

Enhanced photogeneration of E' centers from neutral oxygen vacancies in the presence of hydrogen in high-purity silica glass

Hiroyuki Nishikawa, Ryuta Nakamura, and Yoshimichi Ohki

Department of Electrical Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Yoshimasa Hama

Science and Engineering Research Laboratory, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku Tokyo 169, Japan

(Received 29 December 1992; revised manuscript received 16 March 1993)

Electron-spin-resonance (ESR) and ultraviolet–vacuum-ultraviolet (uv-vuv) spectra were measured on two types of oxygen-deficient silicas, i.e., low-OH ($[\text{OH}] < 1$ ppm) and high-OH ($[\text{OH}] \approx 20$ ppm) silicas, and a high-OH ($[\text{OH}] \approx 1000$ ppm) stoichiometric silica. The results of ESR show that the E' concentration induced in an OH-containing oxygen-deficient silica is one or two orders of magnitude higher than in low-OH oxygen-deficient and high-OH stoichiometric silicas when exposed to 6.4-eV or 7.9-eV photons. It is shown from the vuv spectra that the conversion of an oxygen vacancy into an E' center is enhanced in the OH-containing oxygen-deficient silica compared with the low-OH oxygen-deficient silica. The conversion into an E' center is considered to be mediated by diffusion of atomic hydrogen released from the Si-H bond. A slight peak shift of the 5.8-eV absorption band due to the E' center suggests that the formation of an E'_β -like center is involved in the enhanced E' creation. A possible correlation of the enhanced E' creation with the appearance of a 7.4-mT doublet in the ESR spectrum is also discussed.

I. INTRODUCTION

Radiation-induced defect formation in amorphous silicon dioxide ($\alpha\text{-SiO}_2$) has long been a topic of interest, since it concerns the long-term reliability of silica-based optical fibers, bulk silica for ultraviolet-grade optics and thin SiO_2 films used in electronic devices under radiation [x and γ rays and ultraviolet–vacuum-ultraviolet (uv-vuv) photons].¹ Hydrogen is one of the most common impurities incorporated in $\alpha\text{-SiO}_2$. For example, in the case of high-purity silica synthesized by H_2/O_2 flame hydrolysis, hydrogen can be contained abundantly ($[\text{OH}] \approx 10^2\text{--}10^3$ ppm) in the form of hydroxyl. Exposure of $\alpha\text{-SiO}_2$ films to a hydrogen ambience is frequently involved in metal-oxide-semiconductor device processing. It is therefore important to understand the basic mechanisms involved in defect formation in the presence of hydrogen in $\alpha\text{-SiO}_2$.

Hydroxyl is one of the possible forms of hydrogen in $\alpha\text{-SiO}_2$. Several studies have been made to understand the effect of hydroxyls on photoinduced defect formation by means of electron-spin-resonance (ESR),^{2–7} optical-absorption,^{3,6,8–12} and photoluminescence^{8,9,11} measurements. While the incorporation of hydrogen in the form of hydroxyl has generally been thought to be a measure for suppressing the formation of E' centers, enhanced E' creation is reported to be observable in oxygen-deficient silicas treated by hydrogen⁷ and OH-containing oxygen-deficient silicas (20–500 ppm).⁶ Thus the role of hydrogen seems to be so diverse that its identification is one of the most important issues in defect formation in $\alpha\text{-SiO}_2$.

In this paper we will present the results of ESR and optical-absorption measurements in the uv-vuv region on

oxygen-deficient and stoichiometric silicas containing various degrees of OH concentration. Electron-spin-resonance measurements show a significant increase in the concentration of the E' centers induced in an OH-containing oxygen-deficient silica. Optical-absorption measurements in the uv-vuv region reveal the conversion of preexisting oxygen vacancies into E' centers. This paper provides evidence that hydrogen plays a significant role in the formation of E' centers from preexisting oxygen vacancies. Analogy with light-induced defect creation in hydrogenated amorphous silicon ($\alpha\text{-Si:H}$) is also discussed.

