\equiv SiO\cdot$ (NBOHC). The estimated NBOHC concentration from ESR measurements of VAD samples is about $1.0-2.7\times10^{16}cm^{-3}$. Compared with O_3 concentration estimated from an optical cross section of Hartly bands, 10^{16} order seems to be resonable.[24] In Table, O_2, O_3 and NBOHC concentrations were shown.

CONCLUSION

SiO_2 glasses were systematically prepared by using VAD, direct and plasma method by changing preparation conditions with the expectation of changes in O_2 concentration from glass to glass. These samples have VUV absorption above 7eV in the as-prepared state, and the 4.8eV absorption, 1.9eV luminescence and NBOHC were generated in the glasses after irradiation with ArF excimer laser. The VUV absorption above 7eV is attributed to Schumann-Runge bands of O_2 molecule trapped in the silica glass network. The induced 4.8eV absorption band is assigned to Hartley bands of O_3 molecule. The photoluminescence at 1.9eV is thought to be due to a radiative relaxation of an excited $O(^1D) \rightarrow O(^3P)$. The reactions are totally expressed as;

$$O_2\ (\text{trapped}) \xrightarrow{h\nu} 2O\ (h\nu \geq 5.1\text{eV}),$$

$$O + O_2 \rightarrow O_3\ (\text{trapped}),$$

$$O_3 \xrightarrow{h\nu} O(D) + O_2\ (h\nu \geq 4.1\text{eV}),$$

$$O(^1D) \rightarrow O(^3P) + 1.9\text{eV}.$$

Recently, we also reported that Cl_2 molecules were trapped in the silica glasses.[30]

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Table Concentrations of O_2, O_3 and NBOHC generated with ArF excimer laser.

Abbreviated sample names	Trapped O_2 (10^{17}cm^{-3})	Ozone (10^{16}cm^{-3})	NBOHC (10^{16}cm^{-3})
VAD1	2.2	1.5	1.0
VAD3	2.4	1.7	2.0
VAD7	2.9	1.9	2.7
VAD10	3.2	1.9	2.7

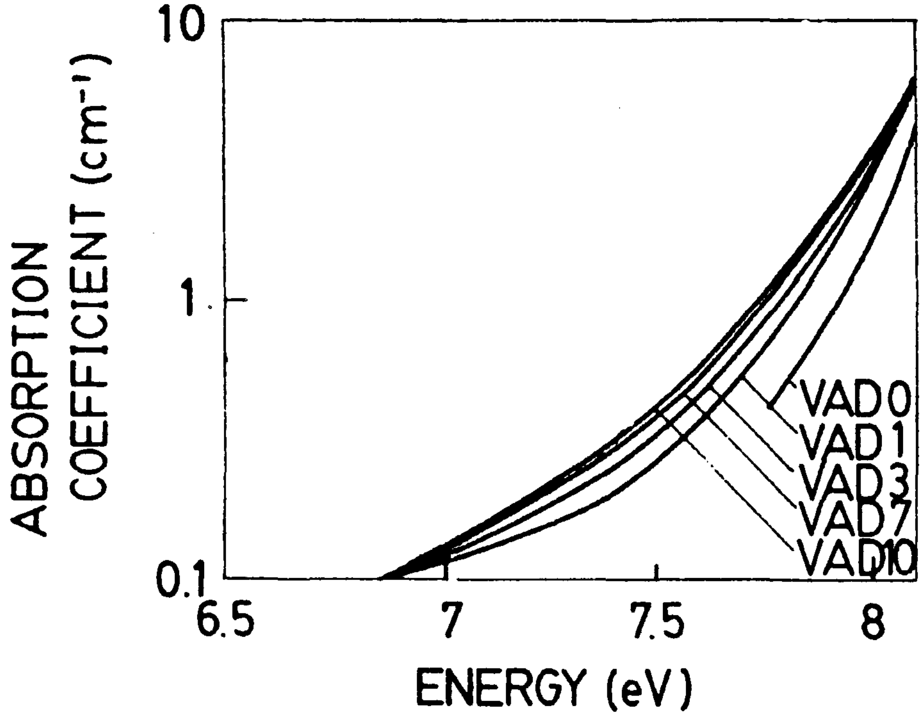

Fig.1 VUV absorption spectra of as-prepared glasses. Characteristics of the glasses are given in Table 1.

