



Thermally activated electron capture by mobile protons in SiO 2 thin films

K. Vanheusden, S. P. Karna, R. D. Pugh, W. L. Warren, D. M. Fleetwood, R. A. B. Devine, and A. H. Edwards

Citation: Applied Physics Letters **72**, 28 (1998); doi: 10.1063/1.121447 View online: http://dx.doi.org/10.1063/1.121447 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/72/1?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Exoelectron emission spectroscopy of silicon nitride thin films Appl. Phys. Lett. **80**, 2743 (2002); 10.1063/1.1469656

Localized charge injection in SiO 2 films containing silicon nanocrystals Appl. Phys. Lett. **79**, 791 (2001); 10.1063/1.1383574

Thermal stability of a- SiN x : H films deposited by plasma electron cyclotron resonance J. Vac. Sci. Technol. A **17**, 1280 (1999); 10.1116/1.582110

Coupled charge trapping dynamics in thin SiO 2 gate oxide under Fowler–Nordheim stress at low electron fluence J. Appl. Phys. **83**, 2662 (1998); 10.1063/1.367029

Recovery of time-dependent dielectric breakdown lifetime of thin oxide films by thermal annealing J. Appl. Phys. **82**, 3462 (1997); 10.1063/1.365662



Thermally activated electron capture by mobile protons in SiO₂ thin films

K. Vanheusden,^{a)} S. P. Karna, and R. D. Pugh

US Air Force Phillips Laboratory, Space Mission Technologies Division, Kirtland Air Force Base, New Mexico 87117-5776

W. L. Warren^{b)} and D. M. Fleetwood Sandia National Laboratories, Albuquerque, New Mexico 87185-1349

R. A. B. Devine

France Télécom/CNET, B.P. 98, Meylan Cedex, France

A. H. Edwards

Department of Electrical Engineering, University of North Carolina, Charlotte, North Carolina 28223

(Received 22 September 1997; accepted for publication 31 October 1997)

The annihilation of mobile protons in thin SiO₂ films by capture of ultraviolet-excited electrons has been analyzed for temperatures between 77 and 500 K. We observe a strong increase in proton annihilation with increasing temperature, and derive an activation energy for electron capture of about 0.2 eV. Based on quantum chemical $[(OH)_3Si]_2$ —O—H⁺ cluster calculations, we suggest photoexcitation of electrons from excited vibrational states of the ground electronic (valence band) state to a nearby excited electronic (SiO₂ gap) state. It is argued that the latter excitation can result in H⁰ formation at elevated temperatures. © *1998 American Institute of Physics*. [S0003-6951(98)01301-1]

In the field of microelectronics, hydrogen is used industrially to passivate dangling silicon bonds or "interface traps" which are present at the SiO₂/Si substrate interface.^{1–4} If atomic hydrogen is present in the SiO₂, it can also depassivate the interface by "gettering" of the bonded hydrogen to form H₂.⁵ Protons can perform a similar function as has been demonstrated in postirradiation and hot-carrier induced interface trap buildup experiments.^{6–10} Here, protons generated during irradiation or hot-carrier stress (from hydrogen present in the SiO₂) drift towards the SiO₂/Si interface where they presumably capture an electron and transform to H⁰ which can depassivate an adjacent bonded hydrogen. Unlike atomic H⁰ motion in SiO₂, which has a thermal activation energy of 0.18 eV,¹¹ protons have a much larger activation energy for drift (diffusion) of about 0.8 eV.¹²

In the present letter, we compare the electron trapping properties of both trapped holes and mobile protons in the SiO₂ network. Instead of using irradiation or high-field stress, we generate the protons in the SiO₂ via a hydrogen anneal technique.¹³ Two different buried oxide materials were used: separation by implantation of oxygen (SIMOX), obtained by implanting 1.8×10^{18} O⁺ cm⁻² with an energy of 190 keV into p-type Si(100) wafers followed by annealing for 6 h at 1320 °C in an atmosphere of Ar+1% O₂, and zone-melt-recrystallization (ZMR) material in which thermally grown SiO₂ ($\approx 1 \ \mu m$ thick) is covered with a film of polycrystalline Si which is then zone-melt recrystallized. We have previously demonstrated¹³ that, if these structures are heated to temperatures above 450 °C in forming gas $(N_2+5\% H_2)$, mobile protons appear spontaneously in the buried SiO₂ network. Following the anneal, the top oxide surface was bared by removing the superficial Si layer in a KOH etch solution. To perform hole injection into these oxides, identical samples (except for the forming gas anneal) were bared by KOH etch and then positive corona ions were deposited on the oxide surface. During irradiation with vacuum ultraviolet light (E=10 eV, $>\text{SiO}_2$ band gap), holes were photoinjected from the surface into the oxide where they can become trapped.