II. EXPERIMENTAL PROCEDURES

Two types of oxygen-deficient samples with different hydroxyl contents were studied. Samples OD1 and OD2 are low-OH ($[\text{OH}] < 1$ ppm) oxygen-deficient type silicas, which contain neutral oxygen vacancies.^{13,14} Sample ODH is an oxygen-deficient-type silica containing hydroxyls ($[\text{OH}] \approx 20$ ppm), in which enhanced E' creation was previously observed.⁵ As a reference, a high-OH silica (OH) produced by flame hydrolysis is also studied, which contains hydroxyls of ≈ 1000 ppm. This sample is thought to be relatively stoichiometric from our previous studies using ESR, optical-absorption, and luminescence measurements.^{5,11} The sample shape is a slab of $0.7 \times 2 \times 25$ mm³ for ESR measurements and a plate with a radius $\phi \approx 10$ mm and a thickness of 0.7–40 mm for optical-absorption measurements.

Excimer-laser irradiation was carried out with a Lambda Physik LPX-105i excimer laser using Ar/F₂/He (193 nm, 6.4 eV) or F₂/He mixture (157 nm, 7.9 eV) as a laser gas. Irradiation was performed at room temperature in

air for the 6.4-eV photons and in a N_2 atmosphere for the 7.9-eV photons. The pulse energy was monitored with a Scientech thermopile power meter.

ESR measurements were performed using a JEOL RE-2XG spectrometer operating at X-band frequency ($\nu \approx 9.25$ GHz) with a modulation amplitude of 0.063 mT. The samples in quartz tubes were kept at 77 K by immersing them in liquid N_2 during measurements. The microwave power was set at $1 \mu W$ for the detection of the E' centers.

Optical-absorption measurements in the region of 6–8 eV were carried out with a 1-m Seya-Namioka type monochromator using synchrotron radiation as a light source (0.38-GeV SOR-RING, The Institute for Solid State Physics, The University of Tokyo, Tanashi, and 0.75-GeV UVSOR, Institute for Molecular Science, Okazaki). A conventional uv spectrometer (Shimadzu UV-160) was employed for the absorption measurements at 3–6 eV.

The time elapsed after the exposure to laser photons until the measurement is several minutes to hours for ESR and uv absorption and is within a few days for vuv absorption. During this period, the sample was kept immersed in liquid nitrogen.

III. RESULTS AND DISCUSSION

Figure 1 shows the ESR spectra of the (a) low-OH oxygen-deficient sample OD1, (b) OH-containing oxygen-deficient sample ODH, and (c) high-OH sample OH, after exposure to 6.4-eV photons (35 mJ/cm^2 per pulse, 30 Hz, 30 min). The central features at ≈ 330 mT ($g \approx 2.001$) observed in all samples indicate the presence

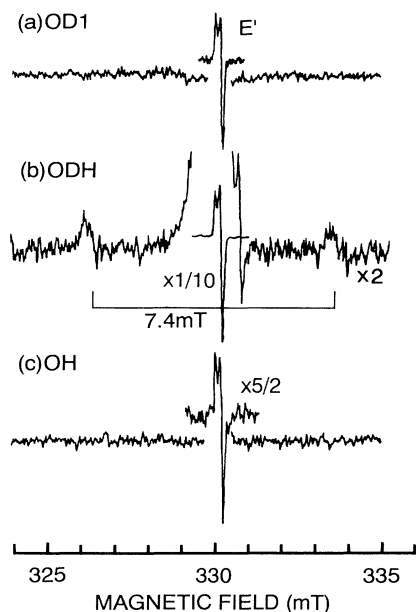


FIG. 1. ESR spectra of (a) oxygen-deficient silica OD1, (b) OH-containing oxygen-deficient silica ODH, and (c) high-OH silica OH after 6.4-eV laser irradiation (35 mJ/cm^2 per pulse, 30 Hz, 30 min).

of so-called E' centers ($\equiv Si\cdot$), comprising an unpaired spin in a sp^3 hybrid orbital of silicon bonded to three separate oxygens (in this paper the dot represents an unpaired spin and the symbols " \equiv " and " $=$ " denote bondings with three and two separate oxygens, respectively). A doublet signal with a magnetic field separation of 7.4 mT can be seen in the spectra of sample ODH [(b)], indicating the presence of an unpaired spin undergoing a hyperfine interaction with a nearby nucleus with a spin of $I = \frac{1}{2}$. The 7.4-mT doublet was identified to be an unpaired spin on a silicon bonded to two separate oxygens and a hydrogen ($=Si-H$), which was proposed by Tsai and Griscom¹⁵ and supported by a theoretical calculation.¹⁶ For sample OD2, a virtually identical spectrum with sample OD1 was obtained.

