Interfacial Defects in SiO_2 Revealed by Photon Stimulated Tunneling of Electrons

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Experiments on the photon stimulated tunneling of electrons at the interfaces of SiO_2 with Si and SiC demonstrate the presence of defects with electron binding energy of 2.8 eV relative to the SiO_2 conduction band, well above the semiconductor band gap. These defects, which so far escaped direct detection, are located near interfacial oxide layers, their density being sensitive to the silicon enrichment of SiO_2. The discovered defects appear to be the origin of the trap-assisted electron injection phenomena in SiO_2. [S0031-9007(97)02708-7]

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A major requirement of an electrical insulator is the ability to sustain a high electric field without dielectric failure. Silicon dioxide, the most widely used insulator in the solid state electronic devices, is superb in this aspect: Thermally grown oxides on silicon and silicon carbide exhibit electric breakdown field strength up to 10 MV/cm or even higher. Admittedly, the best layer is reached the closer the insulator approaches perfect SiO_2 stoichiometry throughout a uniform homogeneous structure, without incorporation of intrinsic or impurity-related defects: It is the degree of mastering these defects that governs the ultimate insulator quality. Defects may be subdivided in two groups, according to whether their electronic energy level occurs within or outside the semiconductor band gap. Thermal oxide exhibits the unique property that, when grown on Si, the density of detrimental interface states distributed *within* the semiconductor band gap is intrinsically low; it can be reduced [1,2] to the 10^9 cm^{-2} eV^{-1} range in standard (100)Si/SiO_2. The question, however, about the presence of interface states *outside* the Si band gap has not been specifically addressed so far as these states were believed not harmful to the electronic properties. Yet, there is one group of worrying interfacial electrical effects which show little correlation with the well studied conventional interface states: the defect assisted electron injection, which is responsible for the leakage current and early breakdown of the insulator. This process appears related to SiO_2 defects with the energy levels located outside the semiconductor band gap.

The interest in the defect mediated injection has increased strongly over the last few years. One reason is that this mechanism dominates leakage currents in the most advanced SiO_2 layers: ultrathin and low-temperature oxides, and buried oxides formed by oxygen ion implantation in Si [3–5]. Also, the application of SiC as a semiconductor for high voltage devices imposes higher demands to the oxide [6], as the electric field strength it has to endure scales with the field in the semiconductor. However, while obviously in need of their identification, little is known about these defects assisting electron injection in SiO_2: This concerns the present study. We found that the photon stimulated tunneling (PST) of electrons at the Si/SiO_2 and SiC/SiO_2 interfaces is controlled by interfacial defects in the oxide. The corresponding energy level $E_B = 2.77 \pm 0.05$ eV was found remarkably reproducible over different interfaces, but the defect density is sensitive to the Si enrichment of the particular oxide. Furthermore, a correlation between the PST quantum yield and the SiO_2 dark conduction is observed, unveiling the isolated defects as the source of the defect assisted electron injection in the oxide.

The samples used were prepared by thermal oxidation of (100) and (111)Si, and (0001) hexagonal SiC (4H-, 6H-polytypes, Si face). On Si, 25–66-nm-thick oxides were grown at 1000 or 1120 °C in dry O_2. The conduction electron concentration (n) in these samples was varied from 3×10^{14} to $\sim 3 \times 10^{21}$ cm^{-3} by implanting P prior to oxidation. The oxides on SiC (25–90 nm thick) were grown using a technology described elsewhere [7]. For the sake of comparison, also studied were buried oxides containing excess Si. These are produced in (100)Si by implantation of oxygen ions and subsequent high-temperature anneal. Fabrication details were published elsewhere [8]. Finally, low-temperature oxides were deposited on (100)Si by plasma enhanced decomposition of silane in the presence of oxygen at 500 °C. Metal-oxide-semiconductor (MOS) structures were defined by evaporation of semitransparent (13-nm-thick) gold electrodes onto the oxide.

