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H-complexed oxygen vacancy in SiO_2: Energy level of a negatively charged state

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The defects generated in SiO_2 during irradiation with energetic (10 eV) photons were found to trap electrons at a level 3.1 eV below the oxide conduction band. The electron spin resonance data and the behavior upon hydrogen passivation indicate that the optically active state may be ascribed to a H-complexed oxygen vacancy in SiO_2. The observed injection of electrons to these traps from Si advances the revealed defects as the possible origin of the degradation-induced electrical conduction of thin SiO_2 layers. © *1997 American Institute of Physics.* [S0003-6951(97)03752-2]

The trend of gate SiO_2 reduction in Si-based metal–oxide–semiconductor (MOS) devices urges for a better understanding of the physical mechanism(s) of the oxide degradation. It is well recognized that during device fabrication or in the course of its operation, charge injection attendant with the release of hydrogen results in the generation of defects which serve as intermediate tunneling states for electrons leading to leakage current and, ultimately, dielectric breakdown of SiO_2.[1–5] However, despite large efforts, the nature of these SiO_2 defects remains unknown. In the present work, we will show that a defect, likely a H-complexed oxygen vacancy ($O_3{\equiv}SiH\ HSi{\equiv}O_3$), generated under optical injection of electron-hole pairs in thermally grown SiO_2 on Si, has an energy level for an extra electron at 3.1 eV below the oxide conduction band, and that these centers may trap electrons from Si when an electric field is applied across the oxide. The correlation between the electrical properties of these H-complexed vacancies and the stress-induced traps in thin oxides advances the generation of this kind of defects as one of the probable SiO_2 degradation mechanisms.

The studied samples were prepared by oxidation of *p*-type (100)Si in dry O_2 at 1000 °C followed by postoxidation annealing in N_2 (1000 °C, 30 min). The oxide thickness ranged from 27 to 66 nm. MOS structures with semitransparent ($\approx$15-nm thick) metal electrodes were fabricated by resistive evaporation of Al and, subsequently, exposed to vacuum ultraviolet (VUV) radiation from a Kr discharge through a MgF_2 window under floating metal conditions ($h\nu = 10$ eV). After irradiation, some of the samples were annealed in forming gas (10% H_2+90% N_2) or in pure H_2 at 400 °C for 30 min. The defects produced in SiO_2 were analyzed previously by avalanche electron injection (AEI), hole photoinjection, and electron spin resonance (ESR) spectroscopy.[6] AEI reveals the generation of electron traps with a capture cross section in the range of 10^{-18} cm^{-2}, which is close to that of a H_2O molecule in SiO_2,[7] while ESR and hole trapping experiments show generation of Si dangling bond centers (E'_γ center: $O_3{\equiv}Si\cdot$). From the matching generation kinetics and densities of the E'_γ centers and H_2O molecules, the effect was hypothesized as removal of an O atom from a Si–O–Si bridge towards an interstitial position followed by H decoration (see Ref. 6).

An important observation for the present work is that the intense ESR signal from E'_γ centers observed after VUV irradiation (Fig. 1) disappears upon annealing in H_2. However, the original signal is restored after a short VUV irradiation of the sample (10^{15} photons cm^{-2}), while the oxide remains electrically neutral. This reversible bleaching of the E'_γ signal thus indicates that Si dangling bond defects remain present in SiO_2, but may be switched between a paramagnetic ($O_3{\equiv}Si\cdot$) and a diamagnetic (H-passivated) ($O_3{\equiv}SiH$) state. We will analyze the trapping of an additional electron by these centers and their subsequent photodepopulation. The electrons were supplied in two ways: applying a large positive bias to the metal electrode, allowing electrons from Si to populate the traps located in the oxide within a tunneling distance (2–4 nm) from the Si/SiO_2 interface, or, alternatively, filling the traps in the oxide by AEI from Si. After filling of the traps, electrons can be detrapped by optical excitation to the oxide conduction band to determine their energy level.[8] Such experiments were performed using a spectral system described elsewhere,[9] where the detrapping was monitored by measuring the photocurrent or the

