

## Stability of Chlorine Termination on Ge(100) and Ge(111) Surfaces

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**Abstract.** The different cleaning solution; HCl and HF solution are used to remove the suboxide and oxide component on Ge surface. The HCl cleaning results chlorine (Cl) termination on Ge surface whereas no Fluorine (F) termination was observed just after HF cleaning. The growth of Ge oxide is studied after treated with HCl cleaning on two surface orientations; (100) and (111), respectively in dry oxygen ambient and cleanroom air by spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS). A clear step and terrace trend was observed for the oxidation growth of Ge (100) and Ge (111) in dry oxygen ambient compared to in clean room air. This trend shows the difference in surface reaction of Ge oxidation as humidity varies. The stability of chlorine termination of Ge (111) than Ge (100) explains the slower growth of oxidation in dry oxygen ambient.

### 1 Introduction

Scaling down of the planar bulk silicon (Si) metal-oxide-semiconductor (MOS) field effect transistors (FETs) has been confronted its fundamental limit associated with performance, on current, power consumption, and short-channel effects which have the trade-off relationship with each other. Therefore, device structures and materials with high carrier mobility are needed for further continues enhancement in device performance. Germanium (Ge) become an emerging and promising material to replace Silicon (Si) because it has the advantages of high electron and hole mobility compared to that of silicon (Si) [1]. However, controlling the interface defects between Ge and oxide interface is the critical issues for Ge MOSFETs. Recently, researchers have interest of Ge because it can be integrated with Si to fabricate optical communication devices [2]. However, GeO<sub>2</sub> is water soluble and not stable if compared to SiO<sub>2</sub>. In addition, the fast native oxidation on Ge surface is one of the key issues that must be overcome. Many efforts have been done to passivate Ge surface to avoid fast oxidation such as organic functionalization of Ge substrates under gas phase of UHV condition [3-13]. Furthermore, various chemical-based methods have been explored to passivate Ge substrate prior to high-k deposition such as sulfur passivation, halogen passivation, and hydrogen passivation [14-19]. Though, the oxygen free was not yet obtained on Ge surface and the kinetics oxidation of Ge is quite fast compared to Si oxidation [20-21]. It is may be due to the lower thermal and chemical stability of Ge hydrides compared to Si

hydrides [22]. Notably, the native oxidation of Si proceed layer- by- layer trend with very flat Si/SiO<sub>2</sub> interface and the origin of layer-by layer growth presumably relates to less structural strain at Si/SiO<sub>2</sub> interface [22-23]. Despite it was reported that HF-last Ge exhibits layer-by layer trend in clean room air, the effect of moisture and stability of chlorine terminated on Ge (100) and (111) on the oxidation growth in dry oxygen ambience at room temperature has been not discussed yet.

In addition, the water absorption on the semiconductor surface play important roles nanotechnology and give the effects on the surface chemistry. As for Silicon case, the water absorbed on hydrophilic silicon oxide surface causes large changes in adhesion and friction of nanoscale contact. This paper shows how the effect of moisture in the air affects the growth rate of oxide in Germanium case. However, these studies have not fully elucidated the evolution of absorbed moisture on the Ge oxide surface as function of relative humidity.

To gain better understanding on Ge oxidation, the HCl and HF cleaning are compared in order to remove oxide completely and to prepare good passivation on Ge surface. Furthermore, the growth of oxidation of HCl last Ge is investigated in dry oxygen ambient in room temperature with crystallographic orientation dependence. The effect of moisture and stability of Cl terminated Ge (100) and (111) on the oxidation growth are discussed and compared.

