

Evidence of the Ge nonreactivity during the initial stage of SiGe oxidation

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(Received 3 June 2008; accepted 20 December 2008; published online 28 January 2009)

Density functional theory calculations are used to identify preferential sites for oxygen adsorption on SiGe. It is shown that Ge atoms hinder O incorporation in their vicinity. Additionally, the silanone structure, known to be the key intermediate prior to silicon dioxide formation, is shown to be not favorable when close to a Ge site on the surface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3076092]

Silicon undoubtedly remains at the heart of microelectronics due to the excellent properties of its interface with silicon dioxide. As the silicon industry looks for new ways and materials to continue the rapid pace of increasing microelectronic device speed, strain and crystal lattice engineering become crucially important. For instance, Si/Ge heterostructures offer potential improvements of actual devices by significantly increasing carrier mobility. This is obtained by strained silicon on SiGe substrate with a larger lattice parameter.^{1,2} Such materials enable the preparation of a Si channel or a Ge-rich or even a pure Ge channel with a respective two-dimensional carrier gas opens the attractive possibility to fabricate high performance *n*- or *p*-type field effect transistors. From the processing viewpoint, it is known that Ge condensation is achieved by thermal oxidation of the SiGe layer whereby Si oxidizes faster than Ge, and the Ge atoms are rejected from the oxide into the SiGe layer below.^{3–5} In the late 1980s, Fathy *et al.*⁶ demonstrated such formation of a SiO₂ layer on nearly pure epitaxial layers of Ge on Si substrates with a very smooth interface. It is known that because of higher negative formation energy of SiO₂ compared to GeO₂ only SiO₂ will be produced under all experimental conditions.⁷ Indeed, Terrasi *et al.*^{8,9} reported on the SiGe oxidation using photoelectron spectroscopy and Rutherford backscattering spectrometry for short oxidation times and found small concentrations of Ge in the oxide. Additionally, Liang *et al.*¹⁰ studied the atomic configuration of the Ge/SiO₂ interface using electron-energy-loss spectroscopy measurements and their results are consistent with those obtained by Terrasi *et al.*^{8,9} In order to investigate all the above features and to optimize the structures, a large experimental processing “window,” in terms of oxidation pressure and temperature and potential associated annealing steps, has to be considered. Therefore a detailed understanding of the oxidation process of a SiGe substrate is now required to serve as a guide for optimizing the processing windows: oxygen incorporation mechanisms into SiGe layers, potential role of oxidation induced strain at the interface, and Ge and Si diffusion across the interface. Density functional theory (DFT) calculations have been used with success along the last decades to shed light into the mechanisms of pure

silicon oxidation.¹¹ Only recently, a coherent scenario of the initial stages of silicon oxidation has been described where specific intermediates, strand oxygen positioning, and silanone structure configurations play the important role.¹² Such knowledge should be now revisited when confronted to SiGe materials where to date, little has been published on the physico-chemical mechanisms of oxidation.

The DFT and plane waves code VASP,^{13,14} using a parametrized generalized gradient approximation^{15,16} have been used to perform these calculations. The atoms (Si, Ge, H, and O) are described by ultrasoft pseudopotentials of the Vanderbilt type, standard for these materials.¹⁷ The energy cutoff for the wave function basis set expansion is set to be 475 eV. Spin polarization has been taken into account. The conjugate gradient method is used for all atomic relaxations. The Brillouin zone is sampled at Γ point.¹⁸ The SiGe model considered in the following is based on a Si(100)-(2×1) surface built according to previous work,¹² where a silicon surface atom is now replaced by a germanium atom. The Si(100) model is constructed by a repeated slab consisting of six layers of eight silicon atoms considering 2×1 reconstruction with buckling along dimer rows. Sixteen hydrogen atoms are used to saturate the silicon dangling bonds underneath the surface and the two lowest silicon layers are kept fixed during relaxations in order to mimic the bulk. The cell dimensions are $a=b=10.91$ and $c=17.91$ Å, leaving a vacuum space of about 10 Å between the slabs that prevents bottom to top slab interaction. SiGe model system has been created by replacing a surface Si atom with a Ge atom and minimizing the energy. The resulting structure does not modify the overall surface morphology. The surface thus remains buckled, the most stable dimer structure for the Si–Ge dimer is found to be down-up as recently published.¹⁹