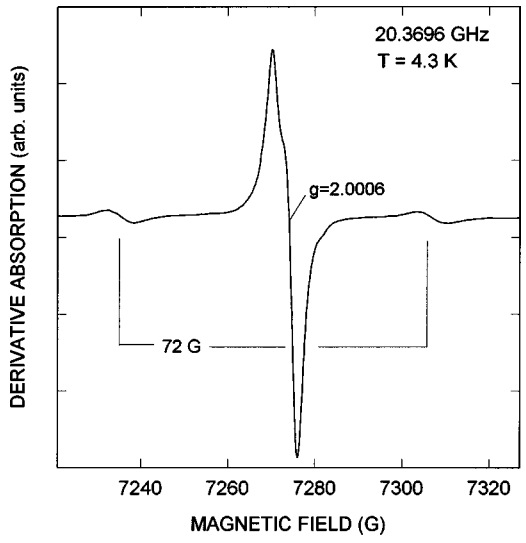

FIG. 1. ESR spectrum (applied microwave power $\approx$0.3 nW) of the Si/SiO_2 (66 nm) structure after VUV exposure of 1×10^{19} photons cm^{-2} through Al (removed prior to the measurements). The signal at $g = 2.0006$ originates from the $O_3{\equiv}Si\cdot$ defect in SiO_2 (E'_γ center), while the 72-G doublet is ascribed to the $HO_2{\equiv}Si\cdot$ center.

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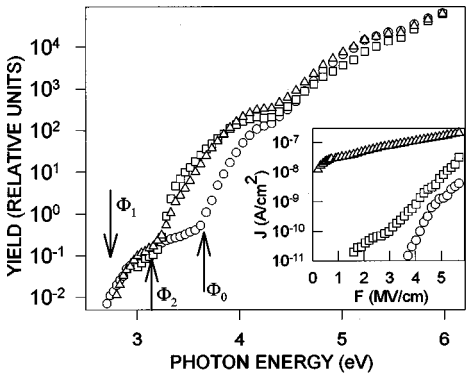

FIG. 2. Photocurrent quantum yield as a function of photon energy in the control Si/SiO_2 (66 nm)/Al structure (○) and in those exposed to 1×10^{19} VUV photons cm^{-2} without (□) and with subsequent H_2 anneal at 400 °C (△) measured at the electric-field strength in the oxide of 4 MV/cm under positive metal bias. The arrows indicate the spectral thresholds. The inset shows current–voltage characteristics (positive metal bias) of the dark current (○) and photocurrents at $h\nu=3.6$ eV (□) and $h\nu=5$ eV (△) measured on the irradiated unannealed sample.

flatband voltage shift on 1-MHz capacitance–voltage $(C-V)$ curves.

The spectral dependencies of the photocurrent quantum yield (Y), normalized to the incident photon flux, are shown in Fig. 2 for the control (nonirradiated) and VUV exposed (10^{19} photons cm^{-2}) samples. All the curves are taken with an applied electric field F in the oxide of $+4$ MV/cm, the metal being positively biased. In the control sample, a first observation is the intense internal photoemission of electrons from the Si: It is characterized by $Y\sim(h\nu-\Phi_0)^3$ and a field-dependent (the Schottky effect) spectral threshold Φ_0, which, when extrapolated to zero field, gives the barrier height of 4.25 ± 0.05 eV, the value characteristic for electron emission from the Si valence band to the SiO_2 conduction band.[10] Second, there is a much weaker emission, characterized by $Y\sim(h\nu-\Phi_1)$ and the field-independent spectral threshold $\Phi_1=2.8\pm0.1$ eV, which we previously ascribed to the electron emission from oxide defects near the Si/SiO_2 interface.[11,12] These reside near as-grown interfaces and correlate with the oxygen deficiency of SiO_2; the irradiation has little effect on the electron emission from these centers. However, VUV exposure is seen to lead to the development of a new band, characterized by $Y\sim(h\nu-\Phi_2)^2$ and the field-independent spectral threshold $\Phi_2=3.1\pm0.1$ eV. We found that this emission gradually increases with VUV exposure of the oxide, and therefore, this band is associated with radiation-induced defects near the Si/SiO_2 interface. Subsequent annealing in H_2 of the irradiated sample causes a weak, though distinguishable spectral redistribution of the quantum yield in this band (see Fig. 2), but does not eliminate it, while no ESR-active E'_γ centers remain in the SiO_2 after this anneal. Hence, the radiation-induced states excited at $h\nu>3.1$ eV appear remarkably stable against passivation by H at 400 °C.

