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Plasma nitridation of Ge(100) surface studied by scanning tunneling microscopy

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ABSTRACT

The geometric and electronic structures of the surface species on Ge(100) after plasma nitridation were investigated in this study. An electron cyclotron resonance (ECR) plasma source was used to directly nitride Ge(100), and scanning tunneling microscopy and spectroscopy (STM/STS) were employed to study the structures of the nitrided surface. Nitridation at room temperature generated a large diversity of adsorbate sites on the surface containing N, O, and displaced Ge atoms, differentiated by annealing between 200 °C and 450 °C. Conversely, nitridation at 500 °C produced Ge–N adsorbate sites which formed ordered and disordered structures on the surface free from oxygen. Density functional theory (DFT) simulations were performed focusing on the ordered nitride structure, and the simulated surface structure showed a good correspondence with the STM data. DFT calculations also found an increase of density of states near the STS results. The DFT results predict H-passivation can unpin the Fermi level of the nitrided surface by reducing the dangling bonds and the bond strain, but the residual plasma damage and the low nitridation rate in UHV are challenges to obtain complementary experimental results.

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1. Introduction

As the scaling of Si-based metal-oxide-semiconductor field effect transistors (MOSFETs) approaches its physical limits, there have been an increasing number of studies of alternative channel materials. Ge has been considered one of the candidates for the new channel material of the next generation MOSFET devices due to its high electron and hole mobility compared to Si. The success of fabricating silicon transistors has relied on an electrically passive SiO₂/Si interface, even when employing high-k dielectrics [1,2]. However, unlike SiO₂, Ge native oxide (GeO₂) is thermally unstable [3] and water soluble [4] which makes it very challenging to fabricate a GeO₂/Ge-based MOS structure comparable to the SiO₂/Si MOS structure with similar process methods. Moreover, the hydrogen passivation via forming gas annealing (FGA) - usually adopted in the Si MOSFET process - is often ineffective at sufficiently reducing the interface states in the GeO₂/Ge interface [5,6]. Therefore, it is crucial to find a way to electrically passivate the Ge surface which can generate a thermally stable and high density layer on Ge to initiate the Ge-based MOS structure.

Several methods have been reported for Ge surface passivation, including epitaxial Si deposition [7,8], halogen (-F, -Cl, -Br)

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incorporation [9–11], sulfur-passivation [12,13], oxidation to form GeO_2 [14–18], and thermal or plasma nitridation [19–21]. While the best electrical properties are usually obtained on GeO_2 passivated surfaces [14–17], the nitridation of Ge surface, which forms Ge oxynitride (GeO_xN_y) or Ge nitride (Ge_3N_4), showed both enhanced electrical properties compared to unpassivated Ge and improved thermal stability compared to GeO_2 passivated Ge [22,23]. When Ge oxynitride and Ge nitride are used as an interfacial layer between a Ge substrate and a high-k dielectric film, an effective suppression of Ge (or GeO) out-diffusion from the substrate into the high-k dielectric was observed [21].

Although the passivation of Ge surface using Ge nitride or Ge oxynitride has been well investigated from the device point of view [19,22], there are very few studies about the atomic and electronic structures of the Ge–N surface species, which are essential to understanding the atomic basis of the combined electrical passivation and enhanced thermal stability. In the current study, electron cyclotron resonance (ECR) plasma nitridation and the scanning tunneling microscopy/spectroscopy (STM/STS) were performed on Ge(100) to determine the initial geometric and electronic structures of the Ge nitride–Ge(100) interface. STM provides a unique opportunity to determine the geometry of Ge–N or Ge–O adsorbates with atomic resolution, while STS provides the electronic structure of the interface prior to any perturbation by gate oxide deposition. Theoretical studies were also performed using density functional theory (DFT) to support experimental results.

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2. Experimental and theoretical methods

2.1. Experimental details

All the sample processes and measurements were carried out in an ultrahigh vacuum (UHV) chamber at a base pressure of 2×10^{-10} Torr. A commercially available *n*-type Ge(100) wafer (Sb-doped, 0.005–0.020 Ω cm) was cut into a small piece and transferred immediately into the UHV chamber. To remove Ge native oxides, the sample was sputtered by a 0.9 kV of Ar⁺ ion beam (EX05, VG Microtech) at 500 °C for 30 min and annealed at 800 °C for 20 min. Both Ar⁺ ion sputtering and thermal annealing procedures were repeated several times to obtain atomically flat Ge surfaces.