Electrons are photoexcited from the SiO₂ valence band into the oxide gap (see discussion below) by exposing the oxide to sub-band gap ($\leq 6 \text{ eV}$) ultraviolet (UV) light at a fixed temperature between 77 and 500 K without applying an external bias. Prior to the subgap UV exposure, the oxide contained either trapped holes or mobile protons, with similar densities ($\approx 2 \times 10^{12} \text{ cm}^{-2}$).

The net charge within the oxide layers was derived from midgap voltage shifts at room temperature using a standard metal-oxide-semiconductor (MOS) capacitance experiment in which a metal electrode is formed on the bared oxide surface (a mercury bead, contact area $\approx 1 \text{ mm}^2$) and the capacitance is measured at a frequency of 1 MHz as a function of applied dc bias across the capacitor. Since the protons are very mobile at room temperature and move in the presence of an applied electric field, a reversible shift is observed in the capacitance-voltage (C-V) curves which can be directly linked to the areal density of protons. These were the only positively charged entities observed with a significant density in the protonated samples.

Figure 1 shows the areal density of mobile protons in the SiO_2 layer (relative to the initial density) as a function of UV exposure time at 77 and 295 K. We observe that, if the protonated sample is exposed to UV at room temperature, the mobile protons are being annihilated. Similar UV exposure carried out at 77 K results in *no* annihilation of protons or charge compensation (electron trapping). These results were reproduced on several different samples. The observed temperature dependence of the H⁺ concentration is not caused

^{a)}Electronic mail: karel@unm.edu

^{b)}Present address: Defense Advanced Research Projects Agency, Arlington, VA 22203.



FIG. 1. Mobile H⁺areal density in the 1 μ m SiO₂ layer of ZMR material, relative to the initial H⁺ density of 2×10¹² cm⁻², plotted as a function of 5 eV UV illumination time at 77 and 295 K. The areal density was obtained from the hysteresis of the *C*-*V* curves. A similar plot for 2×10¹² cm⁻² trapped holes in an identical sample and under identical UV-illumination conditions is shown in the inset.

by direct out diffusion of protons from the oxide since no decrease in proton density was observed in a reference sample that was not exposed to the UV source. In the inset of Fig. 1, we show the result for an identical experiment performed on samples not subjected to the protonation anneal but injected with a comparable density of holes prior to the electron excitation under UV exposure. Here we clearly observe that holes are similarly annihilated by electrons at both 77 and 295 K, in agreement with previous results.¹⁴ We also observe from Fig. 1 that at room temperature there is a dramatic difference in efficiency of hole annihilation during electron injection as compared to proton annihilation. The process would appear to be, in terms of illumination time, about 100 times more efficient for hole annihilation.

In SiO₂ both holes and protons may be expected to act as Coulombic attractive centers for electrons. The significant differences between the annihilation of protons versus trapped holes as shown in Fig. 1 must therefore be intimately related to the detailed electron trapping mechanism. It is most likely that the electrons available for capture are photoexcited from the SiO₂ valence band during UV exposure. A similar mechanism has been suggested by Devine and Francou¹⁵ in bulk SiO₂. Electron injection from the Si substrate into the oxide seems very unlikely since no change in the net oxide charge is observed in the 77 K experiment.

The observed temperature dependent proton annihilation as opposed to the trapped hole annihilation is most likely intimately related to the way the proton is bonded to the SiO₂ network and how the hydrogen, which results from the proton capturing an electron, escapes this bonding. It has been suggested that H⁺ motion in the SiO₂ network occurs by hopping between neighboring O atoms, by forming temporary bonds to the lone pair orbitals of the bridging O atoms (Si—O—Si), resulting in a positively charged, overcoordinated O (Si₂O—H)⁺.⁷ To gain more insight into the microscopic mechanisms involved in the electron capture process, *ab initio* quantum chemical calculations were performed on



FIG. 2. Potential energies for $(OH)_3Si$ —O—Si $(OH)_3$ precursor clusters, as a function of Si₂O—H⁺ bond length. The lowest curve is for the bonding state and was obtained from *ab initio* quantum chemical calculations (Ref. 16). The upper curve is for the antibonding orbital, largely localized at the H site, and is only schematic (not calculated). The left arrow shows an optical transition from the vibrational ground state to the dissociative state. The right arrow shows an optical transition with the same photon energy but from a higher vibrational state, resulting in excess kinetic energy.