The inset in Fig. 2 shows the current–voltage behavior in the irradiated (unannealed) sample of the dark current, and the photocurrent under excitation with photons of $h\nu=3.6$ eV (band Φ_2) and 5.0 eV (band Φ_0). As the dark current in the control samples in the covered field range is found not to exceed 2×10^{-11} A cm^{-2}, it is seen that the defect generation by VUV exposure induces a leakage current. Clearly, there is a considerable difference between the photocurrent curves taken in the spectral ranges corresponding to the excitation of the traps generated in SiO_2 [3.6-eV (□) curve] and to the emission of electrons from Si into the oxide [5 eV (△) in the inset]. Because the electron concentration in the Si valence band may be taken as constant, the emission from this band is determined by the field dependence of the electron emission probability into SiO_2. In the high field range, the latter increases slowly, quite in contrast with the trap ionization curve. Apparently then, the density of the filled traps increases with the field strength as more and more defects are populated by electrons tunneling from Si. Indeed, the trap photoionization current-field curve is well described by the Fowler–Nordheim function[13]

$$J\sim AF^2\ \exp(-B/F), \tag{1}$$

with $B=(5.0\pm0.3)\times10^7$ V/cm.

The photodepopulation results for the *bulk* oxide traps filled by AEI ($\sim10^{18}$ electrons/cm^2, trapped charge to a density of 6×10^{12} electrons/cm^2) are shown in Fig. 3 for the sample with 66-nm-thick oxide subjected to VUV exposure and subsequent 400 °C anneal in H_2. In Fig. 3(a) the depopulation yield is shown, obtained from photocurrent measurements, as a function of photon energy for three positive voltages on the metal electrode. The curves indicate two spectral thresholds, i.e., at 3.1 ± 0.2 and 4.3 ± 0.2 eV. Obviously, the first threshold corresponds to the Φ_2 value measured above after electron tunnel injection for the defects generated by VUV near the Si/SiO_2 interface, as particularly evidenced by the fact that the same power law of the spectral curve $Y\sim(h\nu-\Phi_2)^2$ is observed in both cases. The assignment of the 4.3 eV threshold is less straightforward: both oxide defect ionization and the electron photoemission from Si into SiO_2 may account for the photocurrent increase. To distinguish between these mechanisms, the depopulation spectral curves were measured under the opposite directions of electric field in the SiO_2, where it is observed that the direction of the current flow is reversed. The results shown in Fig. 3(b) indicate no sensitivity of the thresholds to the direction of electron motion, suggesting that the responsible mechanism is detrapping of electrons in SiO_2. Moreover, the depopulation yield determined from the rate of trapped charge removal [measured at $F=+3$ MV/cm to exclude hole photoemission from Si into SiO_2, which has a lowest spectral threshold around 4.5 eV (Ref. 14)] exhibits the same threshold.

There are several important observations as to the nature of the electron trapping site. (i) All the charge available for optical depopulation can be removed at $3.1<h\nu<4.3$ eV as well as at $h\nu>4.3$ eV. This means that the two spectral thresholds born out in Fig. 3 correspond to the photoionization of the *same* electron state. (ii) The H_2O electron traps here observed in the nonirradiated oxides exhibit no photoionization effect although their capture cross section is found hardly distinguishable from the radiation-produced ones.[6] Consequently, the optical activity of the generated center must be related to its oxygen vacancy part. (iii) The spectra shown in Fig. 2 indicate that the passivation of the E'_γ center with H influences the spectral curve of photoionization, in-

