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Oxidation of Germanium and Silicon surfaces (100): a comparative study through DFT methodology

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Abstract. Density Functional Theory calculations are used to map out the preferential oxygen molecule adsorption sites and oxygen atom incorporation on germanium (100) surface. A comparison with primary oxidation mechanisms encountered in pure silicon and silicon germanium (100) surfaces is presented here. This study highlights opposite substrates behaviors facing oxygen molecule adsorption: 1/ surface germanium atoms move from their crystalline positions to adapt to the approaching oxygen molecule resulting in adsorbed peroxide bridge configuration, whereas oxygen molecule is fully dissociated in strand configuration on a silicon surface 2/ oxygen atoms tend to avoid each other on germanium surface whereas oxide nucleus can be observed on silicon surface even at the early steps of the oxidation process. Results show that germanium surface appears to be less reactive than the silicon substrate towards molecular oxygen species.

1. Introduction

With the constant downscaling in microelectronic industry, Si-based devices reach their technological and physical limitations processes such as thermal oxidation require an ineluctable mastering of the Si/SiO₂ to pursue the silicon technological roadmap. In this context, germanium material has received a great attention as a promising candidate for replacing silicon in the next generation of complementary metal-oxide semiconductors (CMOS) technology and metal oxide field effect transistors (MOSFET). This renewed interest is motivated by the similar atomic structures and electronic properties with silicon, i.e. a small electronic band gap of 0.66 eV (1.1 eV for Si), and higher carriers (3,900 cm²/Vs for electrons and 1,900 cm²/Vs for holes) mobility compare to silicon [1].

Moreover this material has a lattice mismatch of 4.7 % and is easily compatible with MOS Si-based technologies, and could provide emerging Si/SiGe/Ge heterostructures. However, for the required oxide layer thickness, an atomic scale understanding of the growth of the germanium oxide layer and on interfaces formation obtained during germanium oxidation process is still lacking.

The objective of this study is to establish an energetic mapping of the oxygen molecule chemical reaction as a function of its position and orientation over the germanium surface. This study has been performed using Density Functional Theory methodology. The result will be the determination of the most reactive sites and the most probable configurations that are obtained during the initial stage of the

germanium oxidation process. The relative stability of configurations containing one and two oxygen atoms incorporated into the surface bonds are characterized and commented. Additionally, we propose a comparison with the first oxygen molecule adsorption on silicon substrate during initial oxidation process. This comparative study between germanium, silicon germanium and silicon materials highlights two different behavior of both substrates and oxygen species facing the oxidation process: - contrary to the case of germanium the oxygen atoms preferentially agglomerate in the silicon oxidation case; - oxygen molecules accommodate to the silicon crystalline network whereas germanium atoms accommodate to the approaching oxygen molecule and move out from their crystalline positions.

2. Details of calculations

Substrates constructions: All surfaces considered in this article, i.e. germanium - silicon - silicon germanium surfaces, are built according to the following model. Slabs consist in periodic cells built as follow:

The germanium surface modeled with eight layers of eight germanium atoms. The cell dimensions for the germanium slab $a = 16.7 \text{ \AA}$, $b = 8.2 \text{ \AA}$, $c = 21.3 \text{ \AA}$.

For the silicon and silicon germanium surfaces, six layers of eight silicon atoms are used in the periodic cell and are detailed in the referred papers [2]. The SiGe model is built by replacing a surface silicon atom of one of the dimers by a germanium atom [3]. We checked that the difference in the chosen number of layers between Ge substrate and, Si and SiGe slabs has no impact on surface reactions and energetics. A deeper substrate was used in the case of germanium material justified by a study to come on atomic oxygen diffusion in the Ge sub-surface.

For each slab, sixteen hydrogen atoms were used in order to saturate the dangling bonds of atoms underneath the slab. The two lowest slab layers and hydrogen atoms are kept fixed during relaxation in order to simulate the bulk. All other layers, as well as the oxygen atoms, are allowed to relax. A vacuum zone of 10 \AA is used in order to create a surface effect. All three surfaces have a (2×1) surface reconstruction pattern exhibiting four dimer units, two channels and a buckling along the dimer rows (Figure 1).

