Investigation of the Detailed Structure of Atomically Sharp Ge/SiO_2 Interfaces

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***Abstract*—**The atomic structure of the interface between Ge and SiO_2 – fabricated by oxidation of Ge-implanted Si – was studied using a combination of density-functional and kinetic-Monte Carlo simulations with atomic-resolution Z-contrast imaging and electron energy-loss spectroscopy with an experimental resolution close to the quantum-mechanical limit. The combination of experimental and theoretical results is consistent with the model of an atomically abrupt Ge/SiO_2 interface with probably small fractions of Ge in the oxide.

Keywords–interface; germanium; SiO_2; ab-initio; Monte Carlo; Z-Contrast; EELS

I. INTRODUCTION

Si is at the heart of the present-day microelectronic industry to a large degree due to the excelling properties of its oxide, SiO_2. Thermally grown SiO_2 is an excellent dielectric, an effective barrier to dopant diffusion, and can be selectively etched with respect to Si, which enables the currently used process to fabricate integrated circuits [1]. The processing and particularly the oxidation of Si-Ge alloys instead of pure Si were motivated by the need for advanced electronic and optoelectronic devices and circuits.

One of the most interesting advances in this area has been achieved by Fathy, Holland, and White in the late 1980s [2], who demonstrated the formation of SiO_2 on nearly pure epitaxial layers of Ge on Si substrates with a very smooth interface. This was achieved by Ge implantation and wet oxidation under the appropriate processing conditions, which are sufficiently high oxidation temperature (> 700 ^oC) and low enough Ge doses (δ 10^{16} cm^{-2}). However, such $SiO_2/SiGe$ systems have been found in the past to have considerably worse electrical properties than SiO_2/Si systems [3,4]. Among the discussed possible causes for this was the nature of the interface, specifically the possible detrimental role of the intermediate Si oxidation states and elemental Ge at the interface [3].

Although the literature provides a multitude of (theoretical) structural models for Si/SiO_2 interfaces, no method for experimental detection of the exact interfacial structure exists to date, which would allow discriminating between the above mentioned possible causes for electron trapping. In this paper, we suggest such a method, where we use impurities – in the present case, Ge atoms – as a probe to determine the interface structure by a combination of theory and experiment, which we call AIDA-TEM (Ab-Initio Dopant Analysis by Transmission Electron Microscopy).

The experimental part of AIDA-TEM consists of two TEM-based methods, Z-contrast imaging to study the segregation of heavy atoms and EELS for light elements, both with single-atom resolution. Z-contrast can detect the segregation sites of impurities with single-atom accuracy relative to the interface in amorphous as well as crystalline materials. EELS can detect the conduction band density of states (DOS) of the different atoms, which depends on the species as well as on the neighboring atoms.

The same dopants are tested in theoretical calculations for their preferred segregation sites and conduction band DOS. The identification of key features of the winning structural models (whose dopant segregation and conduction band DOS patterns match the TEM findings) enables us then to propose realistic models of interface structures.

In this paper, we will apply AIDA-TEM to study the segregation behavior of Ge in oxidized Ge-implanted Si. Our results are commensurate with an atomically sharp interface.

II. Z-CONTRAST MEASUREMENTS

The Ge film on Si substrate was fabricated at Oak Ridge National Laboratory by Ge implantation with 100 keV Ge^+ ions at a fluency of 10^{16} cm^{-2} and subsequent high-temperature wet oxidation as described in [2]. As described previously [2,4], the Ge is ejected during the oxidation step from the oxide and piles up on the substrate side of the interface. In our sample, the pile-up leads to a compact Ge layer which contains within our experimental detection limit of about 5 at.% no Si atoms as probed by EELS (*vide infra*). All the films for Z-contrast and EELS measurements were prepared by standard mechanical polishing and ion milling.