Figure 2 highlights enhanced photogeneration of the E' centers, comparing the concentrations of the E' centers in samples OD1, ODH, and OH as a function of 6.4-eV laser fluence. A monotonic increase is observed in the low-OH oxygen-deficient sample OD1. A significant growth of the E' center is observed in the OH-containing oxygen-deficient sample ODH ($[OH] \approx 20$ ppm) up to $\approx 4 \times 10^{16} \text{ cm}^{-3}$, followed by a saturation. The E' concentration in the high-OH stoichiometric sample OH ($[OH] \approx 1000$ ppm) shows an immediate saturation at $\approx 8 \times 10^{14} \text{ cm}^{-3}$ and a subsequent decrease with increasing laser fluence. The E' concentration in sample ODH is one or two orders of magnitude higher than those in samples OD1 and OH over the whole range of laser fluence. A similar enhanced E' creation was also observed in sample ODH exposed to 7.9-eV photons. Two important features can be noted for the enhanced E' formation. First, from the results of samples OD1 and ODH, the presence of hydrogen appears to be correlated with enhanced E' creation. Second, in comparison with the result of the stoichiometric sample OH, the oxygen deficiency is also responsible for the enhanced E' creation.

Figure 3 shows the vuv absorption spectra of the unir-

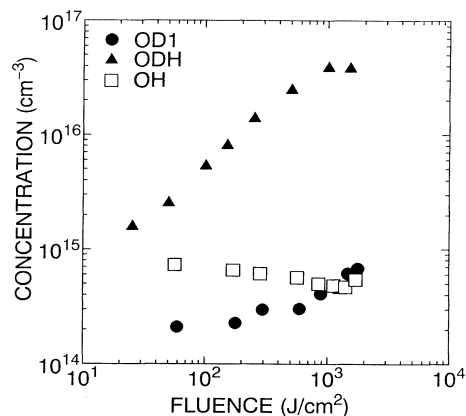


FIG. 2. Concentrations of the E' centers in samples: low-OH oxygen-deficient silica OD1, OH-containing oxygen-deficient silica ODH, and high-OH silica OH, as a function of 6.4-eV laser fluence (35 mJ/cm^2 per pulse, 30 Hz, 1–30 min).

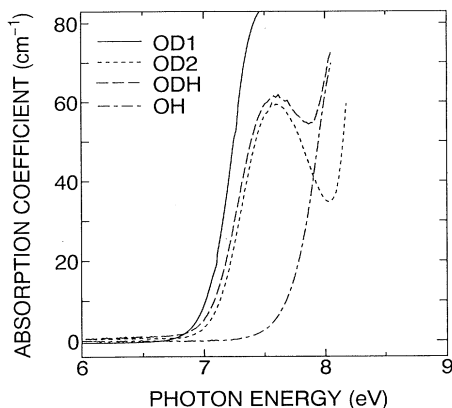


FIG. 3. Vacuum-ultraviolet absorption spectra of unirradiated silicas: low-OH oxygen-deficient samples OD1 and OD2, OH-containing oxygen-deficient sample ODH, and high-OH sample OH.

radiated samples OD1, OD2, ODH, and OH. The oxygen-deficient samples OD1, OD2, and ODH exhibit a 7.6-eV absorption band, which is attributed to preexisting oxygen vacancies ($\equiv\text{Si}-\text{Si}\equiv$).^{13,14} In addition, an absorption tail above 7.5 eV can be seen in the OH-containing samples ODH and OH, which is thought to be due to hydroxyls.⁶