Resulting periodic cells are thus $\text{Ge}_{64}\text{H}_{16}$, $\text{Si}_{48}\text{H}_{16}$ and $\text{Si}_{47}\text{GeH}_{16}$ respectively for pure germanium, pure silicon and silicon/germanium slabs.

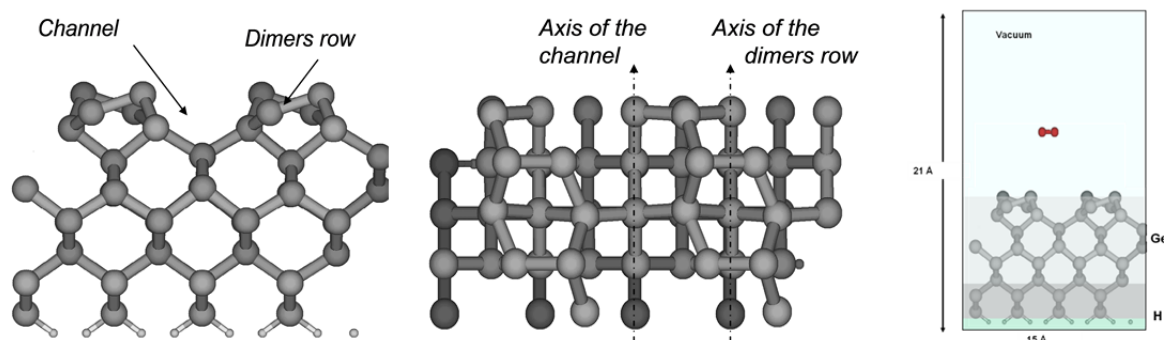


Figure 1. Side (left) and top (in the middle) views of the slab used to mimic Germanium substrate. Ge atoms are in grey and hydrogen atoms are in white. (2×1) surface reconstruction highlight dimers rows and channels. A schematic view of the periodic cell used in DFT calculations is given on the right.

Calculations Parameters. The calculations are performed in the framework of the Density Functional Theory (DFT) and implemented in the periodic VASP code [4,5]. Ultra-soft pseudo-potentials have been used with orbital developed on a basis of plane waves. For the exchange-correlation energy,

Generalized Gradient Approximation (GGA) was used and the cut-off energy fixed at 475 eV. Brillouin-zone integrations are carried out using the Monkhorst–Pack scheme [6] with a spaced mesh of 1x2x1 points in the reciprocal unit cell shifted from the origin at Γ for modeled the germanium surface. We also take into account the spin polarization to describe the oxygen molecule behavior during the adsorption process.

3. Adsorbed configurations through dry thermal oxidation

The adsorption procedure is performed by placing the oxygen molecule above the germanium surface sites with different positions and orientations initially at a height of 4 Å. At this distance, oxygen molecule and slab have no interactions. All starting configurations are schematized in Table 1. Once relaxed, the gravity centre of oxygen molecule is gradually lowered by step of 0.5 Å towards the surface until the adsorption reaction occurs. In all starting configurations, the bond axis of oxygen molecule is taken parallel to the substrate surface to favor the interaction between the occupied molecular orbital $2p\pi_u$ and the half occupied molecular orbital $2p^*\pi_g$.

Table I. Structures and energetics involved in the adsorption process on Ge(100)-(2x1). Starting and final structures are schematized. Adsorption energy gains are given in eV. White spheres represent oxygen atoms, grey squares represent germanium atoms. Grey squares size and darkness vary as a function of the layer depth from a top point of view: Larger the square is the topmost the layer.

