

Study on Native Oxidation of Ge (111) and (100) Surfaces

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1. Introduction

Recently, Ge has been considered as a promising channel material to replace Si used conventionally for higher performance CMOS technology since it gives us higher carrier mobilities than Si. However, because of large differences in surface chemistry between Si and Ge, surface cleaning and passivation of Ge wafers are still matter of research. It is well known that, for Si wafers, the surface passivation with hydrogen, which is usually realized by oxide removal in a dilute HF solution, is quite effective to stabilize the surface against oxidation. In contrast to this, in Ge surface cleaning using HF solutions, the oxygen free surface was not obtained so far and initial oxidation is quite fast [4] presumably due to lower thermal stability of Ge-hydrides than Si-hydrides. In addition, it is also known that the oxidation of Si surfaces proceeds in a layer-by-layer fashion to create a very flat SiO₂/Si interface being compositionally abrupt in an atomic scale and the origin for the layer-by-layer oxidation is often discussed on a structural strain at the SiO₂/Si interface [2,3]. Despite much less stain at the GeO₂/Ge(100) interface than the SiO₂/Si (100) interface, it was recently reported that the native oxidation of HF-last Ge (100) surface is likely to be layer-by-layer growth of GeO₂ with air exposure time [4].

In this work, to gain a better understanding on the native oxidation of Ge surfaces, we have studied the growth of native oxides on HCl-last and HF-last Ge surfaces and examined the influence of crystallographic orientation and conduction type on the native oxidation.

2. Experimental

P-type or n-type Ge (100) and p-type Ge (111) with a resistivity of ~10-20 Ωcm, and n-type Si (100) with a resistivity ~10Ωcm were used in this work. For Ge wafers, they were dipped in deionized pure water for 90s to dissolve native oxide and followed by immersing in 15% H₂O₂ for 60s to reoxidize the surface intentionally. Then the wafer was rinsed with deionized water for 90s and subsequently dipping in either 50% HF or 30% HCl solution to remove the surface oxide layer. Finally, deionized pure water rinse was made shortly to minimize residual chemicals such as fluorine and chlorine. As for Si, after conventional wet-chemical cleaning step, the surface was 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. The thickness of native oxide was determined by high-resolution x-ray photoelectron spectroscopy (XPS) combined with spectroscopic ellipsometry (SE).

3. Results and Discussion

The thicknesses of native oxides grown on HF-last and HCl-last Ge (100) as a function of air exposure time are shown in Fig. 1. The native oxidation of the HF-last Ge surface is likely to proceed in slow time except in very early stages in comparison to the HCl-last surface. Stepwise increases of native oxide thickness every 0.2~0.3nm was observed for both HF-and HCl-cleaned Ge (100). Considering that the Ge-O bond length is about 0.2nm which similar to the stepwise increased of oxide thickness on Ge surfaces [5], the result suggests that layer-by-layer oxide growth occurs on Ge surface as similarly seen in the Si surface [6]. As shown in Fig. 2, Ge3d_{5/2} core-line spectra for HCl-last Ge (100) exposed in clean room air confirm that the signals due to fully-oxide Ge⁴⁺ are increased with exposure time. Also, AFM images confirm no surface roughening with progressive native oxidation as shown in inset of Fig. 2. For the sample surface after 16 days, the root-mean square value of the surface micro-roughness was obtained as small as ~0.18nm.

In order to reveal the influence of crystalline orientation on the native oxidation, the result obtained for HCl-last p-type Ge (100) and (111) surfaces were compared as shown in Fig. 3. The oxidation rate of (100) surfaces is faster than (111). This is because the (111) surfaces has less reactive sites such as atomic steps or microfacets as evidenced by a previous work [7]. Considering that oxygen molecule with a size of 0.271 nm is smaller than that of surface atom void sizes of (100) which has an atom void size of 0.308 nm [8], oxygen molecules are thought to penetrate easily through the (100) surface. To get an insight into the bonding structure at the interface between native oxide and Ge, we examined the suboxide components for natively-oxidized Ge (100) and (111) surfaces. For the natively-oxidized Ge(111), significantly less signals due to Ge²⁺ than others components were observed, implying atomically flat Ge(111) surface in part. On the other hand, for the natively-oxidized Ge(100), relatively large intensities of Ge¹⁺ and Ge³⁺ components were observable, indicating the interface is inferior in atomic flatness to the Ge(111) case.

The oxidation rate of n-type Ge (100) is significantly faster than that of p-type Ge (100) at early stage of oxidation as represented in Fig.5. The oxidation rate of n-type Si (100) is plotted in the figure as a reference that shows the oxidation rate of n-type Si (100) is significantly slower than that of n-type Ge (100) and p-type Ge (100). The oxidation rate of n-type is known to be enhanced by forming O₂⁻ ion through free electron transfer from Ge to adsorbed O₂ molecules. The formation of O₂⁻ ion also induces the

surface electric field which assists the oxidation [9].

4. Conclusions

The layer-by-layer growth of native oxide on HCl- and HF-last Ge (100) and (111) surfaces has been demonstrated. The native oxidation of Ge surfaces is influenced by topological aspects of the surface atom arrangement. The enhanced native oxidation of n-type Ge(100) compared with p-type is attributable to free electron transfers from Ge surfaces to oxygen molecules.

