Monolayer Passivation of Ge(100) Surface via Nitridation and Oxidation

Joon Sung Leea,b, Sarah R. Bishopa, Tobin Kaufman-Osborna,b, Evgueni Chagarova, and Andrew C. Kummela

a Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093, USA
b Materials Science and Engineering Program, University of California at San Diego, La Jolla, California 92093, USA

The monolayer passivation of Ge(100) surface via formation of Ge-N and Ge-O surface species was studied using scanning tunneling microscopy (STM) and density functional theory (DFT). Direct nitridation using an electron cyclotron resonance (ECR) plasma source formed an ordered Ge-N structure on a Ge(100) surface at 500°C. DFT calculations found the hydrogen passivation on this Ge-N ordered structure could reduce the bandgap states by decreasing the dangling bonds and the bond strain. Oxidation of Ge(100) using H2O produced an –OH and –H terminated surface with very few Ge ad-atoms, while e-beam evaporation of GeO2 formed semi-ordered Ge-O structures and Ge ad-species at room temperature. Annealing above 300°C formed suboxide rows on both H2O and GeO2 dosed surfaces, and the scanning tunneling spectroscopy (STS) showed that the Fermi level was pinned near the valence band edge on the n-type Ge surfaces covered by suboxides.

Introduction

Germanium is considered a promising channel material for the next generation MOSFET devices due to its favorable electronic properties (e.g. high electron and hole mobilities) compared to Si. However, high defect densities at the interface between Ge and high-k dielectric layers have been a challenging issue in fabricating scaled devices. Among several different methods to passivate the Ge surface (1-3), nitridation (4-6) and oxidation (7-11) have shown the most promising results.

Nitridation of Ge has been studied using thermal (NH3) (4) or a plasma nitridation (atomic N) (5-6) sources to form Ge oxynitride (GeOxNy) or Ge nitride (Ge3N4). These layers have better thermal stability than Ge oxide (12-13); therefore, they suppress the GeO outdiffusion from Ge surfaces to the high-k dielectric layer during processing at elevated temperatures, resulting in a low interface defect density (5). A stoichiometric GeO2 layer produced by ozone (9) or high pressure oxidation (11) is also effective in passivating Ge surfaces by eliminating interface defects due to suboxides and dangling bonds. However, for a practical MOSFET device with a high-k dielectric layer, these passivation layers should be scaled down to one or two monolayers.

In this study, the geometric and electronic properties of a Ge(100) surface at an initial stage of nitridation or oxidation were studied; the low coverage reactions are crucial to
understanding the physical or chemical origin of defect formation that can occur in the ultrathin passivation layer. Submonolayer nitride structures were formed on a Ge(100) surface by plasma nitridation and were probed using scanning tunneling microscopy and spectroscopy (STM/STS). Density Functional Theory (DFT) calculations were performed on a model structure to support the experimental data. Oxidation of Ge(100) was performed using H₂O and e-beam evaporation of GeO₂, and the results were compared with the O₂ dosed Ge(100) surface (14).

**Experimental Details**

A Ge sample was cut from the n-type Ge(100) wafer (Sb-doped, 0.005-0.020 Ohm-cm), and immediately transferred into the ultrahigh vacuum (UHV) chamber at a base pressure of 2×10⁻¹⁰ Torr. The native oxide of Ge(100) surface was removed using 0.9 kV Ar⁺ ion sputtering at 500°C for 30 min, followed by thermal annealing at 800°C for 20 min. Direct nitridation of Ge(100) surface was performed using an electron cyclotron resonance (ECR) plasma with pure N₂ gas. To avoid oxygen contamination due to trace O₂ or H₂O, the substrate temperature was maintained at 500°C during the plasma nitridation. Oxidation of the Ge surface was carried out using two different oxidants – H₂O and GeO₂. H₂O (HPLC grade) was carefully degassed and dosed onto a Ge(100) surface through a differentially-pumped dosing system. E-beam evaporation was used for the deposition of GeO₂ (99.999%, metals basis). The atomic and electronic structures of the sample surface were observed using scanning tunneling microscopy and spectroscopy (STM/STS), while Auger electron spectroscopy (AES) was used to analyze the chemical elements on the surface. All the STM images were obtained at a sample bias of -2.0V and a set point tunneling current of 0.2 nA.