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## 2 Experimental procedure

The wafer used in this work were p-type Ge (100), p-type Ge (111) with a resistivity of  $\sim 10\text{-}20 \Omega\text{cm}$ , and p-type Si (100) with a resistivity  $\sim 8\text{-}12 \Omega\text{cm}$ . All Ge wafers were dipped in deionized pure water for 90s to dissolve native oxide. The wafers were then immersed in 15%  $\text{H}_2\text{O}_2$  for 60s to reoxidize the surface intentionally followed by rinsing with deionized water for 90s and subsequently dipping 30% HCl solution or 50% HF solution to remove the surface oxide layer. Finally, the wafers were rinsed shortly in deionized pure water. The surface oxide layer must be removed to reduce the defect generation at Ge/ $\text{GeO}_2$  interface. As for Si, the entire wafers were cleaned with standard RCA cleaning step. Then the wafers were dipped in 0.5 % HF and followed by deionized pure water rinse. All the samples prepared were stored in clean room air at room temperature and dry oxygen chamber at atmosphere pressure. The oxygen flow was 30 sccm at room temperature. The humidity of clean room air and oxygen chamber was around 60% and 40%, respectively. The high resolution x-ray photoelectron spectroscopy (XPS) was used to characterize the Ge surfaces bonding feature. The angle between photoelectron detector axis and direction normal to the Ge surface was kept to  $30^\circ$  for the surface sensitive measurements. Spectroscopic ellipsometry (SE) was used to measure the thickness on native oxide on Ge and Si surfaces.

## 3 Results and discussion

The effect of different cleaning solutions is investigated on Ge (100) surface. Figure 1 shows the Ge  $3d_{5/2}$  spectra

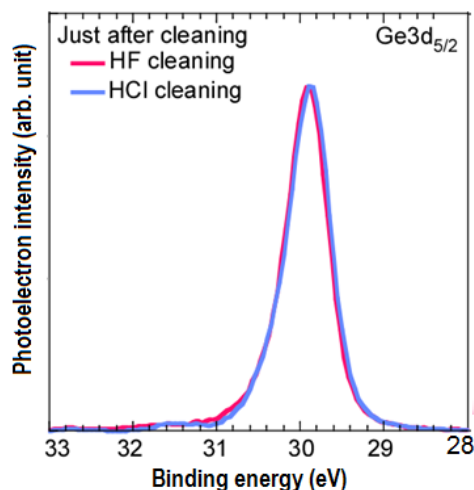


Figure 1. Ge $3d_{5/2}$  just after HCl and HF cleaning

on Ge (100). The results shows no signals originated from suboxide and oxide component were shown at binding energy of 31.5 eV which indicates that almost all of suboxide and oxide components are remove by HCl and HF cleaning. The Cl $2p$  and F $1s$  were measured on Ge (100) to evaluate the surface termination after chemical cleaning. The result shows that the Cl $2p$  signal was clearly observed and no F $1s$  signal was evaluated after HF cleaning which implies that the Ge (100) is