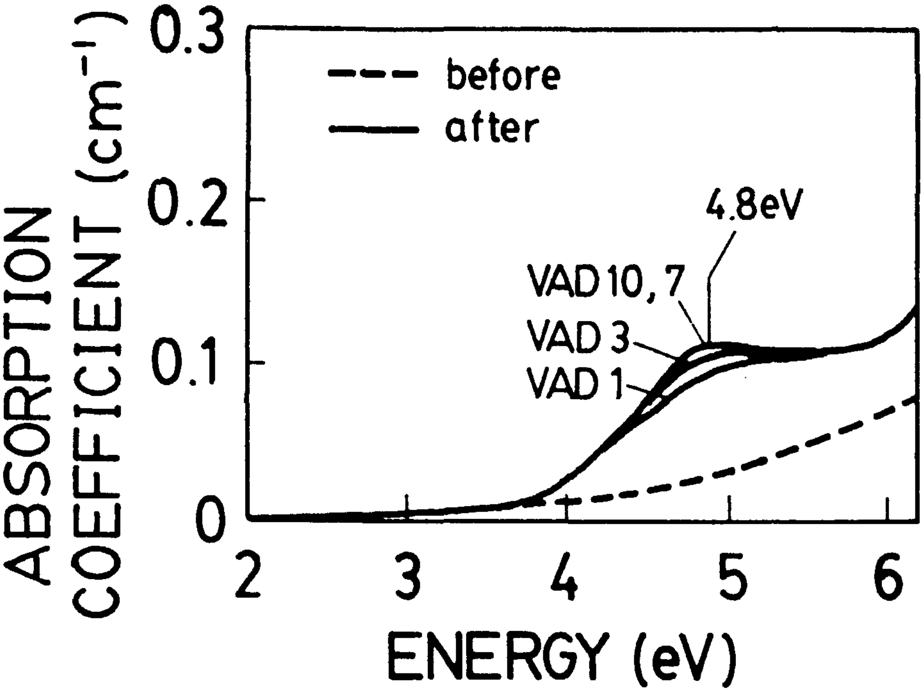

Fig.2 UV-visible absorption spectra of silica glasses produced with VAD method. Dashed lines in the figure shows the spectrum for the as-prepared glasses and these are connected to those shown in Fig.1. Solid lines denote the spectra for the glasses irradiated with ArF excimer laser radiation. Irradiation conditions were 13mJ/cm^2 per pulse, 100Hz for 3min at room temperature.

