IRRADIATION RESPONSE OF MOBILE PROTONS IN BURIED SiO₂ FILMS

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Abstract

We have performed current-voltage, capacitance-voltage and electron-paramagnetic-resonance (EPR) characterization of silicon-on-insulator (SOI) samples, subjected to a wide variety of irradiation and anneal treatments. By comparing transport properties and interfacial reaction mechanisms, we provide evidence for an intrinsic difference in the response of mobile protons in these oxides, depending on whether they are generated by irradiation or by annealing. A radiation effects study of SOI buried oxides containing annealing induced mobile protons is presented to gain insight into the mechanisms behind these fundamental differences. Electrical characterization shows that, for these devices, the initial interface trap and mobile proton densities are largely unaffected by the irradiation. However, if the irradiation is carried out in the presence of positive bias applied to the top Si, the protons become trapped in shallow levels. These proton traps are activated by the irradiation and are located near the oxide/substrate interface [4]. These results may lead to improved radiation hardness of buried oxides for nonvolatile memory and other applications.

I. INTRODUCTION

Buried oxide layers in SOI materials formed using a high-temperature processing step (>1100 °C) have been demonstrated to contain significantly more electron and hole traps than standard, thermally grown oxides [1-3]. Furthermore, annealing of the structures in a hydrogen containing ambient above 500 °C results in the generation of mobile and/or fixed positive charges in the buried oxide layer. The fixed species are located near the buried oxide/Si interface [4], and have been attributed to over-coordinated oxygen sites induced by interaction with hydrogen [5]. The creation of this fixed charge is significantly enhanced when the hydrogen annealing is performed after the Si overlayer is first etched off. The mobile species, on the other hand, have been identified as protons which are imprisoned inside the buried oxide layer of the Si/SiO₂/Si structure [6,7]. Nonvolatile memory devices have been demonstrated based upon the latter phenomenon [6,7].

Previous studies of time dependent radiation effects at the Si/SiO₂ interface [8-11] have been interpreted in terms of radiation induced generation and transport of mobile protons [9-11]. However, unlike our experiments which demonstrate perfectly reversible field induced proton motion, the radiation effect models involve the generation of protons which lose their charge through interface trap generation when they arrive at the oxide/Si-substrate interface [9-11].

In this study we provide further evidence of the intrinsic difference between the response of radiation induced and H₂ annealing induced mobile protons in the Si/SiO₂ system. We compare the transport properties of the mobile protons in our hydrogen annealed Si/SiO₂/Si samples to those generated by irradiation. Next, the radiation response of SOI buried oxides containing mobile protons generated by moderate temperature annealing in H₂-containing atmospheres was investigated. We have looked at the effects of both radiation dose and applied oxide field during and after irradiation. We also monitored the generation of interface traps at both buried oxide interfaces during these experiments. The data demonstrate that the initial interface trap and proton densities are largely unaffected by the irradiation. However, if the irradiation is carried out in the presence of a positive bias applied to the top Si, the protons become immobilized (trapped). This suggests that proton traps located near the oxide/Si-substrate interface have been activated by the irradiation. Release of the protons can be induced thermally, although the traps themselves are not eliminated. A second irradiation step in the

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presence of a negative bias applied to the top Si is required to release the protons and eliminate the traps.

Finally, we investigated the effect of prolonged field and thermal stressing on the mobile protons generated by hydrogen annealing, and show that no loss of protons and no interface trap generation was observed. We were able to generate significant densities of interface traps in our SOI samples, but only by high-vacuum annealing, showing that the passivated interface traps do not directly react with the mobile protons. Our data demonstrate that the response of mobile protons, generated in high temperature annealed Si/SiO2/Si structures by medium temperature annealing in a H2 containing atmosphere, is fundamentally different from the response of protons in irradiated SiO2.

II. EXPERIMENTAL DETAILS

A variety of different Si/SiO2/Si materials was investigated. SOI materials included: (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 × 1018 cm−2 followed by a subsequent anneal at 1320 °C in Ar + 1% O2, 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 [12] formed by implanting hydrogen (~6 × 1017 cm−2) into a wafer, below a thermally grown SiO2 layer (300 nm thick), followed by bonding of 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. We also analyzed 40 nm dry thermal oxides capped with a poly-Si layer. These structures were annealed at 1200 °C in an inert ambient.

Unlike the radiation study method, we generated the protons in the SiO2 using a recently demonstrated technique [6,7]. With this technique mobile protons are introduced into the buried SiO2 layer of the Si/SiO2/Si structures by annealing pieces of wafer in forming gas [N2:H2; 95:5 (by volume)] at 600 °C for 30 min. In some specific cases samples were dehydrogenated by annealing them in vacuum (2-3 × 10−6 torr) at 670 °C for 6 hours.

