Surface Science 602 (2008) 2373-2381

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc



Tyler J. Grassman, Sarah R. Bishop, Andrew C. Kummel*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Dr., #0358, La Jolla, CA 92093-0358, United States

ARTICLE INFO

Article history: Received 4 February 2008 Accepted for publication 1 May 2008 Available online 24 May 2008

Keywords:

Scanning tunneling microscopy Scanning tunneling spectroscopy Density functional calculations Fermi level pinning Oxidation Germanium Suboxides Semiconducting surfaces

ABSTRACT

An experimental atomic-level study of the structural and electronic properties of the oxidation of the Ge(100) surface was performed using scanning tunneling microscopy (STM) and spectroscopy (STS). Room-temperature O_2 -dosed Ge(100) surfaces at sub-monolayer coverages (with and without post-oxidation annealing) were imaged via STM in order to identify the bonding geometries of the oxidation reaction products, and STS spectra were taken for the characterization of the surface electronic structures resulting from those structures. DFT modeling, including STM simulations, was performed for the various potential adsorbate structures indicated by STM imaging in order to elucidate the most likely bonding geometries. Long, low-temperature post-oxidation anneals (325 °C) were used to eliminate some meta-stable oxidation reaction products and to drive the coalescence of the stable products. The O_2 -reacted Ge(100) surfaces, both the disordered pre-annealed and the ordered post-annealed (325 °C), were found to exhibit Fermi level pinning near the valence band. However, proper Fermi level position was restored upon desorption of the GeO at 500 °C, indicating that the presence of germanium suboxide at the Ge(100) surface is a source of Fermi level pinning for annealed surfaces. The pinning observed on the room-temperature as-oxidized surface is most likely also due to the suboxide coverage; it is likely that additional components to the pinning states also arise from the displaced Ge ad-species.

© 2008 Published by Elsevier B.V.

surface science

1. Introduction

Due to the approach of the fundamental limits of classical silicon complementary metal-oxide-semiconductor (CMOS) device scaling, recent years have seen a great deal of work focused on alternative channel materials for high-speed MOS-type field-effect transistors. One such alternative material is germanium, whose greater low-field intrinsic carrier mobilities may provide for a significant increase in saturation current over state-of-the-art silicon metal-oxide-semiconductor field effect transistor (MOSFET) devices. However, in contrast to Si, Ge does not have a suitably stable electrically-passivating native oxide. The Ge native oxide, GeO₂, is both water-soluble and thermally unstable at elevated temperatures; on Ge(100), GeO₂ decomposes and desorbs as GeO above 400 °C [1–3]. Therefore, an alternative dielectric and/or electrical passivation method is needed.

Numerous experiments have attempted the fabrication of Gebased MOSFET or MOSCap (metal-oxide-semiconductor capacitor) devices using a great diversity of insulators, including GeO₂ [4–6], Ge₃N₄ [7], GeO_xN_y [5,8,9], SiO₂ (with and without a Si interlayer/ cap) [10,11], and high-k metal-oxides (BaStTiO₃, ZrO₂, HfO₂) [12– 14]. The success (or failure) of these different dielectric materials has been found to depend on the chemical passivation of the Ge at the semiconductor-oxide interface. In general, devices that were fabricated with interfacial GeO₂ were consistently found to yield poor C-V (capacitance-voltage) characteristics; large frequency dispersion in accumulation, capacitance peaks within the band gap, gate leakage, and/or flatband shifts, all of which are associated with interface states, interfacial or oxide traps, and fixed charge. Those devices that were fabricated with no interfacial GeO₂ were found to exhibit superior C-V characteristics.

Recent work has shown that there are at least two methods that can yield MOS devices that include a GeO₂/Ge interface (using rf-sputter deposited GeO₂ films) with high-quality C-V characteristics: protection (capping) of the deposited GeO₂ film during post-deposition annealing, preventing desorption of GeO, and N-passivation of the Ge(100) surface prior to GeO₂ deposition, preventing the formation of GeO by blocking the GeO2-Ge decomposition reaction [15]. These results strongly indicate that native GeO₂ (i.e. without additional passivation or protection) serves as a poor passivant, most likely due to the formation of suboxide at the GeO_{2-x}/Ge interface, while suboxide-free GeO_2/Ge interfaces can have a low trap and interface state density. However, it is unknown if the oxide/Ge interfacial state/trap formation and associated Fermi level pinning is due to the formation of suboxide Ge–O bonds or due to the properties of bulk suboxide (GeO_{2-x}); it is critical to determine if specific Ge-O bonding alone can pin the Fermi level, as this will help determine the feasibility of interfacial passivation by the direct deposition of other potential gate oxides.



^{*} Corresponding author. Tel.: +1 858 534 3368; fax: +1 858 534 2063. *E-mail address:* akummel@ucsd.edu (A.C. Kummel).

While certain types of Ge–O bonding might pin the Fermi level, we note that the pinning may not be intrinsic to all Ge-O bonds on the Ge(100) surface. For example, while the GeO_{2-x}/Ge interface is pinned, a ZrO₂/Ge interface may be unpinned, even though both interfaces contain Ge-O bonds. Furthermore, even for a given interface, the deposition method itself can change the electronic structure because the bonding geometries of adsorbates on surfaces play a definitive role in the determination of the electronic properties of the resultant interfaces. This is an especially important issue in the consideration of electrical passivation of semiconductor surfaces, where bond angles and coordination numbers can have a large effect on the electronic structure. Therefore, a thorough characterization and understanding of the effect of Ge-O bonding at the Ge(100) surface is paramount for understanding the interfaces made with potential gate dielectric oxides for Gebased MOSFET devices.