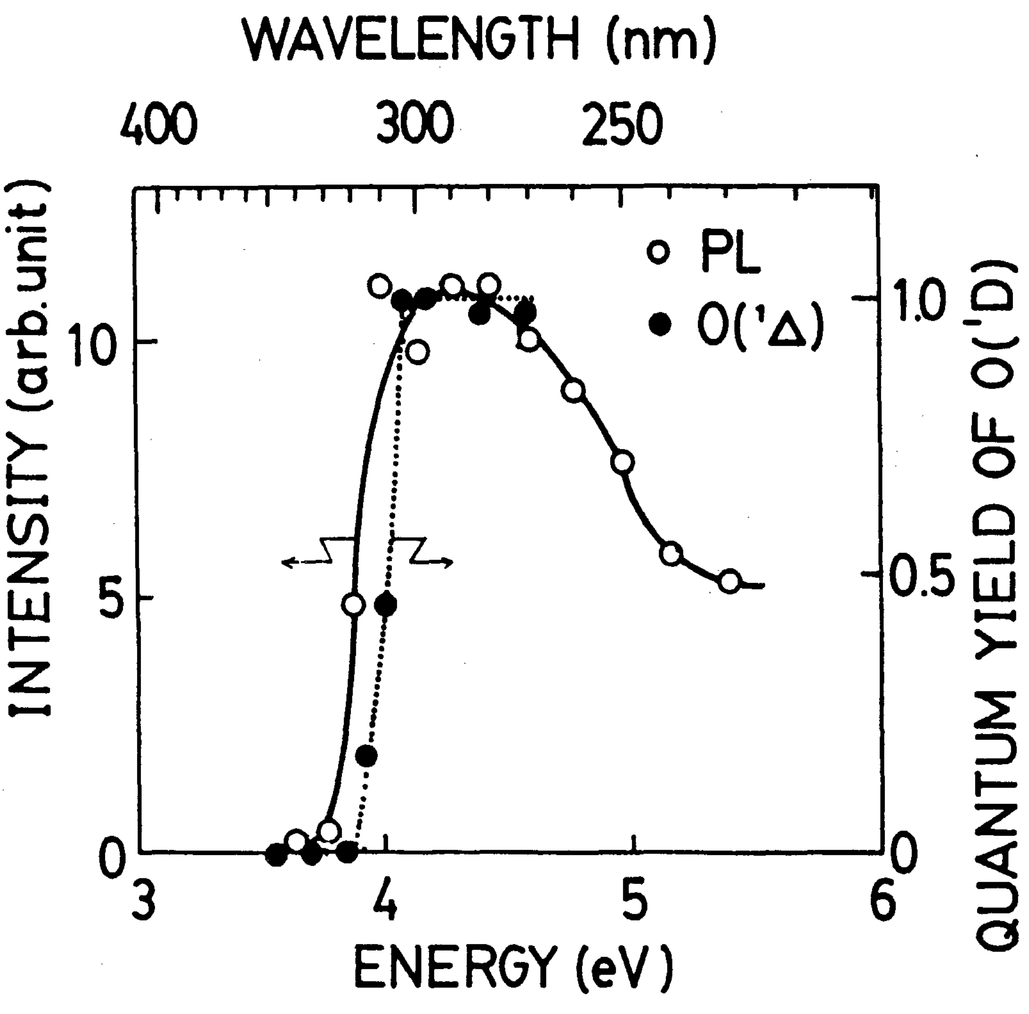

Fig.3 Changes in photoluminescence intensity measured at 1.9eV as a function of incident energy (Solid line and open circles). Dotted line and closed circles show quantum yield of O(^{1}D) in the photolysis of O_3 at -40°C as a function of incident energy.[25]