the interaction of H^0 and H^+ with the bridging oxygen in the SiO₂ network. An (OH)₃Si-O-Si(OH)₃ precursor cluster was used, with a fixed geometry obtained from ab initio restricted Hartree-Fock optimization.¹⁶ It is possible to explain the temperature dependent proton annihilation by examining the O-H⁺ vibrational levels and the different electronic states of this cluster. The lower curve in Fig. 2 is the calculated potential energy as a function of O-H⁺ bond length for the $[(OH)_3Si]_2$ —O—H⁺ cluster, taken from Ref. 16. This curve has a minimum at $R_{\Omega-H} \approx 1$ Å.¹⁶⁻¹⁸ The calculations further show that the highest occupied molecular orbital for this system corresponds to a bonding O—H⁺ orbital, whereas the lowest unoccupied orbital is an antibonding orbital, largely localized at the H site. Hence, a repulsive curve (not calculated) can be associated with this excited state, as shown schematically in Fig. 2. Our model assumes that the UV exposure causes optical excitation between these curves, which can result in a hole in the valence band and a neutral H atom. The hole is mobile and is repelled from the oxide by the remaining protons. It is clear from Fig. 2 that vibrational excitations (stretching of the O—H⁺ bond) result in a significant lowering of the photon energy required for excitation to occur. If we assume that the transition from the vibrational ground state (Frank-Condon transition) requires a photon of the order of 6 eV (upper energy limit of the UV photons), proton annihilation would be very unlikely at low temperatures, in agreement with the observations. Furthermore, if the photon energy is very close to the Frank-Condon transition energy, the neutral hydrogen atom which results from the optical transition at low temperatures would have very little kinetic energy, and would take a significant amount of time to escape. During that time, the excited electron may undergo a radiative decay back to the valence band before the hydrogen atom leaves the vicinity of the nearby oxygen atom. However, at higher temperatures, the optical transition is likely to originate from a higher vibrational state. Moreover, because of the slope of the dissociative curve, the optical excitation would place the resulting hydrogen atom in a region of much higher kinetic energy, as can be seen in Fig. 2. This situation would significantly enhance the probability that the H atom could escape before radiative decay occurs. The proposed reaction mechanisms are summarized in the following reaction scheme:

$$(\text{Si}_{2}\text{O}-\text{H})^{+} + e^{-} + h^{+} \xrightarrow{\alpha} (\text{Si}_{2}\text{O}-\text{H})^{*} + h^{+} \xrightarrow{\nearrow} \gamma$$

$$(\text{Si}_{2}\text{O}-\text{H})^{*} + h^{+} \xrightarrow{\swarrow} \beta$$

$$(\text{Si}_{2}\text{O}+\text{H}^{0,7} + h^{+,7}, \gamma)$$

where α is the rate for electron capture resulting in the formation of a neutral overcoordinated O site $(SiO_2-H)^*$, which is unstable, β is the rate for dissociative decay resulting in the release of a neutral H⁰, and γ is the rate for radiative decay resulting in the initial positively charged state. Little can be said about any temperature dependence of γ since this is a spontaneous decay depending only upon rapid electron-hole recombination, α and β , however, are expected to be temperature dependent, as discussed above. It is beyond the scope of this work to derive an actual equation for the temperature dependence of the [H⁺] decay rate. As a first approximation, a single thermal activation energy process can be defined by assuming a simple Arrhenius dependence:

$$\frac{-1}{[\mathbf{H}_0^+]} \frac{d[\mathbf{H}^+]}{dt} = \kappa \, \exp\left(-\frac{E_a}{k_B T}\right),\tag{2}$$

where $[H^+]$ is the areal proton density in the SiO₂ film and the subscript "O" indicates the initial value, κ is the rate constant, E_a is the activation energy, k_B is the Boltzmann's constant, and *T* is the absolute temperature. To determine E_a for the process, the quantity on the left-hand side in Eq. (2) was measured at various temperatures. Figure 3 shows the Arrhenius plot. From this plot, a thermal activation energy $E_a \approx 0.2 \pm 0.1$ eV was obtained for H⁺ annihilation (H⁰ formation) under UV exposure in SiO₂.