Shown in Figs. 4(a) and 4(b) are the vuv optical-absorption spectra of two different oxygen-deficient silicas (a) OD2 ($[\text{OH}] < 1$ ppm) and (b) OH-containing ODH ($[\text{OH}] \approx 20$ ppm) before and after exposure to 6.4-eV photons (35 mJ/cm^2 per pulse, 30 Hz, 30 min) and 7.9-eV photons (3 mJ/cm^2 per pulse, 50 Hz, 25 min). Since the 7.6-eV band is too intense in sample OD1, sample OD2 was alternatively chosen to observe spectral changes at 7.6 eV due to oxygen vacancies. In the case of the low-OH sample OD2, no significant change is observed when exposed to 6.4-eV photons. When exposed to 7.9-eV photons, the 7.6-eV band appears to grow and the peak shifts to a lower energy in sample OD2. An interpretation of the vuv spectral behavior is beyond the scope of the present paper and will be given elsewhere.¹⁷ On the other hand, a pronounced decrease of the 7.6-eV absorption band is observed for sample ODH exposed to either 6.4- or 7.9-eV photons. In addition, a significant growth is observed around 6 eV, in accordance with the decrease of the 7.6-eV band. The induced absorption around 6 eV is thought to be the high-energy tail of the absorption band around 5.8 eV associated with E' centers.¹⁸ Assuming an absorption cross section at 7.6 eV of $8 \times 10^{-17} \text{ cm}^2$ reported for the oxygen vacancy,⁶ we estimate the decreased concentrations of the oxygen vacancy in sample ODH by 6.4- and 7.9-eV photons to be 5×10^{16} and $1.6 \times 10^{17} \text{ cm}^{-3}$, respectively. These are in good agreement with the E' concentrations of 3.8×10^{16} and $1.2 \times 10^{17} \text{ cm}^{-3}$ determined from ESR data for 6.4- and 7.9-eV photons, respectively. This demonstrates a one-to-one correlation between the annihilation of oxygen vacancies and the generation of the E' centers in sample

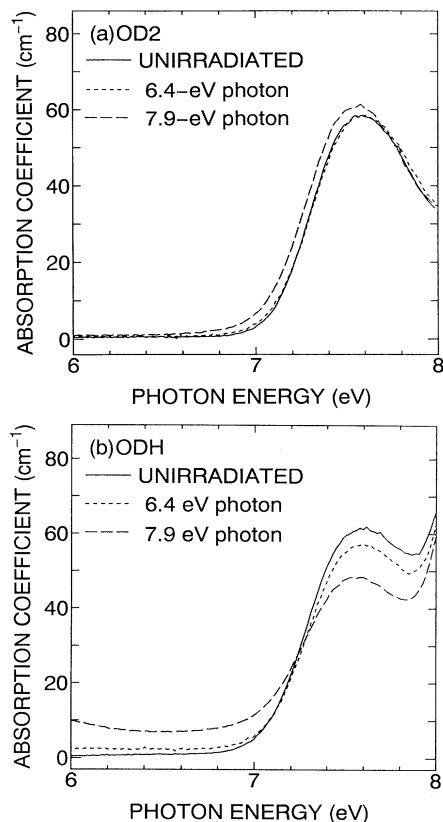


FIG. 4. Vacuum-ultraviolet absorption spectra of (a) low-OH oxygen-deficient silica OD2 and (b) OH-containing oxygen-deficient silica ODH, before and after exposure to 6.4-eV photons (35 mJ/cm^2 per pulse, 30 Hz, 30 min) and 7.9-eV photons (3 mJ/cm^2 per pulse, 50 Hz, 25 min).

ODH. Thus it should be concluded that the enhanced E' creation is due to the conversion of oxygen vacancies into E' centers. The results shown above are summarized in Table I.

A prevailing model for the generation mechanism of the E' center in a low-OH oxygen-deficient silica is a hole trapping at the site of the oxygen vacancy, as proposed by Feigl, Fowler, and Yip:¹⁹



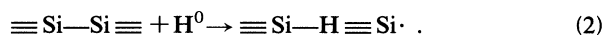
Thus we attribute the E' centers in the low-OH oxygen-deficient samples such as OD1 and OD2 to be generated by the reaction of Eq. (1). Since only a small fraction ($\leq 10^{-3}-10^{-2}$) of the preexisting oxygen vacancies are transformed into E' centers, the decrease in the 7.6-eV absorption band is thought to be negligibly small.

In the case of the OH-containing oxygen-deficient sample ODH, the presence of a substantial amount of hydrogen should be taken into consideration as well as oxygen vacancies. It was previously inferred by Griscom²⁰ that an E' variant labeled as the E'_β center can be formed by diffusion and subsequent trapping of atomic hydrogen at the site of oxygen vacancy, following irradiation by x rays at 77 K:

TABLE I. Summary of the experimental results of ESR and vacuum-ultraviolet absorption measurements (D and ND denote "detected" and "not detected," respectively).