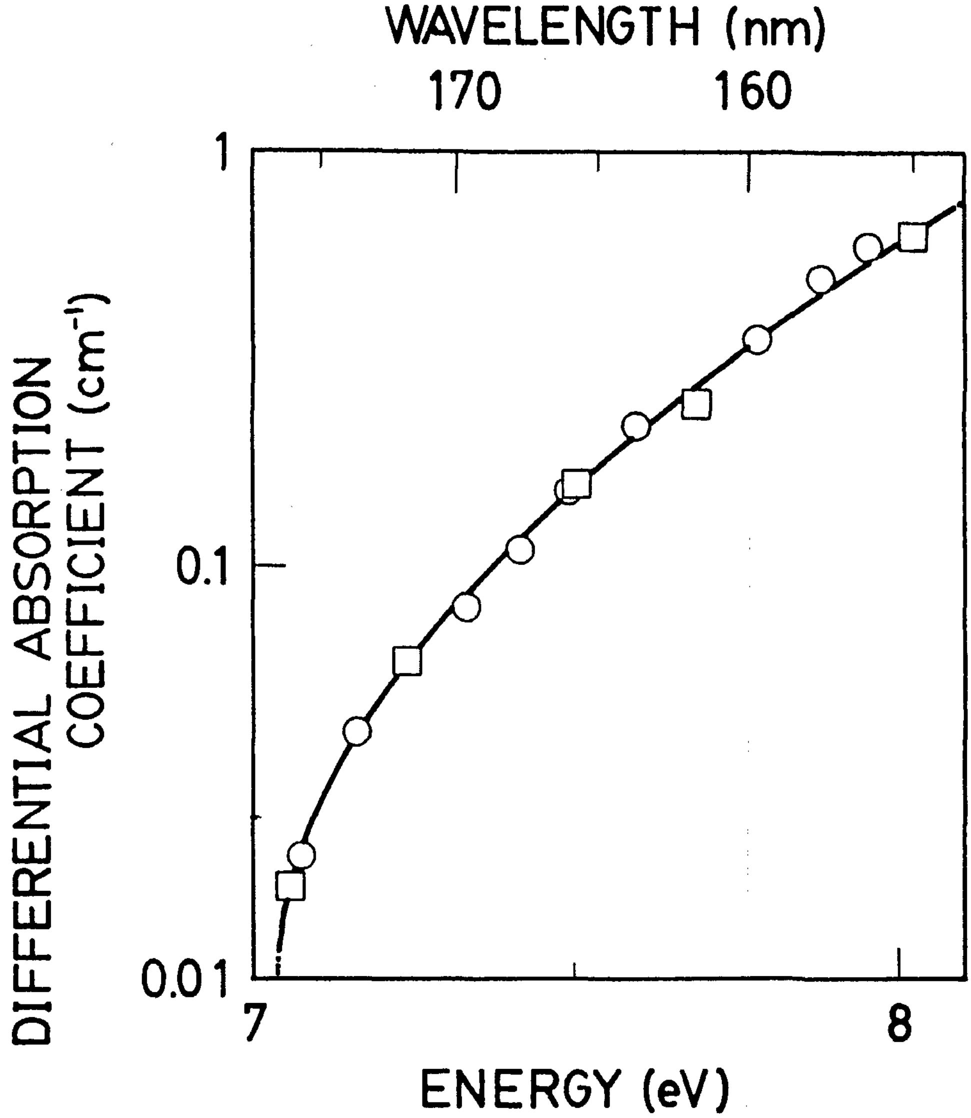

Fig.4 The absorption spectra around 7.5eV. Open circles show the difference spectrum between VAD10 and VAD1 and open squre shows the spectrum of Schumann-Runge bands of O_2 molecule whose concentration is assumed to be $10^{17}cm^{-3}$. Absorption coefficient of the Schumann-Runge bands was taken from Ref. 23.

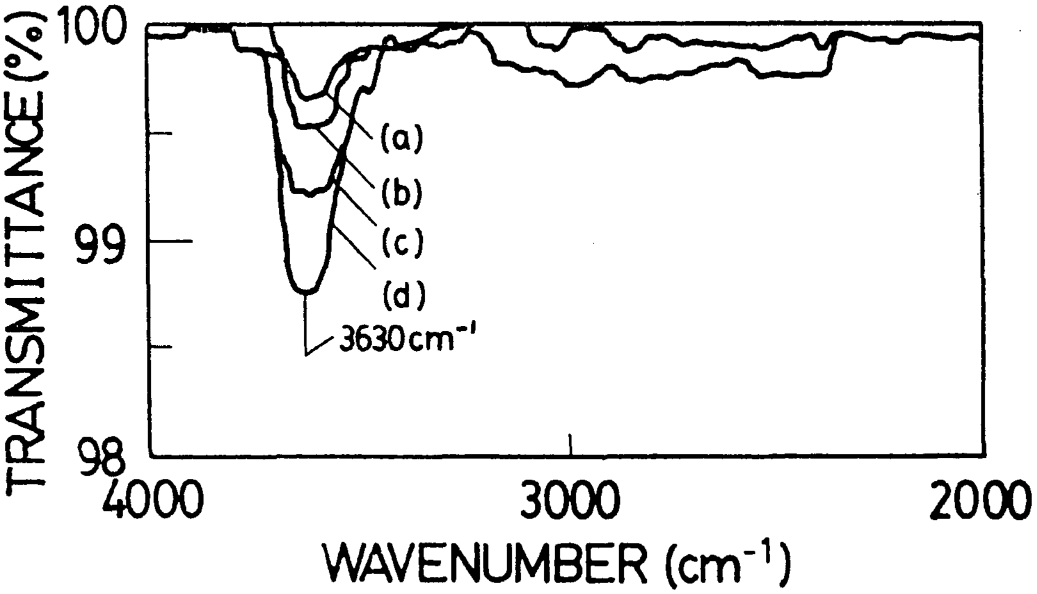

Fig.5 The difference spectra in IR region for VAD1, 3, 7 and 10 samples before and after the H_2 annealing at 800°C for 15hr.

