

Passivation of Ge(100) and (111) Surfaces by Termination of Nonmetal Elements

DongHun Lee¹, Kazuki Kubo¹, Takeshi Kanashima¹ and Masanori Okuyama²

¹Department of Systems Innovation, Graduate School of Engineering Science, Osaka University,

²Institute for NanoScience Design, Osaka University,

1-3 Machikaneyama-cho, Toyonaka, Osaka, 560-5831, Japan

Phone: +81-6-6850-6332 E-mail: donghun@semi.ee.es.osaka-u.ac.jp

1. Introduction

Germanium (Ge) has been attracting a lot of attention as a candidate of channel material for high-performance metal-oxide-semiconductor field effect transistor (MOSFET), because it has higher electron and hole mobilities than Si [1]. However, it is well known that the formation of a high-k/Ge gate stack with good interface is difficult [2]. Especially, dielectrics deposited on a Ge surface treated with diluted HF exhibit a large interface state density, since the Ge surface is not easily passivated by hydrogen (H) [3]. To solve this problem, it is necessary to passivate the Ge surface using an appropriate element before dielectric layer deposition. Therefore, recently, the passivation of the Ge surface using new treatment materials has been studied to reduce the interface state [4]. The studies of the Ge(100) surface have been mainly focused because the (100) orientation has the smallest density of surface dangling bonds. However, the Ge(111) substrate showed better improvement in electron mobility compared to the (100) substrate [5].

In this study, we have theoretically simulated the chemical reactivity of various nonmetal elements with the Ge(100) and (111) surface, in order to look for an adequate ambient treatment by using molecular orbital method. Based on the results of the simulation, we were able to search available elements for the passivation of the Ge surface. Moreover, we have also confirmed the stability of the elements on both the Ge(100) and (111) substrates by experimental work.

2. Calculation method and experimental details

All calculations have been carried out using MOPAC 2009 for the semi-empirical molecular orbital method. The PM6 Hamiltonian and unrestricted Hartree-Fock (UHF) parameter were used for the calculations. Generally, the first-principle calculation is more accurate than that obtained by the semi-empirical molecular orbital method, but this type of calculation is not applicable to large molecular models. However, this study needs to calculate large molecular models for the analysis of reactions on the surface. Thus, we have used the semi-empirical molecular method because it is applicable to giant molecule structures and gives reliable results.

Figure 1 shows the Ge(100) and (111) surface cluster models used for the calculation. Positions of the Ge atoms of the lower 2 atomic layers were fixed during the calculation and those of the Ge atoms of the upper 4 atomic layers were optimized. The dangling bonds located on the bottom of Ge layer system were terminated artificially by H atoms, to make the structure stable.

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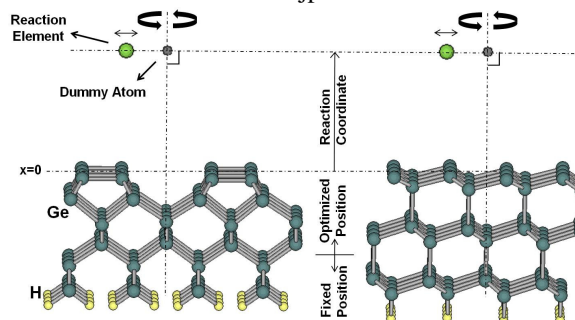


Fig.1. Cluster model for studying reaction on Ge(100) and (111) surface

Ge surface cluster models, various nonmetal elements were made to approach the surface to analyze their reaction with the Ge atoms on the surface. The heat of formation (ΔH_f) of the reaction between the elements and the Ge layer system was calculated as a function of the reaction coordinate. The ΔH_f is defined as:

$$\Delta H_f = E_{elect} + E_{nuc} - E_{isol} + E_{atom},$$

where E_{elect} is the electron energy, E_{nuc} is the nuclear-nuclear repulsion energy, $-E_{isol}$ is the energy required to take all the valence electrons off from all the atoms in the system, and E_{atom} is the total heat of atomization of all the atoms in the system. The stability of the layer system is estimated by ΔH_f , because a stable system has a smaller ΔH_f than an imbalanced system.

