SAN099-1531C

THE EFFECT OF NEAR-INTERFACE NETWORK STRAIN ON THE MOBILITY OF PROTONS IN SiO_2

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35-word abstract

Our data suggest a correlation between near-interface strain in SiO_2 and the ratio of fixed vs. mobile positive charge generated at the interface during forming gas annealing. A model based on first-principles quantum mechanical calculations supports this correlation.

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I. INTRODUCTION

Hydrogen plays an intriguing role in radiation, hot-electron, and annealing-induced effects in the Si/SiO_2 system [1-5]. In particular, hydrogen interactions at the Si/SiO_2 interface play a crucial role in most of the proposed reaction models. For example, it has been found that annealing in hydrogen can generate both fixed and mobile positive charges at the Si/SiO_2 interface. The fixed positive species show remarkable similarities to oxidation induced fixed charge [1] and have recently been attributed to near-interface over-coordinated oxygen sites involving trapped H^+ ions [4]. The mobile species are only observed in $Si/SiO_2/Si$ structures and have been identified as protons imprisoned inside the oxide of these layered structures [5]. In another recent study, radiation induced trapping of mobile protons near the interface has been reported [6]. Interface strain, resulting from a mismatch between the Si and the SiO_2 network and from network defects such as oxygen vacancies, is likely to play an important role in these hydrogen reactions at the interface, and in the stability of the hydrogenous species.

In the present work we report experimental data suggesting a correlation between near interface strain in the SiO_2 network and the ratio of fixed vs. mobile protons generated at the Si/SiO_2 interface. Our data suggest that interface strain may affect proton mobility. First-principles quantum mechanical modeling has been performed to investigate the effect of SiO_2 network strain, measured in terms of the Si-O-Si angle, on the mobility of protons near the Si/SiO_2 interface. The calculations show that the binding energy of a proton to a bridging O atom decreases strongly when increasing the Si-O-Si angle beyond its calculated equilibrium value (at ~128°). These results may offer new fundamental insight into the detailed nature of annealing induced positive charge near the SiO_2 interface, and may also contribute to a better understanding of hydrogen chemistry at and near the Si/SiO_2 interface.

II. EXPERIMENTAL DETAILS

A. Substrates

Both SIMOX and thermal oxide material were investigated. The SIMOX substrates consist of a SiO_2 layer of ~ 400-nm thick SiO_2 layer buried below a 200-nm c-Si layer. We also analyzed 400-nm commercially grown thermal oxides. A 20-nm SiO_2 film was deposited on top of these oxides, which was subsequently covered by a 300-nm poly-Si layer. Both layers were sputter deposited using a Si target and an oxygen partial pressure of 3.6×10^{-4} torr and 3×10^{-7} torr, respectively. A post deposition anneal was performed at 900 °C in Ar for 50 min.

The local density of both fixed and mobile charges present at the substrate interface of SIMOX substrates as shown in Fig. 1 was measured. These substrates were annealed for 600 s in a flow of forming-gas (N_2:H_2; 95:5) at 700 °C. After the anneal the remaining top-Si layer was removed, and small metal gate contacts were deposited on both sides of the substrate for capacitance-voltage characterization. This procedure allowed a comparison between the oxide charge accumulated in the area with the buried oxide exposed to the forming-gas ambient, and the Si-covered area.

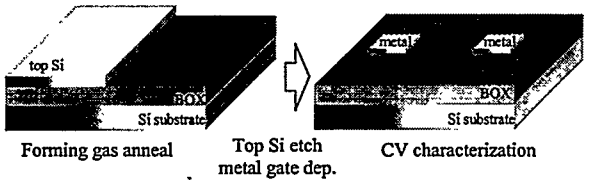

FIG. 1. Schematic of SIMOX sample processing after the forming-gas anneal of the structure on the left.