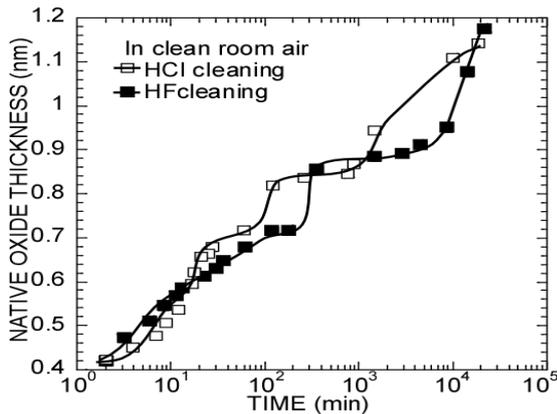


Fig. 1 The growth of native oxides on HF- and HCl-last p-type Ge(100) surfaces in clean room air.

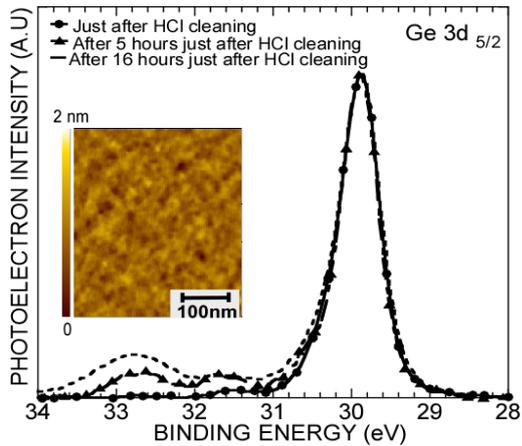


Fig. 2 Ge $3d_{5/2}$ spectra taken after 5 hours and 16 days stored in clean room. An AFM image of the sample stored for 16 days is shown in the inset.

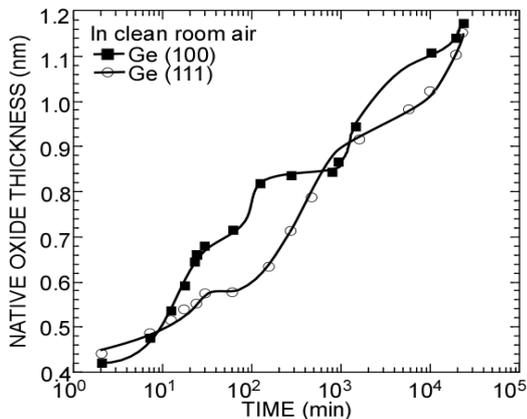


Fig. 3 The growth of native oxides on HCl-last p-type Ge (100) and Ge (111) surfaces.

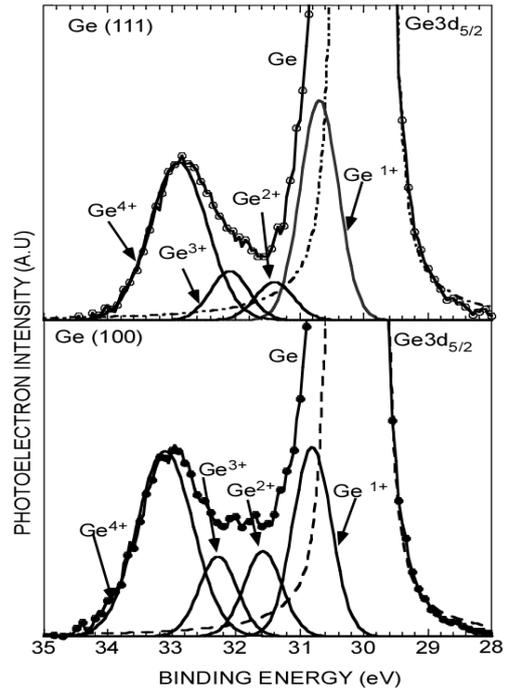


Fig. 4 Ge $3d_{5/2}$ spectra taken after native oxidation of HCl-last Ge(111) and (100) with storage for 6 days

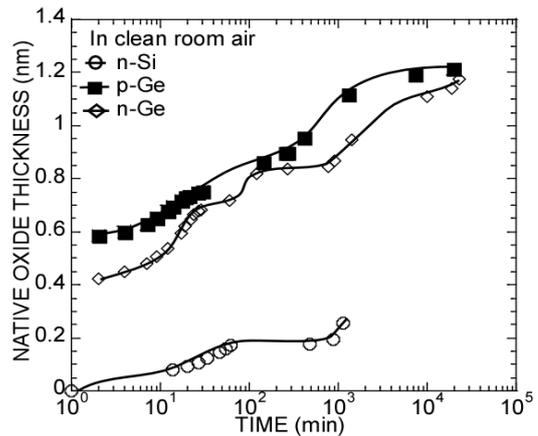


Fig. 5 The growth of native oxides on HCl-last n-Ge (100) and p-Ge (100) surfaces in clean room air

Acknowledgement

A part of this work was supported by Research Institute for Nano-device and Bio Systems (RNBS), Hiroshima University.

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