The nitridation of the Ge surface was performed using an ECR plasma source ("Osprey" Plasma Source, Oxford Scientific) operated at 2.45 GHz with pure N₂ gas. During the nitridation process, the plasma source was differentially pumped by a turbomolecular pump. The N₂ gas was provided through a leak valve with a flow rate of 0.6 sccm (standard cubic centimeter per minute). The nitrogen plasma was directed to the sample surface at normal incidence via an aperture between the differentially pumped plasma source and the main UHV chamber. The pressure in the differentially pumped source was 5×10^{-5} Torr while the pressure in the UHV chamber was 8×10^{-8} Torr during the ECR operation.

The topography of the sample surface was characterized by STM (Autoprobe VP1, Park Scientific Instrument) with the constant current mode. Filled state STM images were obtained at a sample bias of -2.0 V and a tunneling current of 0.2 nA. STS experiments were performed with the variable-z method using a modulation bias of 0.1 V at 1.4 kHz from an external lock-in amplifier (SR850, Stanford Research Systems).

All sample preparation processes (cleaning, nitridation, and annealing) were performed *in situ* while the Ge sample was mounted on a water-cooled manipulator equipped with direct sample heating electrodes. After each process, the sample was transferred to the STM for imaging the surface. Auger electron spectroscopy (AES) was performed after the STM/STS measurements to analyze the surface species.

2.2. Computational methods

Density functional theory (DFT) plane-wave calculations with periodic boundary conditions were performed using the Vienna Ab-Initio Simulation Package (VASP) [24–27]. All simulations were performed with the Perdew–Burke–Ernzerhof (PBE) variant of the generalized gradient approximation (GGA), and the atoms were modeled using the projector augmented wave (PAW) pseudopotentials that were supplied with VASP [28,29]. A $4 \times 4 \times 1$ Monkhorst-Pack *k*-point mesh generation scheme led to a total of 4 irreducible *k*-points in the first Brillouin zone. A plane-wave basis cut-off was set to 450 eV. The structural relaxation of the slab was obtained once the interatomic forces were below 0.01 eV/Å per atom.

The system studied consisted of an Ge(100) slab supercell with a 4×2 surface dimer reconstruction. The Ge slab was 8 atomic layers thick with 12 atomic layers of vacuum. The bottom 3 layers were frozen and H-terminated to simulate bulk-like conditions. Both a single unit cell and a double unit cell in the *y*-direction were relaxed consisting of 64 and 128 atoms respectively. Low coverage nitrogen sites were simulated on the single unit cell, while the subsurface nitride was simulated on the double unit cell. Energy calculations were determined with respect to both atomic and molecular nitrogen resulting in exothermic and endothermic results respectively. In addition to the atomic structure and simulated STM images were calculated. Within standard DFT, the band gap is underestimated for semiconductor materials. For Ge(100), the simulated electronic

structure results do not contain a true bandgap, rather a local minima in the Fermi level region. Conclusions were made based on whether there is an increase, decrease, or no change of density in the Fermi level region as to whether the N adsorption site impacted the electronic structure of the surface, similarly to previous work [30]. While hybrid exchange functional methods produce accurate electronic structure results [31,32], they are computationally expensive and have not been performed for this study. Grassman et al. found DFTbased STM simulations using the Tersoff-Hamann approach to correspond with experimental STM images of both the clean and oxidized Ge(100)-(4×2) surface [33]. Similar DFT methods were employed in this study to correlate experimental results with computational results.