Figure 1(a) shows a typical Z-contrast image of our sample with the substrate side aligned in [110] direction. The Ge layer is brighter since Ge is heavier then Si. The ellipse-like bright double spots correspond to atomic columns. These spots (so called "dumbbells") are formed by electron scattering on two neighboring columns of Si or Ge, and should

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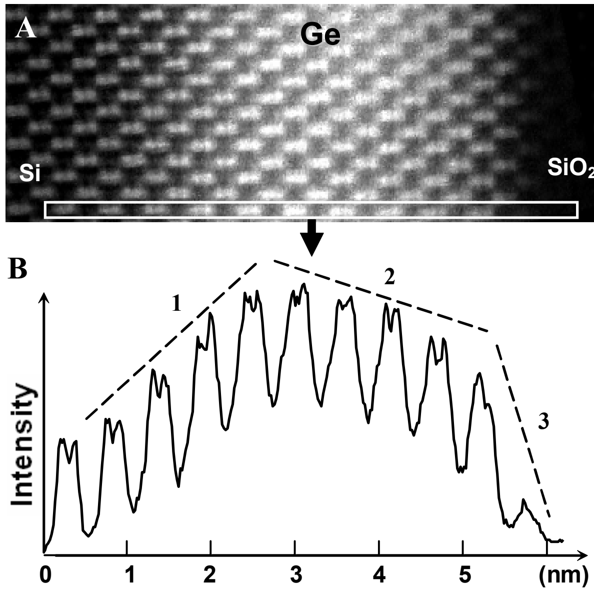

Figure 1. (a) Z-contrast image of Si substrate with Ge film covered by SiO2; (b) signal intensity profile across the interface.

show as two circular spots that touch. The distance between the neighboring atomic columns in (110) projection is 1.4 Å in Ge (larger than the electron probe size) and can be resolved. The dumbbell structure is clearly seen as double peaks in the intensity profile across the $Si/Ge/SiO_2$ interface in Fig. 1(b). We did not find any steps in any of the studied samples, which indicates a very smooth interface.

Different slopes can be identified in the intensity profile [Fig. 1(b)]. Slope 1 results mostly from the atomic mass increase at the transition from Si to Ge. Slope 2 corresponds to a nearly linear change of the Ge film thickness as a result of the wedge-shaped sample preparation. The sudden drop in intensity (slope 3) indicates a compositional change in the last dumbbell layer before the interface, while there are no signs of Ge on the oxide side. Thus, nearly all of the compositional change from pure Ge to pure SiO_2 takes place within one transitional layer right below the interface. In order to clarify the kinetics which favor the formation of such a layered structure vs. the formation of Ge pockets in the oxide reported mainly for lower-temperature oxidation [3], we investigate in the following the oxidation process by Monte Carlo modeling.

III. Monte Carlo Simulation of SiGe Oxidation

Reaction-diffusion [7] and kinetic lattice Monte Carlo [8] models for the oxidation of silicon-germanium alloys have been suggested in the past. In order to understand the thermal oxidation process of SiGe better for different Ge distributions and oxidation conditions, we formulate a Monte Carlo model similar to the model in [8].

First we use density-functional based *ab initio* calculations to determine the energy per bond for Si and Ge atoms with different numbers of Si, Ge, and O neighbors. We thus obtain an energy expression as a function of the number of bonds that is used as our acceptance/rejection criterion in the Monte Carlo simulation,

$$E[\mathrm{eV}] = -2.71\, n_{\mathrm{SiSi}} - 2.23\, n_{\mathrm{GeGe}} - 2.47\, n_{\mathrm{SiGe}} - 7.07\, n_{\mathrm{GeOGe}} - 8.94\, n_{\mathrm{SiOSi}} - 8.05\, n_{\mathrm{SiOGe}}, \quad (1)$$

where the subscript represents the bond type and n is the number of the given bond type. Since in such a model the exact structure of the disordered oxide is not important, just the coordination, our modeled oxide structure is based on the initial diamond structure and thus consists of (compressed) high-cristobalite. Although the different numbers are highly dependent on the strain, the energy *differences* remain nearly unchanged when homogeneous pressure is applied to the system. Thus, assuming homogeneous strain, we neglect the local-pressure dependence for now. Equation (1) indicates that the formation of Ge-O-Ge bonds will dramatically increase the system energy as compared to Si-O-Si bonds. In other words, from an energetics point of view, Ge atoms "prefer" to stay away from the oxide region.

