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**THE EFFECTS OF IRRADIATION AND PROTON IMPLANTATION
ON THE DENSITY OF MOBILE PROTONS IN SiO₂ FILMS**

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35-word abstract

Proton implantation into the buried oxide of Si/SiO₂/Si structures does not introduce mobile protons. The cross section for capture of radiation-induced electrons by mobile protons is two orders of magnitude smaller than for electron capture by trapped holes.

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I. INTRODUCTION

In microelectronics technology, annealing in a H_2 containing atmosphere at temperatures $< 450^\circ C$ is commonly used to passivate electrically active interface traps. However, the role hydrogen plays in the Si/SiO₂ system is far more complex as reflected in the vast research effort in this field. Recently, we have begun to explore the effects of annealing at temperatures $> 450^\circ C$, and have found that hydrogen can generate both fixed and mobile positive charges in thin film amorphous SiO₂. The fixed positive species show remarkable similarities to oxidation induced fixed charge [1] and have recently been attributed to near-interfacial over-coordinated oxygen sites induced by interaction with hydrogen [2,3]. The mobile species are only observed in Si/SiO₂/Si structures and have been identified as protons imprisoned inside the oxide of these layered structures [4]. These protons are rapidly rearrangeable at room temperature by applying a bias and immobile in the absence of a bias, which makes this phenomenon potentially useful as the basis for a new generation of nonvolatile memory devices [4,5].

It has been shown that mobile protons can be generated during a forming-gas anneal ($>450^\circ C$). It was furthermore evidenced that this reaction is induced by hydrogen which diffuses laterally into the buried oxide (as opposed to through the Si overlayer). In this study we explore the technologically interesting alternative of introducing the mobile protons into the oxide by proton implantation, instead of the forming-gas anneal. It is shown that proton implantation, with or without post-implantation anneal, does not yield a significant number of mobile protons in the buried oxide of Si/SiO₂/Si structures. In a second part of this work, we investigate the radiation tolerance of the mobile protons introduced into thermal oxides capped with poly-Si. These protons were introduced using standard forming gas anneal treatments. Proton densities were analyzed as a function of radiation dose, temperature and applied oxide field during irradiation. The irradiation data show that the mobile protons in the oxide can tolerate doses over 10 Mrad(SiO₂) before their density drops to half of the initial value. No post-irradiation trapping of mobile protons was observed in these thermal oxides. This is in contrast with the

behavior of SOI material, where proton trapping was observed near the substrate interface when irradiation was performed with a positive bias applied to the Si overlayer [6]. Our data provide new insights into the atomic mechanisms governing the generation and radiation tolerance of mobile protons in SiO₂. This can lead to improved techniques for production and radiation hardening of radiation tolerant memory devices based on this phenomenon [4,5].

II. EXPERIMENTAL DETAILS

Both SOI and thermal oxide material were investigated. We used Unibond® SOI material formed by implanting hydrogen ($\sim 6 \times 10^{17} \text{ cm}^{-2}$) into a wafer, below a thermally grown SiO₂ layer (380 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 $1100^\circ C$ is used to strengthen the bonding interface. We also analyzed 40-nm dry thermal oxides grown at Sandia's Microelectronics Development Laboratory. These were capped with a poly-Si layer and annealed at $1100^\circ C$ in Ar + 1 % O₂. Finally, titanium silicide was formed on the poly-Si overlayer by depositing Ti, and reacting it in nitrogen at $700^\circ C$, stripping the unreacted Ti, and annealing again at $800^\circ C$ in Ar.

Mobile protons were introduced into the thermally grown oxide of the Si/SiO₂/Si structures (density $\sim 1 \times 10^{12} \text{ cm}^{-2}$) by annealing in forming gas [Ar:H₂; 95:5 (by volume)] at $600^\circ C$ for 5 min. Details of this process are discussed elsewhere [4]. These samples were subsequently irradiated using a 10-keV x-ray source at a dose rate of 4 krad(SiO₂)/s. Samples were irradiated with and without applied bias, and different biases and substrate temperatures were used during irradiation.

Protons were implanted into SOI substrates at room temperature with an energy of 40 keV to doses of 0.5, 1.0, and $4.0 \times 10^{14} \text{ cm}^{-2}$. TRIM-90 simulation shows that the vast majority of the protons are stopped inside the buried oxide layer. For a number of samples, post-implantation anneals were performed in pure Ar or in forming gas at $600^\circ C$ for 5 min.

FIG. 1. Current-voltage characteristics for Unibond pseudo-MOSFET structures, starting from a positive and a negative bias.

Areal densities of mobile protons and trapped charge in the buried oxide of the SOI samples were determined by studying the top-Si threshold voltage shift using pseudo-MOSFET (Ψ -MOSFET) current-voltage (IV) curves. Capacitance-voltage (CV) measurements were utilized to characterize the mobile and trapped charge in the poly-Si capped thermal oxides. Paramagnetic defects were analyzed with Electron Paramagnetic Resonance (EPR) using an X-band (9.43 GHz) Bruker spectrometer.