Much work has been performed over the past decade using scanning tunneling microscopy (STM) experiments to characterize the initial oxidation of the Ge(100)- 2×1 surface, including the effect of post-oxidation annealing and elevated-temperature oxidation [16-22]. A few studies utilizing density functional theory (DFT) modeling have also been produced [23,24], but these have mostly concentrated on the initial metastable oxygen adsorption sites. While these various works have provided much insight into the physical nature of the Ge(100) oxidation reaction, a thorough and unambiguous identification of the various adsorbate and reaction product geometries has remained elusive, as well as has a characterization of electronic structure of the oxidized Ge(100) surface. STM- and DFT-based studies are ideal for the study of these suboxide-type bonding structures, as sub-stoichiometric oxidation is easily achievable in the relevant experimental conditions, and DFT allows for a truly atomic-level analysis of the resulting geometry and their effect on the interfacial electronic structure. While the local environment around the suboxide structures may be different in the device-level (buried interface) vs. the atomiclevel (surface vacuum interface), the resultant electronic structures, and their effects on device operation, are likely to be similar since defect electronic structure is mostly determined by the local bonding configuration.

We have performed an atomic-level study of the structural and electronic properties of the O_2 oxidation reaction on the Ge(100) surface utilizing scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) modeling, in order to obtain a fundamental understanding of the atomic geometries of the surface binding sites (STM, DFT) and the resultant electronic structure of those sites (STS). DFT was used to model and simulate the bonding structures observed in the STM images from the clean and oxidized Ge(100) surfaces. Long, low-temperature post-oxidation anneals allowed us to eliminate various metastable and/or transitional reaction sites from the room-temperature oxidation reaction so that the effect of specific reaction products on the electronic structure could be elucidated. For definitive determination of the effect of O₂ dosing and annealing on the electronic structure, we measured the STS spectra on the clean and oxidized Ge(100) surfaces of both n-type and p-type substrates.

2. Methods

2.1. Experimental setup

All experiments were performed under ultra-high vacuum (UHV) conditions with a base chamber pressure of $2-3 \times 10^{-10}$ Torr. The UHV chamber is equipped with a water-cooled manipulator and sample holder, a differentially-pumped ion gun (VG Micro-

tech EX05), a custom-built differentially-pumped deposition source chamber (allowing for the low-background pressure deposition of various oxides from high-temperature effusion cells), a room-temperature scanning tunneling microscope (Park Scientific Autoprobe VP1), and a standard set of analytical instruments: Auger electron spectrometer (AES), low-energy electron defractometer (LEED), and quadrupole mass spectrometer (QMS).

Experiments were performed on $6 \text{ mm} \times 18 \text{ mm}$ samples cut from *n*-type (Sb-doped, 1.88×10^{17} - 1.54×10^{18} cm⁻³, 0.020-0.005 Ω -cm) and *p*-type (Ga-doped, 1.58 \times 10¹⁷-1.12 \times 10¹⁸ cm⁻³, 0.040–0.010 Ω -cm) 100 mm Ge(100) wafers purchased from Wafer World (epi-grade, ±1° orientation tolerance). The samples were lightly cleaned of oils and particles using a lint-free cloth wetted with methanol or isopropanol prior to insertion into the vacuum chamber. The Ge(100) samples were prepared by successive sputter/anneal cycles as follows: sputtering at normal incidence with 800–1000 V Ar⁺ ions at a sample temperature of 500 °C. followed by resistive annealing at 700 °C for 20 min, with a 1 °C/min ramp down to room temperature. Typically, about three such cycles were required to reach peak surface cleanliness and order. This treatment produced large, well-ordered, defect-free terraces. Surface cleanliness and order was checked with Auger electron spectroscopy, low-energy electron diffraction, and scanning tunneling microscopy (STM).

Following a successful STM-based check for surface cleanliness and order and an STS check for electronic structure, the sample was then dosed with high-purity O_2 through a leak-valve in the main UHV chamber (either with the sample still on the STM stage or after being picked up with the manipulator). Subsequently, the dosed sample was either transferred back to the STM for scanning of the room-temperature reacted surface, or annealed at temperatures ranging between 300 °C and 500 °C before being returned to the STM.

Filled-state constant-current STM images were generally taken at -1.8 V to -2.0 V sample bias and 0.2-0.5 nA tunneling current with electrochemically etched tungsten tips. Scanning tunneling spectroscopy (STS) was performed using the variable tip-sample separation method developed by Feenstra et al., yielding a unitless spectrum that is an approximation to the surface density of states [25–31] (which were subsequently normalized to unity). A 1.4 kHz, 0.2 V sine wave was used for the bias modulation and the signal was extracted with a digital lock-in amplifier (Stanford Research Systems SR850).

2.2. Computational details

All density functional theory (DFT) calculations presented in this paper were performed using the Vienna Ab-Initio Simulation Package (VASP) [32–35] in the generalized gradient approximation (PBE exchange-correlation functional), with projector augmented wave (PAW) potentials [36,37] (as supplied by the VASP group), a $4 \times 4 \times 1$ Monkhorst–Pack *k*-point mesh generation scheme (for a total of four irreducible *k*-points), and plane-wave basis cut-off of 450 eV. All parameters (i.e. *k*-points, cut-off energy, vacuum space, slab thickness, etc.) were chosen such that they were each individually converged to within 1 meV/atom for the system of study.