We assume diffusion-limited oxidation, which was simulated by adding O atoms at the interface at a rate commensurate with experimental oxidation rates [4] and theoretical results for O_2 and H_2O diffusion through SiO_2 [5,8]. Since Ge is the much more mobile atom in the alloy, only hopping of Ge was considered with local-concentration dependent hopping rates adjusted to experimental results of Ge diffusion in SiGe alloys [6] and in oxide [8].

The mechanism of the snow-plowing effect that leads to the Ge pile-up can be demonstrated on a reduced-scale model with a shallow Ge implant. We assume an implanted Ge dose of 1×10^{16} cm^{-2} with a Gaussian distribution peaking at 11 nm with a lateral straggle of $\sigma = 4$ nm. Our Monte Carlo simulation results for high temperatures (1000 ^{o}C) are shown in Fig. 4. At this temperature, Ge becomes mobile in the Si matrix, and is also ejected out of the growing oxide at an appreciable rate due to the strong repulsive interaction between Ge and O [Eq. (1)]. This results in the formation of pure SiO_2 right above an increasing pile-up of Ge as shown in Fig. 4. However, once the Ge concentration reaches about 3.0×10^{22} cm^{-3} (~60 at.%), the room for the Ge escaping from the oxide front becomes too limited despite the Ge diffusion deeper into the substrate, and the oxide starts to incorporate Ge. The predicted Ge concentration is never higher than 5 at.% for the thin oxides that we can grow in our small simulation system and is on the order of magnitude of 1/10 of the Ge concentration on the substrate side. Our threshold of ~60 at.% is in agreement with all previous literature which reports the formation of mixed oxides [9]. There, however, usually low-temperature oxidation had to be employed to produce an appreciable amount of Ge in the oxide.

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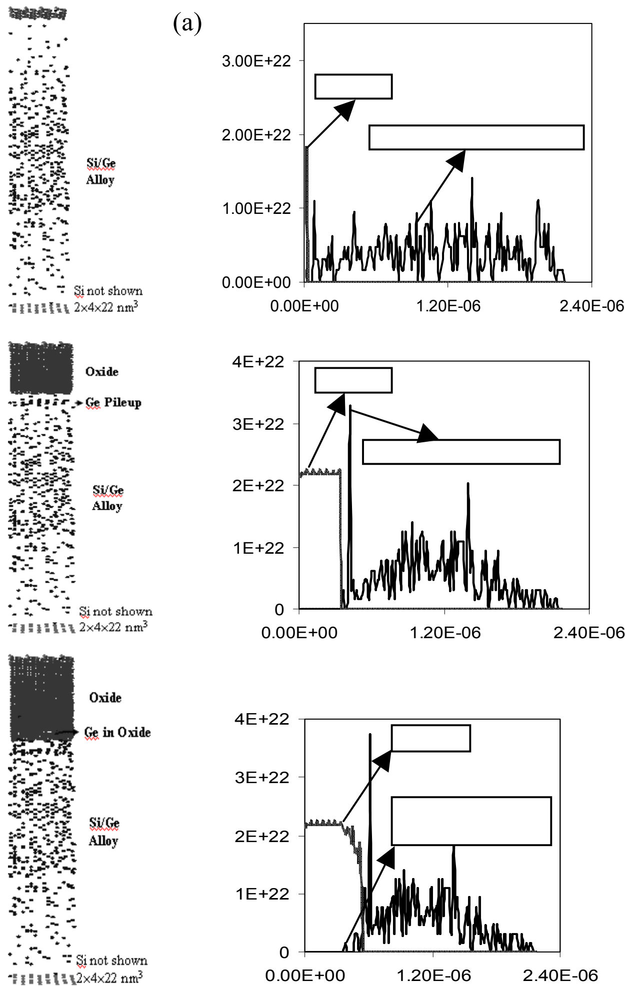

Figure 2. Monte Carlo simulation on oxidization shows a selective oxidization process: a) initial conditions; b) right before Ge incorporation into oxide; c) end of oxidation.

