

Evidence for a wide continuum of polymorphs in α -SiO₂

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The irradiation of vitreous amorphous silica with subband-gap laser radiation at 248 nm induces reversible-irreversible compaction. The former is consistent with the creation of a wide continuum of densified amorphous silica (α -SiO₂) polymorphs, whilst the second stage corresponds to the ablation through laser radiation of the damaged α -SiO₂. These observations are discussed in terms of conformational structure modifications (i.e., changes in the distribution of planar rings) and stable superficial defect creation.

In wide-band-gap insulators, radiation of a primarily ionizing character is found to produce diverse effects such as surface desorption of constituent materials^{1,2} and bulk defect creation leading to volumetric effects [e.g., in amorphous³⁻⁶ SiO₂ (α -SiO₂)]. Of particular interest, because of the increasing technological importance of such materials, is the evolution of bulk-surface damage or modification of insulators when the ionizing radiation is significantly less energetic than either the band gap or the energy necessary to create a core hole leading to Auger-electron ejection and subsequent structure modification.¹ Although various studies have been devoted to breakdown induced in an insulator^{7,8} (mainly characterized by the appearance of macroscopic structural defects, i.e., cracks and fissures) by subband-gap laser radiation, studies related to atomic arrangement modifications induced by such radiation have been few. Such modifications produced in α -SiO₂ before the onset of irreversible damage are presently the subject of intensive research. In the present work we have studied for the first time changes induced in thin α -SiO₂ films induced by 248-nm laser radiation at energy densities (~ 0.3 -J/cm² pulse) well below the observed macroscopic damage threshold.⁸ The results presented here are discussed in terms of defect models which may lead, as a function of the accumulated uv dose, to the creation of a continuous range of α -SiO₂ "polymorphs"⁹ followed by photoetching when high, superficial defect density is generated. It is demonstrated that amorphous SiO₂ prepared by thermal oxidation of Si can be continuously transformed into compressed forms of polymorphic α -SiO₂. We show, furthermore, that as in the case of allotropic forms of crystalline silica (c -SiO₂), the refractive index of α -SiO₂ and its density obey a linear relationship.

The SiO₂ samples used in the study were grown on n -type $\langle 100 \rangle$ -orientated Si wafers using standard technological conditions; both annealed wet and dry oxides were studied. Irradiations were carried out in a vacuum $\sim 10^{-6}$ torr at room temperature using an excimer laser operating at $\lambda = 248$ nm. A pulse energy density of 300 mJ/cm² arrived at the sample surface. The pulse duration was ~ 20 ns and the repetition frequency maintained at < 3 Hz to avoid sample heating (through the underlying Si substrate). Oxide thickness was ascertained ellipsometrically at fixed wavelength ($\lambda = 632.8$ nm), as was refractive index. Validity of thickness results was checked initially relative to spectroscopic ellipsometry and mechanical Talystem measurement. Further characterization was made by forming

metal-oxide-semiconductor structures using a mercury probe as the metal-SiO₂ contact and using capacitance-voltage measurement at 1 MHz to obtain the density of fixed oxide charge in the irradiated oxide.

In Fig. 1 we show the variation of the oxide thickness (normalized to unity for the unirradiated case) as a function of accumulated uv dose. The results presented were for a nominal 1000-Å oxide, but thicknesses down to 250 and up to 4200 Å were also studied. One observes a linear compaction of the silica at an accumulated dose ~ 2000 J/cm², and, after annealing for 60 min at 950°C in vacuum $\sim 10^{-6}$ torr, this linear compaction (which attains $\sim 16\%$; see the inset of Fig. 2) is found to be reversible (the original thickness and refractive index were retrieved). This result was general, within the limits of experimental error, for all oxides studied. Beyond the reversible compaction regime, irreversible compaction and etching occurred until, for the 1000-Å oxide, the film was totally etched for an accumulated dose ~ 17000 J/cm². Figure 2 shows the results of fixed oxide charge measurements in wet and dry oxides subjected to laser radiation. As expected,⁴ the important result from Fig. 2 appears to be the ability of 248-nm radiation to create significant numbers of charged defects in the oxide. We note that 5×10^{11} charges/cm² correspond to a bulk density in a 1000-Å film (if uniformly distributed) of

