

## Effects of Post-Deposition Annealing Temperatures on the Composition of Interfacial Layer at Germanium (Ge) /Aluminium Oxide (Al<sub>2</sub>O<sub>3</sub>)

(Kesan Suhu Penyepuh Lindapan Pasca Pemendapan ke atas Komposisi Antara Muka Lapisan Oksida Germanium (Ge)/Aluminium (Al<sub>2</sub>O<sub>3</sub>))

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### ABSTRACT

*The understanding of chemical bonding structure of high k dielectrics/Germanium (Ge) interface is utmost importance in order to form a good quality dielectric/Ge interface in fabricating Ge metal oxide semiconductor field effect transistor (MOSFETS). In addition, there is still no detail explanation on the interfacial growth of dielectrics/Ge under the influenced of different temperature of post deposition anneal. In current work, the effects of post deposition anneal (PDA) temperature between 400°C and 600°C on the chemical composition of interfacial layer between Ge and Al<sub>2</sub>O<sub>3</sub> were examined by X-ray photoelectron spectroscopy (XPS). Investigation on thermal stability and structural characteristics for gate structure of Al<sub>2</sub>O<sub>3</sub> dielectric grown on Ge by RF sputtering was done by analyzing X-ray photoelectron spectroscopy (XPS) spectra. It is observed that the oxygen deficient region in interfacial layer (IL) is enhanced rather than fully oxidized Al<sub>2</sub>O<sub>3</sub> with increased PDA temperatures. These undesired phenomena caused shrinkage of IL at Ge/Al<sub>2</sub>O<sub>3</sub> interface at higher temperature of 600°C.*

*Keywords: Al<sub>2</sub>O<sub>3</sub>; germanium; interfacial layer; post deposition anneal*

### ABSTRAK

*Pemahaman tentang struktur ikatan kimia yang tinggi dielektrik/antara muka Germanium (Ge) adalah sangat penting untuk membentuk antara muka dielektrik/Ge berkualiti baik dalam fabrikasi Ge kesan medan transistor logam oksida semikonduktor (MOSFETS). Di samping itu, masih belum ada penjelasan terperinci mengenai pertumbuhan antara dielektrik/Ge di bawah pengaruh suhu yang berlainan bagi pemanasan pasca sepuh lindap. Penyelidikan kesan suhu pemendapan pasca sepuh lindap (PDA) antara 400°C dan 600°C pada komposisi kimia lapisan antara muka Ge dan Al<sub>2</sub>O<sub>3</sub> diperiksa oleh spektroskopi fotoelektron x-ray (XPS). Dalam makalah ini, kami mengkaji kestabilan terma dan pencirian struktur untuk struktur gerbang Al<sub>2</sub>O<sub>3</sub> dielektrik yang ditanam di Ge oleh percikan RF oleh spektroskopi fotoelektron x-ray (XPS). Difahami bahawa rantau kekurangan oksigen dalam lapisan antara muka (IL) ditingkatkan daripada Al<sub>2</sub>O<sub>3</sub> sepenuhnya teroksida dengan suhu PDA yang meningkat. Fenomena yang tidak diinginkan ini menyebabkan pengecutan IL pada antara muka Ge/Al<sub>2</sub>O<sub>3</sub> pada suhu lebih tinggi 600°C.*

*Kata kunci: Al<sub>2</sub>O<sub>3</sub>; Ge; lapisan antara muka; pos pemendapan rawatan haba*

### INTRODUCTION

Germanium(Ge) can be used to replace Silicon (Si) as a channel because it has four times higher hole mobility and two times higher electron mobility than Si (Wallace et al. 2009). The replacement of Si by Ge reopens the space for high-k dielectric Ge metal oxide semiconductor field effects transistors (MOSFETS) development. However, besides fabrication handling of Ge as a channel, the quality of the surface and interface between high k and Ge is still a main technological issue that must be overcome for development of MOSFETS. The poor quality of Ge/dielectrics with high interface states density and high interface roughness have been shown on the high permittivity dielectrics such as HfO<sub>2</sub>, ZrO<sub>2</sub>, on Ge substrate (Han et al. 2013; Ngai et al. 2000;

Wu et al. 2005). Therefore, to improve the quality of interface between high k and Ge, the implementation of IL between high k and Ge has been proposed (Shang et al. 2007). For the case of Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), the formation of interfacial layer (GeO<sub>x</sub>) between Ge and Al<sub>2</sub>O<sub>3</sub> resulted in low defect states density (10<sup>-11</sup>cm<sup>-3</sup>) (Zhang et al. 2013). To resolve the issues of surface and interface between high k and Ge, the selection of annealing ambience during the fabrication is to be taken into account. Previous research showed that the selective passivation of low interface traps can be influenced under multiple conditions of annealing (Zhang et al. 2015). In addition, surface treatment with HBr, HCl, HF, H<sub>2</sub>S-based have been used to obtain a well passivated at Ge and high k interface (Bai-Qing et al. 2012; Elshochta et. al. 2006).