It has been shown that one can detect H^0 in SiO₂ using electron paramagnetic resonance (EPR).¹⁸ However, we did not observe any H^0 EPR signal after UV exposure of the protonated oxide layers over the entire temperature range. This can be explained by the fact that the activation energy for electron capture E_a that we derived here (0.2 eV) is similar to the activation energy for H^0 diffusion in SiO₂.¹³ As a result, H^0 formation—like H^0 diffusion—occurs very slowly at 77 K, while at higher temperatures, once H^0 is formed by electron trapping, it can diffuse and will dimerize with another $H^{0, 19}$ thus escaping EPR detection.

In summary, we have studied the temperature dependence of photoinduced H^+ annihilation in protonated SiO₂ thin films. We observe that the proton annihilation during UV exposure strongly increases with increasing substrate temperature. An Arrhenius expression for the H^+ annihilation yields a thermal activation energy of 0.2 eV. Based on first-principles quantum chemical calculations, a model is proposed for proton annihilation by photoexcitation of electrons from the SiO₂ valence band. The model suggests that, compared to the ground level, higher vibrational levels of the $(O-H)^+$ bond are more likely to trap electrons, and the remaining kinetic energy facilitates dissociation before elec-



FIG. 3. Arrhenius plot of the normalized initial rate of proton decay in SiO_2 during UV exposure. The values were obtained by taking the initial slope of the [H⁺] decay curves like the ones shown in Fig. 1 at various temperatures. The line is a linear least squares fit to the data.

tronic deexcitation can occur. In order to provide more quantitative support for this model, calculations of the excited state and transition probability are underway.

The part of this work performed at Sandia National Laboratories (SNL) was supported by the U.S. Department of Energy (DOE) under Contract No. DE-AC04-94AL85000, and by the Defense Advanced Research Projects Agency. SNL is operated by Sandia Corporation, a Lockheed Martin Company, for DOE.

- ¹E. H. Poindexter, Semicond. Sci. Technol. 4, 961 (1989).
- ²K. L. Brower, Phys. Rev. B **42**, 3444 (1990).
- ³E. Cartier, J. H. Stathis, and D. A. Buchanan, Appl. Phys. Lett. **63**, 1510 (1993).
- ⁴A. Stesmans, Phys. Rev. Lett. **70**, 1723 (1993).
- ⁵J. H. Stathis and E. Cartier, Phys. Rev. Lett. 72, 2745 (1994).
- ⁶P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. **50**, 3492 (1979).
- ⁷F. B. McLean, IEEE Trans. Nucl. Sci. NS-27, 1651 (1980).
- ⁸D. J. DiMaria, J. Appl. Phys. **68**, 5234 (1990).
- ⁹N. S. Saks and R. W. Rendell, Appl. Phys. Lett. 61, 3014 (1992).
- ¹⁰ R. E. Stahlbush, A. H. Edwards, D. L. Griscom, and B. J. Mrstik, J. Appl. Phys. **73**, 658 (1993).
- ¹¹D. L. Griscom, J. Appl. Phys. 58, 2524 (1985).
- ¹²S. R. Hofstein, IEEE Trans. Electron Devices ED-14, 749 (1967); P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, IEEE Trans. Nucl. Sci. NS-35, 1168 (1988).
- ¹³ K. Vanheusden, W. L. Warren, D. M. Fleetwood, J. R. Schwank, P. S. Winokur, R. A. B. Devine, and Z. J. Lemnios, Nature (London) **386**, 587 (1997).
- ¹⁴J. M. Aitken and D. R. Young, J. Appl. Phys. 47, 1196 (1976).
- ¹⁵R. A. B. Devine and J.-M. Francou, Phys. Rev. B 41, 12 882 (1990).
- ¹⁶A. M. Ferreira, S. P. Karna, C. P. Brothers, R. D. Pugh, B. K. Singaraju, K. Vanheusden, W. L. Warren, and R. A. B. Devine, in *Amorphous and Crystalline Insulating Thin Films*, edited by W. L. Warren, R. A. B. Devine, M. Matsumura, S. Cristoloveanu, Y. Homma, and J. Kanicki (Materials Research Society, Pittsburgh, 1997), Vol. 446, p. 187.
- ¹⁷A. H. Edwards, J. A. Pickard, and R. E. Stahlbush, J. Non-Cryst. Solids 179, 148 (1994).
- ¹⁸J. Robertson, in *Physics and Technology of Amorphous SiO*₂, edited by R. A. B. Devine (Plenum, New York, 1988), p. 91.
- ¹⁹K. L. Brower, P. M. Lenahan, and P. V. Dressendorfer, Appl. Phys. Lett. 41, 251 (1982).