Samples were irradiated using a 10-keV x-ray source at a dose rate of 4 krad(SiO2)/s. Samples with and without mobile protons were irradiated, and different oxide fields (between -1 and +1 MV/cm) were applied during irradiation.

Figure 1. Pseudo-MOSFET configuration used to measure the IV curves [13].

Areal densities of mobile protons, trapped charge in the buried oxide, and interface traps were determined by studying the top-Si threshold voltage shift using pseudo-MOSFET (Ψ-MOSFET) current-voltage (IV) curves [13]. In this technique two metal probe tips are placed on the top Si layer to form the source and drain point contacts (Vφ = 0.2 V), while the substrate and the buried oxide act as gate and gate oxide respectively, as shown in Fig. 1. In addition, dual capacitance-voltage (CV) measurements [14] were utilized to characterize both the top and bottom buried-oxide/Si interfaces simultaneously. EPR measurements were performed at room temperature with an X-band (9.43 GHz) Bruker spectrometer to study paramagnetic defects.

III. RESULTS AND DISCUSSION

III.A. DIFFERENT H+ MOTION MECHANISMS

Field assisted motion of protons in SiO2 has been measured and discussed by various authors [8-11,15-19]. In some of these experiments, proton motion has been inferred by examining the post irradiation buildup of radiation-induced interface traps (with density DIT) in MOS field effect transistors. This effect has been studied as a function of applied electric field and oxide thickness [17,19]. In Fig. 2 we show data taken from Ref. [17] for oxide thickness of the order of 46 nm, similar to one of the oxides studied in our work. Here, the gate electrode of the MOSFET was polarized negatively during the irradiation sequence and for 10 ms following the irradiation pulse (LINAC). The gate polarity was then reversed and the variation of the interface trap density with time was measured. In both positive and negative polarization cases the magnitude of the electric field was 2 MV/cm; the irradiation dose was in the range 20-50 krad(Si). We see that the
interface trap density appears to reach 90% of its total variation after 10^3 seconds. Similar radiation-induced interface-trap buildup rates were observed in other studies [8-11,15-19].

Figure 2. Comparison of post irradiation buildup of interface traps in a MOS field effect transistor (taken from Ref. 17) and buildup of source-to-drain current in our pseudo-MOSFET structure with comparable gate oxide thickness, resulting from buildup of positive charge near the oxide/substrate interface.

We show in the same figure the variation of the source-drain current (I_d) in our pseudo-MOSFET structure as a function of time for an applied electric field of 0.5 MV/cm. In this case we had first pulled the mobile protons, generated by annealing in forming gas, to the gate (substrate) electrode/oxide interface by application of a negative potential on the gate. Subsequently, a positive bias was applied to the gate in order to drive the protons to the top-Si/buried-oxide interface. One sees clearly that the time scale for the proton motion in our experiments is at least 10^4 times shorter than that observed in radiation induced interface trap buildup experiments [17]. This indicates that there are fundamental differences between the two experiments, possibly the presence of reactive sites, a difference in the hopping mechanism, effective mass, or even in the very nature of the mobile species. Note also that, since the interface trap buildup experiments used a driving field of 2 MV/cm as compared to our field of 0.5 MV/cm, the actual discrepancy between the two different proton drift experiments is expected to be even larger than 10^4 times. However, we must re-emphasize that we measure a variation in I_d resulting from the accumulation of mobile protons near the top Si/buried-oxide interface, whereas the radiation experiment senses interface trap buildup, presumably due to protons interacting at the interface. It is worth noticing that we observe no evidence for this reaction in our experiments.

III.B. RADIATION INDUCED H⁺ TRAPPING

Figure 3. 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(SiO₂) irradiation under a field of +0.5 MV/cm (taken from Ref. 20).

The IV curves in Fig. 3 (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 [6,7]: 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 number of mobile protons in the buried oxide. Figure 3 (b) shows the results of the same measurements as performed in Fig. 3 (a), but here the samples received 100 krad(SiO₂) x-rays irradiation at positive top-Si bias (negative substrate bias), prior to the IV measurements. The data show that, after irradiation at +0.5 MV/cm
oxide field, the number 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 4. 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(SiO₂) irradiation at +0.5 MV/cm.

Figure 4 shows dual CV data on forming-gas annealed Unibond SOI material. The sequence of data acquisition is similar to that in Fig. 3. The dual capacitance goes through two transitions, one at a negative (small step in capacitance) top-Si bias and one at a positive (large step in capacitance) 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. 4 (a) is caused by mobile proton drift [6,7]. Figure 4 confirms that, after the samples received a dose of 100 krad(SiO₂) of x-rays with a positive bias applied to the top-Si layer, the protons are no longer mobile. In addition, the small shift at the top interface (large step at ±15 V), and the large shift at the substrate interface (small step assumed to be lower than -100 V, not detected) show that the charge trapping (trapped holes and trapped protons) occurs mainly near the substrate interface, as would be expected from the bias applied during irradiation.