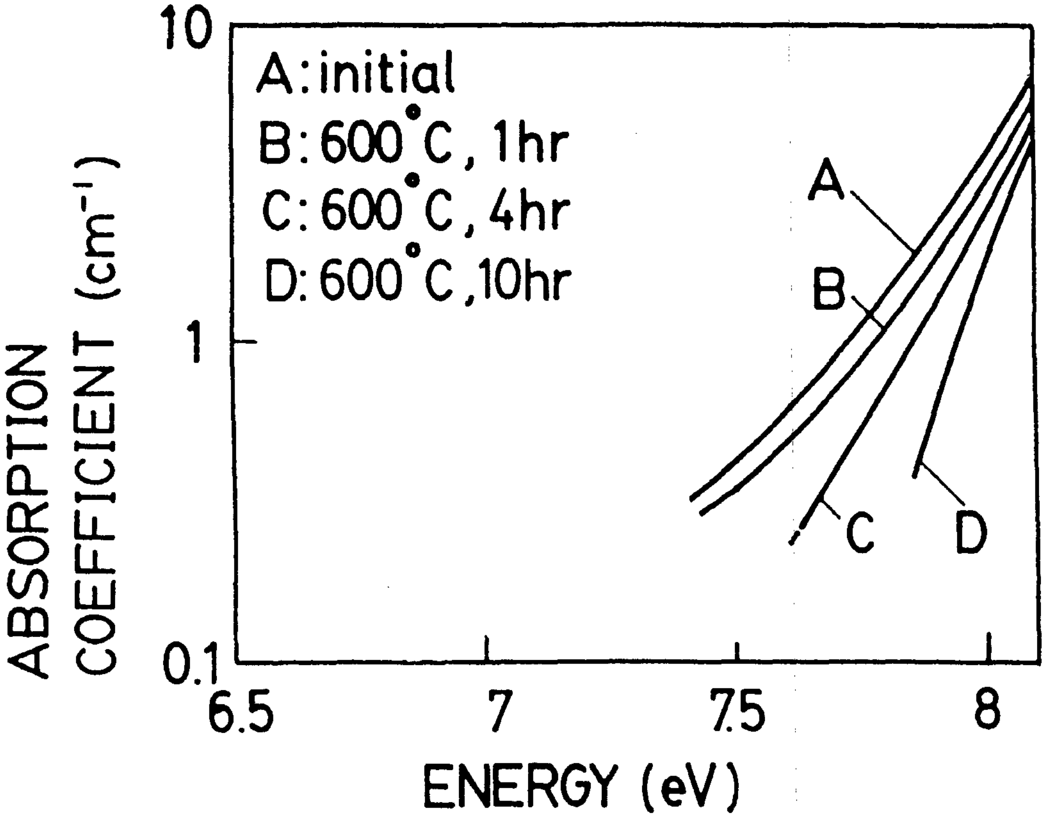

Fig.6 Changes in VUV absorption spectra of the glasses annealing under H_2 atmosphere (1atm pressure) at an elevated temperature.

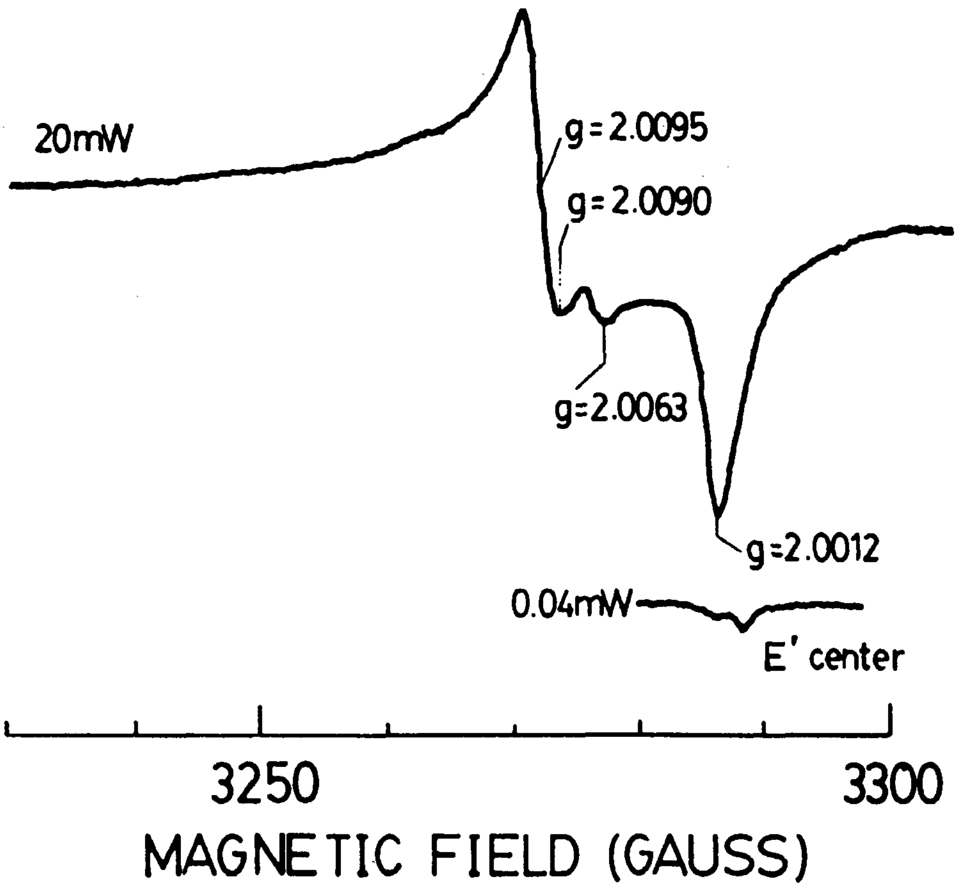

Fig.7 ESR spectrum of VAD1 sample irradiated with ArF excimer laser at room temperature.