The system studied consisted of a Ge(100) slab supercell with a 4×2 surface dimer reconstruction, as this is the lowest energy configuration (compared to the 2×1 flat dimer and 1×1 unreconstructed geometries). For all results presented in this work, the germanium slab was eight atomic layers thick. For most work, each atomic layer was 2×4 atoms in area, for a total of 64 Ge atoms per unit cell (for the clean Ge surface/substrate calculations), with the bottom of the slab unreconstructed and terminated with 16 hydrogen atoms (two H atoms per Ge). In some cases, in order to properly model the larger observed reaction sites (i.e. post-an-

nealed extended dark structures), larger slabs consisting of 96, 128, or 160 (i.e. 1.5, 2.0, and 2.5 times the size of the original 64 atom slab). In all cases, the total energies were found to scale properly with these systems; calculated enthalpies of adsorption were found to change by less than 0.1 eV for the expanded slabs, well below the estimated uncertainty of the calculations. The clean Ge supercell contained 12 atomic layers of vacuum space in the z-direction. The bottom three Ge layers were constrained to the minimum-energy bulk DFT geometry, which was found through a series of bulk Ge calculations to have a lattice parameter of 5.795 Å (2.4% larger than the experimental room-temperature result of 5.658 Å due to the well-known GGA overestimation of lattice parameters). The terminating H atoms were initially allowed to relax and were kept fixed at these optimized positions for all subsequent calculations. All other atoms (upper substrate, adsorbate, gas-phase) were allowed to structurally relax with respect to interatomic forces to a tolerance of 10 meV/Å.

DFT-based STM simulations were produced using the Tersoff-Hamann approach, wherein the charge density is calculated for the energy range of interest – in this case 0 eV to -2 eV, to match the STM conditions - and an isodensity plot of the computational slab surface is produced as an approximation to a constant-current style STM image. In order to try to best match the sites observed in the experimental STM images, surface sites based upon both the 2×1 and 4×2 dimer reconstructions were modeled. Because the 4×2 dimers on the experimental Ge(100) surface buckle rapidly at room temperature, and faster than the sampling time of the STM, much of the surface appears to consist of flat 2×1 dimers instead of the tilted 4×2 . Therefore, it was found that a combination of 4 \times 2- and 2 \times 1-based STM simulations was needed to provide a full, consistent picture of the various sites observed on the oxidized Ge(100)- $2 \times 1/4 \times 2$ surface. It must be noted, however, that while STM simulations were generated for both the 2×1 and 4×2 reconstructions, only the energies for the 4×2 sites are considered in this report, as the clean Ge(100)-4×2 reconstruction is the energetically preferred surface.

2.2.1. Discussion of estimated uncertainties/errors from DFT calculations

Since this computational work is being used to calculate thermodynamic quantities such as the enthalpy of adsorption/reaction, it is important to provide estimates of the errors and uncertainties of the method. The mean absolute error of atomization energies from the G2-1 small molecule test set using VASP with the PBE exchange-correlation functional and PAW potentials has been reported to be 0.37 eV [38], but it is difficult to determine exactly how this error applies to the O/Ge(100) system presented here. Since the systems being studied in this work all contain the same atomic species with similar bonding configurations, one should expect the relative computational errors to actually be quite small (<<0.37 eV) and systematic, regardless of absolute numerical accuracy. Under optimal circumstances, the authors would claim a conservative estimated uncertainty of \pm 0.10 eV for the work presented in this manuscript.

However, an additional issue that comes into play in this discussion is that of the infamous DFT band gap problem [39,40], wherein semiconducting and insulating materials' band gaps are under-predicted by usually 30–50%. However, in the case of the small gap semiconductors (Ge, InAs, GaSb, InSb), the band gap is predicted to be non-existent; Ge exhibits an overlap of the valence and conduction bands of almost -0.1 eV [41,42]. It is for this reason that DFT-calculated electronic structures are not being presented in this manuscript; an example density of states calculated for clean Ge(100)-4×2, however, will be made available in the Surface Science Supplementary material for the sake of reference.

Because of the overlap of the valence and conduction bands, or in a more chemistry-related nomenclature, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), one would expect an unphysical filling of what should be empty states (non-bonding and anti-bonding orbitals), and even a slight emptying of what should be completely full states (bonding orbitals). These unphysical orbital occupancies are likely to negatively affect the final calculated bonding structures and energies, most likely producing weaker bonds that would normally be expected. Additionally, because of the \sim 0.1 eV valence and conduction band overlap, one might expect some unphysical quantum mechanical mixing of the HOMO and LUMO states, producing orbitals, and therefore bonding configurations, that may be somewhat different from what would be the case for a HOMO and LUMO separated by the proper 0.67 eV Ge band gap. As a result, our estimated numerical uncertainties for the calculated enthalpies of adsorption must be larger than originally assessed, but are most likely no larger than the absolute accuracy values previously mentioned. Therefore, we will assume a relative numerical uncertainty of at least ±0.30 eV for the calculated values presented in this manuscript.