Thus, our model predicts that what was originally interpreted as pure SiO_2 in [2] might indeed contain a small amount of Ge, provided that the Ge incorporation into the oxide is not eliminated by out-diffusion of Ge for longer oxidation times. This surprising finding was not confirmed by our Z-contrast measurements, which however is not significant since the Ge concentration present might be below the detection limit of ~5 at.%. However, there are very recent experiments based on X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry for short oxidation times that confirm our modeling and indeed find Ge in the oxide in small concentrations – usually 1/10 of the Ge concentration in the substrate which is in excellent agreement with our Monte Carlo prediction – even for high-temperature oxidation [9]. Furthermore, the XPS spectra suggest Ge^0 and Ge^{4+} as well as Si^0 and Si^{4+} as the only oxidation states occurring in non-negligible concentrations. Although XPS might not detect the oxidation states around the interface due to their low fraction of the overall examined volume, this result shows that the Ge in the oxide should be predominantly in the form of GeO_2 or in the form of elemental clusters. The formation of Ge nanoclusters in SiO_2 has been observed experimentally for Ge concentrations > 0.7 at.% at temperatures 600 °C [10].

IV. Near-Edge Electron Energy Loss Spectroscopy

To get insight into the atomic configuration of the Ge/SiO_2 interface and Si oxidation states we also employed EELS measurements of the Si-$L_{2,3}$ edge in combination with *ab initio* calculations of the EELS spectra [11]. Duscher *et al*. [11] have shown that the Z+1 approximation, where the examined atom is replaced by the element with atomic number Z+1 in order to compensate for the core-hole shift that is caused by the electron-excitation process, predicts the near-edge EELS spectrum reasonably well within standard pseudopotential density-functional calculations. Two structures were selected for our theoretical EELS calculation. The first structure has an atomically sharp interface, where all-perfect Si has one transition layer with Si^{2+} atoms (two O neighbors each), followed by perfectly 4:2 connected SiO_2 (Fig. 3, left). In the second structure, we introduce suboxide characteristics by removing the O atom from one Si-O-Si bond, which results in a structure with Si^{1+} and Si^{3+} atoms (Fig. 3, right). If we calculate now the orbital and spatially resolved electronic conduction band DOS for the Si atoms in the different oxidation states and line them up as described in [11], we see that each oxidation state has its distinct shape and peak position in Fig. 3. Whereas Si^0 and Si^{4+} have very distinct spectra with prominent peaks at 102 eV for bulk Si and 108.5 eV for Si^{4+} respectively that can be easily detected, it is more difficult to sort out the intermediate oxidation states in the measured spectra. Thus, EELS allows us to probe not only the species (overall energy loss), but also the bonding of the atoms with the help of the near-edge structure.

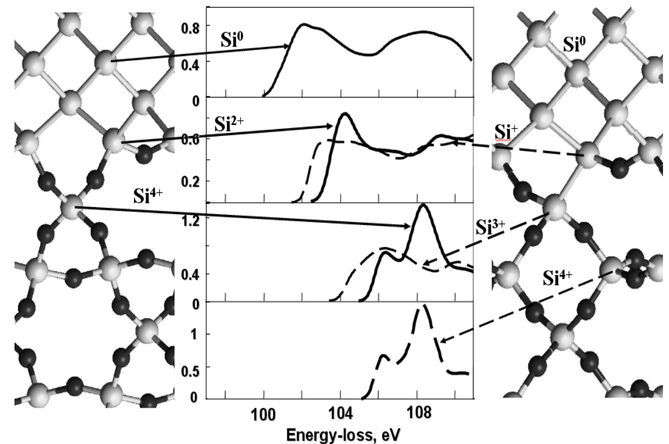

Figure 3. Calculated Si-$L_{2,3}$ edge at the Si/SiO_2 interface

The experimental EELS spectra of our Si:Ge/SiO_2 sample are shown in Figure 4. The spectra are taken with a spatial step of about 1 – 1.5 Å which is about the inter-plane distance perpendicular to the interface on the crystalline side and thus have a resolution of single atomic layers.