3. Results and discussion

A clean, ordered Ge(100) surface was obtained after several cycles of Ar⁺ ion sputtering and thermal annealing. Fig. 1(a) shows the filled state STM image obtained from a clean Ge(100) surface with atomically flat and large terraces. On the clean Ge(100), the surface structure with the mixture of (4×2) and (2×1)-like reconstructions was always observed. It is well known that the (2×1)-like reconstruction is a dynamic superposition of buckled dimers of the



Fig. 1. (a) (left) Filled state STM image ($V_s = -2.0 \text{ V}$, $I_t = 0.2 \text{ nA}$) of a clean Ge(100), and (right) dimer structures of c(4×2) (green circle) and (2×1) (red circle) surface reconstructions. The Ge dimers normally flip between buckled structures so they appear symmetric (2×1) except near defects where they are frozen in the c(4×2) structure. (b) STS spectra of clean *n*-type Ge(100). Fermi level (E_F) is located near the conduction band(CB) consistent with an unpinned surface. For Ge(100), pinning states on *n*-type material move the Fermi level to the valance band (VB).

 (4×2) reconstruction [34,35]; therefore, the Ge dimers appear flat unless they are frozen by surface defects, adsorbates, or step-edges. In these reconstructions, the surface Ge atoms have half-filled dangling bonds. The dI/dV spectra obtained by STS measurements on the n-type surface is presented in Fig. 1(b). The conduction band and valence band edges are well defined in the STS spectra, with the Ge bandgap consistent with reported values (0.67 eV) and the Fermi level located closer to the conduction band edge than the valance band edge as expected for an *n*-type sample. This confirms the Fermi level is unpinned on the clean n-type Ge(100) surface. It has been reported that oxidation and impurities tend to pin the Fermi level of Ge(100) near the valance band [33]. For *p*-type Ge(100) samples, the Fermi level is at the valance band edge, making pinned and unpinned *p*-type Ge(100) indistinguishable in STS. Conversely, *n*-type Ge(100) has a Fermi level which shifts from being closer the conduction band to being closer to the valance band when the surface becomes pinned, which is readily observed in STS [33]. Therefore, experiments in this study were performed only on n-type Ge(100) to determine the impact of plasma nitridation on the electronic structure of the nitrided Ge(100) interface.

After ECR plasma nitridation of the clean Ge(100) surface at 300 K for 2 min, STM images show various adsorbate sites (Fig. 2). Previously, Grassman et al. studied oxidation of the Ge surface using STM, and identified the O displacement and the Ge ad-atom sites on the oxygen-dosed Ge surface [33]. The O displacement site has one or two oxygen atoms replacing a surface Ge atom or dimer; these oxygen sites appear dark in the filled state STM image (0.6 Å or 1.0 Å below the surface), while the displaced Ge ad-atoms bond on top of undisturbed surface Ge dimers and appear bright (1.2-1.4 Å above the surface) [33]. The as-nitrided Ge surface has very similar surface features such as dark oxygen-like sites (Fig. 2, circle), and bright Ge ad-atom sites (Fig. 2, square). Even though high-purity N2 gas is employed for the plasma source, trace water or oxygen also can be introduced into the plasma source from the gas line which reacts on the Ge surface during the plasma nitridation [20]. The existence of oxygen contamination is verified by the Auger spectra obtained from the surface nitrided at 300 K for 30 min which shows the O peak in addition to N and Ge [36]. Meanwhile, another kind of bright site (Fig. 2, hexagon), distinct from Ge ad-species, is also found which has a typical height of 0.8 Å above the surface, and is provisionally assigned as nitrogen-related adsorbates.

To verify the assignment of the nitrogen-related site, the 300 K nitrided Ge surface was annealed to elevated temperatures. Since GeO desorbs from Ge surface above 425 $^{\circ}$ C [3] while Ge nitride evaporates



Fig. 2. Filled state STM image of a Ge(100) surface nitrided at room temperature for 2 min. Dark oxygen-like sites (circle), bright Ge ad-atom sites (square), and bright N-related sites (hexagon) are observed. The Ge ad-atoms and N-related sites can be distinguished by their height and annealing properties.

above 600 °C [23,37], it is expected that the nitrogen-related sites would stay stable on the Ge surface at the annealing temperatures between 425 and 600 °C.

Fig. 3 presents the STM images of the nitrided Ge surface, with corresponding height analysis histograms and annealing conditions. Note that the *x*-axis in the histogram indicates the height relative to the substrate Ge atoms. Therefore, the peak of total height distribution (blue curve) is defined as 0 Å, corresponding to the height of the background Ge(100) surface. The as-nitrided Ge surface contained bright and dark sites, covering approximately 17% and 7% of the surface, respectively (Fig. 3(a)). Up to 200 °C, no significant changes are observed for the coverage of bright and dark sites (16% and 6%), though these sites are partially coalesced into larger bright and dark islands (Fig. 3(b)). For the Ge surface annealed at 400 °C, the bright sites are reduced to 5% while the dark sites decrease to 0.5% (Fig. 3(c)).