3. Results and discussion

3.1. O/Ge(100) adsorbate bonding geometry characterization

3.1.1. Clean Ge(100)-2×1/4×2

Fig. 1a is a typical filled-state STM image of the clean Ge(100)- 2×1 surface. The 2×1 dimer row reconstruction is a 4×2 buckled dimer reconstruction with a low activation energy to intra-dimer rocking (giving it an overall 2×1 periodicity and making the dimer rows appear flat). In addition to the flat-looking 2×1 rows, there are other rows, as well as small domains, where the 4×2 buckled dimer configuration has been frozen due to stabilization by step-edge and/or lattice defects; this is also observed on Si(100) at cryogenic temperatures. Also in Fig. 1a are DFT-based STM simulations



Fig. 1. (a) Filled-state STM image (V_s = -2.0, I_t = 0.2 nA) of the Ge(100)-2×1/4×2 surface. (b) Ball-and-stick diagrams of the 4 × 2 and 2 × 1 dimer reconstructions.

of the 2 \times 1 and 4 \times 2 reconstructions, overlaid on 2 \times 1 and 4 \times 2 regions of the surface, respectively.

Fig. 1b displays ball-and-stick models of the top three layers for the two different dimer reconstruction geometries. We note that the 4×2 buckled dimer structure is significant because it is accompanied by electron transfer from the "low" dimer atoms to the "high" dimer atoms, which changes the reactivity of the two respective dangling bonds.

3.1.2. Room-temperature oxidized Ge(100)

Fig. 2 is a typical filled-state STM image of the Ge(100)-2×1 surface after exposure to 100 L O_2 at room temperature (no post-oxidation anneal). Two main types of sites, with two sub-types each, are found on the unannealed oxidized surface: "bright sites", which image above the original Ge(100) lattice, and "dark sites", which image below the original Ge(100) lattice. According to the site designation nomenclature introduced by Fukuda, the four different site sub-types indicated in Fig. 2 are as follows: type A (square), type B (hexagon), type C (diamond), and type D (circle). The sites are catalogued in Table 1.

There are two distinct types of bright sites observable with STM on the room temperature oxidized Ge(100) surface; these sites can be clearly differentiated by line scan analysis. The brighter and larger of the two, type A, are found to image 1.2–1.4 Å above the surface (the dimer plane), which is consistent with the Ge(100) step height, indicating that these sites are Ge ad-atoms. The dimmer and smaller of the two sites, type B, are found to image at a range of 0.6–0.9 Å above the surface. These sites are consistent with metastable oxygen adsorption sites - the dimer adsorption/insertion site and the back-bond insertion site – suggested by previous theory work [23,24]. In these sites, a single O atom inserts into a Ge-Ge bond without displacing any Ge atoms. Insertion into and adsorption onto the surface dimers is denoted as "dimer insertion" and "dimer adsorption", respectively, while insertion into the bond between 1st and 2nd layer Ge atoms is denoted as "backbond insertion". As can be seen by the STM simulations in Table 1, the dimer insertion site is unlikely to be observable in the experimental images, but the dimer adsorption and backbond insertion sites should be visible.

There are also two different observable dark sites. Type C sites exist on the edge of the dimer row and image about 0.6 Å below



Fig. 2. Filled-state STM image ($V_s = -2.0$ V, $I_t = 0.2$ nA) of room-temperature Ge(100) surface exposed to 100 L O₂. Examples of the major types of post-oxidation features (A, B, C, and D) are highlighted with geometric symbol.

Table 1

Summary of computational results for the post-oxidation features indicated in Fig. 2, including ball-and-stick diagrams for both 4 \times 2- and 2 \times 1-based geometries, STM simulations for both 4 \times 2 and 2 \times 1 geometries, and enthalpies of adsorption (only for 4 \times 2)



Enthalpies of adsorption are given per adsorbed O, and calculated with respect to molecular O_2 reactant and the formation of Ge ad-dimers.

the surface. They are somewhat difficult to distinguish between the "holes" formed by buckled dimers, but they do image slightly deeper and more distinct. These sites stabilize the dimer buckling, locking it into place. This site is consistent with a single oxygen displacement site, where a single Ge atom has been displaced by an oxygen atom, producing type A sites. Type D sites image as a dark cut across the dimer row 1.0–1.2 Å deep below the surface. This site is consistent with a double oxygen displacement site, where a full Ge dimer has been displaced by two oxygen atoms, also producing type A sites. Both types of dark sites have previously been reported to image as bright sites in empty-state imaging, confirming the presence of oxygen rather than being merely missing Ge defects [18,21].

In order to provide additional evidence for the identification of the various features observed in the STM images, DFT modeling was employed to simulate the various O/Ge(100) reaction sites suggested by experimental results, standard chemical reasoning, and claims in the literature. Table 1 provides the results from the DFT modeling of the observed and suggested reaction sites from the O/Ge(100) oxidation process, including ball-and-stick diagrams of the surface bonding configurations, STM simulations (with the computational unit cell indicated by the dashed red line), and calculated adsorption enthalpies. Note that the adsorption energies in Table 1 are only provided for the 4×2 reconstruction and that these calculations were performed at a coverage (25%) such that the adsorbate and/or reaction sites were not adjacent within the computational unit cell, making them essentially isolated.