In our previous study, we have shown that the Chlorine (Cl) termination after HCl treatment on Ge surface was confirmed by Cl2p spectra of XPS measurement and this can prevent slightly the intermixing between Ge and Al<sub>2</sub>O<sub>3</sub> after PDA of 400°C (Sahari et al. 2017b, 2017a). In this study, we continue the study by investigating on the effect of Cl- termination by increasing the temperature up to 600°C. This study aims to observe the evolution process of formation intermixing during post deposition anneal of Al<sub>2</sub>O<sub>3</sub> on Ge substrate. This was accomplished by monitoring the growth of suboxides components as a function of post deposition anneals temperatures.

In this work, thickness of interfacial layer between Ge and Al<sub>2</sub>O<sub>3</sub> was measured using FESEM. The x-ray photoelectron spectroscopy (XPS) was performed to measure the chemical composition of IL.

#### MATERIALS AND METHODS

In this work, p-type Ge wafers with surface orientation (100) with resistivity 0.001-10 ohm/cm were used. The cleaning process is similar with the previous study (Sahari et al. 2015, 2014). First, the wafers were cleaned with deionized water before dipped in 15% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). After that, the wafers were rinsed with deionized water and subsequently dipped in 30% hydrochloric (HCl) acid. The final step of cleaning method is dipping the wafers in deionized water. Then, the Al<sub>2</sub>O<sub>3</sub> layer was deposited on cleaned Ge wafer by RF sputtering at 250 W with pure Argon flow of 20 sccm, and the partial pressure of chamber was maintained at 24 mTorr during the sputtering process. The deposition time was 2 min. After that, post deposition anneals (PDA) were performed at temperature ranges between 400°C and 600°C for 30 min in a furnace with flowing N<sub>2</sub> at a rate of 5L/min under atmospheric pressure. The composition of IL was characterized by x-ray photoelectron spectroscopy (XPS) at take-off angle 0° and 15° with an AlK $\alpha$  radiation source operating at 1486.6 eV. The thickness of IL was evaluated by XPS from the measured intensity ratio Ge metal 3d/Ge(oxide) 3d with considering the escape depth of 2.3 nm for AlK $\alpha$ .

#### RESULTS AND DISCUSSION

Figure 1 shows the post deposition anneal temperature dependence of IL thickness. The thickness of IL between Ge and Al<sub>2</sub>O<sub>3</sub> increases upon increasing the post deposition anneal temperature up to 550°C. However, it decreases when the PDA temperature increased to 600°C. This result is consistent with the previous report that showed the shrinkage of IL at Ge/HfN interface after high annealing temperature in nitrogen ambience may be caused by bond breaking in the IL which leads to GeO desorption or densification of IL during high PDA temperature (Ching et al. 2006). To investigate the phenomena in detail, we evaluated the chemical bonding structure between Ge and Al<sub>2</sub>O<sub>3</sub> with PDA temperature dependence as shown in Figure 2. In the figure, Ge 3d of 2 min Ge thermal oxidation

is shown as a reference. It is observed that the binding energy originated from Ge oxide peak at 33.2 eV, separated by 3.4 eV from Ge3d<sub>5/2</sub> metal, originated from Ge bound to oxygen. This binding energy was shifted to lower binding energy after deposition of Al<sub>2</sub>O<sub>3</sub>. It may be attributed to the non-uniform reaction that affects the formation of oxygen vacancies and caused defects during sputtering as reported in previous work for Silicon substrate (He et al. 2005). Moreover, after PDA was performed, this oxidized peak is shifted slightly to higher binding energy corresponds to the changes of chemical composition at IL. With increasing of PDA temperature up to 550°C, no changes are observed on the binding energy difference between Ge metal and Ge oxide peak. However, after PDA at 600°C, the energy separation between Ge metal and GeO<sub>2</sub> decreases to 2.5 eV. This result may be attributed to the GeO<sub>x</sub> undergo different structural rearrangement under N<sub>2</sub> annealing that produce different intermediate phases before ultimately turning into metallic Ge (Zhao et al. 2015).