	1	2	3	4	5	6	7	8
Starting positions								
Final configurations								
Eads (eV)	2.00	4.81	2.79	2.79	1.64	1.64	1.27	2.54
Remarks d(O-O)(Å)	1.47	/	1.49	1.49	1.57	1.56	1.48	1.46
	9	10	11	12	13	14	15	16
Starting positions								
Final configurations								
Eads (eV)	2.56	1.63	1.43	1.32	1.54	2.31	0.39	1.63
Remarks d(O-O)(Å)	1.47	1.57	1.36	1.36	1.47	1.48	unreacted	1.56

The sixteen initial oxygen molecule positions over the germanium surface and the final adsorbed configurations are presented in Table I. Adsorption energy gains and oxygen atoms distances obtained

in the final configuration are also given. Among all tested positions, only one leads to a spontaneous dissociation of the oxygen molecule. It corresponds to a narrow channel for the dissociation of one oxygen molecule initially perfectly centered between two dimers and perpendicular to the dimer row (configuration 2) [7,8]. In this adsorbed configuration, one oxygen atom is inserted into one Ge-Ge dimer bond, the second oxygen atom is stabilized in 'on top' configuration on the up-tilted atom of the adjacent dimer like a strand position as defined precisely in Ref. 9 and 10. The associated energetic gain is as large as 4.8 eV that is the highest energetic value encountered during adsorption procedure associated to the full dissociation of the oxygen molecule.

For all other adsorbed molecule configurations, a non-dissociative adsorption of the oxygen molecule is observed on the germanium surface in a good agreement with Fan's results [11]. Two configurations exhibit an adsorption of the oxygen molecule having an energetic gain of 1.3-1.4 eV (configurations 11, 12). This molecular chemisorption is characterized by a slightly stretched bond ($d(\text{O-O}) = 1.36 \text{ \AA}$) and an oxygen molecule attached to a surface germanium dimer atom by a single oxygen atom. Four configurations exhibit a partially dissociative chemisorption of the oxygen molecule on the same up-tilted germanium atom of the dimer (configurations 5, 6, 10, 16) associated with energetic gains slightly higher in the order of 1.6 eV. Both oxygen atoms are stabilized in an 'on top' configuration and are distant by 1.64 \AA . We can note that this adsorption type is possible on the low-tilted germanium atom of the dimer (configuration 7). In this case, adsorption is less favorable considering its energy gain (1.27 eV) and the oxygen molecule is less stretched ($d \text{ O-O} = 1.48 \text{ \AA}$). Configurations 11 and 12 will result in partially dissociative adsorbed configurations after an atomic migration of strand oxygen atom as observed for cases 5, 6, 10, 16.

Other configurations (#1, 3, 4, 8, 9, 13, 14 in Table I) exhibit a partial dissociative chemisorptions of the oxygen molecule on two distinct germanium atoms: in all these configurations, stretched or not peroxy surface bridges (Ge-O-O-Ge where $d(\text{O-O}) = 1.39$ to 1.5 \AA) are created. These adsorbed states are the more energetically favorable non-dissociative configurations involved during adsorption. The associated energetic gain range from 2 eV to 2.8 eV depending on the adsorption occurring a single Ge-Ge dimer or on two adjacent Ge-Ge dimers: a peroxy bridge can be obtained through an adsorption of two oxygen atoms on a single dimer with an energetic gain of 2.8 eV (Configurations 3, 4). This peroxy-adsorbed state can also arise from one up and one low-tilted germanium atoms of two adjacent dimers to form an inter-dimer peroxy bridge (configuration 8, 9). An unexpected configuration is also produced by the adsorption of non-dissociated oxygen molecule on two up-tilted germanium atoms from adjacent dimers, i.e. on opposite side of the axis of the dimers row (see configuration 1). These three last cited configurations are possible thanks to a lattice deformation of the substrate. Germanium atoms bonded to the adsorbed oxygen atom move out from their crystalline site to adapt to the presence of molecular oxygen species. O-O bond is quite stretched but not dissociated with a typical length of $1.46 \text{ \AA} - 1.47 \text{ \AA}$ (to be compared with referred data of 1.22 \AA for gaseous specie). This peroxy inter-dimer adsorbed configuration allows the linking of two germanium atoms initially distant by 4.20 \AA (Configurations 8, 9) and even by 4.94 \AA (configuration 1). But lattice deformation costs in energy: the more the germanium network is deformed, the lower the adsorption energy (2 eV for configuration vs 2.5 eV for configurations 8 and 9). The two positions above the channel (configurations 13, 14) can be associated to the peroxy-type adsorption except that it involves germanium atoms of the backbond of the sub-surface.