Sample	Unirradiated [Si—Si]	Concentration (cm^{-3})				6.4 eV 7.4 mT
		6.4 eV ^a		7.9 eV ^a		
		[E']	$-\Delta[\text{Si—Si}]$	[E']	$-\Delta[\text{Si—Si}]$	
OD1	$> 10^{18}$	6.8×10^{14}		2.3×10^{16}		ND
OD2	8×10^{17}					ND
ODH	7×10^{17}	3.8×10^{16}	5×10^{16}	1.2×10^{17}	1.6×10^{17}	D
OH		5.7×10^{14}		4.9×10^{15}		ND

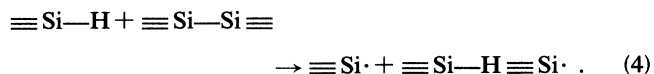
^aThe value at the total laser fluence of $\approx 1.9 \times 10^3 \text{ J/cm}^2$ for 6.4-eV photons and $\approx 2.3 \times 10^2 \text{ J/cm}^2$ for 7.9-eV photons.



Here the puckered configuration of the unpaired spin against the Si—H bond is based on the absence of hyperfine structure in the ESR spectrum of the E'_β center, implying a separation between the unpaired spin and hydrogen by more than 5 \AA .²⁰ Indeed, we observed the ESR signal of atomic hydrogen at 77 K in sample ODH (data not shown), following irradiation with 6.4-eV photons at 77 K, though we could not observe it in the sample irradiated at room temperature. There are two possible candidates for the source of atomic hydrogen, Si—OH and Si—H bonds. The Si—OH bond can be ruled out for the source of H^0 based on the absence of nonbridging oxygen hole centers ($\equiv \text{Si—O}\cdot$), the counterpart of H^0 formed by the radiolysis of O—H bond:



Particularly in sample ODH prepared under an oxygen-deficient condition, the Si—H bond is thought to be another form of oxygen deficiency in addition to the Si—Si bond. Our previous study demonstrates that dissociation of the Si—H bond is much more likely to occur than that of the O—H bond under 6.4-eV laser irradiation.⁵ In the case of the 7.9-eV photons where dissociation of the O—H bond is thought to be possible,⁵ the NBOHC concentration [$5.4 \times 10^{15} \text{ cm}^{-3}$ (not shown in Table I)] in the 7.9-eV-irradiated sample ODH is two orders of magnitude smaller than the E' concentration ($1.2 \times 10^{17} \text{ cm}^{-3}$). Thus it is considered that atomic hydrogen released from a Si—H bond rather than from a Si—OH bond plays a dominant role in the conversion of the oxygen vacancy into an E' center, either in the case of 6.4- or 7.9-eV photons. In view of the reaction of Eq. (2), the following scheme involving diffusion and trapping of atomic hydrogen at the site of Si—Si is proposed:



Note that the sites of the two defects, $\equiv \text{Si—H}$ and $\equiv \text{Si—Si} \equiv$, are not necessarily nearby since the diffusion of H^0 is considered to be involved. The reaction of Eq. (4) indicates that annihilation of one $\equiv \text{Si—Si} \equiv$ bond leads to the formation of a pair of E' centers. This is consistent with the present results in terms of the

ESR-vuv correlation, within an error in the absolute ESR spin concentrations (see Table I). The model of Eq. (4) also explains the observation by Imai and co-workers that the growth of a Raman-scattering peak at 2250 cm^{-1} due to a $\equiv \text{Si—H}$ bond was observed in low-OH oxygen-deficient silica after hydrogen treatment at 800°C , in accordance with the decrease of the 7.6-eV band due to the oxygen vacancy.^{6,21} Although they attributed the efficient E' creation in the H_2 -treated oxygen-deficient silica solely to the dissociation of the Si—H bond,



our results clearly demonstrate that the conversion of the oxygen vacancy is the main reaction for enhanced E' creation. In fact, as Imai *et al.*⁶ themselves pointed out, the 7.6-eV band cannot be bleached out by a hydrogen treatment at temperatures between 600 and 1000°C ; i.e., oxygen vacancies still remain in their sample. Thus their results can be well accounted for in the context of the reaction model of Eq. (4), in which the coexistence of Si—Si and Si—H bonds is required.