**Results and Discussion**

**Nitridation of Ge(100) Surface**

After ECR plasma nitridation at 500°C for 30 min, the Ge(100) surface was covered by ordered and disordered Ge-N structures as shown in Figure 1(a). Only Ge and N peaks were detected in AES spectra, confirming the surface structures were formed purely due to nitrogen (data not shown). Figure 1(b) shows the STS results obtained from a clean n-type Ge(100) surface (dotted line) and a Ge surface nitrided at 500°C (straight line). On a clean n-type Ge(100) surface, the Fermi level (E_F) appeared near the conduction band (CB) edge. However, after plasma nitridation, the Fermi level of a n-type Ge surface was pinned near the valence band (VB) edge. To investigate the relation between bonding and electronic structure of the ordered nitride, the DFT calculations were performed on a model structure with two subsurface N atoms tri-coordinated underneath the surface Ge dimer (Figure 2, upper left). After full relaxation, the topmost Ge dimers are slightly pushed up and tilted, consistent with the STM data (Figure 1(a)). The adsorption reaction is exothermic with respect to an atomic N (ΔH = -3.77 eV/N), consistent with the thermal stability of the ordered nitride structure at 500°C. However, the adsorption is endothermic with respect to molecular N₂ (ΔH = 1.45 eV/N), consistent with the relatively low coverage of the ordered nitride structure even after a long exposure to atomic N.

DFT calculations of density of states showed that plasma nitridation increases the states near the Fermi energy, consistent with the Fermi level pinning on the nitrided Ge
surface (Figure 2, right). However, terminating all the dangling bonds on the nitride structure with H atoms is found to remove the tilt of Ge dimers (Figure 2, lower left) and reduced the bandgap states near the Fermi energy, possibly unpinning the Fermi level of the surface (Figure 2, right). This implies both dangling bonds and the bond strain due to the subsurface N atoms contribute the increase of the band gap states. Complementary experimental data were not available for the H-passivation due to the low nitridation rate and the residual plasma defects.

Figure 1. STM and STS of Plasma Nitrided Ge(100). (a) Filled state STM image of a Ge(100) surface nitrided at 500°C. Ge-N ordered (rectangle) and disordered (circle) structures are shown. The dotted box is expanded for geometric analysis. (b) STS results on a clean Ge(100) (dotted) and a nitrided Ge surface (straight). Note that the Fermi level of n-type Ge is pinned near the valence band (VB) edge after plasma nitridation.

Figure 2. DFT Models of Nitrided Ge(100). (upper left) DFT model of subnitride with backbond insertion N sites. Each Ge surface atom has two half filled dangling bonds; (lower left) DFT model of H-passivated subnitride; (right) DFT calculations of the density of states shows the subnitride produces density near the Fermi energy, but hydrogen passivation removes the density around the Fermi energy unpinning the Fermi level of Ge surface.
Oxidation of Ge(100) using H$_2$O

Figure 3(a) shows the STM image of a Ge(100) surface dosed with 1.5 L of H$_2$O at room temperature. The Ge surface is covered by approximately 0.1 monolayers (ML) of dark sites, which are due to the –OH and –H termination of Ge dangling bonds and consistent with the dissociative chemisorption of H$_2$O on a Ge(100) surface (15). In the case of the O$_2$-dosed Ge(100) surface, an equal amount of dark (O displacement) and bright (Ge at-atom) sites were produced due to the strong reactivity of each O atom to displace a Ge surface atom (14). In contrast, H$_2$O dosing produces very few Ge ad-atoms, which makes H$_2$O as a promising oxidant for a monolayer passivation of Ge. However, there are also Ge dimer vacancies (DV) observed on the H$_2$O dosed surface (Figure 3(a), diamond), which are distinguished from the H$_2$O adsorbate sites by different depths (0.9 Å for H$_2$O sites, 1.2 Å for DV). These dimer vacancies are possibly due to H$_2$O etching resulting in the Fermi level pinning of the $n$-type Ge surface after H$_2$O dosing (Figure 4(a)).