Fig. 3. STM images and height analysis histograms of Ge(100) surface nitrided at room temperature with (a) no-anneal, (b) 200 °C anneal, (c) 400 °C anneal, and (d) 450 °C anneal. Note that the height is measured relative to the substrate Ge atoms, and the height distributions of bright and dark sites are denoted in green and red colors respectively in the histogram while the total height distribution is represented in blue color. In (c) and (d), bright and dark site distributions are magnified by a factor of 10 for readability purpose. The dark sites are due to O displacements while both Ge ad-atoms (fitting curve A) and N adsorbates (fitting curve B) contribute to the bright sites.

Finally, annealing at 450 °C results in nearly complete removal of the dark sites, whereas bright sites are still observed covering 2% of the surface (Fig. 3(d)). The disappearance of the dark sites at 450 °C is consistent with the O displacement sites observed on the oxygen-dosed Ge surface [33]. Therefore, the dark sites on the as-nitrided Ge surface are assigned as O displacement sites.

The height distribution of bright sites consists of two components; (i) the distribution centered at 1.2 Å (bright site A), and (ii) the distribution centered at 0.8 Å (bright site B), which are also distinguished by their different behaviors in the annealing process. The fitting curves of components A and B are overlaid on the height distribution of bright sites in Fig. 3. Bright site A is continuously reduced as the annealing temperature increases (200-400 °C), and nearly disappears at 450 °C. This is consistent with the thermal behavior of Ge ad-atoms since they diffuse out to step edges at elevated temperatures. On the contrary, bright site B still remains at 450 °C, which is not associated with the Ge ad-species because virtually all Ge ad-atoms diffuse out at this temperature [33]. The partial reduction of bright site B is likely due to desorption of metastable oxygen sites which are 0.6–0.9 Å above the surface [33]. Considering thermal behaviors and height differences, bright site A is assigned as Ge ad-atoms and bright site B remaining at 450 °C is assigned as N-related adsorbates.

Table 1 shows various N adsorption sites obtained from DFT calculations with atomic geometries, STM simulations, and adsorption energies. The possible nitrogen adsorption sites include N insertion between Ge dimer atoms, N backbond insertion, N single displacement, and N double displacement. The modeled sites are similar to the adsorption sites modeled for low coverage oxidation of the Ge surface, with more exothermic adsorption energies for the nitrogen sites [33]. The thermodynamic DFT results are consistent with the experimental data, with oxygen desorption occurring at lower temperatures than nitrogen on the Ge(100) surface. Although all the sites in Table 1 are stable with respect to an atomic N (note negative values of adsorption energy), none of their STM simulations correspond with the nitrogen-related adsorbates observed in the experimental STM images (Figs. 2, and 3(d)); the simulated sites are dark while the experimental

nitrogen-related sites are bright. In each case of Table 1, the N atom only forms two bonds to the Ge surface upon adsorption. The result is a remaining half-filled dangling bond directly on the N atom. The low coverage adsorption sites should be reactive to the displaced Ge atoms or formation of extended nitride. In addition, further interaction with atomic N during plasma nitridation could induce desorption of molecular N₂ from the surface. Therefore, it is likely the N adsorbates in Figs. 2 and 3(d) have subsurface N atoms which push up the surface Ge atoms to create bright sites rather than single N adsorption sites shown in Table 1 which only produce dark sites. Experimental STM images of the N adsorbates at higher coverage and low energy ordered structures with annealing are required to determine the detailed geometry.

