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IRRADIATION RESPONSE OF MOBILE PROTONS IN BURIED SIO$_2$

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35-word abstract

Trapping of mobile protons is observed in various SOI materials, but only upon irradiating under a positive top Si bias. Thermal detrapping shows that the proton traps are shallow and located near the substrate Si/SiO$_2$ interface.

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I. INTRODUCTION

Due to the high-temperature formation anneal, the buried oxide of SOI materials has been shown to have significantly more electron and hole traps than standard thermally grown SiO_2 [1,2]. It has been found that annealing of SOI material in a hydrogen containing ambient above 500 °C can generate both fixed and mobile positive charges in the buried oxide layer. The fixed positive species are located near the interfaces and have been attributed to over-coordinated oxygen sites induced by interaction with hydrogen [3]. The mobile species have been identified as protons imprisoned inside the buried oxide layer. A novel nonvolatile memory device has been demonstrated based on the latter phenomenon [4,5].

In this study we investigate the radiation response of the mobile-proton/buried-oxide system as a function of radiation dose and applied oxide field during irradiation. Our irradiation data show that the initial density of mobile protons in the oxide is not affected by the irradiation. However, if the irradiation is performed under a positive top Si bias, the protons become trapped (immobilized). It is found that irradiation under positive bias activates a proton trap in the buried oxide near the substrate interface. The data provide new insights into both electron trapping by protons and about the distribution of defects in the buried oxide, and may lead to improved techniques for reducing the concentration of buried oxide defects and improving the radiation hardness of buried oxides for nonvolatile memory and other applications [5].

II. EXPERIMENTAL DETAILS

Different types of SOI material were used: (1) standard separation by implantation of oxygen (SIMOX) samples formed by implanting *p*-type Si(100) wafers with 190-keV O^+ ions to a dose of 1.8×10^{18} cm^{-2} followed by a subsequent anneal at 1320 °C in Ar + 1% O_2, resulting in a 150-nm Si layer on top of a 400-nm buried oxide, (2) SIMOX with a supplemental oxygen implantation followed by an anneal at 1100 °C, (3) Unibond® material formed by implanting hydrogen ($\sim 6 \times 10^{17}$ cm^{-2}) into a wafer, below a thermally grown SiO_2 layer (300 nm thick), followed by bonding this wafer to another wafer. Splitting of the first wafer occurs at the boundary defined by the implant. Finally a high temperature anneal at 1100 °C is used to strengthen the bonding interface.

To introduce mobile protons into the buried SiO_2 layer of the $Si/SiO_2/Si$ structures, a forming gas [N_2:H_2; 95:5 (by volume)] anneal was performed at 600 °C for 30 min. Finally, the samples were irradiated using a 10-keV x-ray source at a dose rate of 4 krad(SiO_2)/s. Different buried oxide fields (between -1 and +1 MV/cm) were applied during irradiation. Areal densities of mobile protons and trapped charge in the buried oxide were determined by studying the top-Si threshold voltage shift using pseudo-MOSFET (Ψ-MOSFET) current-voltage (IV) curves [6] measured on devices as shown in the inset of Fig. 1(b). In addition, dual capacitance-voltage (CV) measurements [7] were utilized to characterize both the top and bottom buried-oxide/Si interfaces simultaneously.

III. RESULTS

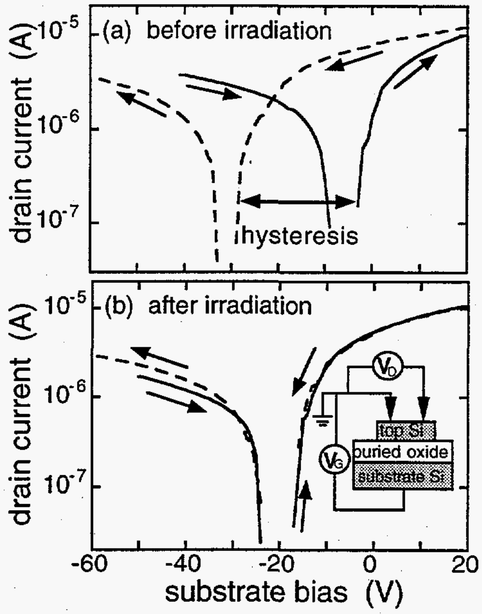

Figure 1. IV curves measured on 600 °C forming-gas annealed SIMOX using point-contact FET devices as shown schematically in the inset. The solid/dashed curves were recorded with an increasing/decreasing substrate (gate) bias, after keeping the bias at -50V/+50 V for 5 min. Curves in (a) were measured before, and in (b) after 100-krad irradiation under +0.5 MV/cm (taken from Ref. 8).

