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LETTER TO THE EDITOR

Photon-stimulated tunnelling of electrons in SiO_2: evidence for a defect-assisted process

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Abstract. Photon-stimulated tunnelling (PST) of electrons at Si–SiO_2 and SiC–SiO_2 interfaces is shown to be insensitive to the density and energy distribution of electrons in the semiconductors. Instead, the observed relation of PST to the type of the oxide layer indicates a defect level in the oxide as the initial state of electrons contributing to PST. The defect's energy level was found to be positioned 2.8 eV below the conduction band of SiO_2, the defect density increasing with silicon enrichment of the SiO_2. The observed correlation between PST yield and dark conductance of the oxide suggests the isolated defect states to be involved in the high-field electron transport of SiO_2 layers.

The wide bandgap and outstanding purity of SiO_2 layers produced by thermal oxidation of silicon make these about the best insulating films known to date. With the present microelectronic technology demands driving the thickness of SiO_2 down to the nanometre range, 'ideal' insulating behaviour becomes even more crucial. Injection of electrons in SiO_2 layers is routinely considered to be band-to-band tunnelling or over-barrier transport of electrons excited from the bulk bands of silicon [1]. However, observations of low-field conductance [2], current fluctuations [3], stress-induced leakage currents [4, 5], and early breakdown [6] phenomena rather suggest defect-dominated conductance of the metal-oxide–semiconductor (MOS) structures with ultrathin oxides. Thus, questions arise about future applicability of thermal SiO_2 as the preeminent gate insulator when its thickness approaches the thickness of the interfacial Si–SiO_2 transition layer [7].

In qualifying this quest, at least one problem arises due to the lack of adequate physical tools to characterize the defects assisting electron injection into SiO_2. Obviously, defect-dominated conduction requires a higher probability for electron transition via defects than for direct transport between the Si and SiO_2 conduction bands. In the former case, the energy of the electron in the defect state may be above the bottom of the Si conduction band, but can be populated when shifted to below the Si Fermi level by an electric field in the oxide. This makes the defect levels hard to detect by conventional capacitance or conductance methods which lose sensitivity at high fields [1]. Therefore, a transport analysis based on photon-stimulated tunnelling (PST) of electrons has been carried out in this work. We will show a relationship of the electron PST to the near-interfacial oxide defects, which in turn correlates with the electrical conduction behaviour of SiO_2 layers. The ability of the PST technique to monitor these centres provides a new powerful tool for SiO_2–semiconductor interface analysis.

Samples used were prepared by thermal oxidation of (100) and (111) Si or (0001) hexagonal SiC (4H, 6H polytypes, Si face) samples. Ultrathin oxides (5 nm thick) on Si

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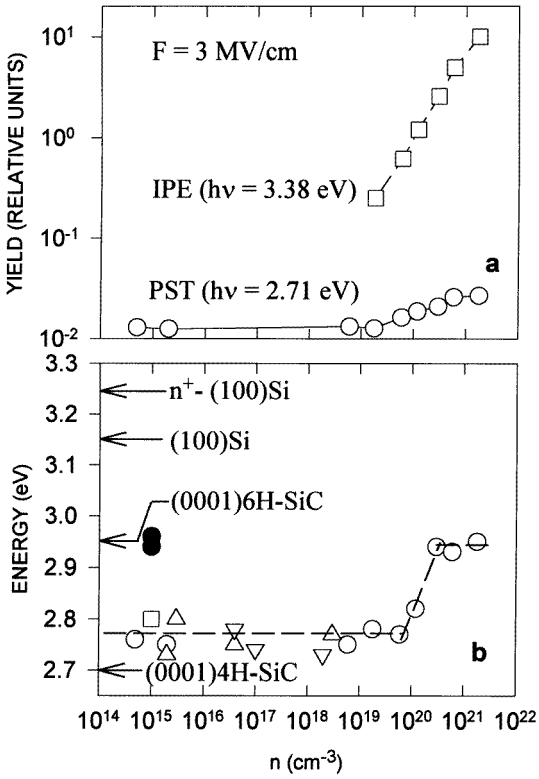

Figure 1. (a) Relative yield of PST (circles) and IPE (squares) at the interfaces of SiO_2 (thick oxides) with (100) Si of different nominal electron concentrations. (b) Energy E_B of the initial state of PST transitions measured relative to the conduction band of SiO_2 at the interfaces with (100) Si (○), (111) Si (□), (0001) 6H-SiC (△) and (0001) 4H-SiC (▽) with different nominal concentrations of electrons in the substrate. Open symbols refer to thick oxides and filled circles represent 5 nm thick oxides on (100) Si. The arrows indicate the conduction band offsets at the corresponding interfaces as determined from IPE spectroscopy. Lines are guide to the eye.