III. RESULTS AND DISCUSSION

The IV data in Figs. 1 (a) and (b) show how a proton implant results in a small negative shift and some broadening of the IV characteristics relative to the unimplanted sample. However, the proton implant does not induce any detectable IV hysteresis (i.e. mobile protons) in these samples. This is in strong contrast with the effect of a 5-min forming-gas anneal at 600 °C, as shown in Fig. 1 (c). The broadening of the IV dip (distance

FIG. 2. Room temperature K-band EPR spectrum from Unibond SOI material implanted with 40 keV proton ($4 \times 10^{14} \text{ cm}^{-2}$).

between flat band and threshold voltage) in Fig. 1 has been reported previously and is due to an increase in the density of interface traps [7]. The data in Fig. 1 further demonstrate that the amount of trapped positive charge in the oxide is only a small fraction of the implanted dose ($5 \times 10^{13} \text{ cm}^{-2}$ vs. about $1 \times 10^{11} \text{ cm}^{-2}$). This means that the vast majority of protons trap an electron during the stopping process.

Figure 2 shows an EPR spectrum taken after the proton implantation. No resonance features were observed prior to implantation. The big central resonance is attributed to the E'_γ center (an unpaired electron in a dangling orbital of a Si atom bonded to only three O atoms in the SiO_2 network). These defects are a direct manifestation of the implantation damage. The small features left and right of the spectrum are the well-known 74 G hyperfine doublet. This signal is attributed to an E'_γ center with one of the backbonded O atoms replaced by a H atom. Detection of this defect after proton implantation offers direct proof for the presence of a large density of hydrogen in the buried SiO_2 network [8]. The signal to the left of the E'_γ resonance is due to P_b defects at the buried Si/SiO₂ interfaces. These interface traps are activated by the proton implant. The most likely scenario is that atomic hydrogen diffuses towards the interfaces and engages in hydrogen-induced interface trap creation along the reaction [9]

which occurs at room temperature. It has been argued that the generation of mobile H^+ during a forming-gas anneal also involves an interfacial

reaction with H^0 as one of the reactants. The present observations, however, indicate that this reaction does not occur at room temperature.

Several proton-implanted samples received a 600 °C post-implantation anneal in Ar for 5 min. This anneal was performed to test whether it would activate the interfacial proton generation reaction as observed in a standard forming gas anneal. Surprisingly, this post-implantation anneal did still not result in any increase in hysteresis; only a slight decrease in the negative threshold voltage shift was observed (data not shown). Finally, a number of implanted samples were subjected to a 600 °C forming-gas anneal. This treatment did result in IV hysteresis similar to the one shown in Fig. 1 (c). These results seem to suggest that there is a fundamental difference in the chemistry of hydrogen implanted into the oxide as compared to hydrogen which enters the buried oxide during a forming-gas anneal. The majority of the implanted hydrogen is still present in the buried oxide at the time of the post implantation anneal, either in molecular form at interstitial sites (H_2 , H_2O) or bonded to the SiO_2 network. Even if the latter form dominates, a 600 °C anneal should liberate at least a fraction of the implanted hydrogen. One possible explanation for the observed difference is that an interfacial reaction, occurring as the hydrogen diffuses into the system from the annealing ambient, is crucial for the proton generation mechanism. To clarify some of these issues, a study of implantation at elevated temperatures is underway.

The data in Fig. 3 show the results of a total dose experiment for poly-Si capped thermal oxide capacitors. The samples were first annealed in forming gas at 600 °C to generate the mobile protons, and subsequently irradiated at room temperature under floating bias conditions. It can be seen that the density of mobile protons drops with increasing dose while the density of net trapped positive charge increases. Figure 4 compares the proton decay vs. total dose for exposure at room temperature and at 200 °C. The main conclusion from this figure is that the decay at room temperature occurs faster compared to decay at 200 °C. The decrease in mobile proton density in these samples can be explained in two ways. Proton annihilation may occur due to capture of radiation-induced electrons, resulting in H^0 . A similar mechanism has been suggested to explain the proton annihilation observed during

FIG. 3. Density of mobile protons and net oxide-trapped charge density vs. total dose for poly-Si capped thermal oxide capacitors, irradiated at room temperature with floating gate.

exposure to UV light. [10]. Alternatively, it cannot be ruled out that proton trapping occurs at radiation induced defects in the SiO_2 network, resulting in either positive or neutral centers. The observed decrease in proton decay with increasing temperature seems to argue in favor of a Coulombic attractive capture process. However, the most striking conclusion from this experiment is that the effective cross section for the capture of radiation-induced electrons by mobile protons is at least two orders of magnitude smaller than the effective cross section for electron capture by trapped holes in thermal SiO_2 [11].

In a previous radiation study of SOI material

FIG. 4. Density of mobile protons vs. total dose under floating gate for poly-Si capped thermal oxide capacitors.

we identified a shallow proton trap in the buried oxide near the substrate interface[6]. In this experiment, trapping of mobile protons was observed when irradiation was performed with a positive bias applied to the Si overlayer. These experiments were repeated in the present work, analyzing the poly-Si capped thermal oxide capacitors. However, no shallow proton trapping could be observed in these samples. This suggests that there are structural differences between SOI buried oxides and poly-Si capped thermal oxides subjected to high-temperature anneals.

IV. CONCLUSIONS

We observe that, unlike forming gas annealing, proton implantation does not introduce any mobile protons in the buried oxide of Si/SiO₂/Si structures. These results demonstrate a fundamental difference between the chemistry of hydrogen implanted into the oxide and hydrogen which diffuses into the buried oxide from the annealing ambient.

We also show that the effective cross section for capture of radiation-induced electrons by mobile protons is at least two orders of magnitude smaller than for electron capture by trapped holes. No evidence was found for trapping of mobile protons in the thermal oxide network. This is in contrast with the properties of the buried oxide in SOI material, where proton trapping was observed near the substrate interface. A more detailed study of the radiation tolerance of protons, both as

a function of dose and temperature will be presented at the conference.

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