The IV curves in Fig. 1 (a) show the changes in the top-Si threshold voltage shift measured on SIMOX after it received a 600 °C forming gas anneal. The solid curve was recorded with an increasing substrate (gate) bias, after keeping the gate bias at -50 V for 5 min. The dashed curve was recorded using a decreasing gate voltage sweep, after keeping the gate at + 50 V for 5 min. It has been shown in previous work that this reversible threshold voltage shift is caused by mobile H^+ ion drift [4,5]; the positive substrate bias drifts the protons to the top Si interface, and the negative bias drifts them to the substrate interface, resulting in the observed difference in top-Si threshold voltage shift. The amount of reversible threshold voltage shift obtained in this way is directly proportional to the amount of mobile protons in the buried oxide. Figure 1 (b) shows the results of the same measurements as performed in Fig. 1 (a), but here the samples received 100 krad x-rays under a positive top-Si bias (negative substrate bias), prior to the IV measurements. The data show that after irradiation under +0.5 MV/cm oxide field the amount of *mobile* protons in the buried oxide has dropped to zero. Similar effects were observed when looking at SIMOX with a supplemental O implant and Unibond SOI material.

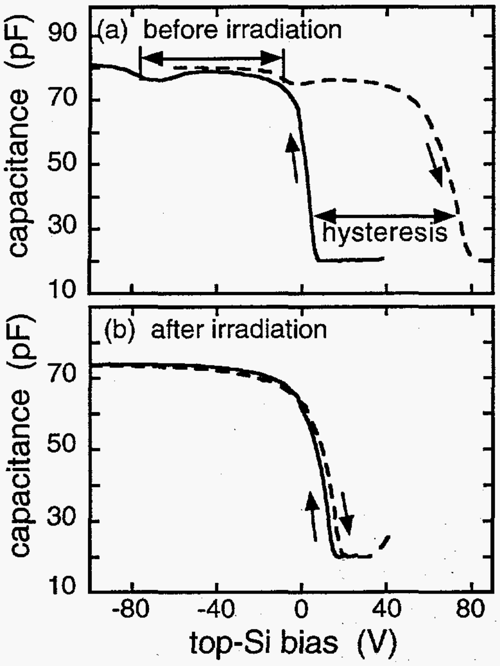

Figure 2. Dual CV curves measured on 600 °C forming-gas annealed Unibond samples. The solid/dashed curves were recorded with an decreasing/increasing (top-Si) bias, after keeping the bias at +50 V/ -50 V for 5 min. Curves in (a) were measured before, and in (b) after 100-krad irradiation under +0.5 MV/cm.

Figure 2 shows dual CV data on Unibond SOI material. The sequence of data acquisition is similar to that in Fig. 1. The dual capacitance goes through two transitions, one at a negative (small step in C) top-Si bias and one at a positive (big step in C) top-Si bias, marking the threshold voltage shift at the substrate and top-Si interface, respectively. Notice that the substrate Si is p-type, while the top Si layer is n-type. Again, the reversible threshold voltage shift in Fig. 2 (a) is caused by mobile proton drift [4,5]. Figure 2 confirms that after the samples received 100 krad x-rays under a positive top-Si, the protons are no longer mobile. In addition, the small shift at the top interface (big step at ≈ +15 V), and the large shift at the substrate interface (small step lower than -100 V, not detected) show that the charge trapping (trapped holes + trapped protons) occurs mainly near the substrate interface.

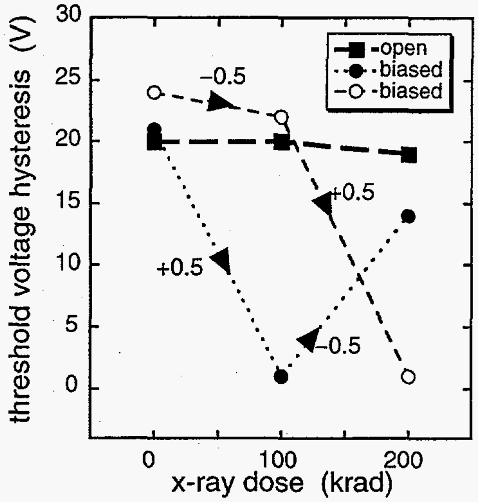

Figure 3. Reversible threshold voltage shift (hysteresis) of the top Si channel as a function of irradiation under different top-Si biases. The oxide fields (MV/cm) applied during the x-ray exposure are indicated next to the curves (taken from Ref. 8).

