

A molecular dynamics study of the causes of defects at dielectric/substrate interface of Ge MOSFETs

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ABSTRACT

We employed a classical molecular dynamics approach to study the defects of the GeO₂/Ge interface in MOSFETs fabricated on a germanium substrate. A Ge film sandwiched by two layers of GeO₂ oxide was simulated using a reactive force field. The transition of Ge native oxide was studied within the oxide thickness where the amorphous nature of GeO₂ at the interface was exhibited. The influence of parameters such as oxide thickness and fusing temperature on the number of interfacial dangling bonds was investigated. Four types of dangling bonds with different oxidation states were observed in this work.

Keywords: Ge MOSFETs, dielectric/interface defects, MOSFETs reliability, interface defects mitigation, interfacial dangling bonds

1 Introduction

The superior electrical properties of Germanium (Ge), such as higher electron and hole mobility, compared to that of other semiconductor materials (respectively twice and four times that of Si), have been one of the factors to cause germanium to return to be of focal interest in R&D. In particular, bulk Ge offers a higher hole mobility compared to the members of group IV and III-V semiconductor elements. On the other hand, for Ge n-MOSFETs, electron mobility is poor, and most of the III-V elements have a higher bulk electron mobility than Ge, but MOSFETs are easier to be fabricated in Ge than the rest of III-V elements [1]. It is also easier to use Ge-based MOSFETs with high-k materials, due to needing a lower processing temperature compared to Si [2, 3]. In addition, the Ge energy band gap is lower than that of Si, leading to further reduction in power consumption of advanced integrated circuits [4]. However, the inferior quality of the dielectric/substrate interface of Ge-based MOSFETs compared to its Si counterparts has been reported to be a challenge in manufacturing Ge-based MOSFETs, causing reliability issues for the devices (including Negative-Bias Temperature Instability - NBTI). Overall, SiO₂/Si gate stacks have a better interface than any other gate stacks. Typically, the interface state density (D_{it}) of SiO₂/Si has been reported

to be around $2 \times 10^{10} \text{ cm}^{-2}$, while that for high-k/Ge gate stacks is between 10^{11} to 10^{12} cm^{-2} , changing the threshold voltage considerably.

Hydrogen passivation is a technique that is efficient for reducing high-k/Si interface defects, but it is not effective for high-k/Ge. There have been various suggested methods to reduce the interface state density, including passivating the dielectric-Ge active interface (active sites) with a few monolayers of silicon, sulfur, and germanium nitrides [5]. The electrical reliability of gate oxides is attributed to the charge trapping of the defects [6]. Hence, using group IIIB oxides such as Y₂O₃ is beneficial for stabilizing amorphous germanium oxide, leading to the electrical reliability improvement of the gate oxide [7, 8]. In fact, the stabilizing effect of yttrium incorporation causes a more robust oxide network [7]. From Density Functional Theory (DFT), there are two types of defects in a GeO₂ structure: O vacancy and Valence Alteration Pairs (VAP) [6]. In the case of SiO₂, the vacancy energy of formation is much higher than that of GeO₂ [6] and that is why GeO₂ is a more unstable oxide compared to SiO₂.

Furthermore, another issue is that GeO₂ is water-soluble which incurs problems in the process of fabricating devices because once the device is exposed to air, it absorbs water, leading to the degradation of electrical properties. By incorporating the materials above into GeO₂, the etching time of the Metal-GeO₂/Ge will increase, improving water resistance. This strengthening effect is proportional to the number of Metal-O bonds which make the network stronger, more water resistive, and more thermally stable [8].

Interface states are a result of Ge dangling bonds at the interface. Hence, reducing interface state density is one of the significant challenges for Ge MOSFETs. These states can lead to higher leakage currents and the degradation of threshold voltage over time. Specifically, the number of Ge dangling bonds at the interface can play a crucial role in deteriorating electrical properties over time. Many factors in the process of MOSFETs fabrication can affect the number of interface states. These include oxidation temperature, oxide thickness, dopant nature and concentration. In this work, classical molecular dynamics simulations were carried out using LAMMPS software [9, 10] to gain an insight into

the interfacial properties of GeO_2 on Ge channels. Also, ReaxFF [11, 12], which is capable of modelling chemical reactions, is employed here. This allows for non-equilibrium dynamics including bond formation and dissociation in an extensive system of atoms.

2 Method and Theoretical Basis

The reactive force field used in this work has been developed by Zheng et al. [13]. The visualization of simulation results was performed using Ovito software [14]. Initially, a 45.26 Å thick slab of Ge(100) was sandwiched by two cleaved layers of alpha-quartz $\text{GeO}_2(100)$, with an initial two-angstrom gap between the layers, and placed in a simulation box with the dimensions of $22.63 \times 22.63 \times 87.41$ Å. Meanwhile, the time step of choice was set to 0.2 fs, and a periodic boundary condition was applied in all three dimensions. Next, the system energy was minimized, followed by an energy equilibration at 300 K using a micro-canonical ensemble. Afterwards, using a Noose-Hoover thermostat [15, 16] for temperature regulation, the system was heated up to 500 K and kept at this temperature for 100 ps, performed by an NVT ensemble¹ to ensure the chemical reaction between both the oxide and substrate. Subsequently, the system was linearly cooled down to 300 K, and, then equilibrated with an NPT ensemble to set the pressure and temperature at 1 atm and 300 K, respectively. Finally, the whole structure is thermally annealed to relieve the internal residual stress introduced during surface oxidation. Accordingly, the system was similarly heated up to 900 K (which is nearly half of the melting point of GeO_2) and cooled down to 300 K.