Adsorption enthalpies were extracted from the computational work using the Hess's law method of "products minus reactants." The calculated values can strongly indicate which of the potential simulated geometries are thermodynamically favorable (and therefore stable at room temperature and above) and those that are unlikely to occur. The reported adsorption enthalpies are per adsorbed O atom, with respect to an O₂ molecule reactant. Reaction sites that involve the displacement of Ge atoms from the surface to form ad-atoms and/or ad-dimers are calculated with respect to the formation of ad-dimers, as ad-dimers are the lower energy configuration of the two ad-species (-0.78 eV decrease in total energy due to dimerization). This combination of experiment and theory allows for the unambiguous assignment of low-coverage O₂ reaction sites and resultant bonding geometries.

All of the calculated adsorption enthalpies indicate room and somewhat elevated temperature stability, with dimer and lowbackbond insertion yielding the highest adsorption enthalpies, -2.65 eV and -2.43 eV, respectively, and the high and low-single displacement geometries having the lowest, -1.87 eV and -2.02 eV, respectively. It is interesting that the displacement sites, especially the full dimer displacement, with an adsorption enthalpy of -2.11 eV, yield lower enthalpies than the insertion sites, considering the prevalence of these sites in the experimental STM images. The computational results, however, are consistent with the initial-stage Ge oxidation mechanism calculations reported by Soon et al. [24], which used a Gaussian-type basis set and Ge clusters, compared to the plane-wave basis and slabs used in the work presented in this manuscript. The STM simulations indicate a very subtle appearance for the single displacement sites in the experimental images, so it is difficult to quantify the site surface coverage. The dimer displacement sites, however, are quite obvious in both the simulations and the experimental images, and they are of significant coverage.

This apparent theory-experiment discrepancy, however, is explained by the increase in configurational entropy introduced by the Ge displacement reaction due to the large number of potential ad-atom adsorption sites available on the surrounding surface, especially at elevated temperatures, where significant diffusion is possible, providing for an essentially irreversible reaction. Each O atom may reversibly sample any of the insertion reaction products before settling on the dimer or low-backbond insertion, but any displacement sites sampled are final products by the nature of their irreversibility because the Ge atom that gets displaced is effectively removed from the reaction environment.

3.1.3. Annealed oxidized Ge(100)

Following the work of Fukuda et al., the oxidized samples were annealed at 325 °C, well below the GeO desorption temperature of about 425 °C [16,18,20,21]. The continued presence of oxide on the surface after the long, low-temperature anneal was also verified by measuring a simple thermal desorption spectrum while monitoring O_1 , O_2 , GeO, and GeO₂ with a quadrupole mass spectrometer (QMS); GeO was found to be the only detectable desorption product; furthermore, GeO was detected only at surface temperatures above 400 °C. The 325 °C gentle anneal of the oxidized sample helped to eliminate many of the different room-temperature oxidation reaction sites so that the effect of the few remaining sites on the electronic structure could be elucidated. As depicted in Fig. 3, the 325 °C anneal appears to convert the oxygen insertion sites (B sites) to displacement sites, and coalesces the individual oxygen displacement sites (sites C and D) into long, dark troughlike structures. These extended dark structures existed as both single and double atomic width rows (designated as S and 2S rows by Fukuda). These dark rows have been previously verified as oxide structures with ultraviolet photoelectron spectroscopy (UPS) [20].

In contrast to Fukuda et al., however, we performed much longer anneals (20 min vs. 5 min). It was found that if the room-temperature oxidized sample was subjected to this longer anneal time, the O dark sites coalesced into much longer rows (often 600+ Å long; see Fig. 3b) than reported by Fukuda, and the Ge ad-atom reaction products tended to either coalesce into larger regrowth areas or were diffusively driven to the step edges, leaving behind very few isolated Ge ad-atoms or ad-dimers compared to the unannealed room temperature oxidized surface. Shorter anneal



Fig. 3. Filled-state STM images ($V_s = -2.0 \text{ V}$, $I_t = 0.2 \text{ nA}$) of 100 L O₂-dosed Ge(100) after 20 min anneal at 325 °C: (a) 300 × 300 Å² and (b) 800 × 800 Å². Note: both images have been skew-corrected for excessive scanner drift.

times were found to yield surfaces still containing most of the Ge ad-species (ad-atoms, ad-dimers, small regrowth islands) on the terraces and shorter O dark site rows.

A blown-up high-resolution STM image of the extended dark trough structures is given in Fig. 4a; note that areas with both staggered (zigzag) and in-line (linear) trough structures are visible. With regard to the nature of these extended dark trough structures, Fukuda et al. originally surmised that they consisted of a reconstructed trough dimer structure in the second atomic layer [16,18,20,21], as depicted in the models and STM simulations presented in Fig. 5a. Such a configuration would necessarily produce a site with a depth, as measured from a row dimer to a trough dimer, equal to that of a Ge(100) step height, 1.4 Å. However, line scan measurements performed on the images taken in this work actually yield depths of only 0.6–0.7 Å for the bright portions of the extended dark trough sites and 1.8-2.2 Å for the dark portions (see line-scans in Fig. 4b-d; depths measured with respect to "flat" row dimers), indicating a different structure than that suggested by Fukuda. Additionally, the Fukuda structure would seem to preclude the continuing presence of oxygen on the Ge(100) surface, but our thermal desorption results performed after the 20 min 325 °C anneal prove otherwise.



Fig. 4. (a) Section of a high-resolution filled-state STM image ($V_s = -2.0 \text{ V}$, $I_t = 0.2 \text{ nA}$) of 100 L O₂-dosed Ge(100) after 20 min anneal at 325 °C, blown-up to reveal details of the extended dark trough structures. Note the existence of both staggered (top, bottom) and in-line (right) structure types. The image was corrected for excessive scanner drift. (b) Line scan over a staggered dark trough structure (squares). (c) Line-scan over the bright portion of an in-line dark trough structure (circles). (d) Line-scan over the dark portion of an in-line dark trough structure (triangles).