If the E' centers induced in sample ODH are in the form of E'_β centers ($\equiv \text{Si—H} \equiv \text{Si}\cdot$), there should be some differences in the ESR and uv spectral signatures from those induced in the low-OH oxygen-deficient samples OD1 and OD2. Although Griscom distinguishes the E'_β center by the small deviation in the value of g_1 ($\Delta g \approx 0.00008$) from the E'_γ center ($\equiv \text{Si}\cdot + \text{Si} \equiv$),²⁰ the present ESR measurements do not allow one to detect such a subtle difference in the g value. Figure 5 shows the uv spectra of samples OD1, OD2, and ODH exposed to 6.4-eV photons (35 mJ/cm^2 per pulse, 30 Hz, 30 min). The well-known 5.8-eV (5.75-eV) band due to E' centers¹⁸ is seen in the low-OH oxygen-deficient samples OD1 and OD2. On the other hand, the peak slightly shifts by 0.1 eV (to 5.65 eV) in the OH-containing oxygen-deficient sample ODH. A radiation-induced band at 5.4 eV in α -quartz has been correlated with the E'_2 center.¹⁸ Since the E'_β center is analogous to the E'_2 center in α -quartz as discussed by Griscom,¹ the peak shift can be interpreted as the creation of E'_β centers exhibiting a peak around 5.4 eV which overlap with the 5.8-eV band due to the E'_γ center. This result supports the above-mentioned mechanism of Eqs. (2) and (4) for enhanced E' creation in sample ODH.

Recently, similar phenomena have been reported for

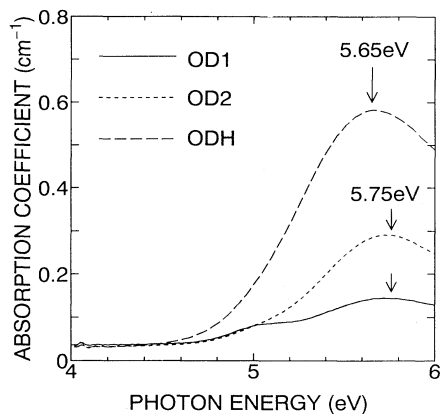
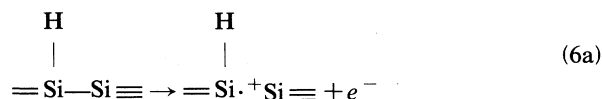


FIG. 5. Ultraviolet absorption spectra of low-OH oxygen-deficient silicas OD1 and OD2 and OH-containing oxygen-deficient silica ODH, after exposed to 6.4-eV photons (35 mJ/cm² per pulse, 30 Hz, 30 min).

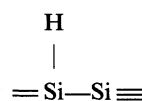
thermal oxides and buried oxides formed by the separation of silicon by implantation of oxygen (SIMOX) process.^{22,23} For both oxides, the formation of the E' center induced by γ rays is significantly enhanced by the pre-hydrogen-treatment above 600°C.²³ They argued that the Si—H bonds are responsible for enhanced E' creation.^{22,23} If we assume the presence of oxygen vacancies as well as Si—H bonds in thermal oxides and buried oxides, the increased E' creation in the H₂-annealed thermal and buried oxides can be also understood in terms of the oxygen-vacancy- E' conversion model. Especially in SIMOX oxides, relatively high concentrations of oxygen vacancies might be expected by the very nature of their manufacturing process, as discussed by Devine, Leray, and Margail.²²

We should also mention the stability of the E' centers formed by the reactions of Eqs. (1), (2), and (4). In the case of Eq. (1), the neutral Si—Si bond can be reformed by trapping an electron at the site of the E' center or positively charged oxygen vacancy ($\equiv\text{Si}^+\text{Si}\equiv$). The reverse reaction of Eq. (1) was in fact demonstrated in electron injection experiments on thermal oxides by Warren *et al.*²⁴ This means that creation and annihilation of E' centers can simultaneously occur during irradiation, since free electrons can be generated by two-photon absorption during exposure to 6.4- or 7.9-eV photons.⁵ In contrast, the back reaction of Eq. (2) or (4) will be inhibited by the diffusion of atomic hydrogen away from the initial bonding site and subsequent trapping at another Si—Si bond to form a distant pair of an E' center and a new Si—H bond. Enhanced E' creation is thought to be a manifestation of the stability of the E' centers produced by the mechanism of Eq. (2) or (4).