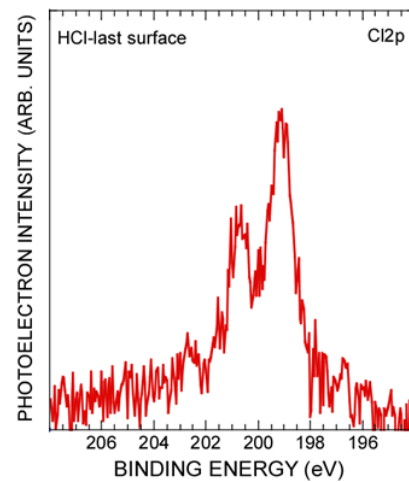


Figure 2. Cl $2p$  just after HC cleaning

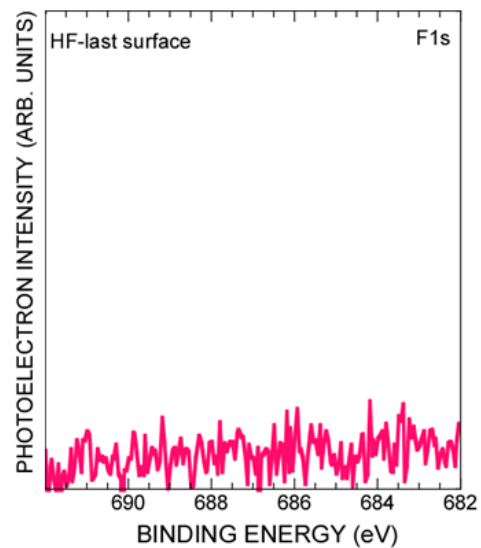


Figure 3. Just after HF cleaning

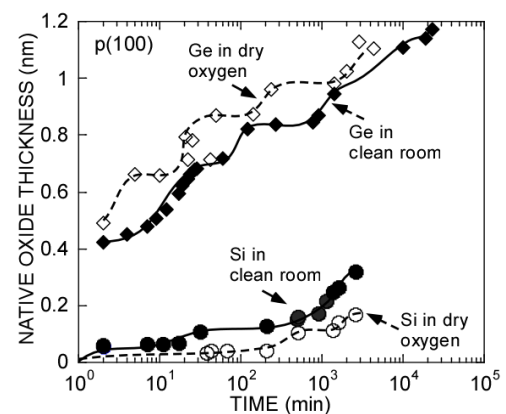
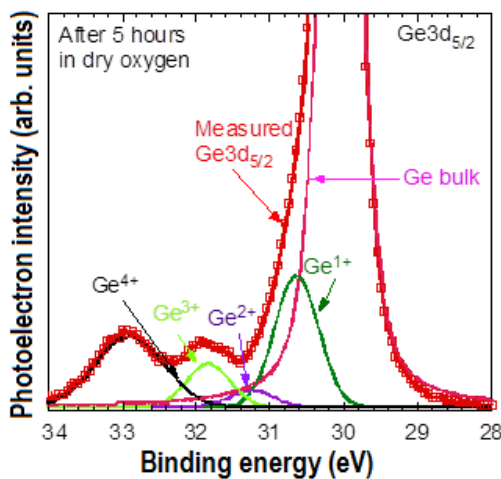
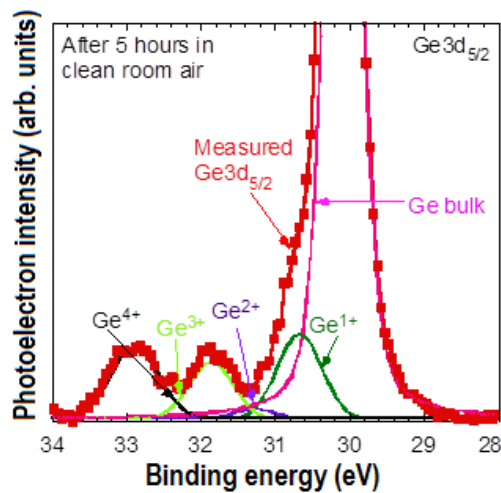


Figure 4. The growth of native oxide thickness of HCl-treated Ge (100) surface in clean room air and dry oxygen.

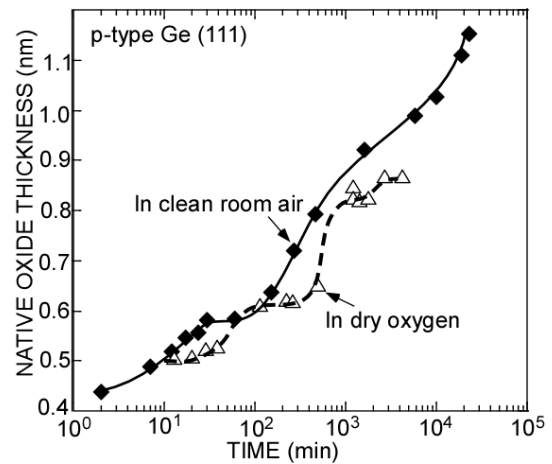
terminated with Cl passivation after HCl treatment as shown in Figure 2 and 3. Therefore in preceding experiments, the HCl cleaning was used to clean the Ge surface. The moisture effect on oxidation of Ge (100) in

cleanroom air and dry oxygen ambient are evaluated. Figure 4 shows the thickness of native oxide on Ge (100)