Fig. 5. Atomic-structure models and STM simulations for the post-oxidation post-annealed Ge(100) extended dark trough structures: (a) the model originally suggested by Fukuda et al., and (b) the modified configuration proposed by the authors of this manuscript.

While the original Fukuda model (Fig. 5a) does not appear to match the extended dark structures observed in the STM images, it does posses the correct periodicity, and the second layer Ge redimerization would indeed be expected due to the significant energy reduction it provides. Using the original Fukuda structure as a starting point, a number of different configurations incorporating oxygen into the trough redimerization structures were modeled with DFT. Of the various structures considered, the only one found to visually match the STM results consisted of O atoms adsorbed onto the reconstructed Ge trough dimers (see STM simulations and ball-and-stick models for staggered and in-line structures in Fig. 5b).

For a more quantitative structural analysis, the predicted structural dimensions (trough depth, distances between features) from the DFT "trough oxide" model were compared with those measured in the STM images (see Fig. 4b–d). The trough oxide model yields a depth for the bright portions (O adsorbates) of the extended dark trough structures of 0.7 Å, which is exactly equal to the experimental value. The O–O distance for the in-line dark trough structure was predicted by the trough oxide model to be 4.3 Å, the same as measured in the STM images (4.4–4.6 Å). These results indicate that the trough oxide model is very consistent with the extended dark trough structures observed on the post-oxidized 325 °C annealed Ge(100) surface.

In principle, the relative populations of the in-line vs. staggered structures can be estimated using Maxwell–Boltzmann statistics and the calculated enthalpies of formation (or total energies, since the numbers and types of atoms in both systems are the same). In this case, a room-temperature Maxwell–Boltzmann population ratio equal to that experimentally observed (~10% in-line) requires a difference in energies of only 0.055 eV, far below the limit of uncertainty for the computational work reported in this manuscript, and arguably below the threshold of DFT calculations in general. It is interesting to note, though, that the total energies for the two structures were actually calculated to be degenerate.

It must also be noted, however, that there do remain some questions regarding the veracity of our model, regardless of the excellent qualitative and quantitative match. Specifically, the model structures that are most consistent with the experimental results are not the structures that are predict to be the most energetically preferred. It was found that, given the same basic modified structures for the in-line and staggered dark trough features (see Fig. 5b), there are two simple configuration changes that produce more stable structures: Ge trough dimer tilt (vs. the current flat dimers) and O adsorbate dimer insertion (vs. the current O atom adsorption onto of the Ge dimers).

According to the calculations, a total of -0.34 eV (per Ge-O-Ge dimer complex) of stabilization can be gained by both tilting the Ge trough dimers (similar to the stabilization of the 4×2 vs. the 2×1 terrace dimers) and inserting the O atoms *into* the Ge dimers rather than adsorbing *onto* the dimers, as was the case in the model. This value is right on the edge of our estimated uncertainty (due to the poor DFT-calculated Ge electronic structures) for the computational work reported in this manuscript; we cannot, at present, fully account for this apparent discrepancy.

However, given the well-known room temperature active buckling of the 4×2 Ge terrace dimers, it may be possible, even likely. that the reconstructed Ge trough dimers in the dark trough features will also exhibit this dynamic feature. This buckling motion would thereby eliminate the tilted- vs. flat-dimer energy discrepancy, but should leave the visual appearance of the extended dark trough features basically the same. While we cannot say anything definitive about the O adsorbate bonding structure discrepancy, it is possible that improved electronic structures from higher-order computational techniques may yield different results. It must also be noted that there is an additional potential source of error due to the periodic boundary conditions of the plane-wave DFT method used in this work. Because the finite slab supercell is repeated infinitely in all three Cartesian directions, the extended dark trough features are necessarily modeled as being infinitely long, while they are in fact finite. It is possible that long-range physical phenomena that cannot be accounted for in the computational modeling, such as surface strain, may influence the experimental surface and lead to a slight discrepancy between calculated and actual energetics. Nonetheless, the current calculations clearly show that the trough oxide model captures the most important aspects of the extended dark trough features. The STM simulations perfectly match the STM images, and the predicted structural dimensions are also completely consistent with experimentally measured values.

3.1.4. Oxide desorption and surface recovery

Finally, upon annealing the oxidized sample to 500 °C, the clean surface could be recovered due to desorption of all of the GeO reaction products, as verified by the thermal desorption spectra, and diffusion of Ge atoms to fill in vacancies and reorder the surface

(see Fig. 6). STM images indicate that all oxygen has been removed from the surface, as the surface appears identical to that of clean, unoxidized Ge(100).

