Creation of Quasistable Lattice Defects by Electronic Excitation in SiO$_2$

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The transient volume change of α-quartz and fused silica induced by irradiation with
an electron pulse has been measured above 80 K. It is shown that transient changes of
volume and optical absorption due to the E_1' centers (oxygen vacancies) decay in parallel
and that the volume change per E_1' center is of the order of a unit molecular volume.
The results show unambiguously that recombination-induced defect formation occurs in
SiO$_2$ but the defects created are not stable even at low temperatures.

It is known that intrinsic photolytic reactions, the creation of intrinsic lattice defects by electronic excitation, occurs in some ionic solids such as alkali and silver halides.[1] In alkali halides, of which the photolytic reaction has been understood most satisfactorily, the primary process is known to be the ejection of a halogen atom to a neighboring interstitial position from a highly excited nonbonding state of the self-trapped exciton.[1,2] Whether such intrinsic photolytic processes are induced in other solids, such as oxides and semiconductors, is a problem of general interest. In these materials it is generally believed that the knockon process creates point defects[3,4] but not the electronic excitation.

In SiO$_2$, Griscom[5] and Hobbs et al.[6] have suggested that a close pair of an oxygen vacancy and an interstitial oxygen is generated by electronic excitation. Griscom has found that a transient optical-absorption band in the ultraviolet region is induced by bombardment of α-quartz and fused silica with an electron pulse, and he ascribed the optical-absorption change to creation of a singly ionized oxygen vacancy (the E_1' center), of which the yield is much higher than that expected from the knockon process. It is not yet clear, however, whether the transient optical-absorption band arises from momentary trapping of holes at isolated neutral oxygen vacancies existing before irradiation or from newly created ionized vacancies by a photolytic reaction. Hobbs and co-workers have observed, by an electron microscope, formation of heterogeneously nucleated disordered strain centers and a subsequent homogeneous crystal-amorphous transformation by irradiation with low-energy electrons that does not cause any knockon processes. They suggested that the strain centers are vacancy-interstitial pairs originating from an intrinsic photolytic reaction. The phenomena they observed are nonlinear effects that are observed only under dense electronic excitation and apparently are not a simple photolytic process. Thus direct experimental proof of the intrinsic photolysis for SiO$_2$ is needed. Since the generation of vacancies and interstitials by photolytic reactions is proportional to the absorbed energy of ionizing radiation and gives always a considerable volume change,[7] the volume change per absorbed energy is the most direct measure whether such intrinsic photolysis is effective.

The present Letter reports the result of measurements of the volume change of α-quartz and fused silica induced by an electron pulse. It is shown that a transient volume change of an order of a unit lattice volume per defect is induced by an electron pulse, with an efficiency much higher than that expected from the knockon process up to a defect concentration of over 10^{18} cm^{-3}. Thus the present results are the first observation of intrinsic quasistable defect formation by electronic excitation of an oxide.

The specimens are Z-cut Toyocom α-quartz[8] synthetically grown and Suprasil fused silica having a size $10 \times 10 \times 1$ mm^3. They were placed in a conventional cryostat, in which the volume change and the optical-absorption change induced by a 10-ns pulse of 2-MeV electrons from a Febetron 707 were measured. A single pulse is capable of generating an excitation density of 10^{19} cm^{-3} but less than 10^{14} cm^{-3} knockons. The volume change was obtained with the photoelastic method,[9,10] in which a specimen was placed between two crossed polarizers. A part of the specimen was bombarded with an electron pulse so that strain is induced at the boundary. The strain-induced optical rotation, which is proportional to the volume change, was determined by measuring the light transmitted through the crossed polarizers. To measure the volume change of the α-quartz, a dummy specimen with the optical axis perpendicular to that of the bom-
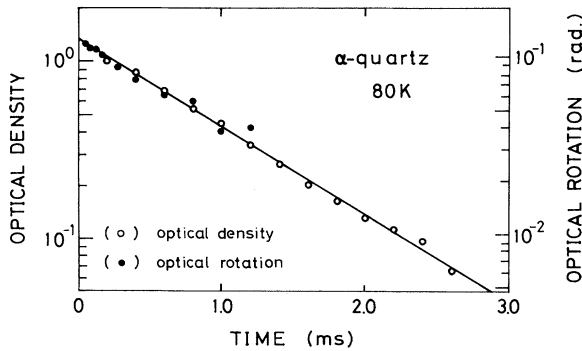