were grown in $N_2 + 10\%$ O_2 at 850 °C, or in pyrogenic H_2O at 700 °C, while 25–66 nm thick oxides were grown at 1000 °C in dry O_2. The concentration of electrons in these samples (doping level) was varied from $n = 3 \times 10^{14}$ to $n \sim 3 \times 10^{21}$ cm^{-3} by implanting P prior to oxidation. Oxides on SiC (25–90 nm thick) were grown using a technology described elsewhere [8]. For the sake of comparison, SiO_2 layers produced in (100) Si by implantation of oxygen ions and subsequent high-temperature anneal were studied as well. Details of the latter preparation have been published elsewhere [9]. MOS structures were prepared by evaporation of semitransparent (13 nm thick) gold electrodes of 0.5 mm^2 area onto the oxide.

PST was studied 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 $h\nu = 2.41$–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 (2.8–5.5 eV) [10]. The relative electron yield

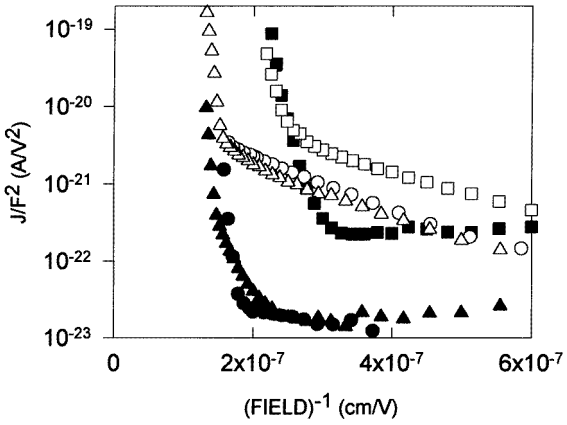

Figure 2. An FN plot of the dark (filled symbols) and PST ($h\nu = 2.71$ eV; open symbols) I–V curves of 52 nm thermal oxide (circles), 360 nm oxide produced by oxygen ion implantation in Si (squares), and 5 nm thermal oxide (triangles). All structures are prepared on (100) Si substrates.

(Y) of PST and IPE was calculated from the photocurrent normalized to the incident light power.

The IPE and PST yield at the (100) Si–SiO_2 interface (oxide thickness >25 nm) is shown in figure 1(a) as a function of nominal bulk electron concentration n in Si for a fixed electric field strength ($F = 3$ MV cm^{-1}) in the oxide. It is seen that the IPE yield increases nearly proportionally with n, bearing out the conduction band of Si as the source of electrons. By contrast, the PST yield and n appear uncorrelated as the PST yield increases only by a factor of two to three when n increases by two orders of magnitude. At the same time, both the IPE and PST yield were found to be independent of the light intensity in the power range studied, revealing first-order processes in both cases.

Following previous researchers [11–13], the dependence of the PST yield on photon energy (not shown) were fitted as $Y/F^2 = A\exp[-6.83\times10^7(m_{ox}/m_0)^{1/2}(E_B - h\nu)^{3/2}F^{-1}]$, where A is a constant, $m_{ox} = 0.5m_0$ 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 SiO_2 conduction band. A and E_B are the adjustable parameters. E_B is found to be field independent in the range $F = 2$–6 MV cm^{-1}; an average is plotted for different structures in figure 1(b) as a function of n. A remarkable observation is that we found an identical $E_B = 2.77 \pm 0.05$ eV for all low-doped Si and SiC thick oxide structures. In the 5 nm oxides on (100) Si and those formed on heavily doped n-type Si, by contrast, E_B increases by approximately 180 meV. For reasons of comparison, the conduction band offsets at the Si–SiO_2 and SiC–SiO_2 interfaces as determined by IPE are indicated in the same figure by arrows [10]. A shift of the IPE threshold in the heavily doped n-Si was observed previously [14], and ascribed to Si bandgap narrowing. Note that the measured E_B value is the same for Si and SiC MOS structures despite the ~ 0.5 eV difference in conduction band offset at the (100) Si–SiO_2 and (0001) 4H-SiC–SiO_2 interfaces: this indicates there is no direct relationship of the initial state of electrons involved in PST to the spectrum of electron states in the semiconductor.