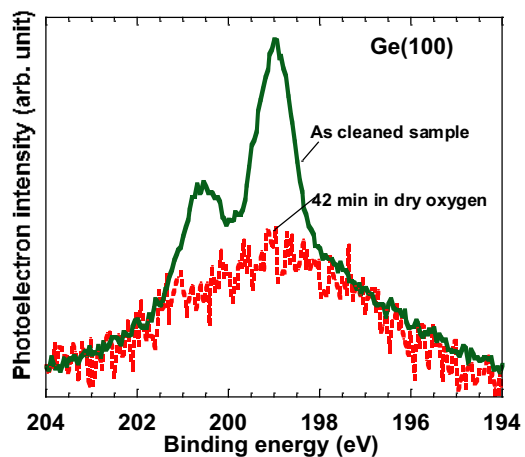


**Figure 5.** Deconvolution of Ge3d<sub>5/2</sub> signal of Ge (100) stored in cleanroom air and dry oxygen ambient

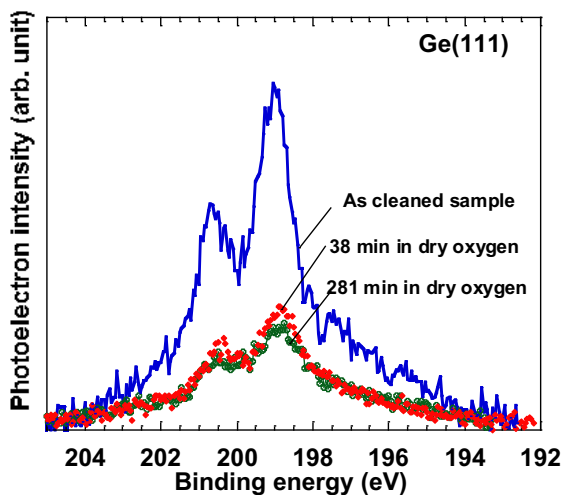
surfaces as a function of time after stored in clean room air and in dry oxygen chamber. Si oxidation was also evaluated and as a reference. The oxidation on Cl terminated Ge (100) in clean room air is slower compared to that of in dry oxygen chamber. In contrast, the oxidation on Si (100) in clean room air is faster compared to that of in dry oxygen ambient. The longer plateau region of Si oxidation is thought caused by the higher strain at Si/SiO<sub>2</sub> interface compare to Ge/GeO<sub>2</sub> interface [20]. To get insight into chemical bonding structure, Ge3d<sub>5/2</sub> spectra was measured. Each Ge3d<sub>5/2</sub> of Ge (100) stored in clean room air and dry oxygen ambient in 5 hours was compared as shown in Figure 5. The Ge 3d spectra was deconvoluted into Ge 3d<sub>5/2</sub> by considering the spin orbital splitting of Ge 3d core line. The energy splitting of Ge3d is 0.58eV as indicated in previous research [24]. For both samples, the suboxide components were clearly observed at binding energy around 31.5eV. To investigate the Ge 3d<sub>5/2</sub> in detail, the signal is deconvoluted into six components; Ge<sup>0+</sup>: Ge-substrate, Ge<sup>1-3+</sup>: Ge suboxides, Ge<sup>4+</sup>: GeO<sub>2</sub>, and Ge<sup>at+</sup> using the same method as described [24]. From the