Figure 3 shows the reversible threshold voltage shift of the top-Si channel as a function of x-ray dose for irradiation under different gate biases. The hysteresis values are obtained from IV curves as described in Fig. 1. One sample was irradiated without any external bias applied, while the two others were exposed under different top-Si biases. The data show that the hysteresis drops to zero after irradiation with a positive top Si bias, in agreement with the data in Fig. 1 and 2. When the sample is subsequently irradiated under negative bias the hysteresis reappears, i.e., the effects of the initial exposure are totally erased. If a negative or no bias is applied during the initial exposure, the hysteresis remains approximately constant. These data show that the protons can become *trapped* as a result of irradiation, but only when a *positive* top Si bias is applied during irradiation. Subsequent exposure under negative bias de-traps the protons and annihilates the proton traps.

To study the dependence of the proton trapping mechanism on oxide field strength, different positive fields were applied during 100-krad irradiation. It was found that fields in excess of +0.2 MV/cm are required to observe any significant proton trapping.

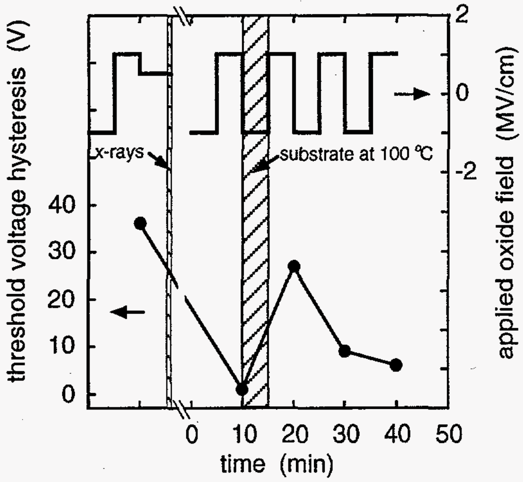

Figure 4. Evolution of threshold voltage hysteresis (●) and applied oxide field (upper curve) vs. time, in Unibond material. The dashed areas mark a 100-krad x-ray irradiation and a 100 °C heat treatment. (taken from Ref. 8)

Dose effects were analyzed by varying the exposure between 0 and 5 Mrad at open bias. Although a large number of electrons is generated during the prolonged exposures, no proton annihilation ($H^+ + e^- \rightarrow H^0$) could be detected at room temperature. To further explore this unexpected result, the temperature dependence of electron capture by protons during UV exposure was analyzed. We observe that the proton annihilation strongly increases with temperature. From an Arrhenius plot for the H^+ annihilation, a thermal activation energy for electron capture by protons of 0.2 eV is derived. First principles quantum chemical calculations were performed on $[(OH)_3Si]_2O—H^+/H^0$ clusters, to obtain potential energy curves as a function of $O—H^+/H^0$ bond length. Using these curves, a potential energy model has been developped which shows that a thermal activation energy (phonon) is required to stretch the $(O—H)^+$ bond to a bond length where the formation of the neutral species becomes energetically more favorable, and permanent electron trapping can occur. This model can explain why no significant proton annihilation is observed, even for irradiation up to 5 Mrad.

To gain more insight into the nature of the radiation induced proton trapping, devices were exposed to 100 krad at +0.5 MV/cm, resulting in trapping of the protons as shown in Fig. 1 and 2, and then heated to 100 °C at -1 MV/cm to release the protons. IV measurements were performed to keep track of mobile and fixed charges. Figure 4 shows how the applied oxide field was varied over time and the points in time when the device was irradiated and heated. The dots in the lower curve show how these treatments affect the reversible threshold voltage shift (i.e., the density of mobile protons) on the same time scale. Figure 4 reaffirms that irradiation under positive bias neutralizes the reversible shift. However, a subsequent heat treatment while applying a negative oxide field re-activates it. This re-activation was not observed when the device was heated under a positive applied field (not shown). The two last data points in Fig. 4 show that the heat induced re-activation is temporary: At room temperature, the hysteresis decreases again over time as the bias is repeatedly switched from negative to positive. These data show that the proton traps are not annihilated because re-trapping of the liberated protons occurs at room temperature.