To further investigate purely N-related sites on Ge(100), the plasma nitridation was performed with the substrate temperature at 500 °C, which is consistent with a published method of forming a pure nitrided surface [38]. Even though there are several reports on forming a pure Ge nitride layer at lower temperatures [21,37], the annealing study described above implies nitridation at 500 °C would eliminate any chance for oxygen to adsorb on the Ge surface during the nitridation. Furthermore, the nitridation time was increased to 30 min to produce a higher coverage of the Ge nitride. Fig. 4(a) shows the STM image of the Ge(100) after nitridation at 500 °C for 30 min followed by UHV annealing at 500 °C for an additional 5 min. During annealing, the pressure in the UHV chamber was maintained at 2×10^{-10} Torr. Highly ordered structures along the surface Ge dimer rows (Fig. 4(a), rectangle) are observed with disordered features (Fig. 4(a), oval) and dark sites (Fig. 4(a), diamond). Within the detection limit of AES, Auger spectra showed that the Ge(100) surface nitrided at 500 °C contains only N while the Ge surface nitrided at 300 K contains both N and O [36]. Therefore, the ordered features in Fig. 4(a) are assigned as Ge-N-related surface structures, and the dark sites are assigned as defect sites due to the residual plasma damage rather than O displacements. The disordered features are consistent with Ge or Ge-N clusters, but a definitive assignment is not possible without an extensive DFT modeling. The STS result shows that the Fermi level of

Table 1

Results of DFT calculations of various N adsorption sites with (4×2) -based atomic geometries, STM simulations, and adsorption energies.

Adsorption Site	Geometry (4×2)	STM Simulations (4 × 2)	$\Delta H_{ads}(eV)^{a}$
N insertion, between Ge Dimer atoms	\$		-3.97
N insertion, backbond	**		-3.80
N single displacement	*		-4.10
N double displacement			-3.01

a: Calculated adsorption energies, ΔH_{ads} , are given per adsorbed N atom, with respect to atomic N. All sites are endothermic with respect to molecular N₂. Displacement sites are calculated with respect to the formation of Gead-dimers

Ge 🔴 N 🔘

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Fig. 4. (a) Filled state STM image of the *n*-type Ge(100) after nitridation at 500 °C for 30 min followed by annealing at 500 °C for 5 min. The ordered structures (rectangle), disordered structures (oval), and plasma damage sites (diamond) are observed. The DFT simulated STM image of the ordered structure is overlaid in the black rectangle. (b) STS spectra obtained on the same surface. Fermi level of *n*-type surface is near the valence band (VB) consistent with pinning.

the *n*-type surface is pinned near the valence band (Fig. 4(b)). The possible causes of Fermi level pinning include the surface states induced from ordered and disordered structures, and the defect sites due to plasma damage. The Fermi level pinning of the Ge surface with plasma nitridation could be confirmed by photoelectron spectroscopy (PES) which was not performed in this study due to lack of equipment, nor was available in the literature at the time of submitting this manuscript.

In Fig. 5, the geometry of the ordered structure is analyzed using line traces on the STM image of the 500 °C annealed nitrided surface. The ordered structures always appear as paired rows of bright spots parallel to the (4×2) -reconstructed Ge dimer rows neighboring them. The spacing between each row is 11 Å + /-0.5 Å (line trace a), apparently wider than the distance between two dimer rows of Ge (100)- (2×1) reconstruction (8 Å) (line trace c). The height of the rows relative to the Ge surface is 0.6 to 0.8 Å (line trace a) which is distinct from the typical height of the Ge ad-atom (1.2 to 1.4 Å). The spacing between the neighboring bright spots is 8 Å + /-0.5 Å (line trace b), which is twice of the spacing between the adjacent Ge dimer rows in the (2×1) reconstruction (4 Å) (line trace d). The schematic ball-and-stick diagrams of a Ge-N ordered structure and a Ge(100) (2×1) reconstruction satisfying these dimensions are shown at the bottom of Fig. 5. The ordered structures primarily form at step edges; however, they do exist on the terrace of the Ge(100) surface.



Fig. 5. The geometric analysis of the ordered structure of 500 °C nitrided surface. The rows of ordered structure are 0.8 Å above the (2×1) reconstructed surface and separated approximately 11 Å apart along the direction of the line trace a (green), which is wider than the distance between two dimer rows of (2×1) reconstruction (8 Å) (line trace c, red). The distance between bright sites along the line trace b (blue) is 8 Å, which is twice of the spacing between dimers in the (2×1) reconstruction (line trace d, black). The line traces in the horizontal direction (b and d) are calibrated considering 1.2 times elongation of the STM image due to the thermal drift of the piezoelectric scanner. The schematic ball-and-stick diagrams of the Ge–N ordered structure and (2×1) -reconstructed Ge(100) surface are shown at the bottom.