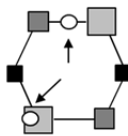
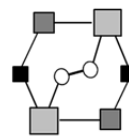
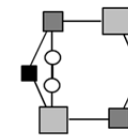
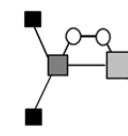
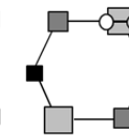
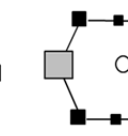
4. Discussion

Table II and III summarize all adsorption results for germanium and for silicon substrates respectively. The corresponding average energy gains and characteristic final adsorbed configurations are detailed and discussed.

We briefly detail adsorption results that we obtained in a previous study on silicon substrate [7,9]: fourteen structures exhibit an 'on top' configuration, and only one is spontaneously dissociated and

incorporated within two adjacent dimers. These results are given in Table III: partially dissociative chemisorbed states have been observed with eight adsorbed states on a single dimer silicon atom, three occur upon a single surface dimer unit and three others react within two adjacent dimer units (one reacts in the channel separating the dimer rows). In the case of reacting oxygen molecule with two adjacent dimer units, a spontaneous dissociation of oxygen molecule is produced to favor an ‘on top’ position and keep unchanged the silicon lattice.

Table II. Summary of the oxidation of Ge(100) surface obtained in Table I. Starting positions are referred compared to starting positions described in Table I and final typical structures are schematized. Adsorption energies are given in eV. White spheres represent oxygen atoms, grey squares represent germanium atoms. Grey squares size and darkness vary as a function of the layer depth from the top: Larger the sphere is, topmost the layer.

Adsorption mechanism	Above or near a single dimer germanium atom					
	Above the dimers row	Above the channel				
Starting Positions	2	1,13,14	8,9	3,4	5,6,7,10,16	11,12
Final Structure-types						
Eads (eV)	4.8	1.54 to 2.31	2.56	2.79	1.27 to 1.64	1.32 to 1.43
d(O-O) (Å)	Fully dissociated	1.47	1.47	1.49	1.48 to 1.57	1.36

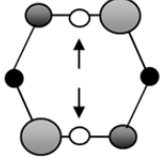
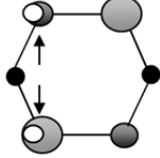
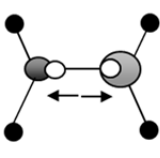
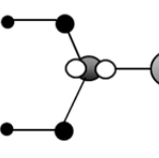
At a first glance, one can notice that germanium oxidation is less exothermic than silicon oxidation process by looking at equivalent adsorption energies of comparable adsorbed structures. Both in silicon and germanium oxidation processes, the insertion of oxygen atoms into the surface bonds is energetically most favorable. Only one final configuration for germanium material leads to the full dissociation coupled to incorporation of O atom in Ge-Ge dimer bond (4.8 eV Configuration 2 Table II). This is to be compared with 6.67 eV in silicon substrate (Configuration 2 Table III) [7,9] and defined as a ‘narrow barrierless channel for dissociation’.

Actually, many metastable steps are observed at the initial stages of oxidation. Table III highlights that a primary partial dissociative chemisorptions occur initially where both peroxy O-O bridge and ‘on top’ configurations appear to be key intermediates during germanium oxidation (Table II). On top-type of configuration was majority during silicon oxidation, whereas in the case of germanium surface, peroxy adsorption configurations are pivoted to further oxidation (further atomic diffusions deeper in the substrate, from Configuration 2 for instance). Indeed, in silicon, peroxy bridge state was only obtained when oxygen molecule was initially placed in a perfect symmetrical site above the dimer unit and only within the same dimer unit with the oxygen molecule axis parallel to the dimer axis. No adsorbed configuration in so-called inter-dimer peroxy bridge was found between Si-Si adjacent dimer bond: when a peroxy-bridge structure is observed in Germanium material, a full dissociation occurs in silicon as illustrated in Figures 2 (Four cases 1,9,13,14).

