Photon-Induced Oxygen Loss in Thin SiO_2 Films

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Ultraviolet irradiation of thin ($\sim$ 15-Å) laser-grown SiO_2 in vacuum renders the oxide unstable and it desorbs when heated to around 760 K. From electron spin resonance and Auger spectroscopy we conclude that irradiation produces a dense defect structure leaving thin films oxygen deficient, SiO_x $(x < 2)$. Observed Auger-spectra modifications then correlate well with calculated band structures for defects in SiO_2.

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Understanding the general physical properties of thin SiO_2 films formed by oxidation of Si, either thermally or laser assisted, is a subject of current interest[1-6] not only because of their technological importance (interface states,[7] thin oxide formation, ...) but also because SiO_2 is one of the simplest semiconductor-oxide systems. In the present work we have used the techniques of Auger-electron spectroscopy (AES) and electron-spin resonance (ESR) to study the influence of ultraviolet irradiation (248 nm) under vacuum on bulk oxide and thin laser-assisted oxides. We demonstrate that laser irradiation produces a defect structure including oxygen-vacancy–related defects. On this assumption we correlate observed modifications in the AES spectrum with recent band-structure calculations for defects in SiO_2. A consistent picture of a dense superficial defect structure in vacuum-irradiated thin and bulk oxides emerges.

Intrinsic *n*-type (minimum resistivity 3000 Ω cm) Si(111) samples were prepared in an ultrahigh-vacuum system (pressure $\sim 5\times10^{-10}$ Torr) in order to obtain a perfect 7×7 low-energy electron-diffraction surface structure emitting neither carbon nor oxygen AES signals. Laser-assisted oxidation was performed as follows: The Si(111) surface was exposed to O_2 at a pressure of 10^{-3} Torr and simultaneously irradiated with the photon beam of an excimer laser at 248 nm. The average power density at the Si surface was 5 W/cm^2 and the growth time, 180 min. The thickness of the silica layers was deduced by measuring the intensities of the *KLL* Auger signal for oxygen and Si (I_O and I_{Si}) and using the formula[2] $d_{SiO} = 1.65 I_O/I_{Si}$. The validity of this formula was verified by comparison with ellipsometric measurements on thicker oxides and found to be accurate to better than 10%. Film thicknesses were of the order of 15 Å. A typical Auger spectrum for a laser-grown oxide is shown in Fig. 1(a)—it is very similar to the spectrum of bulk, vitreous silica[8] (a-SiO_2) having Auger transition derivatives centered on 36, 64, and 74 eV. In Fig. 1(b) we show the spectrum of the laser oxide subsequently exposed to 248-nm laser irradiation for 1 h at an energy density of 100 mJ/cm^2 (pulse duration 10^{-8} sec, repetition frequency 20 Hz) in a vacuum of 5×10^{-10} Torr. The 64- and 74-eV transitions appear to shift by +3 eV to higher energy and a new transition is observed peaked at 84.5 eV. We estimate the center to be at 86 eV.

The Auger peaks at 36 and 74 eV obtained in the laser-assisted oxide correspond to those observed in bulk oxide[8] and originate from the O_{2p}-$Si_{3s/3p}$ bands situated +5 to +10 eV below the valence-band edge. These transitions are $5a_1$ and $4t_2$ in the usual T_d (SiO_4) group nomenclature. The peak at 64 eV is attributed to the O_{2s}-$Si_{3s/3p}$ band centered about 18 eV below the valence-band edge. In vacuum-irradiated laser oxide the Auger transitions shift to 67 and 77 eV and the new transition occurs at 86 eV. At the same time as the extra Auger transition

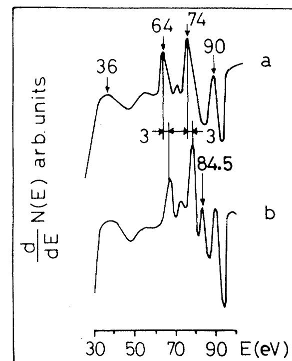

FIG. 1. Auger spectra for thin, amorphous SiO_2 layers ($\sim$ 15 Å) for (a) laser-assisted oxide growth (same as thermally stable oxide); (b) the same sample after irradiation with 8×10^{23} photons/cm^2 at a wavelength of 248 nm. The peak indicated at 84.5 eV corresponds to a transition centered on 86 eV. The peak observed at 90 eV originates from the silicon substrate.