Figure 5. Hysteresis in the IV curves measured on 600 °C forming-gas annealed SIMOX as a function of substrate temperature. Samples were first exposed to 100 krad(SiO₂) while applying an oxide field of 0.5 MV/cm, to cause trapping of the protons.

To gain more insight into the nature of the radiation induced proton trapping in the forming-gas annealed structures, devices were exposed to 100 krad(SiO₂) at 0.5 MV/cm (positive top-Si polarity), resulting in trapping of the protons as shown in Figs. 3 and 4. Following this treatment the samples were heated to various temperatures, and IV hysteresis measurements were performed as shown in Fig. 3. The amount of hysteresis is shown in Fig. 5 as a function of substrate temperature. The resulting curve shows how more and more protons are released from the proton traps as the substrate temperature is increased. Saturation (all protons liberated) occurs around 100 °C, indicating that the proton traps are rather shallow. When the samples are cooled down to room temperature, following the experiment shown in Fig 5, the hysteresis decreases again over time if the bias is repeatedly switched between negative and positive values. This effect is shown in Fig. 6.

These data show that the proton traps are not annihilated during the heat treatment, because re-trapping of the liberated protons occurs at room temperature. The fact that proton trapping occurs under positive field stress (protons drifted to the substrate interface) and release 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. 3 (b) and 4 (b) show that trapping of the protons results in a fixed top-Si threshold voltage shift. This was observed to be similar to the shift observed in a control sample (a similar oxide not exposed to a forming-gas anneal) which did not contain
mobile protons. The shift in the top-Si channel threshold voltage in Fig. 3(b) and 4(b) is due to the formation of the more usual trapped holes in the buried oxide. This shift is smaller than the threshold voltage hysteresis due to the mobile protons before the irradiation. After the protons were released in the heat/negative field stress experiment described in Fig. 5, and accumulated near the top Si, the threshold voltage shift was observed to increase. 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. 4 agree with this asymmetric model. Figure 7 illustrates the effect of irradiation at positive bias, resulting in trapping of the protons, and the subsequent release when heating at a negative oxide field.

Figure 6. Hysteresis in the IV curves measured on SIMOX after it received a 600 °C forming-gas anneal. The sample was first exposed to 100 krad(SiO₂) x-ray irradiation while applying an oxide field of 0.5 MV/cm, followed by heating for 10 min while applying a negative bias to the top Si layer (-1MV/cm), and finally switching the bias between +0.5 MV/cm and -0.5 MV/cm for 5 min intervals at room temperature.

A variety of irradiation experiments were performed using different doses and different bias conditions. These data show that, if a negative bias or no bias is applied during the initial exposure, the hysteresis remains approximately constant. As shown above, the hysteresis drops to zero after irradiation with a positive top Si bias, but reappears after heating with the opposite bias applied. These particular results indicate that the protons can become trapped (not annihilated) as a result of irradiation, but this trapping only occurs when a positive top Si bias is applied during irradiation. To study the dependence of the proton trapping mechanism on oxide field strength, different positive fields were applied during 100-krad(SiO₂) irradiation. It was found that fields in excess of +0.2 MV/cm are required to observe any significant proton trapping.

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 may very well be related to the previously suggested oxygen gettering from the buried SiO₂ film into the Si substrate and the Si overlayer [21,22]. The diffusion is driven by the solubility of oxygen in the adjacent Si. It thus becomes obvious that this effect predominantly occurs at the substrate interface, since the substrate represents a much larger sink for the incoming oxygen as compared to the very thin top Si layer. The measured proton trap precursor profile in the buried oxide matches this proposed oxygen deficiency profile, linking the two together. The atomic nature of the proton trap may be related to the positive fixed oxide charge observed near the Si/SiO₂ interface after forming gas annealing [5]. This is a reasonable assumption since this charge trap was also observed to be enhanced in high temperature annealed (oxygen depleted) buried oxide interfaces.