PST was studied at 77 and 300 K by measuring current in the MOS structures with positive metal bias under monochromatic illumination by an Ar-ion laser of tunable oscillation frequency (Spectra Physics 168B); the latter provides nine spectral lines in the photon energy range $h\nu = 2.41$ to 2.73 eV with output power 25–200 mW. Internal photoemission of electrons (IPE) from Si or SiC into SiO_2 was studied by illuminating the MOS structures by photons of energy sufficient to excite electrons from the semiconductor valence or conduction band above the edge of the SiO_2 conduction band [7]. The electric field strength (F) at the oxide-semiconductor interface was calculated using the applied bias value, oxide thickness, and the semiconductor-metal work-function difference measured by IPE [9]. The relative electron yield (Y) of PST and IPE was calculated from the photocurrent normalized to

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the incident photon flux. The latter is justified as the photocurrent was verified to increase linearly with the light intensity (constant Y). This additionally assures one that the electron energy distribution is not significantly affected by optical excitation or sample heating.

PST is expected to be described by the Fowler-Nordheim (FN) tunneling model. In the case of electron tunneling from a *metal* this model predicts a field dependence of the tunneling current arising only from the field dependence of the barrier penetration probability [10]. But, in the case of electron tunneling from a nondegenerate *semiconductor,* both the energy of quantum subbands and their population become additionally field dependent [11,12]. Therefore, in order to keep the energy spectrum and the density of electrons at the semiconductor surface unchanged, we analyzed the PST yield as a function of photon energy at fixed F. Typical spectral curves for the $(111)\mathrm{Si}/\mathrm{SiO_2}$ interface observed at 300 K for different F are shown in Fig. 1(a). These were fitted by the expression [13–15]

$$Y/F^2 = A\exp[-6.83 \times 10^7 (m_{\mathrm{ox}}/m_0)^{1/2} \times (E_B - h\nu)^{3/2} F^{-1}], \qquad (1)$$

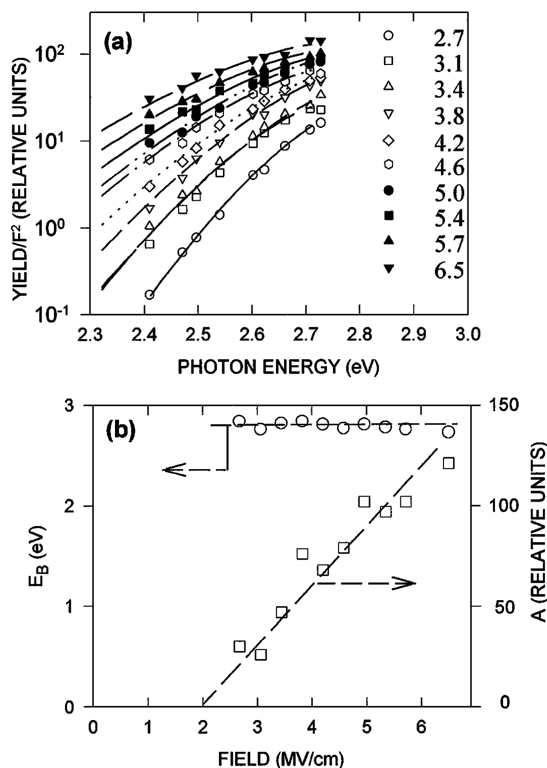

FIG. 1. (a) Relative yield of PST at the $(111)\mathrm{Si}/\mathrm{SiO_2}$ interface as a function photon energy at different strengths of the electric field in the oxide, denoted in MV/cm. The lines represent fitting results. (b) Binding energy E_B of the initial state of PST and the preexponential factor A as a function of the electric field as obtained from the data fitting. Curves are guides to the eye.