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occurs, the thermal stability of the thin films becomes reduced; this is shown in Fig. 2 where Auger results are presented for laser oxides which have been vacuum irradiated for 1 h as described previously, then heated for a few min in vacuum. One observes a progressive decrease in the intensity of the 67-, 77-, and 86-eV transitions with reappearance at 765 K of the spectrum appropriate to pure Si at which point the oxide has clearly desorbed. Similar behavior is found in oxygen-deficient films,[6,9,10] SiO_x ($x < 2$), and in thin native oxides when heated in vacuum. *It is not found for bulk oxides or laser-assisted oxides.*

In order to obtain some feeling for the effects likely to have occurred as a result of laser irradiation of the thin SiO_2 film we have performed ESR measurements at room temperature and *X*-band frequencies on oxide samples before and after laser irradiation. Because laser-grown oxides were too thin to give detectable ESR signals and because of possible reabsorption of oxygen in superficial layers, we studied 2500-Å thermally grown oxides. In this case, the sample was irradiated and the Auger spectrum monitored continuously. After a dose 8×10^{23} photons/cm^2, the observed Auger spectrum was identical to a vacuum-irradiated, laser oxide [Fig. 1(b)]. A single ESR line was observed with a g factor of 2.0004 and a peak-to-peak linewidth of 2.4 ± 0.2 G, characteristic[11] of an overmodulated E_1' oxygen-vacancy-center resonance.[12] The density of centers was roughly estimated to be $4\times10^{17}/\text{cm}^3$ on the assumption of a uniform distribution throughout the oxide volume. Prior to irradiation, no E_1' centers were detectable (sensitivity limit $\sim 7\times10^{16}$ E_1'/cm^3 for our sample). It must, however, be noted that during irradiation, some heating was observed so that, given the low activation energy for E_1' annealing,[9] we do not exclude the probability that some centers were annealed out. The results clearly demonstrate that 248-nm laser irradiation of amorphous SiO_2 will produce stable structural defects such as oxygen vacancies.

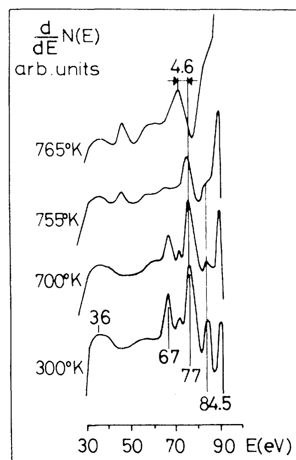

FIG. 2. Auger spectra during thermal desorption of the irradiated oxide shown in Fig. 1(b). The sample was heated in a vacuum of 5×10^{-10} Torr.

It is well known[10] that electron irradiation of SiO_2 in the kiloelectronvolt range produces surface oxygen desorption and that high-energy irradiation may produce stable vacancy centers.[13] It is estimated[10] that about 10^{20} electrons/cm^2 of 1-keV energy will desorb half the number of surface oxygens. Recent AES studies[14,15] on bulk amorphous and monocrystalline SiO_2 indicate an Auger spectrum similar to the laser-grown oxide. If the electron beam used in analysis is maintained on, then after about 30 min at 4 μA/cm^2 a supplementary transition appears centered around 87 eV consistent with the 86-eV peak we observe due to laser irradiation of our thin amorphous oxide. Comparing these irradiation results with electron-induced surface desorption[15] we find that the oxygen-loss–induced Auger peak becomes visible after a loss of about 2% of surface oxygen. Since the approximate Si/O ratio can be determined by comparison of the Si and O *KLL* line intensities we have performed this measurement on laser oxides subsequently irradiated with 8×10^{23} photons/cm^2 at 248 nm in vacuum. We deduce our irradiated oxide to be 18% deficient in oxygen which is clearly consistent with the importance of the intensity of the 86-eV transition shown in Fig. 1(b).