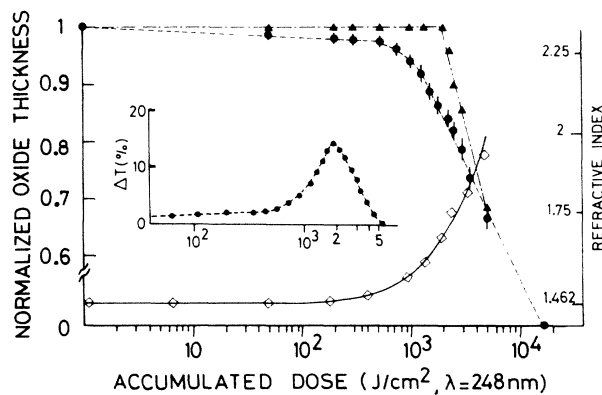


FIG. 1. ●, observed compaction of a 1000-Å-thick oxide as a function of the uv accumulated dose; ▲, the same sample after thermal annealing at 950°C in vacuum ($\approx 10^{-6}$ T) for 60 min. The inset shows the difference between these two results. ◇, evolution of the refractive index during the laser irradiation.

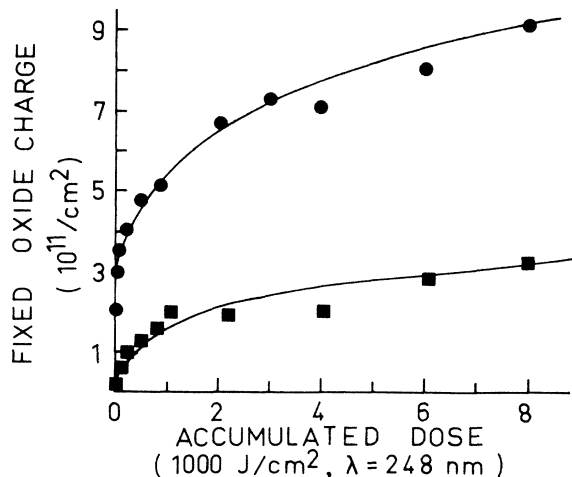


FIG. 2. Measured fixed oxide charge density as a function of accumulated uv dose for the following: ●, 1000-A dry and ■, 2000-A wet oxides.

$10^{17}/\text{cm}^3$. The number is traditionally smaller for wet oxides due to the reduced radiation sensitivity associated with the presence of OH groups. Finally, in Fig. 3 we plot the evolution of the measured refractive index of the irradiated silica during the reversible compaction phase (see Fig. 2) as a function of observed densification. Note that the linear compaction ($\Delta t/t$) is translated to a volume compaction assuming $\Delta V/V \approx 3(\Delta t/t)/(1+2\sigma)$, where σ is Poisson's ratio (~ 0.165 for fused silica).

The presence of reversible compaction coincident with defect creation is consistent with results obtained in fused sili-