In the experiment, after the HF cleaning treatment, p-type Ge(100) and (111) wafers were treated with HCl (35%) or $(\text{NH}_4)_2\text{S}$ (50%) solution for 20 min. Next, HfO_2 thin films were prepared on the wafers by using photo-assisted MOCVD [4]. Then, the samples were annealed at 300 °C for 30 min, in a N_2 ambient (post-deposition annealing, PDA). To characterize electrical properties, Pt (top) and Al (bottom) electrodes were formed on the samples by sputtering through a shadow mask and thermal evaporation, respectively. Finally, PMA (post-metallization annealing) was performed at 300 °C for 30 min in N_2 ambient.

3. Results and discussion

Figure 2 shows the calculated ΔH_f for the reaction between the nonmetal elements and the Ge layer system as a function of the reaction coordinate. The stabilization energy is an important factor defined as the formation energy for the reaction, and is equivalent with the difference between the maximum and the minimum in the curve of the heat of formation. First, the reaction between VII group elements, which have only one dangling bond, and Ge(100) layer system is shown in Fig. 2-(a). The results

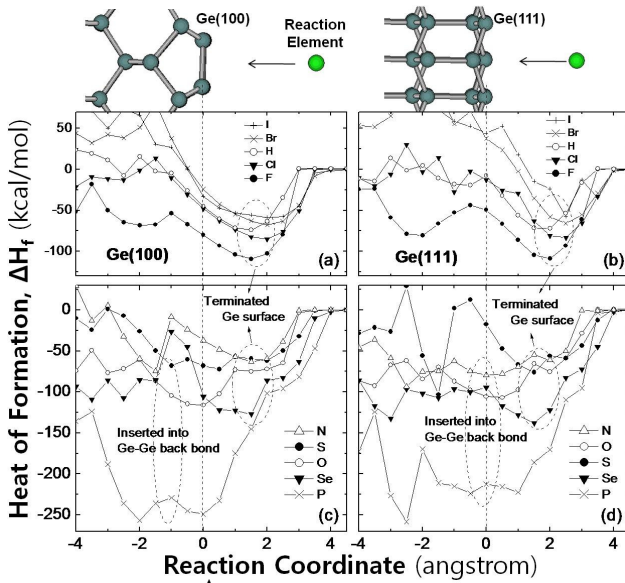


Fig.2. Calculated ΔH_f for the reaction of elements (upper: VII group, lower: V and VI groups) and Ge (left: (100), right: (111)) layer system as a function of reaction coordinate

show that all VII group elements terminated one dangling bond of the Ge surface near 1.5 Å, and reactions are similar to that occurring in the case of H. The reaction of fluorine (F) (stabilization energy: -111 kcal/mol) and chlorine (Cl) (-85 kcal/mol) atoms on the Ge(100) layer system is more stable than H (-76 kcal/mol) atom. Moreover, we can see that the reaction on the Ge(111) layer system is similar to that on the Ge(100) layer system, as shown in Fig. 2-(b). The reactions between one dangling bond of one atom and one dangling bond on the surface are very stable regardless of the surface structure. Because these terminated atoms have no extra dangling bond, the reactions are unaffected by another dangling bond of the Ge surface. We found that F and Cl are more effective and more stable for terminating the Ge(100) and (111) surface than H.

However, the V and VI group elements have another type of reaction on the Ge(100) and (111) surfaces, as shown in Fig. 2-(c) and (d), respectively. The structure of the Ge surface is broken after the reactions, because more than one dangling bond of the element react with the Ge-Ge back-bonds and the atom breaks the Ge surface. However, selenium (Se) on the Ge(100) layer system terminated the dangling bonds of the Ge surface by making a bridge-bond and stabilized the system because the extra dangling bond of the atom reacted with the next dangling bond on the surface, instead of the back-bond. On the Ge(111) layer system, sulfur (S) and Se made the bridge-bond and terminated the surface. It is thought that S and Se react more easily with the next dangling bond of the Ge surface and easily create bridge-bonds because the ionic radius of S (1.70 Å) and Se (1.84 Å) are larger than those of N (1.57 Å) and O (1.28 Å). Especially, as the distance between dangling bonds on the Ge(100) (5.57 Å) surface is larger than that on Ge(111) (4.02 Å) because of the dimer structure of the Ge(100), S does not make bridge-bonds on the Ge(100) surface as easily as on the Ge(111) surface.