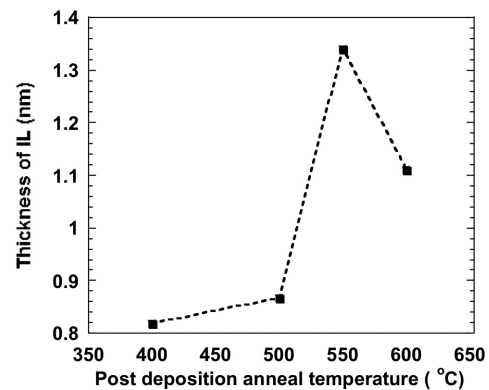


FIGURE 1. Thickness of interfacial layer at different post deposition anneal temperature

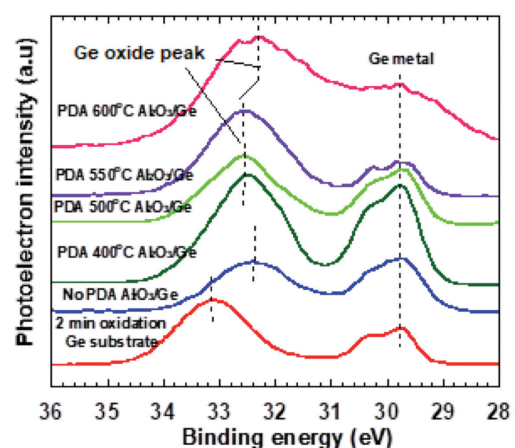


FIGURE 2. Ge 3d spectra of Al<sub>2</sub>O<sub>3</sub>/Ge at post deposition anneal between 400°C and 600°C

To observed the composition of IL between Ge and Al<sub>2</sub>O<sub>3</sub> in detail, the Ge 3d spectra were divided into 5 components; Ge3d<sub>5/2</sub> and Ge3d<sub>3/2</sub> (Ge<sup>0+</sup>) for metal,

suboxides ( $\text{Ge}^{1+}$ ,  $\text{Ge}^{2+}$ ,  $\text{Ge}^{3+}$ ) and  $\text{GeO}_2$  ( $\text{Ge}^{4+}$ ) using Shirley background and 6 Gaussian peaks as shown in Figure 3. The interval of the peak energies for each component of suboxides components was set to 0.8 eV as similar with the reported values for  $\text{GeO}_2/\text{Ge}$  interface (Lucovsky et al. 2013; Matsui et al. 2011; Schmeisser et al. 1986; Shiyabama et al. 2014). The existence of the Ge suboxide components indicates the formation of chemical bond between Ge-O and Ge-Al/Ge between thin film and Ge substrate (He et al. 2016). From the figure, it shows the intensity of  $\text{Ge}^{2+}$ ,  $\text{Ge}^{3+}$  and  $\text{Ge}^{4+}$  increases with increasing PDA temperature between 400°C and 550°C. The percentage of  $\text{Ge}^{3+}$  and  $\text{Ge}^{4+}$  increased almost 50% when PDA temperature is increased from 400°C to 550°C. These results indicate the existence of the oxidation phenomena at the surface of Ge substrates. On the other hand, for the case of PDA at 600°C, the peak intensity of  $\text{Ge}^{4+}$  and  $\text{Ge}^{3+}$  were decreased. In addition, it is observed that the peak intensity of  $\text{Ge}^{3+}$  component is larger than  $\text{Ge}^{4+}$  for the PDA temperature between 400 and 550°C. By taking consideration of electronegativity Ge ( $\chi_{\text{Ge}}=2.0$ ), Al-Germanate peak is expected to appear around  $\text{Ge}^{3+}$  component (Song et al. 2007). The peak for  $\text{Ge}^{3+}$  might thus include Al-Germanate component. These results indicate that the Al-Germanate increased with increasing PDA temperature.

The O1s core level spectra shown in Figure 4 are evaluated to examine the nature of oxide formed on

Germanium. Before sputtering, the O1s peak substrate present only at 532.5eV, corresponding to the binding energy of native  $\text{GeO}_2$ . After  $\text{Al}_2\text{O}_3$  deposited on Ge substrate, the peak of O1s shifts to 531.3eV. This peak shifting suggested that the formation of interfacial oxide or the formation of germanate by the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{GeO}_2$  on Ge surface. From Gibbs free energy, these two processes have the possibility to take place. With increasing temperature from 400°C to 550°C, this peak keeps shifted towards higher binding energy and fixed at 532 eV. According to Wang and Mayer (1998), oxygen deficient oxide has higher binding energy than that of fully oxidized metal oxide. Therefore, according to the XPS result, non-uniform reaction occurs during sputtering which results in the formation of oxygen vacancies and defect. By increasing the annealing temperature, the oxygen deficient region and intermixing are enhanced. The further increased of IL for the PDA temperature up to 550°C indicates the additional Al-germanate layer after high temperature processing.