Comparison of the ESR data on uv-irradiated bulk amorphous SiO_2 and Auger data on electron-irradiated bulk oxide and uv-irradiated laser-grown oxide strongly suggests the effects of uv irradiation to be to produce oxygen desorption in thin, amorphous SiO_2 films. It would be satisfying to attach a physical identification to the origin of the 86-eV transition and explain the movement of the 64- and 74-eV transitions. In electron-irradiation studies[14] it was suggested that the high-energy transition might arise from E_1' oxygen vacancy centers. Band-structure calculations have been presented recently[16] for various types of defects in the amorphous SiO_2 structure. For defects such as the nonbonding oxygen (Si–O), peroxyl bridge (Si–O–O–Si), peroxyl radical (Si–O–O), and Si dangling bond one can summarize that because of charge-transfer effects[16] one expects the O_{2s}-$Si_{3s/3p}$ and O_{2p}-$Si_{3s/3p}$ bands to move to higher energy, closer to the valence-band edge by energy shifts of

the order of those found for the 64- and 74-eV Auger peaks (+3 eV). The formation of a significant density of states in the SiO_2 band gap between 5 and 7 eV above the valence-band edge capable of contributing to the Auger spectrum (i.e., occupied states) is predicted for the peroxyl radical and the Si dangling bond and these could explain the 86-eV Auger transition. The latter is in agreement with the observation of E_1' centers by ESR in irradiated, bulk SiO_2.

The results presented in Fig. 2 show that the defect structure in vacuum-irradiated laser oxide dissociates and desorbs when heated in vacuum to around 760 K. In damaged, bulk SiO_2 it has been demonstrated[9] that around these temperatures generalized damage recovery occurs which is at first sight inconsistent with desorption. However, models for vacancy formation suggest that[17] oxygens which are liberated go into molecular solution provided they escape a capture radius typically ~ 5 Å. Since the laser-oxide film thicknesses were $\geqslant 15$ Å, it is very possible that significant numbers of liberated oxygens escaping from vacancies were desorbed as well as being trapped in molecular solution or as peroxyl radicals. Furthermore, for those which did trap, if the average diffusion distance from the vacancy was > 15 Å, there is a high probability that they desorbed in trying to diffuse back to their vacancy center of origin during high-temperature annealing. Consequently, the remnant defect structure can be expected to have been oxygen deficient (SiO_x, $x < 2$) and unable to recover through heating. At temperatures where movement appears to occur in SiO_2, the unstable oxide desorbs as found for SiO_x films made deliberately oxygen deficient.[18] Note that at the present time, data do not appear to exist indicating the desorption temperature as a function of x.

We believe that the Auger transition observed at 86 eV in uv-irradiated laser oxide and at 87 eV in electron-irradiated bulk SiO_2 must be associated with an oxygen-vacancy–defect structure, i.e., E_1' or peroxyl radical defects, or both. On the basis of the energy of the Auger transition it must be related to states in the SiO_2 band gap. One might ask what justification exists for invoking a defect approach rather than a fully bonded, substoichiometric silicon oxide model which is known[19] to produce gap states. To answer this we note that experimentally, the oxygen-desorbed film was subjected to no ulterior thermal treatment to "heal" the broken bonds left by the desorbed oxygens. We also observed ESR in bulk oxide, inconsistent with a fully bonded structure.

The present study demonstrates that low-energy ionizing radiation can create oxygen-vacancy–related defects in amorphous SiO_2. In thin films (15 Å) the SiO_2 can be rendered sufficiently oxygen deficient that it desorbs when heated in vacuum to 760 K. The Auger spectrum can thus be correlated with the formation of a dense defect structure. An open question remains the mechanism of defect creation. In electron irradiation, the processes usually involved[20] require minimum energies considerably in excess of the 5 eV associated with the photons in laser irradiation. On this basis, the mechanism of vacancy creation apparently remains an open question.

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