According to these calculation results, the Ge(100)

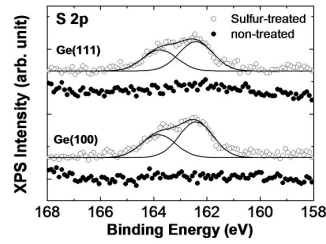


Fig.3. S 2p XPS spectra on Sulfur-treated Ge(111) and (100) surfaces after 300 °C annealing

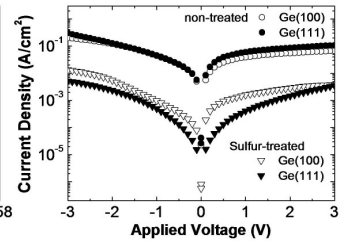


Fig.4. J-V characteristics of HfO_2/Ge gate stacks with/without Sulfur treatment

and (111) surfaces are better terminated and stabilized by elements such as F, Cl, S, and Se than by H. Moreover, in a previous study, we confirmed that the F-termination on the Ge substrate is more appropriate by F_2 gas treatment than by HF solution treatment [4]. However, we used HCl and $(\text{NH}_4)_2\text{S}$ solution treatment method, as simpler and more riskless treatment methods than the F_2 gas treatment. First, the Cl-terminated HfO_2/Ge gate stack treated with a 35% HCl solution has lower leakage currents than the nontreated sample. However, this method was inefficient in a high temperature system for making a HfO_2 film, because the Cl disappeared from the Ge surface directly with increasing the temperature. On the other hand, after $(\text{NH}_4)_2\text{S}$ solution treatment, S remains on the Ge (100) and (111) surface annealed even at 300 °C, as shown in Fig. 3. Moreover, S-treated HfO_2/Ge gate stack by $(\text{NH}_4)_2\text{S}$ solution treatment has lower leakage currents than the nontreated. Specifically, as shown in Fig. 4, we can see that the leakage currents decrease more on the Ge(111) substrate than on the Ge (100) substrate, following S-treatment. It is considered that S can terminate the dangling bonds on the Ge(111) surface more easily than the Ge(100) surface in shown at calculation data. Finally, we are also measuring other electrical properties of the S-treated HfO_2/Ge MOS devices for an intensive verification.

4. Conclusions

In this study, we have instigated the energy states of small nonmetal atoms approaching the Ge(100) and (111) surface using the semi-empirical molecular orbital method. As a result, we found several elements (F, Cl, S, and Se) appropriate as treatment materials of the Ge surface. In experimental work, we succeeded in improving the high-k/Ge gate stack by HCl and $(\text{NH}_4)_2\text{S}$ solution treatment. Especially, we found that the S-treatment is more useful on the Ge(111) surface than on the Ge(100) surface, because S easily terminated the dangling bonds on the Ge(111) surface by making the bridge-bonds.

References

- [1] S. V. Elshocht, M. Caymax, T. Conard, S.D. Gendt, I. Hoflijk, M. Houssa, F. Leys, R. Bonzom, B. D. Jaeger, J. V. Steenbergen, W. Vandervorst, M. Heyns, and M. Meuris: Thin Solid Film. **508** (2006) 1.
- [2] K. Prabhakaran, and T. Ogino: Surf. Sci. **325** (1995) 263.
- [3] S. Rivillon, Y. J. Chabal, F. Amy, and P. Pianetta: Appl. Phys. Lett. **87** (2005) 253101.
- [4] D. H. Lee, H. Imajo, T. Kanashima, and M. Okuyama, Jpn. J. Appl. Phys. **50** (2011) 04DA11.
- [5] D. Kuzum, A. J. Pethe, T. Krishnamohan, and K. C. Saraswat: IEEE Trans. Electron Devices. **56** [4] (2009) 648.