Based on this geometric analysis, the ordered structure was modeled via DFT with two subsurface N atoms under each surface Ge dimer defined as 'subnitride' in this article. Fig. 6 shows the atomic structure of the ordered Ge subnitride resulted from the DFT calculation. In this structure, each N atom forms the preferred *sp*²-like hybridization with adjacent Ge atoms. The Ge dimer which has two N atoms underneath will be pushed up having slightly higher configuration than the Ge dimers on the surface. The adsorption energy is exothermic with respect to an atomic nitrogen ($\Delta H = -3.77 \text{ eV/N}$), consistent with the spontaneous formation of the ordered structure in an atomic N ambient and the thermal stability of the structure during high temperature processes (nitridation and anneal at 500 °C). However, the adsorbate adsorption is unstable with respect to molecular N₂ ($\Delta H = 1.45 \text{ eV/N}$); consistent with the observation of low coverage, even with long exposures of atomic nitrogen. After full relaxation, the Ge dimers on the subnitride structure are tilted symmetrically with the outer Ge atoms pointing upward. The distance between these two outer Ge atoms is 11.4 Å, and the height from the surface to one of the outer Ge atom is 0.93 Å. The distance between the Ge dimers with subsurface N atoms along the row direction is 8.0 Å. This is consistent with the experimental values (11 Å, 0.8 Å, and 8 Å) obtained by the geometric analysis in Fig. 5. The STM simulation on this structure correlates well with the experimental STM image as shown in Fig. 4(a).

The Ge subnitride structure, shown in Fig. 6, is capped with dicoordinated Ge atoms which have partially-filled dangling bonds. If left unpassivated, these partially-filled dangling bonds are both highly reactive and very likely to create midgap states which pin the Fermi level. However, in a real passivation layer, an oxide layer would be deposited on top of the Ge nitride which will certainly bind to the Ge dangling bonds [39,40]. The hydrogen passivation of surface atoms acts as a simplified model of oxide bonding and/or a model of post oxide deposition hydrogen passivation of residual dangling bonds. Therefore, the electronic properties of the subnitride structure can be



Fig. 6. Ball-and-stick diagram of the ordered Ge subnitride obtained from DFT calculation. After full relaxation, the subnitride Ge dimers are tilted symmetrically with the outer Ge atoms pointing upward. The distance between these two outer Ge atoms is 11.4 Å. Also the outer Ge atoms are 0.93 Å above the surface Ge atoms. The subnitride site is exothermic with respect to an atomic nitrogen ($\Delta H = -3.77 \text{ eV/N}$).

elucidated by performing a DFT calculation of the density of states considering the effect of H-passivation.

For the DFT modeling, H atoms are bonded to all dangling bonds created by subnitride formation to maximize the effect of H-passivation. It was necessary to passivate the di-coordinated Ge dimer atoms directly bonded to the N with two H atoms, and the nearest neighbor tri-coordinated Ge dimer atoms with one H. After H-passivation, the tilt of Ge dimers is completely removed on the subnitride structure [41].

Fig. 7(b) depicts the total density of states (DOS) of the clean Ge (100) structure, subnitride structure, and H-passivated structure. Comparing the DOS for unpinned Ge(100) (dotted black curve) with the subnitride structure (blue curve), a large increase of density at the Fermi energy occurred on the subnitride structure suggesting pinning states in the Fermi level region, which is consistent with the observed STS results. However, the density near the Fermi energy disappears upon H-passivation of the subnitride surface (red curve) with a DOS that resembles the DOS for the clean Ge(100) surface. The DFT results suggest the Fermi level can be unpinned upon H-passivation or even the deposition of an oxide layer which bonds covalently to the undercoordinated Ge atoms with a similar electronic structure to the clean Ge(100) surface.