3.2. O/Ge(100) electronic structure characterization

Scanning tunneling spectroscopy (STS) measurements yield (dI/ dV/(I/V) curves that give an approximation to the local surface density of states [25-31]. Therefore, these spectra possess the same features as a standard DOS plot, namely a valence band (VB), conduction band (CB), band gap, and Fermi level. The Fermi level is found at the zero volt position; a negative sample bias probes "filled" electronic states (VB), and a positive sample bias probes "empty" electronic states (CB). In between the finite VB and CB DOS edges is the band gap (i.e. where the DOS is equal to zero). Therefore, in STS spectra, an unpinned *p*-type sample has a Fermi level position near the VB and an unpinned *n*-type sample has a Fermi level position near the CB. It is this property that will be employed in this work, since a misplaced Fermi level is consistent with electronic pinning due to a high density of surface states within the band gap [43,44]. STS experiments have been performed on both *p*- and *n*-type Ge(100)- $2 \times 1/4 \times 2$ surfaces under various conditions (clean, room-temperature oxidized, post-oxidized annealed, and oxide-desorbed clean).

Fig. 7a presents spectra for clean *p*- and *n*-type Ge(100)- $2 \times 1/4 \times 2$ surfaces. For the clean *p*-type sample, the Fermi level is found to be located near the VB (negative sample bias), and for the clean *n*-type sample the Fermi level is located near the CB (positive sample bias).

Fig. 7b presents STS spectra taken on the room-temperature p- and n-type Ge(100) surfaces after exposure to 100 L of O₂ (corresponding to a surface coverage of about 20%), without post-oxidation anneal. The p-type surface displays a Fermi level position near the VB, the same as on the clean surface, but the n-type surface Fermi level is also found near the VB, opposite to what is seen on the clean surface, indicating surface Fermi level pinning. Clearly, this result is direct consequence of the sub-monolayer oxidation reaction, and is presumably due to the induction of electronic states within the semiconductor band gap. However, because there is such a wide range of reaction sites on the room-temperature oxidized Ge(100) surface, including displaced Ge ad-species and



Fig. 6. Filled-state STM image ($V_s = -2.0$ V, $I_t = 0.2$ nA) of 100 L O₂-dosed Ge(100) after annealing for 5 min at 500 °C. All oxide has been desorbed from the sample, thereby restoring the surface to its original "clean" state. The image was corrected for excessive scanner drift.



Fig. 7. Scanning tunneling spectra, with inlayed associated STM images for reference, for both p- and n-type (a) clean Ge(100), (b) as-is room-temperature 100 L O₂-dosed Ge(100), (c) room-temperature oxidized Ge(100) annealed to 325 °C, and (d) room-temperature oxidized Ge(100) annealed to 500 °C. Note that for both the clean (a) and recleaned (d) surfaces the Fermi level (0 V) lies near the valence band (VB) for p-type and conduction band (CB) for n-type, but for both room-temperature oxidized and post-annealed (325 °C) oxidized samples the Fermi level lies near the VB for both p- and n-type, indicating Fermi level pinning.

various O adsorbate structures, it is difficult to elucidate the exact cause of the Fermi level pinning. We note that we would expect a large density of Ge ad-atoms to pin the Fermi level since they have two partially filled dangling bonds.

In order to help better determine the nature of the Fermi level pinning on the oxidized Ge(100) surface, the room-temperature oxidized samples were annealed for 20 min at 325 °C to remove the small Ge ad-species and metastable O adsorbates from the terraces. STS spectra taken on the post-annealed samples (Fig. 7c) reveal the same Fermi level pinning as observed on the as-oxidized samples: both the *p*- and *n*-type samples display a Fermi level position near the VB. Because the only substantial reaction products remaining after the gentle anneal are the extended dark trough structures (the great majority of the Ge ad-species are found to coalesce into regrowth islands and can be considered benign), it is hypothesized that these oxygen-containing (suboxide) dark trough structures are the source of the Fermi level pinning on the post-annealed post-oxidized surface. Therefore, the pinning on the unannealed room-temperature oxidized surface is likely to be, at least in part, due to the various O adsorbate structures. Further detailed computational work utilizing higher-order theoretical methods to produce accurate electronic structures will enable the identification of the pinning species and allow for the exact nature of the pinning mechanism to be elucidated.

Finally, the samples were annealed at 500 °C to desorb the GeO oxidation products completely from the surface. STS spectra taken on these desorption-cleaned samples (Fig. 7d) reveal recovered electronic structures identical to that observed on the clean surface: the *p*-type samples display a Fermi level position that is still near the VB, and the *n*-type samples display a Fermi level that has returned to the original clean-surface position near the CB.

4. Conclusions

We have found that both the room-temperature as-oxidized $Ge(100)-4\times2/2\times1$ surface and the post-oxidation 325 °C annealed surface suffer from Fermi level pinning, with the Fermi level pinned near the valence band for both *n*- and *p*-type Ge(100) samples. This pinning appears to be the result of the induction of electronic states within the semiconducting band gap by at least one of the oxidation reaction products. While the as-oxidized surface contains too many various reaction sites to reliably identify the exact cause of the pinning, the results from the 325 °C annealed surface indicate that it is the suboxide adsorbates and structures that induce Fermi level pinning. These findings point to a potential source of at least some of the problems encountered in Ge-based MOSFET devices that possess germanium native oxide at the semiconductor/dielectric interface.

Acknowledgements

The authors would like to acknowledge the SRC (2006-VC-1437), MARCO (887.011), and the Intel/UCDISCOVERY program for funding this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.susc.2008.05.019.

References

[1] R.H. Kingston, J. Appl. Phys. 27 (2) (1956) 101.