This peroxy-bridge configuration that was few observed during silicon oxidation (three cases 3,4,5), is possible thanks to the ‘softness’ of the germanium surface. The germanium softness allows atoms to accommodate to the electronic charge redistribution by moving out from their crystalline positions, driven by the approaching oxygen molecule interaction, giving rise to metastable adsorbed species such as inter-dimer bridges (see Figure 2). This softness is visible in all peroxy bridge configurations: for peroxy bridge configurations on a single dimer unit (# in Table II) germanium atoms are displaced to shorten the molecular oxygen bond (1.45 Å) whereas for similar final positions in silicon (# in

Table III) O-O bond is stretched to 1.52 Å. Another evidence is the presence of stretched O-O physisorbed on two germanium atoms of two adjacent dimers (configuration 1, 8, 9) whereas in silicon a full dissociation is observed as shown in Figures 2 a and b respectively. Moreover, in silicon, no starting positions were able to bond adjacent dimers.

Table III. Summary of the oxidation of Si(100) surface extracted from Ref. 7. Starting positions are referred with regard of the starting positions described in Table I for Ge substrate and final structures are schematized. Adsorption energies are given in eV. White spheres represent oxygen atoms, grey ones represent silicon atoms. Grey spheres size and darkness vary as a function of the layer depth from the top: Larger the sphere is the topmost the layer.

Adsorption mechanism	Above the dimers row	Above or near a single dimer silicon atom Above the channel		
	2	1,9,13,14	3,4,5	6,7,8,10,11,12,15,16
Starting Positions	2	1,9,13,14	3,4,5	6,7,8,10,11,12,15,16
Final Structure-types				
Eads (eV)	6.67	1.7 to 2.3	3.2	2 to 2.2
d(O-O) (Å)	Fully incorporated	Fully dissociated	1.52	1.59

In a preliminary conclusion, we unravel that different oxidation intermediates are found for initial oxidation stage on Si and Ge (on top; peroxy bridge, configuration respectively). In the next part, we perform a static study for evaluating oxygen atom ability to insert into germanium material.

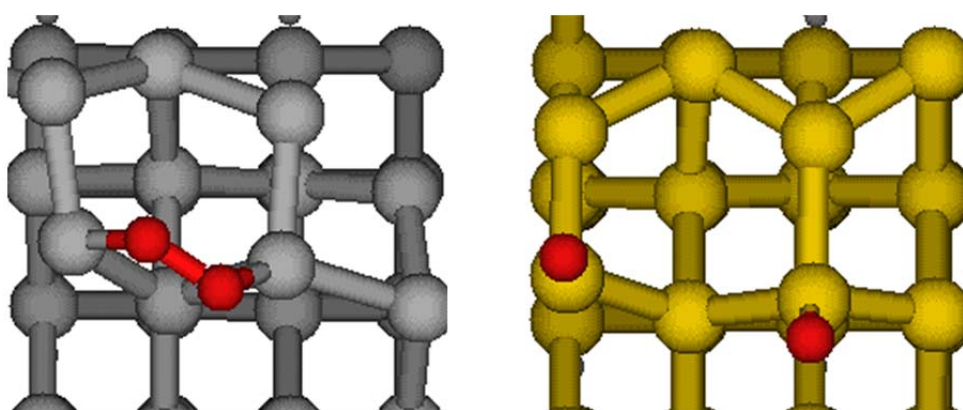


Figure 2. Top views of adsorbed configuration #9 on Germanium substrate (left picture) and on silicon substrate (right picture). Ge atoms are in grey, Si atoms are in yellow and hydrogen atoms are in white.