**Figure 6.** The growth of native oxide thickness of HCl-treated Ge (111) surface in clean room and dry oxygen



**Figure 7.** Cl 2p core level peak on Ge (100) in dry oxygen ambient



**Figure 8.** Cl2p core level peaks on Ge (111) surfaces stored in dry oxygen for various lengths of time and just after HCl clean

spectral deconvolution of Ge3d<sub>5/2</sub> signal into suboxide

components of p-type Ge (100) after air and dry oxygen ambience exposure for 5 hours, we found that the signal due to  $\text{Ge}^{1+}$  on Ge (100) stored in dry oxygen are slightly higher than that of in clean room air. This result indicates that the atomically flat interface of oxidation in cleanroom air compare to that of in dry oxygen ambient. If compared to  $\text{Ge}3d_{5/2}$  spectra of sample stored in clean room air, only signals originated from suboxide ( $\text{Ge}^{1+}$ ,  $\text{Ge}^{2+}$  and  $\text{Ge}^{3+}$  states) components are increased for the sample stored in clean room air but little or no growth of the 4+ state ( $\text{GeO}_2$ ). These results confirmed that the existence moisture in the air increased the oxidation of suboxide of Ge. The effect of crystallographic orientation on Ge oxidation is investigated. The results obtained by spectroscopic ellipsometry is compared for HCl-last Ge (111) stored in clean room air and dry oxygen ambient as shown in the Figure 6. For the case of Ge (111) surface, the result shows that the growth of oxide on the Ge (111) surfaces stored in dry oxygen is slower compared to that of in clean room air as shown in Fig. 7. This result is different with the growth of oxide of Ge (100) as shown in Figure 4. This result indicates that the Cl-termination of Ge surface is more stable in dry oxygen ambience for Ge (111) case. This result consistent with previous report that explains the Cl terminated Ge (111) surface after HCl immersing is thermodynamically stable, well-ordered, atop adsorption, and similar to the surface formed by Cl adsorption in vacuum [25]. However, the step wise trend can be seen clearly on the growth of oxide in dry oxygen ambient for both orientations, Ge (100) and Ge (111) compared to in clean room air. In the early oxidation stage (oxidation time less than 100 min), the thickness of oxide in cleanroom air increases rapidly for both surface orientations and then retards giving a “kneelike” shape. On the other hand, for the samples stored in dry oxygen ambient, the plateau region can be seen clearly at the oxidation time less than 10 minutes. The initial rise of the oxide thickness store in clean room air is attributed by the moisture effect where it induces the growth of oxide and does not stop at the completion of a monolayer; instead it continues growing up to three layers as discussed in the previous research [26]. This reaction is due to the hydrogen bonding in water molecules. In addition, the shorter plateau region of oxide thickness stored in cleanroom air implies that the effect of moisture on the structural relaxation at the oxide/Ge interface oxidation of which the details have not been clarified yet.

As the oxidation time increases above 1000 mins, the thickness of oxide is rapidly increased in clean room air for both surface orientations which implies the increase of amount of water molecules induce the oxidation when storing in the clean room air in longer period of time.

To investigate the Cl termination on Ge (100) and Ge (111), Cl 2p spectra was measured with time dependence as shown in Figure 7 and Figure 8. As in Figure 3, no Cl-terminated on Ge (100) was observed even just after 40 minutes stored in dry oxygen. In contrast, the Cl  $2p_{3/2,1/2}$  peaks was occurred on Ge (111) even after 281 minutes in dry oxygen as shown in Figure 4. These results shows that Ge-Cl bond in dry oxygen ambient is strong on Ge(111) surface compared to Ge

(100) surface. This result shows that the Cl terminated Ge (111) is stable compared to Ge (100) which slow the growth of native oxidation in dry oxygen ambient. The stability of HCl-treated Ge (111) is attributed to the surface dangling bonds being terminated by monochloride [26].

## 4 Conclusion

The effect of different cleaning solution was investigated to remove suboxide and oxide on Ge surface. In addition, the effect of moisture on the growth of oxide is also studied. In low humidity (in dry oxygen ambience) shows perfect step and terrace trend on the growth of oxide for both surface orientations, Ge(100) and Ge(111). These trends have profound effects on the water absorption and the behavior of the Ge oxide in the different environment. In terms of surface orientation dependence, the Cl termination on Ge(111) is more stable compare to that of Ge(100) even after store more than 40 min in dry oxygen ambience.

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