Capacitor structures were formed on the thermal oxide samples by etching part of the top-Si layer. These substrates were then annealed in forming gas as described above. Capacitance-voltage characterization was used to measure the charge generated in the oxide layer during the anneal treatment. We also measured the initial local distribution of the charges inside the oxide over the top and bottom interface, i.e., the H^+ distribution present in the oxide right after the forming gas anneal is performed. This was done by first obtaining the flatband voltage shift on the small capacitors right after the forming-gas anneal, without disturbing the initial charge distribution. Subsequently, the voltage shift is measured after applying a positive (+50 V) prebias to the gate for 5 minutes. This will

accumulate all the mobile positive species at the substrate interface, resulting in a maximum voltage shift. Finally a measurement after a negative (–50 V) prebias is performed, which will accumulate all the mobile protons at the poly-Si-gate interface.

B. Calculations

Calculations were carried out using *ab initio* Hartree Fock (HF) level theory using the 6-31G** basis set [7]. The clusters used in this study are $(OH)_3Si\text{-}O\text{-}Si(OH)_3$ and $(SiH_3)_3Si\text{-}O\text{-}Si(OH)_3$ with and without a proton attached to the bridging O atom (see Fig. 2). The first cluster represents a close-up of the SiO_2 network, the second cluster was chosen to model the Si / SiO_2 interface. The equilibrium Si-O-Si angle, φ, without a proton attached, using this basis set, was found to be 131° and 140° for the SiO_2 and interface clusters, respectively. Subsequently, the Si-O-Si angle was fixed at preset non-equilibrium values from 100° to 175°, and the geometry was reoptimized for all other degrees of freedom. The same procedure was carried out with a proton attached to the bridging O atom. The equilibrium geometry for the Si-O-Si angle in this case was 128° and 130°,

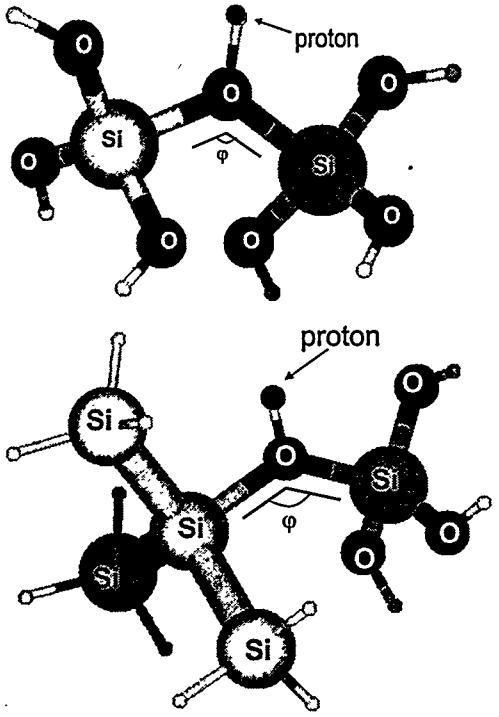

FIG. 2. Clusters used in the *ab initio* Hartree Fock (HF) level theory.

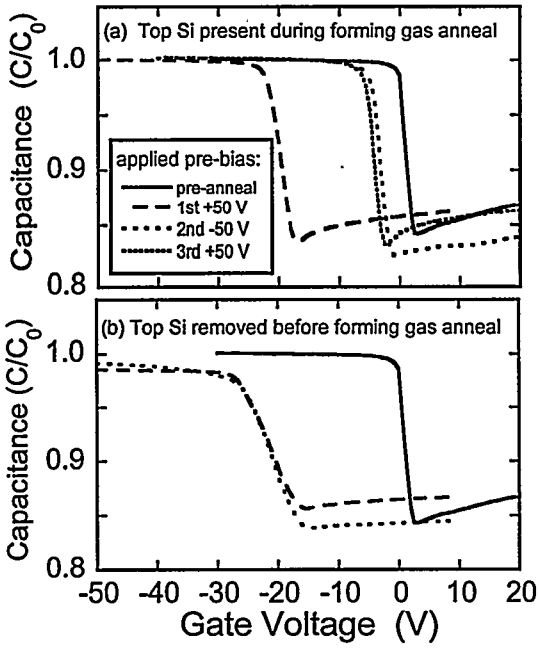

FIG. 3. Sequence of CV data before and after forming gas annealing of both exposed and Si-covered buried oxides.