As a starting point, we consider a set of structures having one or two oxygen atoms attached and/or inserted into germanium surface. Germanium results will be compared to previous conclusions relative to the stability of Si and SiGe oxidized structures having one and two oxygen atoms incorporated in similar surface configurations. The structures and associated stability are listed respectively in the Tables IV and V. In each case, the 0 eV energy reference is taken as the most stable structure. Even if similar structures can be found in silicon and germanium slabs, one can see that their stability varies as a function of the substrate nature.

The insertion of one oxygen atom into the surface dimer is denoted as 'dimer insertion', while insertion into the bond between the first and the second layer is referred to as 'backbond insertion'. One oxygen atom not incorporated and stabilized on a single dimer atom is called 'on top' configuration and one in bridging position between two dimers is a 'bridging' configuration.

Table IV. Comparative energetic diagrams of one oxygen atom adsorbed a. on the Ge(100)-(2x1), b. on the Si(100)-(2x1) and c. on the SiGe(100)-(2x1) surfaces. Relative energies are given in eV. Top view surface structures are schematized. White spheres represent oxygen atoms, grey and dark spheres represent silicon atoms and grey and dark squares represent germanium atoms. Spheres and squares size vary as a function of the layer depth from a top point of view: Larger the sphere or square is the topmost the layer.

	A	B	C	D	E	F
a/ 1O-atoms structures on Ge(100)-(2x1)						
ΔE (eV)	0	0.22	0.40	1.09	1.20	1.25
b/ 1O-atoms structures on Si(100)-(2x1)						
ΔE (eV)	0	0.18	0.22	0.53	1.27	1.48
c/ 1O-atoms structures on SiGe(100)-(2x1)						
ΔE (eV)	0	0.54	0.79	1.20	2.63	unstable

We first consider the case of one oxygen atom incorporated into the topmost layer (Table IV).

For all three substrates, one oxygen atom fully incorporated into Si-Si or Ge-Ge bond is the most favorable configuration that can be observed: oxygen atom in an 'on top' configurations is thus a metastable oxidation, mainly observed at the early stages of oxidation process and already known as an unavoidable step during silicon oxidation [7,9,12]. Insert into substrate is therefore a two steps process (thermodynamically more favorable). In the case of germanium material, dimer insertion is reached whereas in silicon, a backbond insertion is preferred. One can notice here that a reversed

stability order exists between these structures: in a germanium surface, a dimer insertion (Table IV.a-A) will be more stable by 0.22 eV than a backbond insertion (Table IV.a-B), compared to silicon, where a backbond configuration (Table IV.b-A) is more energetically favorable by 0.22 eV than dimer oxidized structure (Table IV.b-C). Interestingly, in the SiGe system, the oxidized Si-Si backbond is the most stable configuration, highly larger than a dimer insertion by 0.54 eV. The ‘on top’ configuration is less stable by roughly 1.25 eV than the energy reference structure (structure IV.a-F and structure IV.b-E for Ge and Si respectively).

Inter-dimer bridge structure given in IV.a-D is a clue that characterizes the softness of germanium surfaces: this structure (Table IV.a-D) is more stable than an on top configuration by 0.16 eV (Table IV.a-F) compared to silicon case, where a inter-dimer bridge structure (Table IV.a-F) is less stable by 0.21 eV than the on top configuration (structure IV.a-E). In silicon material, we see that an inter-dimer bridging state costs in energy and is a non-favorable step at the primary stages. This trend changes when more than two oxygen atoms are inserted in the surface due to charge transfers effects [13].

Table V. Comparative energetic diagrams of two oxygen atoms adsorbed a. on the Ge(100)-(2x1), b. on the Si(100)-(2x1) and c. on the SiGe(100)-(2x1) surfaces. Relative energies are given in eV. Top view surface structures are schematized. White spheres represent oxygen atoms, grey and dark spheres represent silicon atoms and grey and dark squares represent germanium atoms. Spheres and squares size vary as a function of the layer depth from a top point of view: Larger the sphere or square is the topmost the layer.