Figure 2 presents a Fowler–Nordheim (FN) plot of the PST ($h\nu = 2.71$ eV; open symbols) and dark (filled symbols) current–voltage (I–V) characteristics of 52 nm thermal

oxide (circles), 360 nm oxide produced by O^+ ion implantation into Si (squares), and the ultrathin 5 nm thermal oxide on (100) Si (triangles). The dark conductivity of the oxide formed by ion implantation is enhanced by excess silicon present in the oxide, and the onset of the FN behaviour shifts to lower fields as compared to thermal SiO_2 due to trap-assisted electron tunnelling [15]. It is noteworthy that the PST I–V curve of the ion-implanted structure (open squares) is also positioned above those of thermally grown oxides, showing an increase in PST current correlated with the increase in dark current; this again, is associated with trap-assisted transitions. Comparing the dark I–V curves of the 52 and 5 nm thick oxides reveals an earlier onset (lower field) of the tunnelling current in the ultrathin oxide, which is ascribed in the literature to trap-assisted direct tunnelling of electrons from Si into the metal [5]. In the same electric field range, with increasing values, the PST I–V curve of 5 nm oxides starts to deviate from the FN dependence, which may indicate the involvement of the same defects in the trap-assisted tunnelling in ultrathin oxides and PST. Apparently, field-assisted population of the defects with electrons governs the increase of both dark and PST currents.

Previously, it has been assumed that the PST, like the dark tunnelling, is related to the electrons in the Si accumulation (inversion) layer [13]. In contrast, the present results indicate that the PST characteristics are mainly controlled by the properties of the oxide, showing no relationship either with the density of electrons or their energy distribution in the substrate. Thus, there must be another source of electrons for the PST current, namely, defects in the near-interfacial oxide layer. The observation of FN type I–V curves, the linearity of the PST current as a function of the light intensity, and its weak temperature dependence (the current decreases about two to threefold when cooling the (100) Si MOS structure from 300 to 77 K, which is comparable to the dark-tunnelling behaviour of electrons from Si into SiO_2 [16]) reveals the process of PST of electrons from defect levels into the SiO_2 conduction band as the rate limiting process.

The observed PST currents are stable in time except for a slow decay associated with trapping of electrons in the oxide, which is independently detected by the attendant shift of the capacitance–voltage curves. In order to maintain a constant current of defect depopulation, they must be located in vicinity of the Si–SiO_2 interface: only the near-interfacial states can be rapidly refilled by electrons from the substrate. The shift of the initial energy level E_B in the heavily doped Si structures and in those with ultrathin oxides (figure 1(b)) refers to the proximity of a conductive (n^+-Si or Au) electrode as originating this (the fact that about the same numerical values are found is probably coincidental). Probably, this is related to the image-force lowering of the energy level of an electron trapped by a neutral centre. Taking the static relative permittivity of SiO_2 as 3.9 [1], a 180 meV image potential would correspond to a silicon substrate–trap distance of 1.6 nm. Thus, the states will be readily filled by electron tunnelling when shifted below the Si Fermi level, which is consistent with the observed absence of limitation in PST current up to a density of 10^{-6} A cm^{-2}.

The atomic nature of the interfacial oxide defects observed in the PST experiments is still unclear at present; to our knowledge, no defect with an energy level 2.8 eV below the SiO_2 conduction band has been identified yet. The increase of the PST signal in oxygen-deficient oxides produced by oxygen implantation would point to a centre related to excess silicon. Importantly, investigation of the photo-ionization of defects in these oxides reveals a threshold for optical excitation of electrons of $\sim$ 2.8 eV [17], that is, coinciding with the energy level of the initial state of PST. Moreover, the absence of a shift of the energy with changing size of Si inclusions refers to a relationship of the 2.8 eV level to a localized electron state at a defect in SiO_2. At this point, it is interesting to remark that silicon

enrichment of the oxide may also be achieved by implanting Si^+ ions. Investigation of such oxides has shown generation of both electron and hole traps, which have been assumed to originate from one type of amphoteric defect associated with Si–Si linkages in the oxide [18]. The energy barrier for electron transition to the neutral trap has been estimated as 2.97 eV, which is close to the value measured in the present study. However, an immediate association of this energy value with the energy level of the defect is doubtful, because the $Si–SiO_2$ conduction band offset has been estimated in [18] to be nearly the same (2.95 eV). Thus, it is hard to distinguish between the trap filling by direct tunnelling of an electron from Si into the trap, and an electron tunnelling to the oxide conduction band followed by a trapping event. In any case, the relation of electron traps to the Si enrichment of the oxide seems to be independent of the excess Si incorporation mechanism.