where A is a constant proportional to the density of initial electron states, $m_{\mathrm{ox}} = 0.5m_0$ is the electron effective mass in the oxide, m_0 the electron rest mass, and E_B the energy of the initial state of the electron measured relative to the $\mathrm{SiO_2}$ conduction band. The curves shown represent the fitting results indicating the PST data to be well accounted for by the FN model. The inferred values for the parameters A and E_B are shown in Fig. 1(b) as a function of field. The preexponent A is seen to increase nearly linearly with the field starting at $\sim$2 MV/cm, while the binding energy appears independent of F within the accuracy of $\sim$0.05 eV; the latter result was found in all the studied samples. Tunneling current should generally show only a weak temperature dependence [10,16]. This was verified by reducing the observational temperature to 77 K: the PST current is seen to decrease only about 2–3 times without change, however, in field and spectral dependences of Y_{PST} (not shown), which is consistent with the temperature behavior of the dark tunneling current in Si MOS structures [16]. From the above characteristics, it is clear that the photocurrent involves a tunneling process: PST is determined by the tunneling of optically excited electrons.

We next address the nature of the involved electron states in the PST. Average E_B values are shown in Fig. 2 (open symbols) as a function of n for the $\mathrm{Si}/\mathrm{SiO_2}$ and $\mathrm{SiC}/\mathrm{SiO_2}$ interfaces. The conduction band offset at these interfaces measured by IPE are indicated by arrows. For the Si substrate, it is seen that heavy doping ($n^+ > 2 \times 10^{19}$ cm^{-3}) induces a shift in the conduction band position. This has been observed previously and was ascribed to Si band gap narrowing [17]. A major finding is that in all the "low" doped structures ($n < 2 \times 10^{19}$ cm^{-3}) E_B remains constant and remarkably insensitive to the

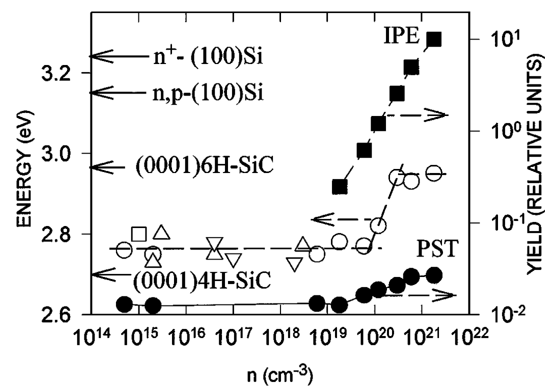

FIG. 2. Energy E_B of the initial state of PST transitions measured relative to the conduction band of $\mathrm{SiO_2}$ at the interfaces with (100)Si (○), (111) Si (□), (0001) 6H-SiC (Δ), and (0001) 4H-SiC (∇) for different nominal concentration of electrons in the substrate. The solid arrows indicate the conduction band offsets at the corresponding interfaces as determined from IPE spectroscopy. The relative yield of PST (filled circles) and IPE (filled squares) at the interfaces of $\mathrm{SiO_2}$ with (100)Si are also shown. Lines are guides to the eye.

differences in the conduction band offset. For higher $n(>2 \times 10^{19}\ \mathrm{cm}^{-3})$, however, E_B is seen to increase by $\sim$180 meV; but, as a similar shift is observed in the low-doped Si/SiO_2 structures with ultrathin (5 nm) oxide (not shown), the image-force reduction of the electron energy by a proximate conductive surface is concluded as the reason for this variation in E_B.

The quantum yields of transbarrier (PST) and overbarrier (IPE) electron photoinjection into SiO_2 measured for fixed $F = 3$ MV/cm are shown in Fig. 2 (filled symbols) as a function of n. The Y_{IPE} increases proportionally with n, which implicates the Si conduction band as the source of electrons, while the Y_{PST} increases only by a factor of 2–3 for n increasing by 2 orders of magnitude. The absence of correlation between n and Y_{PST} as well as between E_B and the conduction band offset both indicate that the initial states of electrons involved in the PST are not related to the semiconductor conduction band, in contrast with previous belief [15]. Instead, the reproducibility of E_B among different structures and its weak field sensitivity suggest that the PST current originates from oxide defects located so close to the substrate that they may be permanently refilled so as to provide a stable-in-time PST current.