The shrinkage of IL after 600°C is still in question. Therefore, Angle Resolved XPS (ARXPS) for Ge3d was conducted to allow us to investigate the decreasing of IL thickness after very high PDA temperature at 600°C. Figure 5 shows the ARXPS at takeoff angle 0 and 15°. The intensity was normalized with the signal originated by Ge metal. The ARXPS indicates that the ratio of Ge suboxides ( $\text{Ge}^{1+}$  -  $\text{Ge}^{3+}$ ) intensity to Ge metal intensity increased as

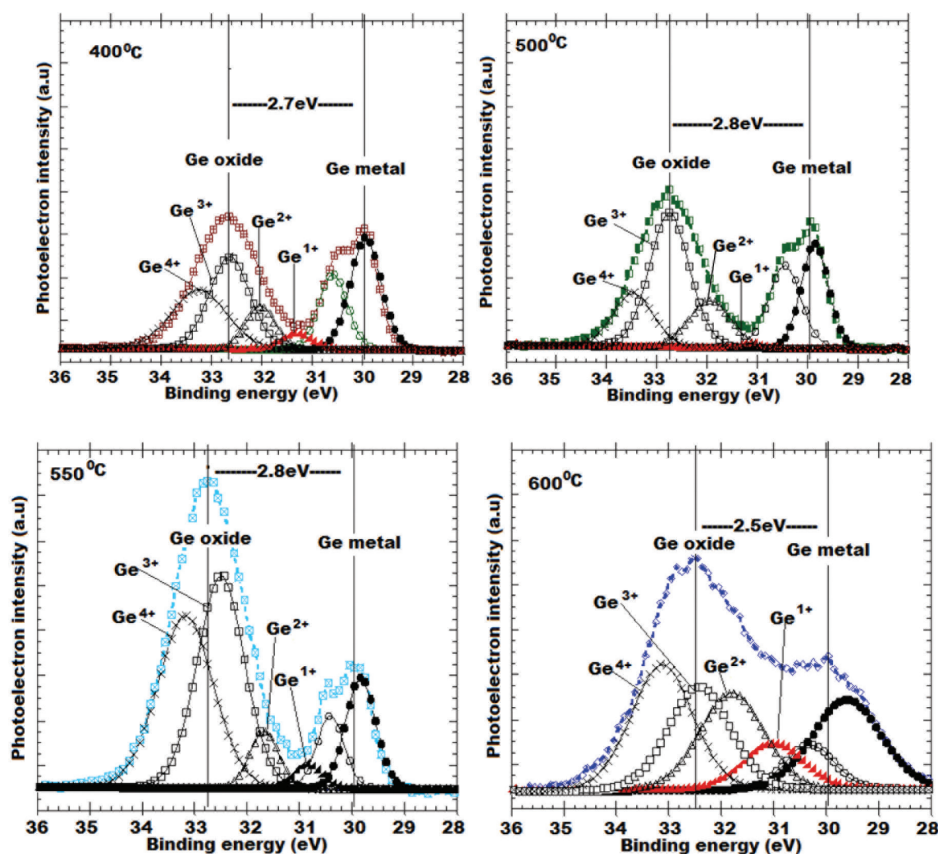


FIGURE 3(a). Evolution of Ge 3d with PDA dependence

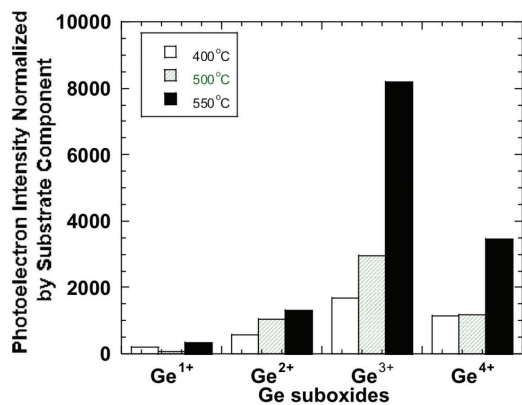


FIGURE 3(b). Ge oxide components on PDA temperatures dependence

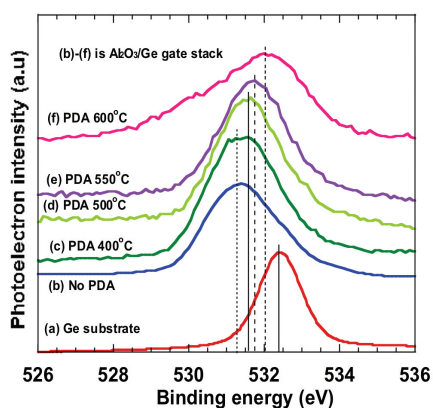


FIGURE 4. O1s signal at different PDA temperature between 400 and 600°C

take-off angle was getting smaller, which means that  $\text{GeO}_x$  at the upper portion of gate dielectric ( $\text{Al}_2\text{O}_3$ ). This result is inconsistent with Shibayama et al. (2014) where they reported that only  $\text{Ge}^{3+}$  and  $\text{Ge}^{4+}$  on the upper portion of  $\text{Al}_2\text{O}_3$ . The inconsistency of these results may be caused by different PDA temperatures of these works. There are two possible mechanisms involved in the  $\text{GeO}_2$  incorporation into  $\text{Al}_2\text{O}_3$  thin film. First is the diffusion of Ge atom from dissociated IL or substrate itself which is then oxidized with the residual oxygen, second is the oxidation of volatile GeO. From these results, we believe that the out-diffusion occurred during PDA  $\text{Ge}/\text{Al}_2\text{O}_3$  gate stack and enhanced with the increasing of PDA temperatures. Thus, the dissociation of the IL is believed to be the real cause of shrinkage of IL thickness with increasing temperatures because the detection of  $\text{GeO}_2$  within the bulk of gate dielectric.