To further determine the cause of the Fermi level pinning and unpinning, the projected density of states (PDOS), or density of states localized on each atom, of selected atoms (depicted in Fig. 7(a)) on the subnitride structure were also calculated. It is found that the Ge atom in the top layer dimer of subnitride (Ge12 in Fig. 7(a)) gives the largest contribution to the density of states near the Fermi level (blue curve in Fig. 7(c)). It can be inferred that the Ge atom in the top layer dimer is sp-hybridized having two half-filled dangling bonds which result in the formation of states near the Fermi level. However, there are also contributions from the second and third layer Ge atoms as well as N atoms to the states in the Fermi level region (see Fig. 7(c)). This suggests the subsurface N atoms induce strain to the surface structure resulting in surface state formation which impacts the electronic structure. Since the subsurface N atom (N1 in Fig. 7(a)) is bonded to the Ge atom in the second layer (Ge26 in Fig. 7(a)), it can consequently distort the bond angles with all next neighboring Ge atoms (Ge26 and Ge45 in Fig. 7(a)) and finally affect their electronic structures.

After H-passivation, there is a large reduction in the PDOS contributions (Fig. 7(d)) to near Fermi level states from the atoms which induced Fermi level states on the unpassivated surface. H atoms on the surface Ge atoms induce sp^3 -hybridization, eliminating states due to the dangling bonds. The sp^3 -hybridization also gives symmetric bond angles to the surface Ge atoms, eventually removing the dimer tilts. The improvement in electronic structure and increase in bulklike bonding for the H-passivated subnitride structure are consistent with the dangling bonds and the bond strain caused by subsurface N atoms being the main sources of the Fermi level pinning on the subnitride structure.

The effect of the H-passivation on the subnitride structure can partially explain the improvement of electrical property after forming gas annealing on the high-k/GeN/Ge MOS devices [22]. It is also likely that the covalent bonding of an oxide layer would improve the electronic structure of the nitrided Ge(100) surface in a manner similar to H-passivation since the oxide bonding would eliminate dangling bonds and restore *sp*³-hybridization. However, the electronic effects of defect sites and disordered features regarding the Fermi level pinning were not clarified in this study. Furthermore, the residual plasma defects and disorders, along with a limited nitridation rate in UHV condition, makes it challenging to obtain the experimental results with ordered subnitride structure at a higher coverage. A careful optimization of plasma nitridation or a different method of nitridation (e.g. atomic layer deposition (ALD)) would be required to avoid plasma damage and disordering, thereby determining the impact on the Fermi level pinning and increasing the coverage of the ordered subnitride structure.

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Fig. 7. Total Density of States (DOS) and Projected Density of States (PDOS) for the clean Ge, subnitride, and hydrogen passivated (H-pass.) systems. (a) Ball-and-stick diagram with atom # labeled for identification of density contributors in the PDOS. Atom 1 represents N, atom 10 and 12 represent first layer Ge, atom 26 represents second layer Ge and atom 45 represents third layer Ge. (b) Total density of states for the subnitride (blue, with increased density in the Fermi level region) and H-passivated subnitride (red, similar to the clean Ge DOS) compared to the clean Ge substrate (dashed black). (c) Projected DOS for the subnitride surface where all atoms strained by the subnitride contain density in the Fermi level region, with the largest contribution from the first layer dimer atoms. (d) PDOS for the H-passivated subnitride surface which shows the density is reduced for the atoms strained by the subnitride

4. Conclusions

ECR plasma nitridation of the Ge(100) surface was performed to investigate the geometric and electronic structures of the Ge-N bonds using STM and STS. The plasma nitridation at room temperature produced surface structures containing O displacement sites, Ge adatoms, and probable N-related adsorbates. The post-nitridation annealing experiments differentiated these adsorbate sites, and finally removed most of O displacements and Ge ad-atoms at 450 °C. The nitridation at 500 °C for 30 min produced an ordered subnitride structure on Ge(100) surface without O displacements and Ge ad-atoms. However, the Fermi level of this surface is pinned due to the increase of dangling bonds and the bond strain. DFT calculations on the atomic and electronic structures of the ordered subnitride show a good correspondence with the experimental STM and STS results. Finally, simulated H-passivation is found to unpin the Fermi level of the subnitride surface structure by eliminating the partiallyfilled dangling bonds and by reducing the strain from the subsurface N atoms. The thermal stability of nitride passivation and the effect of nitride passivation with forming gas annealing at the interface between Ge and high-k dielectric layer can be partially understood based on the findings of this study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.susc.2010.03.030.

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