In the following, we compare and discuss the oxidation process of pure Si and SiGe surfaces. Both systems are partially oxidized by incorporating one, two, or three oxygen atoms at various positions onto the surface; that is either within Si–Si bonds or stabilized “atop” of surface silicon atoms. The oxygen positioning follows the reaction pathways found in a previous work on pure silicon oxidation.¹² Total energy of both Ge-containing and pure Si surfaces for each oxygen-inserted configuration are calculated, after relaxation of the system, and compared to each others. For each of the following three groups, 1, 2, and 3 oxygen-containing

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Structures [1-10] [110]	A	B	C	D	E	F
	ΔE (eV)	■ = Si Ref. = 0 ■ = Ge Ref. = 0	0.08	0.54	0.79	1.26
	Same as A			Same as D		unstable

FIG. 1. Relative stability of dimer units containing one oxygen atom inserted into the first monolayer of the silicon substrate. The two cases of pure Si and SiGe alloy (1 Ge on the Si surface) are considered. The most stable structure in each case is taken as reference. Energy values are in eV. Grey circles are surface Si atoms, small black circles are Si atoms of the subsurface, oxygen atoms are in white circles, and gray squares are germanium or silicon atoms depending on the case studied. Full lines are the dimer bonds and the dashed lines correspond to the backbonds. The formation energy reference is -3.66 eV for Si and -3.78 eV for SiGe.

configurations, the most stable configuration of, respectively, Si and SiGe systems are taken as the reference of energy to facilitate the comparison between different structures in the same group. Figures 1–3 picture the most pertinent calculated configurations for the three cases, respectively. Relative energies ΔE , all positive, are given with respect to the reference energy E_s as $\Delta E = E_i - E_s$, where E_i is the total energy of the configuration i , for each system (SiO_x and SiGeO_x ; $x=1,2,3$). All structures noted as “unstable” in respective figures have a positive energy of formation.

The incorporation of a single oxygen atom onto the Si and SiGe surfaces is considered first (see Fig. 1). In both Si and SiGe cases, the most stable structures are found when the oxygen atom is incorporated into the surface backbonds (structures A). The formation energies of these structures are -3.66 and -3.78 eV for SiO and SiGeO, respectively. Further, in the case of the SiGe surface, the oxygen atom preferentially incorporates in a Si–Si backbond leaving the Ge–Si backbond unoxidized. Forcing the incorporation of the oxygen atom into this Ge–Si backbond has a cost of 0.79 eV compared to the reference structure (Fig. 1, structure C, Ge case). We also observe that the oxygen atom inserted in the dimer remains the second most stable configuration in both cases (structure B). Nevertheless, in the case of pure silicon surface, the difference in energy with respect to the reference is tiny and amounts to 0.08 eV. However, in the SiGe case, this difference increases up to 0.54 eV. This last structure exhibits a drastic asymmetry of the oxygen atom positioning. The third remarkable configuration is the oxygen in atop position (structure E). In the case of pure silicon, it has been demonstrated that this position ($+1.26$ eV compared to the reference) is an important intermediate step for

Structures [1-10] [110]	G	H	I	J	K
	ΔE (eV)	■ = Si Ref. = 0 ■ = Ge 0.29	Same as G 0.39	0.15 Ref. = 0	0.19
				0.66	0.65

FIG. 2. Same as in Fig. 1 but with two oxygen atoms inserted into the first monolayer of the silicon substrate. The formation energy reference is -7.28 eV for Si and -7.45 eV for SiGe.

Structures [1-10] [110]	L	M	N	P
	ΔE (eV)	■ = Si Ref. = 0 ■ = Ge Unstable	0.59	0.20
			0.82	0.25
				Ref. = 0

FIG. 3. Same as in Fig. 1 but with three oxygen atoms inserted into the first monolayer of the silicon substrate. The formation energy reference is -10.81 eV for Si and -10.86 eV for SiGe.

oxygen incorporation and diffusion.¹⁴ The equivalent atop GeO key configuration hardly exists on the SiGe surface, its energy cost having more than doubled: $+2.63$ compared to $+1.26$ eV. As a preliminary conclusion, incorporation of single oxygen atom is not energetically favorable in the vicinity of Ge atom. The last position that plays a crucial role in the oxidation of pure silicon is the bridging dimer position (structure F) discussed in Ref. 20. As shown in Fig. 1, this structure, where the oxygen atom bridges the Ge atom with its adjacent Si atom, becomes unstable and no longer exist in the presence of germanium atom.