FIG. 1. Decays of the optical rotation and the optical-absorption change at 5.4 eV of α-quartz after bombardment with an electron pulse at 80 K.
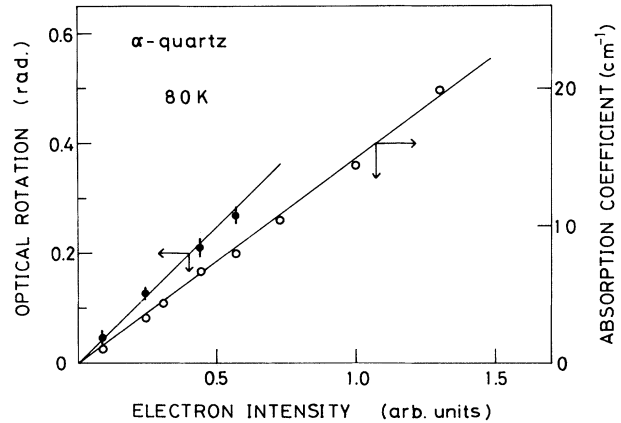

FIG. 2. Dependence of the optical rotation and the optical-absorption change at 5.4 eV of α-quartz on the intensity of the electron pulse.

barded specimen was inserted to eliminate the effect of the optical rotation of quartz. The light source for the photoelastic measurement was a He-Ne laser and that for the optical-absorption measurement was a deuterium lamp. The electron beam is incident upon the 10×10-mm^2 surface of the specimen, while the light beam from the He-Ne laser is incident upon a 10×1-mm^2 surface. This arrangement has an advantage of detecting a small volume change even though the accuracy in the absolute value of the volume change may be lost to some extent.[9] The detection system of the optical signal consists of a monochromator, photomultipliers, and oscilloscopes. The details are reported elsewhere.[11]

The decay of the optical rotation induced by an electron pulse at 78 K was compared with that of the optical absorption at 5.4 eV for α-quartz in Fig. 1. Time-resolved spectroscopic measurements show that the transient absorption band for α-quartz has a peak at 5.4 eV, agreeing with the result by Griscom.[5] The magnitudes of the transient optical rotation and optical absorption at 5.4 eV and 78 K are plotted as a function of the fluence of the electron pulse in Fig. 2. The linear relation between the absorbed energy and the optical rotation and absorption as well as the agreement of their decay times indicate that the same defect centers induce the optical-absorption band at 5.4 eV and the optical-rotation change. In order to substantiate the conclusion that formation of the 5.4-eV absorption band is associated with the change in the optical rotation, we measured their decay times as a function of temperature of irradiation. The result is shown in Fig. 3. The figure also includes the temperature dependence of the decay time of the 2.8-eV luminescence band, which has been first observed by

Sigel and Griscom.[12] The same quenching characteristics for three decay times are evident.

The decays of the changes of the optical absorption and rotation for fused silica were found to be composed of transient components and stable components. It was found that their transient components decay in parallel with each other and with the luminescence at 2.8 eV. The transient optical-absorption band has a peak at 5.5 eV in
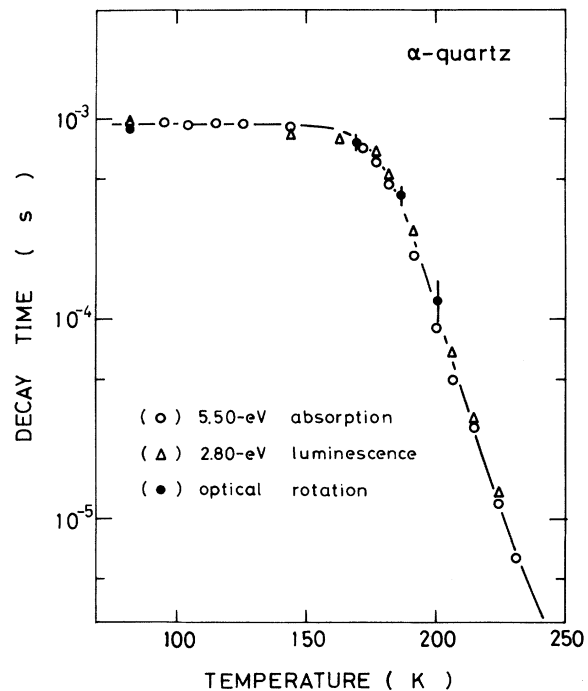

FIG. 3. Decay times of the optical rotation, optical-absorption change at 5.4 eV, and luminescence at 2.8 eV as functions of temperature.

fused silica.