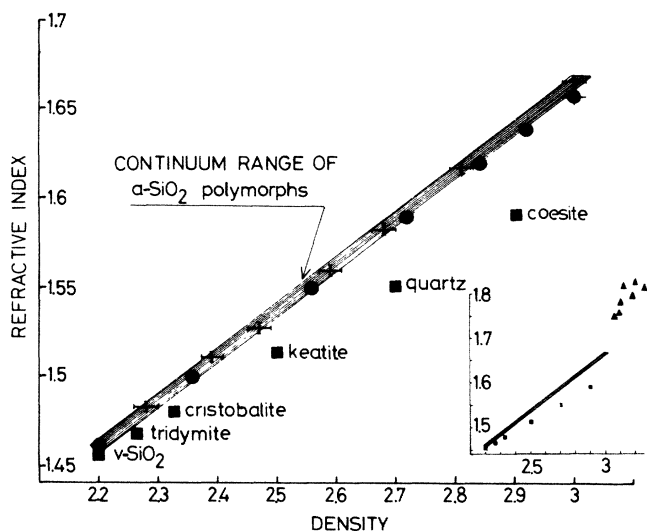


FIG. 3. +, relationship between the measured density and refractive index for the observed α -SiO₂ polymorphs; ● shows the same result deduced from the Lorentz-Lorenz law assuming the measured volume changes (see text); ■ shows the measured density and refractive index for crystalline silica polymorphs. The inset shows randomly distributed points, ▲, relative to the observed irreversible compaction regime, which no longer follow the apparently linear relationship.

ca using charged particle implantation.¹⁰ Here a maximum volume compaction $\sim 5\%$ is obtained for doses $\sim 10^{23}$ keV/cm³ into ionizing processes. The results presented in Fig. 1 indicate a reversible volume compaction which is $\Delta V/V \approx 36\%$, much larger than that observed to date. We also show in Fig. 1 the evolution of the refractive index which increases rapidly from its equilibrium value ≈ 1.462 to much larger values > 1.75 . From the Lorentz-Lorenz relationship for the refractivity¹¹ $R = (n^2 - 1)/\rho(n^2 + 2)$ (where ρ is the specific gravity and n the refractive index) we obtain by differentiation,¹²

$$\Delta n = -\frac{(n^2 + 2)(n^2 - 1)}{6n} \left(1 - \frac{\Delta R}{R \Delta V/V} \right) \frac{\Delta V}{V}, \quad (1)$$

so that, providing $(V/R)\Delta R/\Delta V < 1$, compaction produces (as observed) an increase in refractive index. The first term in the parentheses has been demonstrated¹³ to be simply related to volume changes in the structure, whilst the second has been interpreted¹¹⁻¹³ as being related, for the case of SiO₂, to the volume of the oxygen ion itself. Using the measured maximum volume compaction during the reversible phase, calculations suggest $\Delta n = 0.190$ in good agreement with the measured value of $\Delta n = 0.207$. Bearing in mind the experimental errors, this strongly suggests that effects due to modification of the ionic volume are negligible during α -SiO₂ compaction. This result is in direct contradiction with that found previously,¹² which suggested that in amorphous SiO₂, $\frac{1}{3}$ of the observed volume change arose from ionic volume effects. However, the result agrees well with observation¹⁴ of n variation in c -SiO₂ for monocrystalline polymorphs. We note¹⁴ that the mean Si-O bond length in coesite ($\rho = 2.9$) and tridymite ($\rho = 2.28$) is only a few parts per thousand, so that little variation in ionic volume is anticipated over this density range. Consequently, index variations must be attributed primarily to conformational structure variations induced by the laser radiation.

The observed maximum compaction ($\sim 36\%$) of our α -SiO₂ sample may be compared with a value of 30% obtained¹⁵ in a sample subjected to a hydrostatic pressure of 17 GPa. For this stable densified silica, it was found^{15,16} that although the glass remained ostensibly amorphous, many of its physical characteristics (birefringence, infrared spectrum, Brillouin frequency shift) resembled those observed in coesite (high density c -SiO₂). Furthermore, it has been suggested¹⁶ that in these compressed α -SiO₂ samples, randomly distributed, small amounts of coesite exist. Our present results are in good agreement with these different observations, since both the measured refractive index (1.67) and corresponding density (2.99) of the most compacted form of α -SiO₂ are close to those found for coesite^{17,18} ($\rho = 2.9$; $n = 1.6$).