respectively. The geometry was again reoptimized for the same Si-O-Si angle range from 100° to 175°, again fixing only the Si-O-Si angle and letting all other degrees of freedom optimize

III. RESULTS AND DISCUSSION

Figure 3 shows the results for the SIMOX substrate both for the Si-covered (a) and the exposed (b) buried oxide. A +50 V bias was applied to the metal gate for 300 s, followed by a CV scan. Subsequently, this procedure is repeated with a –50 V prebias, and finally again with a +50 V prebias. The data show that annealing the closed $Si/SiO_2/Si$ structure introduces predominantly mobile positive charge in the buried oxide. Only a small fraction was found to be trapped near the substrate interface. The data further show that, after sweeping the mobile charge towards the gate, reversing the bias does not result in reversing the mobile charge drift towards the substrate interface. This observation implies that the mobile protons get trapped near or absorbed by the metal gate electrode. The results in Fig. 3 (b) show that a forming-gas anneal performed on the open Si/SiO_2 structure results in

about the same amount of positive charge in the oxide. However, unlike in the closed structure, all the positive charge is fixed near the substrate interface. Hence, the presence (or absence) of the top Si layer has a drastic impact on the mobility of the positive charge being generated at the substrate interface. We speculate that removing the top Si layer and subsequently performing a 600 °C anneal may reduce the stress at the substrate interface. We propose that a reduction in the local strain at the substrate interface may favor permanent trapping of the generated protons near the interface.

The data in Fig. 4 show CV measurements performed on poly-Si gated capacitors after the forming-gas anneal. These capacitors have stacked structures consisting of c-Si / thermal SiO_2 / deposited SiO_2 / poly-Si. The initial CV curve was taken right after the anneal, without applying any bias across the oxide. Applying a positive gate bias will drift all mobile positive charges to the substrate interface, while a negative bias will drift all the mobile positive charges to the top Si interface, resulting in a maximum and minimum flatband voltage shift, respectively. Comparing the initial curve to the curves taken after a positive and negative prebias, leads us to conclude that the positive charge at the substrate interface is mainly fixed charge, while the positive charge present near the top-Si interface is largely mobile. Note that these two interfaces are not identical. The substrate interface is a c-Si / thermal-oxide interface, while the top interface is a sputtered-oxide / poly-Si interface. The sputter deposition technique used to deposit the thin oxide film is likely to yield oxygen deficient SiO_2. Thus, the top SiO_2/Si interface is likely to be more oxygen deficient than the lower interface. This excess Si is likely to cause additional local strain in the near-interface oxide network as compared to a stoichiometric thermal oxide interface. In fact, it is not unreasonable to assume that this interface has certain similarities to the buried oxide/Si interfaces in SIMOX material, as it has been suggested that the high temperature anneal induces oxygen depletion of the buried oxide interfaces [8,9].

The results of the two sets of Hartree Fock calculation for the $(OH)_3Si\text{-}O\text{-}Si(OH)_3$ cluster are shown graphically in Fig. 5 where the difference in HF energy with respect to the equilibrium geometry was plotted against the Si-O-Si angle. The results in Fig. 5 show that the angular strain

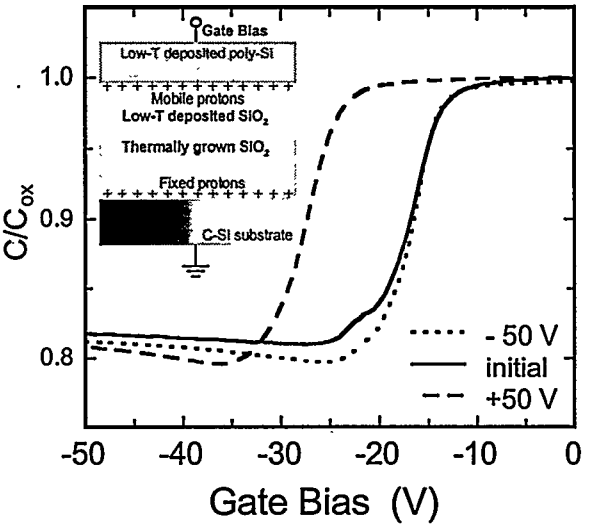

FIG. 4. Sequence of CV data before and after applying positive and negative biases to the gate.