	A	B	C	D	E	F	G
a/ 2O-atoms structures on Ge(100)-(2x1)							
ΔE (eV)	0	0.30	0.67	0.70	0.85	1.03	1.1
b/ 2O-atoms structures on Si(100)-(2x1)							
ΔE (eV)	0	0.15	0.19	0.35	0.46	0.64	1.36
c/ 2O-atoms structures on SiGe(100)-(2x1)							
ΔE (eV)	0	0.29	0.39	0.65	0.66	/	/

This first static study suggests an important role of the ‘on top’ configuration during the initial stage of both germanium and silicon oxidation processes. It also exhibits two different insertion pathways: germanium oxidation proceeds via oxygen atom incorporation into the dimer bond whereas silicon has a more complex oxidation phenomenon with a preferential incorporation site into the backbond but a kinetically favorable insertion into the dimer [2]. This behaviors are also is also illustrated in the SiGe case. For hybrid system, oxygen atom seems to avoid the close neighborhood of Ge atom and prefers to incorporate into Si-Si bond. Then, a mixed Ge-Si ‘dimer insertion’ (structure IV.c-B) is energetically better than a mixed Ge-Si ‘backbond insertion’ (structure 2c-D).

The most stable germanium configuration has oxygen atoms inserted into two adjacent dimers (Table V.a-A). In opposition, the most stable configuration observed in silicon surface is obtained on a single dimer unit with a more “compact” oxide structure: one oxygen atom in a backbond and one oxygen atom attached on top, this structure is known as the silanone structure and detailed can be found in Ref. 9 We observe in germanium substrate that it is tricky to adsorb two oxygen atoms in the vicinity of each other. Here again, an opposite remark can be derived from Ge and Si oxidation mechanisms: a structure with two oxygen atoms adsorbed on the same dimer unit (structure V.a-C) is less stable by 0.67 eV than the two oxidized dimer units structure. In silicon material, it costs 0.64 eV to adsorb two oxygen atoms, each on adjacent dimers compared to the silanone configuration.

Here, the propensity of oxygen atoms to agglomerate on silicon surface contrasts with germanium material where oxygen atoms seem to repeal each other. In his publication Soon [14] has proposed different reaction pathways for the decomposition of one oxygen molecule one a germanium cluster. In this study the author connects two initial configurations presented in the Table 1 (configuration 2 and 3) to structures presented in the table V.a. He shows that structure V.a-C and structure V.a-D are resulting from the adsorption and decomposition of one oxygen molecule centered between two dimers and perpendicular to the dimer row (configuration 2) via the structure V.a-G. It also connects the structure V.a-B to the adsorption and decomposition of one oxygen molecule initially above and parallel to one dimers unit (configuration 3) via the structure V.a-A. Even if the stability order of the structure presented in this paper is different to those presented in our present paper, probably due to bordering interactions in the cluster approach used to simulate the surface, the considerable activation barrier found by Soon to take on oxygen atom in the dimer unit and to insert it in the backbond support the idea of a preferential oxidation of dimer.

5. Conclusion

In this paper, the first stages of germanium oxidation are studied by DFT calculations and a systematic comparison with silicon and silicon germanium data is done. Both oxygen in on-top and peroxy-bridge configurations appear as intermediate metastable unavoidable steps in germanium oxidation process. Peroxy bridge formation is allowed thanks to the softness of the germanium surface giving the possibility to germanium atoms to move out from their crystalline position to adapt to the approaching oxygen molecule. Dissociation is observed in silicon where inter-dimer bridging configurations occur in germanium. So, in pre-oxidation regime Germanium material, germanium atoms adapt to the oxygen species, whereas in silicon material, oxygen molecule adapts to the silicon surface topology. The oxygen atoms tendency to agglomerate on the surface is described in opposition to the favorable spreading of isolated bridging oxygen configurations on germanium surface.

These elemental but fundamental differences in behavior of both silicon and germanium surfaces towards oxidation is key to unravel the dramatic differences observed in providing high quality semiconductor oxide interfaces with these materials. On going research effort is engaged to shad light into the next oxidation stages.

5. References

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