With $E_B = 2.77$ eV invariant, the field dependence of A may be calculated from the PST current-voltage (I-V) data using Eq. (1). Figure 3(a) shows the results obtained on $(100)Si/SiO_2$ and $(0001)4H\text{-}SiC/SiO_2$ interfaces for three photon energies. The marginal effect of $h\nu$ on the $A(F)$ curves indicates an insignificant modulation of PST by the optical matrix elements or by the energy distribution of excited states. The shift in the $A(F)$ dependence towards lower field values [cf. Fig. 3(a)] without change in E_B results from the decrease in the band offset at the $4H\text{-}SiC/SiO_2$ interface by 0.45 eV relative to the Si/SiO_2 interface. It is explained by the defect filling by electrons, which would require a shift of the E_B level below the Fermi level at the semiconductor surface: at the $4H\text{-}SiC/SiO_2$ interface, with a smaller band offset, this condition is simply met at lower field than at the Si/SiO_2 interface. The A-vs-F behavior of different oxides on (100)Si is compared in Fig. 3(b). Both the deposited oxide and buried oxide show larger values and a lower field onset of A variation than thermal SiO_2, suggesting a higher defect density in the former oxides. The supplemental implantation of oxygen in the buried oxide reduces the PST current, which is reflected by the decrease in A. Hence, as buried oxide is known to be oxygen deficient (Si enriched), the defects involved in the PST are probably related to the oxygen deficiency of the oxide.

The dark I-V curves of the MOS structures (not shown) bear out an enhanced conductivity of the low-temperature oxides and buried oxides relative to the thermal ones. This also complies with the literature where it is routinely ascribed [5] to Si enrichment of SiO_2. The latter inference is supported by the observation of a decrease in the buried oxide conductivity by additional incorporation of oxygen

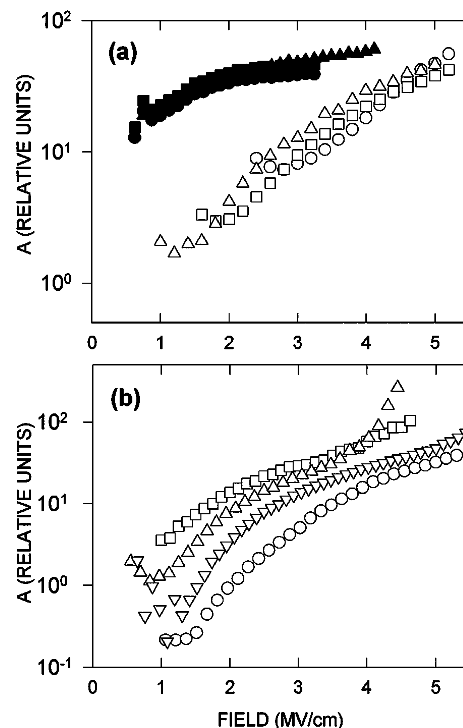

FIG. 3. Preexponential factor A as a function of the electric field strength in the oxide: (a) determined [see Eq. (1)] from the PST I-V curves measured at $h\nu = 2.41$ (circles), 2.54 (squares), and 2.71 eV (triangles) on thermal $(100)Si/SiO_2$ (open symbols) and $(0001)4H\text{-}SiC/SiO_2$ (filled symbols) structures; (b) determined from the PST I-V curves measured at $h\nu = 2.71$ eV on $(100)Si/SiO_2$ interfaces formed by the thermal Si oxidation (○), plasma assisted low-temperature deposition (□), oxygen ion implantation in Si without (Δ), and with (∇) supplemental implantation of oxygen.

[8]. When comparing this with the decrease in PST current after supplemental implantation of oxygen [cf. Fig. 3(b)], a correlation between the dark and PST currents appears. Moreover, the onset field for bulk conduction in buried oxides is observed [5] to be $\sim$2 MV/cm, which is close to the onset value for the variation of A with F derived from the PST data (Fig. 3). This would mean that filling of the same defects by electrons at elevated field augments both the dark and PST currents.