associated with stretching the Si-O-Si angle towards 180° is much larger when a proton is attached to the oxygen. In the absence of the proton, the HF energy increase with increasing angle is small. Figure 5 also shows the difference in HF energy between the two clusters (with and without the proton), which is essentially the change in the proton binding energy vs. Si-O-Si angle. This curve shows that the binding energy between the proton and the cluster decreases significantly for large Si-O-Si angles. Such non-equilibrium angles only exist in the presence of network strain. Similar results were obtained for the $(SiH_3)_3Si\text{-}O\text{-}Si(OH)_3$ cluster, as will be shown at the conference. Hence, these calculations offer support for our suggested correlation between the presence of strained bonds at or near the interface and the mobility of the protons generated at that interface. The lowering of the H^+ binding energy in the presence of strain near the interface may explain why we observe mobile proton generation at the buried oxide interfaces and at sputter deposited SiO_2/Si interfaces.

IV. SUMMARY AND CONCLUSIONS

It has been shown that both fixed and mobile positive charge buildup can occur at the Si / SiO_2 interface during annealing in forming gas at 600 °C. Our data show that mobile charges are typically generated at oxygen deficient interfaces,

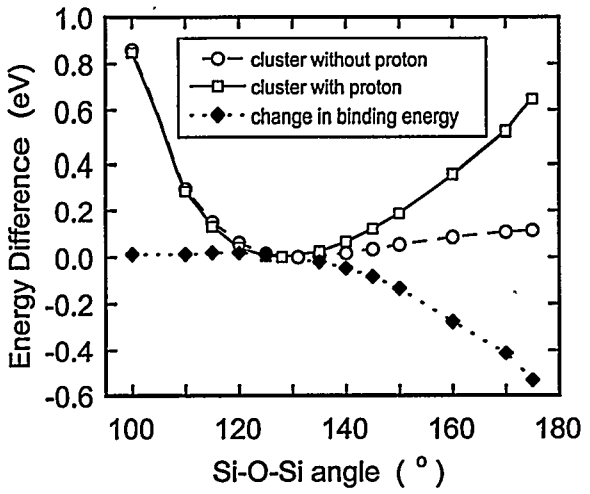

FIG. 5. Results of the Hartree-Fock level cluster calculations for clusters with the proton at its equilibrium position and at infinity.

found in SIMOX or sputter deposited SiO_2. Fixed positive charge buildup was observed at a standard thermal oxide interface, under identical experimental conditions. We tentatively attribute this remarkable difference to a difference in the presence of strained bonds at or near the interface. This is further substantiated by the observation that fixed protons were generated near the substrate interface when performing a forming-gas anneal of SIMOX after the top Si layer was stripped off. We suggest that this may be due to a reduction of strain at the interface caused by annealing in the absence of the top Si layer.

First-principle Hartree-Fock calculations were performed using $(OH)_3Si\text{-}O\text{-}Si(OH)_3$ and $(SiH_3)_3Si\text{-}O\text{-}Si(OH)_3$ clusters with and without a proton attached to the bridging O atom. HF energies were calculated as a function of the bridging Si-O-Si angle. The results show that the binding energy between the proton and the cluster decreases as the Si-O-Si angle increases above its equilibrium value. Together, these data seem to support a model in which the generation of mobile protons at the interface is facilitated by the presence of near-interface network strain. These experimental results and particularly our cluster calculation data provide a new element that may aid to understand the complex hydrogen interaction scheme at the Si / SiO_2 interface.

The authors would like to thank J.A. Ruffner for preparing the sputter deposited films. The part of this work performed at US Air Force Research Laboratory was supported under contract PE62601, Project 8809. H.A. Kurtz acknowledges support from NSF through grants STI-9602656 and CHE-9708517. The portion of this work performed at Sandia National Laboratories was supported by the US Department of Energy (DOE) and by DARPA. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy under contract DE-AC04-94AL85000.

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