We find that just 2 Å away from the last crystalline layer on the amorphous side we observe an ionization edge which corresponds to completely oxidized Si (Fig. 3, last spectrum).

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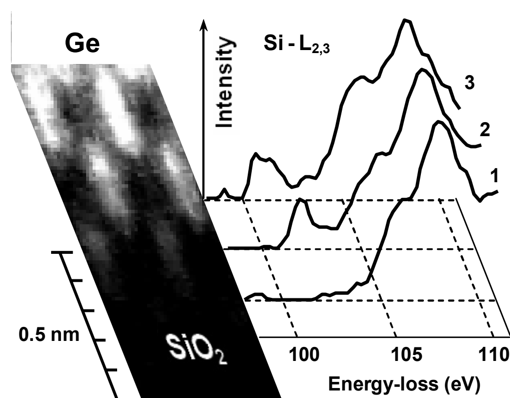

Figure 4. Line-scan EELS of the Si-$L_{2,3}$ ionization edge across the Ge/SiO_2 interface.

Moving one layer away from the oxide to the first crystalline layer, a clear signal of Si^{2+} appears (spectrum 2). In the second crystalline layer, we find a signal typical of bulk SiGe (spectrum 3), which looks different from pure Si due to the core level shift caused by Ge. The EELS data analysis from subsequent atomic layers on the crystalline side of the interface shows a rapid reduction of the Si concentration. Within one or two atomic layers it falls below the detection limit, which we estimated as less than 5 atomic %. In summary, we find an atomically sharp interface for this structure with only one transition layer – containing Si^{2+} – after the last crystalline layer and pure oxide after only ~2 Å. Our result of the high-qualtity interface for the studied sample is consistent with the recent high-temperature oxidation results of [9], but are in contrast with other work [3,12], which however dealt with higher Ge concentrations or lower oxidation temperatures.

V. Electronic Density of States & Charge Traps

In order to assess the quality of the interface, we examine the electronic DOS for the different oxidation states of Si. In a first step, we calculate the DOS for Si in the different oxidation states. For that, we construct virtual bulk structures that contain exclusively one of the 5 possible oxidation states of Si. All structures are derived from the Si diamond structure with relaxed coordinates and lattice constants. Si^0 is represented by bulk Si, Si^{4+} by high-cristobalite, Si^{1+} and Si^{3+} by hexagonal structures with the *c*-axis parallel to the cubic (111) direction, where O is inserted in the appropriate alternating bond layers, and Si^{2+} by an orthorhombic SiO structure containing 4 Si and O atoms each. Si^{1+} results in a material that has within our employed GGA approximation no band gap and thus can give easily rise to electron trapping. All other non-zero oxidation states have insulating band structures with theoretical band gaps of 1.0 eV (Si^{2+}), 4.5 eV (Si^{3+}), and 5.8 eV (Si^{4+}). Thus, structures with a lower percentage of low oxidation states – especially with as little as possible or no Si^{1+} – should have a lower trap density. In this sense, the studied interface is of the best possible quality. The role of the oxidation states with non-zero local gap in creating interface charges depends on the line-up of their DOS with respect to the overall band line-up. This can be done by comparing the atom-projected DOS for the interface structure with the DOS of the corresponding pure-oxidation state structure and shifting the DOS accordingly. This is also a simple way to determine the general band line-up and is the next step in our work. The effect of Ge in the oxide is also still under investigation.

VI. Conclusions

In summary, we suggest that the examined sample has an unprecedented atomically sharp interface with Si^{2+} as the only intermediate oxidation state. This is a strong improvement over common Si/SiO_2 interfaces, which usually introduce Si^{3+} and especially the potentially strongly detrimental Si^{1+} oxidation state [11]. Our modeling suggests small amounts of Ge in the oxide, which might contribute to the enhanced charge trapping in SiGe/oxide systems reported in the literature [3].

Acknowledgments

This work was funded by the Semiconductor Research Corporation under contract number 2002-MJ-1018 and the U.S. Department of Energy under contract number DE-AC05-00OR22725. We also thank the Ohio Supercomputer Center for supercomputer time.

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