To investigate the effect of oxide thickness on the number of dangling bonds at the interface of GeO_2/Ge , a new alpha-quartz $\text{GeO}_2(100)$ was prepared in a simulation box of $22.63 \times 22.63 \times 30$ Å, with a cell density of 3.77 g/cm³. As the $\alpha\text{-GeO}_2$ melting point is 1116 °C [17], to ensure the whole crystal is melted in the short time span of MD simulations, a slightly higher temperature of 1500 K is selected to heat up the system. Next, the simulation cell is kept at that temperature for 30 ps to randomize the system and deform the initial crystal structure, formerly cooled down to 300 K within 600 ps. Afterwards, the cell pressure is equilibrated at 300 K and 1 atm for 50 ps using an NPT ensemble. Then, slices of GeO_2 with different thicknesses were cleaved: 3, 4, 5, and 6 Å; a Ge substrate with a dimension of 22.63 Å in all three directions was sandwiched with the prepared slices. Subsequently, the temperature of the system is elevated to 500 K, and then cooled back to 300 K linearly, similarly followed by equilibration at 300 K and 1 atm.

¹NVT denotes a system with a constant number of particles, volume, and temperature; NPT refers to a constant number of particles, pressure, and temperature.

Again, thermal annealing was performed to release the stress imposed on the structure during the reactions.

3 Results and Discussion

A first observation is that as the distance from the GeO_2/Ge interface increases, the GeO_2 structure becomes more similar to its alpha crystal state. There are different crystal phases for GeO_2 : hexagonal (alpha-quartz structure); tetragonal (rutile structure); and amorphous. The hexagonal and amorphous structures are soluble in water as mentioned earlier [1, 18]. At the end of the NPT equilibration, the Ge native oxide tends to be amorphous when it comes to interacting with the Ge substrate.

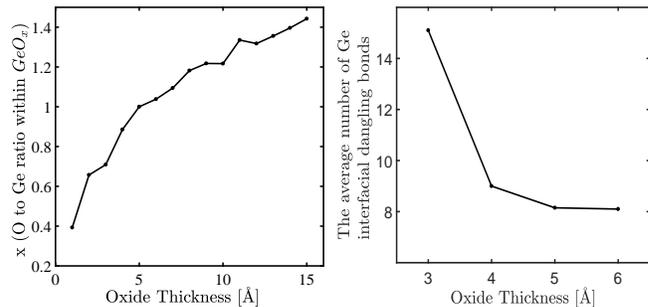


Figure 1: The ratio of Oxygen to Germanium atoms in GeO_x vs. oxide thickness

Figure 2: The effect of oxide thickness on the number of Ge dangling bonds at the interface

In addition to the aforementioned regarding the amorphous nature of GeO_2 at the interface, the ratio of oxygen to germanium atoms was measured. Figure 1 shows the correlation between oxide thickness and x , which is the ratio of O to Ge atoms. As depicted in Fig. 1, by going away from the interface, i.e., increasing the oxide thickness, GeO_x sub oxides shift more towards $\alpha\text{-GeO}_2$, which is aligned with having more amorphous oxide close to the interface. This shows that there is more GeO found near the interface (Fig.1). GeO generation has been recognized to degrade C-V characteristics due to leaving a large amount of defects at the interface by generating charge traps [5].

Dangling bonds are types of defects available at the interface of oxide/substrate. Hence, to investigate the effect of different parameters on interfacial defects, the number of dangling bonds needs to be determined. To do so, some structural properties, with Radial Distribution Function (RDF), bond length, and coordination number as examples, need to be measured. The RDF analysis, at the end of NPT equilibration, turns out the Ge–O bond length to be 1.925 Å and that of Ge–Ge is 2.525 Å. This enabled us to calculate the Mean Coordination Number (MCN) of the constituent atoms of

the system, exhibiting that of Ge and O atoms to be 4.2 and 2.7, respectively.

The results of oxide thickness relation with the number of dangling bonds, represented in Figure 2, show that the lower the oxide thickness, the the higher the number of Ge dangling bonds. As is depicted in Fig. 2, lower thicknesses of oxide definitely have a significant impact on the number of dangling bonds. Nevertheless, as the oxide becomes thicker, this effect is less pronounced. As is clear for the thicknesses of 5 and 6 Å, the number of Ge dangling bonds is approximately the same, revealing that there is an optimum in the relationship between these two quantities.