- [2] P.W. Loscutoff, S.F. Bent, Annu. Rev. Phys. Chem. 57 (1) (2006) 467.
- [3] K. Prabhakaran, F. Maeda, Y. Watanabe, T. Ogino, Appl. Phys. Lett. 76 (16)
- (2000) 2244.[4] V. Craciun, I.W. Boyd, B. Hutton, D. Williams, Appl. Phys. Lett. 75 (9) (1999) 1261.
- [5] O.J. Gregory, E.E. Crisman, L. Pruitt, D.J. Hymes, J.J. Rosenberg, Mater. Res. Soc. Symp. Proc. 76 (1987) 307.
- [6] Y. Wang, Y.Z. Hu, E.A. Irene, J. Vac. Sci. Technol. A 12 (4) (1994) 1309.
- [7] D.B. Alford, L.G. Meiners, J. Electrochem. Soc. 134 (4) (1987) 979.
- [8] S. Huiling et al., IEEE IEDM (2002) 441.
- [9] C.M. Ransom, T.N. Jackson, J.F. DeGelormo, IEEE Trans. Electron Devices 38 (12) (1991) 2695.
- [10] R.S. Johnson, H. Niimi, G. Lucovsky, J. Vac. Sci. Technol. A 18 (4) (2000) 1230.
 [11] M.L. Lee, C.W. Leitz, Z. Cheng, A.J. Pitera, T. Langdo, M.T. Currie, G. Taraschi, E.A.
- Fitzgerald, D.A. Antoniadis, Appl. Phys. Lett. 79 (20) (2001) 3344.
- [12] R.A. McKee, F.J. Walker, M.F. Chisholm, Science 293 (5529) (2001) 468.
- [13] M. Meuris et al., Mater. Sci. Semicond. Process 8 (1–3) (2005) 203.
- [14] K.C. Saraswat, C.O. Chui, T. Krishnamohan, A. Nayfeh, P. McIntyre, Microelectron. Eng. 80 (2005) 15.
- [15] T. Takahashi, T. Nishimura, L. Chen, S. Sakata, K. Kita, A. Toriumi, IEEE IEDM 2007 (2007) 697.
- [16] T. Fukuda, Surf. Sci. Lett. 417 (2-3) (1998) L1149.
- [17] T. Fukuda, T. Ogino, Surf. Sci. 357-358 (1996) 748.
- [18] T. Fukuda, T. Ogino, Phys. Rev. B 56 (20) (1997) 13190.
- [19] T. Fukuda, T. Ogino, Surf. Sci. 380 (1) (1997) L469.
- [20] T. Fukuda, T. Ogino, Appl. Surf. Sci. 130-132 (1998) 165.
- [21] T. Fukuda, T. Ogino, Appl. Phys. A 66 (1998) S969.
- [22] S. Kurokawa, H. Yamashita, J. Yoshikawa, A. Sakai, Jpn. J. Appl. Phys. 38 ((Part 1, No. 6B)) (1999) 3845.

- [23] E.J.J. Kirchner, E.J. Baerends, Surf. Sci. 311 (1-2) (1994) 126.
- [24] J.M. Soon, C.W. Lim, K.P. Loh, N.L. Ma, P. Wu, Phys. Rev. B 72 (11) (2005) 115343
- [25] R.M. Feenstra, J.A. Stroscio, A.P. Fein, Surf. Sci. 181 (1-2) (1987) 295.
- [26] N.D. Lang, Phys. Rev. B 34 (8) (1986) 5947.
- [27] N. Li, M. Zinke-Allmang, H. Iwasaki, Surf. Sci. 554 (2-3) (2004) 253.
- [28] A. Selloni, P. Carnevali, E. Tosatti, C.D. Chen, Phys. Rev. B 31 (4) (1985) 2602.
- [29] J. Tersoff, D.R. Hamann, Phys. Rev. Lett. 50 (25) (1983) 1998.
- [30] J. Tersoff, D.R. Hamann, Phys. Rev. B 31 (2) (1985) 805.
- [31] J.A. Strosico, R.M. Feenstra, in: J.A. Strosico, W.J. Kaiser (Eds.), Scanning Tunneling Microscopy, Academic Press, San Diego, 1993.
- [32] G. Kresse, Thesis, Technische Universität Wien, 1993.
- [33] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (16) (1996) 11169.
- [34] G. Kresse, J. Furthmüller, Comput. Mat. Sci. 6 (1) (1996) 15.
- [35] G. Kresse, J. Hafner, Phys. Rev. B 47 (1) (1993) 558.
- [36] P.E. Blöchl, Phys. Rev. B 50 (24) (1994) 17953.
- [37] G. Kresse, D. Joubert, Phys. Rev. B 59 (3) (1999) 1758.
- [38] J. Paier, R. Hirschl, M. Marsman, G. Kresse, J. Chem. Phys. 122 (23) (2005) 234102.
- [39] J.P. Perdew, M. Levy, Phys. Rev. Lett. 51 (20) (1983) 1884.
- [40] L.J. Sham, M. Schlüter, Phys. Rev. Lett. 51 (20) (1983) 1888.
- [41] A. Fleszar, Phys. Rev. B 64 (24) (2001) 245204.
- [42] M. Städele, M. Moukara, J.A. Majewski, P. Vogl, A. Görling, Phys. Rev. B 59 (15) (1999) 10031.
- [43] W.E. Spicer, P.W. Chye, P.R. Skeath, C.Y. Su, I. Lindau, J. Vac. Sci. Technol. 16 (5) (1979) 1422.
- [44] W.E. Spicer et al., J. Vac. Sci. Technol. B. 6 (4) (1988) 1245.