#### CONCLUSION

The PDA temperatures dependence on the chemical composition of IL between  $\text{Al}_2\text{O}_3$  and Ge has been studied. The results conclude that the formation of  $\text{Ge}^{3+}$  is enhanced with the PDA temperature up to 550°C while  $\text{Ge}^{4+}$  is

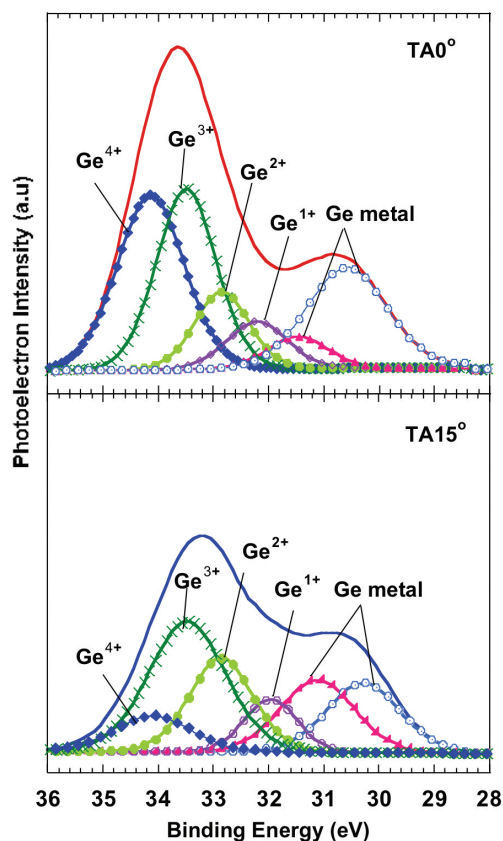


FIGURE 5. Angle resolve XPS of Ge 3d spectrum of  $\text{Al}_2\text{O}_3/\text{Ge}$  stack after PDA at 600°C

dominated during PDA at 600°C. The higher formation of  $\text{Ge}^{3+}$  is related to the formation of Al-germinate while the formation of  $\text{Ge}^{4+}$  is thought related to the re-oxidation when the temperature of PDA is increased. The shrinkage of IL after PDA of 600°C is related to the  $\text{GeO}$  desorption process. As PDA temperature increased, more  $\text{GeO}_2$  is incorporated in  $\text{Al}_2\text{O}_3$  and severe desorption of IL occurs at  $\text{Al}_2\text{O}_3/\text{Ge}$  gate stack. As the overall results, it can be concluded that the Cl-termination of Ge surface is unstable and cannot prevent the intermixing between Ge and  $\text{Al}_2\text{O}_3$  as the PDA temperature increased up to 600°C. Therefore, the continuous optimization of interface structure through process modification can improve the quality of interface between  $\text{Al}_2\text{O}_3$  and Ge.

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