The dark H$_2$O sites are significantly reduced when the surface is annealed to 300°C (Figure 3(b)). Instead, primarily bright sites are observed with some dark suboxide rows which are typically observed on the O$_2$-dosed surface at the same temperature (14). On the Ge(100) surface, H$_2$ desorption occurs around 300°C (16). Therefore, it is assumed that the surface structures remaining at 300°C are mostly due to oxygen. The suboxide species at 300°C can cause the Fermi level pinning (Figure 4(b)), but $E_F$ moves slightly towards midgap, implying there might be other mechanisms involved in the Fermi level pinning at this temperature.

![Figure 3](image-url)
Oxidation of Ge(100) using E-beam evaporation of GeO₂

E-beam evaporation of GeO₂ at room temperature formed semi-ordered structures along the substrate Ge dimer rows and Ge ad-atoms on the Ge(100) surface (Figure 5(a)). It is known that GeO₂ decomposes during e-beam evaporation, producing a substoichiometric film (17). Hence, the semi-ordered structures on the GeO₂ deposited surface are likely Ge suboxides. It is also known that the Ge suboxide films undergo phase separation into Ge and GeO₂ at elevated temperatures on a Si substrate (18). However, in the presence of excess Ge, GeO₂ transforms into GeO by the following reaction (19).

\[
\text{Ge} + \text{GeO}_2 \rightarrow 2\text{GeO}
\]  \[1\]

Therefore, there would be only Ge or Ge suboxides remaining when the GeO₂ deposited Ge(100) surface is annealed at 325°C, consistent with the STM observation of Ge regrowth islands and suboxide rows (Figure 5(b)). The STS of GeO₂ deposited Ge(100) surface indicate the Fermi level of the n-type sample surface is pinned near the valence band edge on both unannealed and annealed cases, probably due to the suboxide species.

Figure 4. STS of H₂O/Ge(100) before and after post deposition annealing. (a) STS of H₂O dosed Ge(100) at room temperature. The Fermi level of n-type Ge surface is pinned near the valence band edge. (b) STS of H₂O dosed Ge(100) annealed at 300°C. The Fermi level of n-type Ge surface is pinned near the midgap.

Figure 5. STM of ebeam GeO$_2$ on Ge(100) before and after post deposition annealing. (a) Ge(100) surface deposited with GeO$_2$ at room temperature. Semi-ordered Ge-O structures (circle) and Ge ad-atoms (square) are observed. (b) Ge(100) surface deposited with GeO$_2$ after annealing at 325°C. Ge regrowth island (rectangle) and suboxide rows (oval) are shown.

Figure 6. STS of e-beam GeO$_2$ on Ge(100) before and after post deposition annealing. (a) STS of GeO$_2$ deposited Ge(100) at room temperature. The Fermi level of $n$-type Ge surface is pinned near the valence band edge. (b) STS of GeO$_2$ deposited on Ge(100) after annealing at 325°C. The Fermi level of $n$-type Ge surface is pinned near the valence band edge.

**Conclusions**

The atomic and electronic structures of Ge(100) surface after nitridation and oxidation were investigated for the monolayer passivation of a Ge surface via Ge-N and Ge-O surface species. ECR plasma nitridation at 500°C produced an ordered Ge-N structure on
Ge(100), consistent with the thermal stability of the nitride passivation. However, the increase of dangling bonds and the bond strain due to the subsurface N atoms generated bandgap states resulting in Fermi level pinning of the Ge surface. DFT calculations showed that hydrogen passivation of the ordered subnitride structure can restore the Fermi level of the surface by eliminating the bandgap states from the dangling bonds and from strain. H$_2$O dosing at room temperature terminated the dangling bonds on a Ge(100) surface with -OH and -H without displacing surface Ge atoms, while GeO$_2$ deposition produced semi-ordered Ge-O structures with Ge ad-atoms. However, annealing above 300°C formed suboxide rows on both H$_2$O and GeO$_2$ dosed surfaces, causing the Fermi level pinning.

Acknowledgments

This work was supported by the MSD Focus Center Research Program (FCRP-MSD-2051.001). In addition, S. R. Bishop was supported by a GLOBALFOUNDRIES sponsored GRC Graduate Fellowship.

References