In order to understand the mechanisms of conformational structure modification under laser irradiation, we note first that the number of defects detected during compaction (Fig. 2), which is $\approx 10^{17}/\text{cm}^3$, is too small for one to argue that the volume changes observed are due to defect creation alone. We then note that^{17,19} covalent solids contain, in general, rings of bonds and that from many experiments^{14,20} and calculations²¹⁻²⁴ it is suggested that α -SiO₂ is composed of a wide distribution of irregular rings of order n ($2 \leq n \leq 6$, where n is the number of Si atoms in the ring). In Fig. 3 we have plotted the refractive index versus density

for a range of c -SiO₂ polymorphs. We recall that tridymite is composed primarily of six membered rings whilst coesite^{14,17,20} is predominately four membered. The densification ($\approx 32\%$) in this case is due to a reduction in the mean ring size¹⁷ (i.e., reduction of the void space encircled by a ring). By direct comparison, then, we argue that the process of compaction in a -SiO₂ is not a defect creation process as previously assumed, but is a process similar to c -SiO₂ involving a reduction in the mean coordination of the planar rings leading to a volume reduction. Results obtained^{15,21} on the Raman spectra of compressed a -SiO₂ strongly support this hypothesis.

It is clear that densification of SiO₂ cannot continue beyond the limit of two-membered rings^{21,24} as indicated by the results for c -SiO₂ polymorphs. We note that further uv irradiation of a -SiO₂ in this regime leads to irreversible compaction and etching, the film shown in Fig. 1 being completely etched after a total dose of 17 000 J/cm². To explain the phenomena of etching, we recall that spin resonance results^{4,25} have clearly demonstrated the ability of uv radiation (sub-band gap) to produce various network defects.²⁶ Furthermore, Auger-electron spectroscopy,²⁵ sensing the superficial oxygen-to-silicon ratio, has revealed the surface defect density to be $> 10^{20}/\text{cm}^3$ for uv doses ≥ 3000 J/cm² consistent with what is found for deposited SiO_x films ($x < 2$). Substoichiometric SiO_x has a band gap strongly sensitive to the x value²⁷ and for $x < 1.8$ the gap is less than the photon energy used in our experiments. In this situation, direct excitation of electron-hole pairs is possible,²⁸ which, via relaxation processes, gives rise to a

means of photon-lattice coupling leading to further defect creation and/or localized heating. Measurements on SiO_x deliberately deposited with $x < 2$ have clearly demonstrated²⁸ the ease with which these substoichiometric films can be removed by uv radiation at 248 nm. The mechanism of initial defect creation (e.g., oxygen vacancy) in a -SiO₂ remains an open question, although²⁵ a significant difference between bulk and superficial densities is readily explained, since oxygen atoms released as interstitials in the bulk have a finite recapture probability, whilst those released at the surface desorb.

We conclude with further comments on Fig. 3. The results demonstrate that, as is the case for the various allotropic forms of c -SiO₂,²⁹ the refractive index and density of the a -SiO₂ polymorphs obey an essentially linear relationship. Furthermore, whereas a finite number of c -SiO₂ polymorphs exist in nature mainly defined by their bonding topology and characterized in terms of their ring order, an "infinite" range of a -SiO₂ polymorphs would appear to be possible. Experimentally, we have demonstrated a wide, continuous domain for a -SiO₂ limited at one end by the most stable form of a -SiO₂, the vitreous amorphous silica (density $\rho = 2.2$), and at the other end by a compressed polymorph of density $\rho = 3.0$. Although stable with time at room temperature, these compressed polymorphs appear unstable against annealing at high temperature ($\approx 950^\circ\text{C}$). The existence of a continuous range of a -SiO₂ polymorphs, unlike the case of c -SiO₂, appears due to the unusual flexibility possible in a system composed of a wide distribution of planar rings.

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⁹It will be seen that by " a -SiO₂ polymorph" we understand a structure composed of various order rings ($2 < n < 6$), where the distribution of the various order rings characterizes the structure as in the crystalline case.

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