The experimental results shown above indicate definitely that the volume change is associated with formation of centers that induces the absorption band near 5.4 eV and the 2.8-eV luminescence band both in α-quartz and fused silica. According to the theory developed by Fowler and co-workers,[13,14] silicon atoms neighboring an oxygen vacancy are asymmetrically relaxed: One of the silicons, Si_I, is nearly at the center of the tetrahedron formed by three oxygens and the vacancy, and the other, Si_{II}, is relaxed onto the plane formed by three oxygens. According to Griscom and Fowler and Shirmer,[15] the 5.8-eV transition of the E_1 center, assigned to the positively charged oxygen vacancy, is a charge-transfer transition from the sp^3 orbital on Si_I to the unfilled $3p$ orbital on Si_{II}. Since the energy of a charge-transfer transition is influenced appreciably by environment, it is most likely that the 5.4-eV band arises from the $Si_I \rightarrow Si_{II}$ charge transfer but not of the isolated vacancy, as suggested by Griscom.[5]

For quantitative discussions of the volume change, we tentatively assumed that the 5.4-eV band has an oscillator strength the same as that of the E_1' center peaked at 5.8 eV.[16] The concentration of the vacancies created by an electron pulse was evaluated by putting the oscillator strength of 0.14 and the half-width of 0.95 eV into Smakula's equation. The magnitude of the volume change $\Delta V/V$ was evaluated with use of the formula developed by Wiegand and Smoluchowski[10] for the isotropic case and that modified by the present authors for the anisotropic case. The energy absorbed by specimens per electron pulse was evaluated with the tabulated values[17] of the electron range, under the assumption that the energy deposition in the specimens is uniform. The obtained values of $\Delta V/V$ and of the number of vacancies per absorbed energy and $\Delta V/V$ per vacancy for α-quartz as well as for fused silica are shown in Table I. The table includes results for KBr, which were obtained to confirm the accuracy of the absolute value of $\Delta V/V$.

From Table I, we note that the defect process induced by electronic excitation in α-quartz is as efficient as that in KBr at 4 K, where the efficiency of defect formation is larger by a factor of 10 than at 78 K.[18] The value of $\Delta V/V$ is an overestimate because of the edge effect.[10] In fact $\Delta V/V$ per F-H pair is known to be 0.6–0.8[19,20] instead of 3.2. Even though there is a little ambiguity in the absolute values of $\Delta V/V$, it is clear

TABLE I. Volume change and number of vacancies per absorbed energy of ionizing radiation for α-quartz, fused silica, and KBr at 80 K.

Substance	$\Delta V/V$ per absorbed energy (molecular volume per eV)	Vacancy per absorbed energy (eV^{-1})	$\Delta V/V$ per vacancy (molecular volume)
α-quartz	1.2×10^{-1}	1.3×10^{-2}	4.7
a-SiO$_2$	3.7×10^{-3}	9.7×10^{-4}	3.8
KBr	6.0×10^{-3}	1.9×10^{-3}	3.2

that creation of a vacancy in α-quartz and fused silica is accompanied by a volume change of at least a molecular volume. Furthermore the fact that the number of the vacancies created by the most intense electron pulse is 1.3×10^{18} cm^{-3} (exceeding the impurity concentration by a factor of ~10) indicates that the creation of vacancies in α-quartz is an intrinsic process. An intrinsic radiation-induced volume change by such a magnitude is an expansion and occurs only by formation of Frenkel pairs. $\Delta V/V$ induced by generation of an E_1' center by neutron irradiation at room temperature is evaluated to be 8.9, from a volume-expansion study by Primak[21] and from an optical study by Ditchburn et al.[22] This value may be also an overestimate since other types of defects (complexes) may be included in the specimen.

The fact that Frenkel pairs generated by electronic excitation have a short lifetime indicates that the interstitial-vacancy distance is small. The electronic structure of the close Frenkel pair is not clear at this stage. The center complementary to the E_1' center is the peroxy linkage.[23] Thus it is most likely that a close pair of an E_1' center and a peroxy linkage is created by electronic excitation, as suggested by Griscom.[5] The high yield in the α-quartz suggests that the creation of the pairs is an excitonic process similar to that in alkali halides, in which an antibonding state of the self-trapped exciton is responsible for defect creation.[1,24] Thus one possible explanation for the relatively lower yield of the defect process in fused silica would be that the antibonding state is less definable in an amorphous material.

The present investigation is the first unambiguous demonstration of a recombination-induced intrinsic defect process in oxides. It bears the

following important implication. Firstly the re-combination-induced intrinsic defect formation is now shown not to be characteristic only of ion-ic crystals. Secondly the transient unstable Frenkel defects may be transformed further into stable defects when the density of excitation is so high that they may be ionized again. Such a proc-ess may explain the formation of strain centers under intense electron irradiation in SiO_2, ob-served by Hobbs.[6]

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