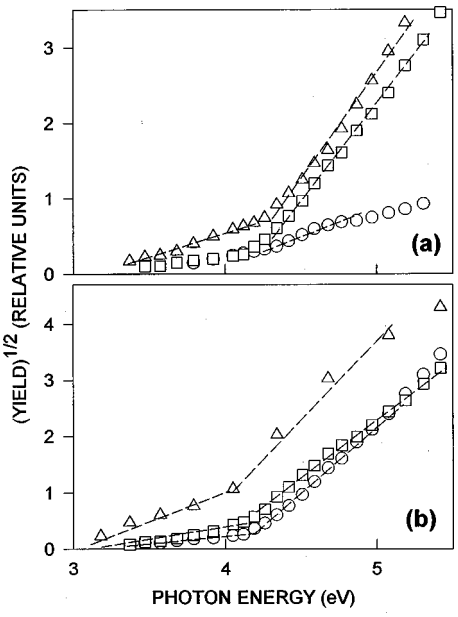

FIG. 3. (a) Photocurrent quantum yield as a function of photon energy in the Si/SiO_2 (66 nm)/Al structure exposed to 1×10^{19} VUV photons cm^{-2}, annealed in H_2 (400 °C, 30 min) and subjected to AEI of 10^{18} electrons/cm^2. The points are taken at the electric-field strength in the SiO_2 of 0.5 (○), 1.0 (□), and 2.0 MV/cm (△) with the metal biased positively. (b) Photocurrent quantum yield as a function of photon energy in the same structure measured for an oxide field of 1 MV/cm with metal biased positively (○) or negatively (□) and the photodischarging yield measured with $F=3$ MV/cm (△) under positive metal bias.

dicating localization of an electron at the O vacancy site in SiO_2. Apparently, there is a variation of the electrostatic trap potential, which determines the power of the photoionization cross-section spectral dependence.[15] (iv) The samples subjected to AEI immediately after VUV exposure show ~100% efficiency of the optical detrapping, which decreases to 90% after 150 °C, and to 40%–50% after 400 °C H_2 anneal. Remarkably, we found no decrease in the density of neither the H_2O electron traps[6] nor the E'_γ centers. This points towards the thermal separation of a H_2O-vacancy complex as the reason for the decrease in photoionization efficiency: when an electron is trapped on a sufficiently remote H_2O, it cannot be transferred anymore to the left oxygen vacancy, and thus remains unavailable for the optical excitation.

Although we have not observed an ESR signal from the negatively charged defect, the above results provide circumstantial evidence that the energy level of 3.1 eV below the oxide conduction band belongs to an additional electron localized on an $O_3{\equiv}SiH$ center in SiO_2. The inferred energy level of the *hydrogenated* oxygen vacancy (3.1 eV below the SiO_2 conduction band) appears to be much deeper in the oxide band gap than the level of negatively charged *intrinsic* O vacancy calculated for α quartz (0.7 eV) (Ref. 16) or at the Si/SiO_2 interface (~1 eV).[17] The latter energies are consistent with the experimental electron trap level in as-fabricated nondegraded MOS oxides.[18] A further overview of theoretical estimates may be found in Ref. 19. In this context, we would like to recall the experimental observations made in Ref. 20 regarding the charging of the Si-implanted and annealed SiO_2 layers. Similar to our case, no ESR signal was detected after the annealing, suggesting saturation of all dangling bonds. Upon biasing of the implanted MOS structure, a leakage current and the SiO_2 negative charging were observed, which may be simulated using an energy level of the negatively charged trap of about 3 eV below the oxide conduction band (our value is 3.1 eV). The way the traps are generated and the reported elimination by reoxidation provide strong evidence of this trap being related to excess Si.[20] This observation of a neutral diamagnetic state and the disagreement with the energy level predicted for the negatively charged intrinsic O vacancy (0.7–1 eV),[16,17] make us suggest that the traps reported in Ref. 20 are likely the hydrogenated ($O_3{\equiv}SiH$) or ($O_3{\equiv}SiH\ HSi{\equiv}O_3$) centers.

There are several observations indicating that some of the electrical stress-induced defects are of the same nature as the presently resolved VUV-radiation generated ones. First, the electron traps generated in the gate oxides of *n*-channel MOS transistors by hot-hole injection were found to be available for optical depopulation with photons of $h\nu{\approx}3$ eV.[21] Second, the filling of the traps responsible for the stress-induced leakage current in thin SiO_2 layers may be described by the Fowler–Nordheim expression (1) with $B=5.27\times10^7$ V/cm,[5] which is close to the value determined for the VUV generated traps in the present study ($B=5\times10^7$ V/cm), suggesting close energy levels of the defects in both cases. Among other complying features, we only mention the recent result of noise measurements in MOS transistors with ultrathin (3.5-nm-thick) oxides, which suggest the energy of the electron level involved in the trap-assisted tunneling across SiO_2 to be 0.96 times the barrier height for electrons at the Si/SiO_2 interface,[22] i.e., ≈3 eV. These matching features point to the H-complexed O vacancy defect as a realistic candidate accounting for the permanent oxide damage during irradiation or hot-carrier injection.

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