III.C. ON THE ROLE OF H⁺ DRIFT IN Dᵦ BUILDUP

To explain the radiation-induced buildup of interface traps, a model has been elaborated over the
past 20 years [8-11,15-19] which involves the field driven diffusion of radiolytic H⁺ across the gate oxide to the interface where it reacts resulting in the appearance of an interface trap. Interestingly, the mobile protons generated by moderate temperature annealing in H₂ containing atmospheres do not follow this well established reaction scheme at all. This is illustrated in Fig. 8, where a protonated point-contact Ψ-MOSFET device using a Unibond SO1 substrate was electric-field stressed with a positive bias applied to the top Si while being heated to various temperatures for prolonged times. Typical initial proton densities are of the order of \( \equiv 1 \times 10^{12} \text{ cm}^{-2} \). Data similar to those shown in Fig. 8 were collected for negative biases applied to the top Si. The data in Fig. 8 imply that, unlike in the irradiation experiments, the H⁺ in the hydrogen annealed SO1 material is not interacting at all at the interface.

![Figure 8](image-url)

**Figure 8.** Evolution of the proton density in protonated Unibond samples subjected to +0.5 MV/cm and heated to various temperatures vs. thermal/field stressing time. Data are taken on Unibond SO1 material relative to the initial proton density (\( \equiv 1 \times 10^{12} \text{ cm}^{-2} \)) generated by a 600 °C forming-gas anneal.

To further investigate this "inert" behavior of the protons in our forming-gas annealed Si/SiO₂/Si structures, x-ray dose effects were analyzed by increasing the dose of previously H₂ annealed (protonated) Unibond devices up to 5 Mrad(SiO₂) with no bias being applied to the oxide. Although a large number of electron hole pairs is generated during these prolonged exposures, no proton annihilation (H⁺ + e⁻ \( \rightarrow \) H) or any significant latent buildup of interface traps [23,24] could be detected in these samples.

Finally, another experiment was performed to try to clarify the relation between \( D_p \) and mobile H⁺ in the buried oxide and at its interfaces. Unibond SO1 material was subjected to a high-vacuum anneal which maximizes the density of \( P_b \) as has been demonstrated by EPR measurements on thermal oxide samples [25,26]. The EPR results are shown in Fig. 9. After the vacuum anneal, a \( P_b \) density of \( \equiv 2 \times 10^{13} \text{ cm}^{-2} \) was observed. From the stretchout of the Ψ-MOSFET IV curves (not shown) we obtained a similar value for \( D_p \).

![Figure 9](image-url)

**Figure 9.** EPR signals from \( P_b \) defects located at the buried oxide interfaces of Unibond material before (a) and after (b) a 700 °C high-vacuum anneal.

Subsequently, these samples, together with a control sample which did not receive the high vacuum anneal, were subjected to a sequence of 30 min forming gas anneals at 600 °C used to generate mobile protons in the buried oxide. The results of this experiment are shown in Fig. 10. It is clear from this figure that the generation of mobile H⁺ is delayed in the sample with the high interface trap density, as compared to the sample which did not receive the high-vacuum anneal. Ψ-MOSFET and EPR data on these structures show that the decrease in \( D_p \) occurs on the same time scale as the buildup of mobile H⁺ in the oxide of the high-vacuum annealed SO1 samples. A simple calculation of the time required for H₂ in-diffusion through the edges of the sample during the forming-gas anneal of the device structures at 600 °C indicates that it takes about 25 min for the buried SiO₂/Si interfaces in the device to be covered with H₂. This time is in excellent agreement with the time required to generate mobile protons in the sample that did not receive any vacuum anneal (all interface traps are hydrogen passivated in these samples), as can be seen in Fig. 10. In these hydrogen-
passivated samples the generation of mobile protons is diffusion limited. In the vacuum-annealed (de-passivated) samples, all the hydrogen that reaches the buried-oxide interfaces during the anneal process is initially consumed by the interface trap passivation mechanism, explaining the delay in \( H^+ \) buildup. It thus seems that the interface trap passivation reaction \([26-28]\) has a lower activation energy than the mobile \( H^+ \) formation reaction, which is also believed to occur at the interface \([29]\).

None of the above phenomena appear to be present in the interface state generation experiment where the mobile protons were themselves generated by the radiation. Moreover, the field induced proton motion in the latter case appears to be considerably slower as compared to that in the forming-gas annealed buried oxides. One is therefore led to conclude that the physical nature of the interaction between the mobile proton and the \( \text{SiO}_2/\text{Si} \) network is different in the two cases. A plausible explanation is that the high temperature anneal, used during the formation of the \( \text{Si}/\text{SiO}_2/\text{Si} \) structures, physically modifies the \( \text{Si}/\text{SiO}_2 \) interface regions, resulting in a different hydrogen chemistry as compared to the unconfined interfaces, such as those used in most radiation effects studies. The proton trapping observed in this work after irradiation may offer a clue to explain the much slower kinetics observed in the radiation induced interface-trap buildup experiments, although we reiterate that the buried oxides used in our experiments are not identical to standard thermal oxide.

These new findings may lead to techniques for increasing the radiation hardness of buried oxides for nonvolatile memory and other applications.

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