IV. DISCUSSION

The mobile protons are not readily annihilated by electrons generated during irradiation. Our data show that this does not occur because the electron capture mechanism involves a thermally activated step. However, if irradiation is performed under a positive top Si bias, the protons become trapped (immobilized, not annihilated). The data in Figs. 3 and 4 show that these trapped protons can be released by x-ray exposure or heating to 100 °C under negative top-Si bias. The latter result shows that the proton traps are rather shallow.

The fact that proton trapping occurs under positive field stress (protons drifted to the substrate interface) and de-trapping only occurs while stressing with a negative top Si bias (protons being drifted from substrate to top interface) suggests that the proton traps are mainly located near the substrate interface.

The data in Fig. 1 (b) show that trapping of the protons results in a fixed top-Si threshold voltage shift which was observed to be similar to the shift observed in a control sample which did not contain mobile protons. The ≈ 15 V shift in the top-Si channel threshold voltage in Fig. 1 (b) and 2 (b) is due to trapped holes in the buried oxide. This shift is smaller than the maximum shift before the irradiation. After the protons were released in the heat/negative field stress experiment described in Fig. 4, the top Si threshold voltage shift was observed to increase again. As the top-Si threshold voltage shift is very sensitive to charge in the buried oxide located near the top Si interface, and not sensitive to charge located near the substrate interface, these observations confirm that proton trapping occurs mainly near the substrate interface. The dual CV data in Fig. 2 agree with this asymmetric model. Additional CV data will be presented at the conference. Figure 5 schematically illustrates the effect of irradiation under positive bias, resulting in trapping of the protons, and the subsequent de-trapping due to heating under a negative oxide field.

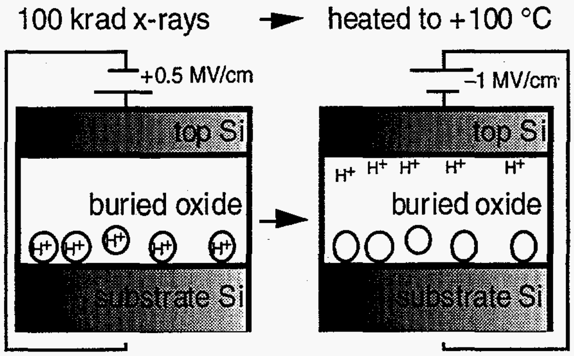

Figure 5. Schematic of protons (H^+) and proton traps (O) in the buried oxide after irradiation under positive bias and after heating under reversed bias. (taken from Ref. 8)

That no proton traps are activated during irradiation under open bias conditions (which favors electron trapping in the buried oxide [2]) indicates that the proton traps are not related to deeply trapped electrons. That no proton traps are activated during irradiation under negative bias is direct evidence for the *asymmetry* of the buried oxide layer: unlike the substrate/buried oxide interface region, the top Si region apparently does not contain a significant density of proton trap precursors. The cause of this asymmetry is still unclear. It may be related to differences in stress near both interfaces (presumably less stress in the SiO_2 near the top Si interface). The nature of the proton trap may be related to the positive fixed oxide charge observed near the Si/SiO_2 interface after forming gas annealing [3].

It is well entrenched in literature that ionizing radiation causes liberation of hydrogen species in the oxide, which can react at the interface [9]. Surprisingly, we do not observe any drastic change in proton density or interface trap density, neither before, nor after irradiation. Additional data and mechanisms will be presented at the conference, addressing these issues.

V. CONCLUSIONS

We observe trapping of mobile protons in the buried oxide of a variety of SOI materials. Trapping occurs during irradiation under positive top Si bias, but not during irradiation in the absence of or under negative bias, providing evidence for the asymmetry of the buried oxide. It is shown that irradiation under positive bias activates a shallow proton trap in the buried oxide near the substrate interface. Additional work (CV, EPR, in combination with etchback) is required to obtain a better insight into the trapping mechanism and the asymmetric distribution of precursors over the buried oxide. These new findings may lead to an improved buried oxide, increased radiation hardness, and reduction of defect precursors.

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