Silicon enrichment of the oxide near the $Si–SiO_2$ interface is usually expected [7], which would cause trapping of electrons from the Si substrate when the energy level of oxide traps is shifted below the Fermi level of Si by the applied electric field. There are two pertinent experimental results in favour of trapping processes when high electric fields are present at the $Si–SiO_2$ interface: (i) there is a noise in the inversion n-channel of MOS transistors ascribed to trapping of electrons by oxide defects [19]; (ii) neutralization of the positive charge (holes) trapped near the $Si–SiO_2$ interface may be described as tunnelling of electrons to a level 6.3 eV above the valence band of SiO_2 [20], i.e., 2.6 eV below the oxide conduction band. Noteworthy here is the fact that the authors of both works relate the observed effects to electron trapping by oxygen vacancies in the near-interfacial SiO_2 layers. While the correlation between these phenomena and the PST current is a matter for future work, it cannot be excluded that the defects isolated in the present study may be involved not only in the oxide conductance, but in other electrical phenomena as well.

In conclusion, we have demonstrated a relationship of photon-stimulated tunnelling of electrons at the $Si–SiO_2$ and $SiC–SiO_2$ interfaces to defects in the near-interfacial oxide layer. These defect generally have an energy level 2.8 eV below the conduction band of SiO_2 and may be related to the oxygen deficiency of near-interfacial SiO_2. The universality of this observation is remarkable. Correlation between photon-simulated tunnelling and the conductance of the oxide layers suggests involvement of the revealed centres in the high-field electrical phenomena in the oxide. Thus, PST is herewith advanced as a powerful new tool for characterization of the oxide defects at the SiO_2–semiconductor interfaces.

References

[1] Sze S M 1981 *Physics of Semiconductor Devices* 2nd edn (New York: Wiley)
[2] Depas M, Vermeire B, Mertens P W and Heyns M M 1995 *Microelectron. Eng.* **28** 125
[3] Andersson M O, Farmer K R and Engstrom O 1992 *J. Appl. Phys.* **71** 1846
[4] Maserjian J and Zamani N 1982 *J. Appl. Phys.* **53** 559
[5] Di Maria D J 1995 *Microelectron. Eng.* **28** 63
[6] Di Maria D J 1996 *Appl. Phys. Lett.* **68** 3004
[7] Sofield C J and Stoneham A M 1995 *Semicond. Sci. Technol.* **10** 215
[8] Afanas'ev V V, Stesmans A, Bassler M, Pensl G, Schulz M J and Harris C I 1996 *Appl. Phys. Lett.* **68** 2141
[9] Afanas'ev V V, Revesz A G and Hughes H L 1996 *J. Electrochem. Soc.* **143** 695
[10] Afanas'ev V V, Bassler M, Pensl G, Schulz M J and Stein von Kamienski E 1996 *J. Appl. Phys.* **79** 3108
[11] Snow E H 1967 *Solid State Commun.* **5** 813
[12] Weinberg Z A and Hartstein A 1976 *Solid State Commun.* **20** 179
[13] Weinberg Z A and Hartstein A 1983 *J. Appl. Phys.* **54** 2517
[14] Goodman A M 1966 *Phys. Rev.* **152** 720
[15] Revesz A G, Brown G A and Hughes H L 1993 *J. Electrochem. Soc.* **140** 3222
[16] Lenzlinger M and Snow E H 1969 *J. Appl. Phys.* **40** 278

[17] Afanas'ev V V, Revesz A G, Jenkins W and Hughes H L 1995 *Proc. 1995 IEEE Int. SOI Conf. (Tucson, AZ, 1995)* (Piscataway, NJ: Institute of Electrical and Electronic Engineers, Inc) p 102
[18] Kalnitsky A, Ellul J P, Poindexter E H, Caplan P J, Lux R A and Boothroyd A R 1990 *J. Appl. Phys.* **67** 7359
[19] Fleetwood D M and Scofield J H 1990 *Phys. Rev. Lett.* **64** 579
[20] Schmidt M and Koster H 1992a *Phys. Status Solidi* b **172** 53
Schmidt M and Koster H 1992b *Phys. Status Solidi* b **174** 403