Similarly, Fig. 2 displays the energy cost in both Si and SiGe systems considered previously but oxidized through the incorporation of two oxygen atoms. The major point here concerns the most stable structure in each case. Their energy of formation is -7.28 and -7.45 eV for SiO_2 and SiGeO_2 , respectively. In the case of pure silicon, the most stable structure (structure G), as described by Chabal *et al.*,²¹ is the silanone configuration. In agreement with both theoretical calculations and low temperature STM experimental observations,¹⁴ this configuration is known to be a key intermediate prior to oxide nucleation. In particular, it expresses (i) the propensity of the oxygen atom in strand position to be mobile and (ii) the difficulty for the strand oxygen to be inserted into the surface Si–Si bonds.¹⁴ The sequencing of this specific structure that leads to quasiordered oxide layers, exhibiting “adjacent dimer bridging oxygen, i.e., an oxygen atom that bridges two adjacent dimer unit,” and described as “surface bridging oxygen” by Yamasaki *et al.*,²⁰ is certainly the basis of the excellent properties of the SiO_2/Si interface. It is therefore of major importance to underline that germanium atom hinders this type of specific structures. In the presence of germanium, the preferential oxidation sites become the backbonds of the silicon atom forming the dimer unit with Ge. This configuration (Ge-containing surface, structure I), taken here as the reference for all 2O–SiGe structures, has a formation energy of 0.15 eV higher than the silanone structure (Si based-structures, case G). This indicates a low stability, with respect to pure Si oxidized surfaces, whatever the relative position of oxygen and germanium atoms.

Forcing a silanone structure on the Ge side costs 0.39 eV. This cost is decreased to 0.29 eV when considering a silanone with an oxygen atom inserted in a Si–Si backbond. Isolated Ge atoms should be seen as a local defect for oxidation process. More generally, like the single oxygen atom within dimer units, the two oxygen atoms tend to avoid direct chemical connection with germanium on the surface.

By increasing the number of oxygen atoms to 3 (see Fig. 3), the most stable structures of SiO_3 and SiGeO_3 are structures *L* and *P*, respectively. Their energies of formation are -10.81 and -10.86 eV. The segregation process between the oxide and the germanium atom becomes even more important. This is particularly clear when comparing configurations *M*, *N*, and *P*. Configuration *P* exhibits a nonbridging oxygen but still is the most stable configuration of all 3O–SiGe configurations and is taken as the reference. It is the only configuration presenting no Ge–O bond. All other higher energy configurations exhibit Ge–O–Si bonds indicating that oxygen atoms prefer to remain close to Si atoms than to connect to Ge. The situation with pure silicon is the opposite: since *L* and *M* structures have, respectively, and energy of formation 0.82 and 0.23 eV lower than that exhibiting a nonbridging oxygen (case *N*). The reference for pure silicon becomes completely unstable when a Ge is added on the surface.

In conclusion, we have determined the most probable positions for the incorporation of oxygen atoms around a germanium atom located in a substitutional site of the silicon (100) surface. We observe that the presence of germanium atom systematically hinders further oxygen insertion around this site. Furthermore, it is seen that the key initial step observed during silicon oxidation is altered. Specifically, the main step before oxide nucleation gives rise to a silanone structure where a “strand” Si=O at the surface has the ability to bind to silicon atoms present on the surface, making the connection between two adjacent dimer units possible. This silanone structure, which is the most stable one in the case of pure partially oxidized silicon, becomes far less stable when a germanium atom is involved. This loss of stability should have a major influence on subsequent atomic arrangement in oxidized SiGe. The results obtained in this work support the experimental findings²² indicating that the presence of Ge catalytically enhances the rate of oxidation of Si for alloys with low Ge concentration.

The authors wish to thank the CCRT and CALMIP supercomputer Centers for calculation facilities. This work was

founded by the French National Research Agency (ANR) through OsiGe_Sim project No. ANR-05-NANO-004.

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