Overbarrier excitation of electrons from defect levels at the Si/SiO_2 interfaces was also observed in low-doped (111) and $(100)Si/SiO_2$ structures formed either by high-temperature (1120 °C) oxidation or by oxygen implantation. These oxides contain a large concentration of oxygen vacancies in SiO_2, as revealed by the hole trapping experiments. The spectral curves (not shown) exhibit a field independent spectral threshold (2.8 ± 0.1 eV) coinciding with E_B within the measurement accuracy. Similar to the PST results, no measurable signal was observed in the thermal oxides for $F < 2$ MV/cm, but the signals increase in the range $2 < F < 4.6$ MV/cm. Additional incorporation of oxygen in the SiO_2 through ion implantation

reduces the photoionization yield, which, again, mirrors the behavior of the PST yield. Thus, the defects observed in the photoionization experiments are likely the same centers as revealed by the PST.

The absence of any significant charge in the oxides, as revealed by capacitance-voltage measurements, indicates that the centers observed in the present work are initially neutral and trap an extra electron upon applying a high electric field. Filling of the traps with electrons occurs likely by tunneling from the semiconductor conduction band, because no significant temperature effect is observed. However, for such tunneling to occur, a shift of the trap level E_B to below the semiconductor surface Fermi level is required, which is possible only if the defects are located in the oxide at some distance from the interface. An estimate of this distance can be obtained from the field threshold of $A(F)$ curves, and the difference between E_B and the Fermi level at the semiconductor surface, which gives a distance of about 2 nm. The latter is consistent with the 1.6–1.7-nm estimate obtained from the image force lowering of the electron energy (180 meV; see Fig. 2) using 3.9 for the relative permittivity of the oxide [1]. Filling of traps located closer to the interface would require a higher electric field to shift their levels below the Fermi level; filling of the more remote traps, on the other hand, is inhibited by an exponential decrease of the tunneling probability with the trap-interface distance.

To the best of our knowledge, no defect in SiO_2 with energy level of 2.8 eV below the SiO_2 conduction band has been identified so far. However, there are indications of electron transitions from Si into oxide defects occurring at high fields: One, there is a noise in the inversion n channel of MOS transistors ascribed to trapping of electrons by oxide defects [18]. Two, neutralization of the positive charge of holes trapped near the Si/SiO_2 interface was ascribed [19] to tunneling of electrons to a level 6.3 eV above the valence band of SiO_2, i.e., 2.6 eV below the oxide conduction band. Three, Si-implanted SiO_2 layers show accumulation of negative charge after application of an electric field, and an effective barrier height for the electron-defect tunneling [20] of 3 eV. In addition, there is the interesting observation that optical detrapping of electrons in buried oxides shows an energy threshold [21] of 2.8 eV, the same as measured in present work. Noteworthy is that all these works relate the observed defects to the oxygen deficiency (excess Si) of SiO_2. While the correlation between these phenomena and the PST current is a matter for future research, it is likely that the defects isolated in the present study are involved not only in the oxide conductance, but in a broad spectrum of other physical effects as well.

In conclusion, the PST is demonstrated to be a powerful tool for characterizing insulator defects in semiconductor-insulator structures with the energy levels outside the semiconductor band gap. Evidence is presented for the existence of interface electron states in SiO_2 with the energy levels in the upper part of the SiO_2 band gap. Both PST and photoionization experiments refer to the universality of these defects over various SiO_2 layers on Si and SiC; the energy level of the negatively charged state is found to be 2.8 eV below the SiO_2 conduction band. The trap mediated electron injection into SiO_2 correlates with the density of these defects, which, in turn, appears correlated with the oxygen deficiency of SiO_2. These correlations point to the unveiled defects as a probable origin of dielectric failure of SiO_2. "Universal" presence of these defects is likely dictated by the SiO_2-semiconductor interface formation in addition to the particular way the SiO_2 network adapts to the substrate lattice. Tracing this intricate relationship, together with the defect identification, must await the help of other techniques with structural and chemical atomic sensitivity.

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