The types of Ge dangling bonds were investigated. As shown in Figure 3, there are four types of Ge dangling bonds based on their oxygen backbonds. First, there is what we based on the oxidation state denoted as Ge^{+0} , shown in Fig. 3a, which is a Ge atom which is threefold coordinated and is only back bonded to Ge atoms. Second, Ge^{+1} and Ge^{+2} shown in Fig. 3b and 3c, are Ge atoms that are threefold coordinated with with one- and two-oxygen back bonded respectively. Finally, there is Ge^{+3} , which is bonded to three oxygen atoms. Although Ge^{+3} is not present at the interface, it is more prone to appear near the interface. The DFT study by Chang et al. [19] reveals that Ge^{+0} states shown in Fig. 3a are below Fermi energy level and these states with this level of energy act as charge traps in n-MOSFETs and Coulomb scattering centres for channel electrons. Our work shows that different Ge oxidation states which have no dangling bonds, do not generate any defects throughout Ge bandgaps. However, Ge^{+1} and Ge^{+2} shown in Fig. 3b and 3c are participating in defects generation because they form gap states near Conduction Band Minimum in Ge bandgap.

We further confirmed one of the known contributing factors causing the interface state density which was reported by Houssa et al. [4]. They found a closed-form expression between the viscoelastic properties of oxide and oxidation temperature. Accordingly, it revealed that there is an inverse relationship between oxidation temperature and density of dangling bonds at the GeO_2/Ge interface. In this reactive molecular dynamics study, we focused on fusing the oxide layer to the substrate, and, then oxidizing it by regulating the temperature to speed up the simulations. A relationship between the fusing temperature and the number of dangling bonds was found which is shown in Figure 4. As is evident from the graph, Ge dangling bonds present at GeO_2/Ge interface decreases by the increasing the temperature. This finding suggests that regulating this parameter during the fabrication of devices will enable the industry to avoid increased number of defects introduced to the interface.

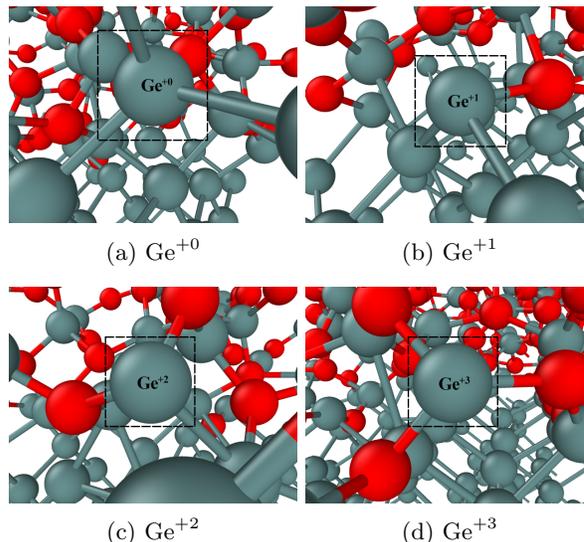


Figure 3: Types of Ge dangling bonds at GeO_2/Ge interface

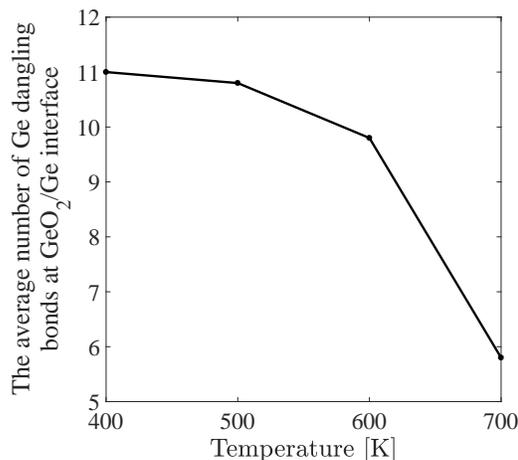


Figure 4: The relationship between fusing temperature and the number of Ge dangling bonds at the interface

4 Conclusion

We identified the mechanisms of dangling bond formation at the GeO_2/Ge interface, and proposed solutions to decrease Ge-based MOSFETs' interfacial Ge dangling bonds which are a type of defects at the interface, causing MOSFETs' reliability problems. We showed that Ge native oxide tends to be an amorphous oxide on the Ge substrate, and it loses its crystallinity near the oxide/substrate interface. While it seems impossible to avoid having an amorphous oxide near the interface, which absorbs water content of the air and damages the device, this study proposed some solutions to improve Ge-based MOSFETs reliability. It was shown out that GeO, known to negatively affect the MOSFETs C-V characteristic, is more available near the interface.

We established a relationship between the oxide thickness and Ge interfacial dangling bonds. It was unveiled that, although having a very shallow oxide layer results in lots of dangling bonds, one cannot cover all the dangling bonds by solely growing a very thick layer of oxide. Also, we further investigated the types of dangling bonds, and identified four such types with different oxidation states. Last, we confirmed that by increasing the fusing temperature, a decline in the number of dangling bonds is achieved, which was in agreement with experimental results of oxidation temperature effect on the density of interfacial defects.

5 Acknowledgement

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