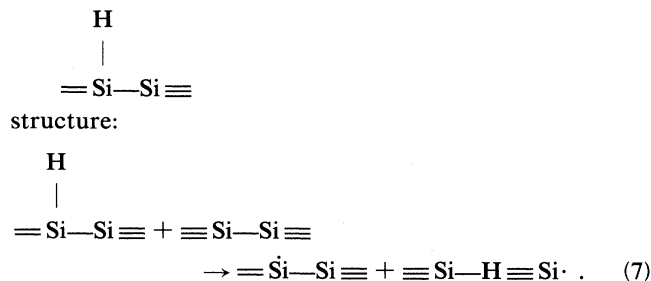
Finally, we will discuss the appearance of the 7.4-mT doublet in the ESR spectrum of sample ODH (see Table I). In view of the reaction of Eq. (1) or (5), the following reactions are considered for the appearance of the 7.4-mT doublet or $\equiv\dot{\text{S}}\text{i}-\text{H}$ bond:



or



structure is assumed for the precursor of the $\equiv\dot{\text{S}}\text{i}-\text{H}$ bond. The mechanism of Eq. (6a) involves a hole trapping at the Si—Si bond, in analogy with the reaction of Eq. (1). The latter scheme in Eq. (6b) involves movement of hydrogen, which is inferred from the so-called weak-bond model proposed in light-induced defect formation in $\alpha\text{-Si:H}$.²⁵ Allowing further movement of hydrogen in the network and trapping at a distant Si—Si bond, the precursor of the 7.4-mT doublet in the left-hand side of Eq. (6) can be also seen as a source of hydrogen. Thus the following scheme can be invoked by replacing the $\equiv\text{Si}-\text{H}$ in Eq. (4) with



In view of the reactions of Eqs. (6b) and (7), the $\equiv\dot{\text{S}}\text{i}-\text{H}$ can be regarded as an intermediate product in a series of reactions leading to the formation of a stable pair of E' centers. It should be noted that the reaction of Eq. (7) is compatible with the reaction of Eq. (4) and can be seen as a variation of the oxygen-vacancy- E' conversion model. Further investigation is needed to clarify the correlation of the 7.4-mT doublet with enhanced E' creation.

IV. CONCLUSION

In conclusion, the mechanism of enhanced E' creation in oxygen-deficient silica in the presence of hydrogen is investigated through ESR and uv-vuv absorption measurements. Enhanced E' creation is observed only in an OH-containing oxygen-deficient type silica. The results of the uv-vuv absorption measurements provide direct evidence that enhanced E' creation is due to the conversion of a preexisting oxygen vacancy into an E' center. In analogy with the E'_β model, we proposed a reaction scheme involving trapping of atomic hydrogen at the site of the oxygen vacancy. The source of hydrogen is considered to be Si—H bonds rather than Si—OH bonds. The peak shift in the absorption band associated with E' centers around 5.8 eV suggests the creation of an E'_β -like center in OH-containing oxygen-deficient silica. The appearance of the 7.4-mT doublet or $\equiv\dot{\text{S}}\text{i}-\text{H}$ structure is

explained as an intermediate produced in the course of reactions involved in the conversion of an oxygen vacancy into an E' center. The present oxygen-vacancy- E' conversion model can be further extended to an explanation of the increased concentration of radiation-induced E' centers observed in technologically important thermal oxides and buried oxides annealed in H_2 above 600 °C.

ACKNOWLEDGMENTS

We acknowledge the advice and technical supports from Professor M. Kamada, Dr. S. Tanaka, and O.

Matsudo at UVSOR of the Institute for Molecular Science, and Dr. M. Fujisawa at SOR-RING of The Institute for Solid State Physics, the University of Tokyo, in the vuv absorption measurements. Some of the samples were provided by courtesy of Shin-Etsu Quartz Products Co., Ltd., and Shin-Etsu Chemical Co., Ltd. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 03452156) from the Ministry of Education, Science and Culture of Japan, and the foundation "Hattori-Hokokai." One of the authors (H.N.) acknowledges the encouragement by Professor K. Nagasawa of Shonan Institute of Technology.

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