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Mechanism of the Initial Oxidation of Hydrogen and Halogen Terminated Ge(111) Surfaces in Air

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The initial stage of the oxidation of Ge(111) surfaces etched by HF, HCl and HBr solutions is systematically studied using synchrotron radiation photoelectron spectroscopy (SR-PES). We perform controlled experiments to differentiate the effects of different oxidation factors. SR-PES results show that both moisture and oxygen contribute to the oxidation of the surfaces; however, they play different roles in the oxidation process. Moisture effectively replaces the hydrogen and halogen termination layers with hydroxyl (OH), but hardly oxidizes the surfaces further. On the other hand, dry oxygen does not replace the termination layers, but breaks the Ge-Ge back bonds and oxidizes the substrates with the aid of moisture. In addition, room light enhances the oxidation rate significantly.

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Recently, Germanium (Ge) has emerged as a promising material for high-performance devices due to its high intrinsic electron and hole mobilities.[1] To fabricate devices on Ge, it is essential to clean and passivate its surface effectively. Although clean Ge surfaces can be achieved by wet chemical etching,[2-4] the passivation layer formed during cleaning is not stable in air,[5] and the surface oxide grow rapidly.[6] Therefore, it is crucial to understand the mechanism of the initial oxidation of the cleaned Ge surfaces in air, which little research has been carried out on. In addition, since Ge is next to Silicon (Si) in the periodic table, this study can also help to understand the mechanism of the initial oxidation of hydrogen terminated silicon (Si) surfaces, which has received considerable attention from both technological and scientific viewpoints.[7-11]

In this work, we study the initial stage of the oxidation of Ge(111) surfaces treated by HF, HCl and HBr solutions using synchrotron radiation photoelectron spectroscopy (SR-PES) at Stanford Synchrotron Radiation Laboratory (SSRL), and the oxidation experiments are performed at room temperature. It is well known that the oxidation in air is complicated, since oxygen, moisture, trace oxidants such as ozone etc. and illumination conditions can all affect the oxidation process[8-11,17]. Therefore, controlled experiments are performed to differentiate the effects of different oxidation factors. Specifically, first we do the oxidation experiments without room light, and then we repeat all the experiments with room light to study the effect of the room light illumination. Under either illumination condition, we try to oxidize the surfaces with dry oxygen alone, moisture alone, combination of oxygen and moisture, and room air, respectively, to understand the roles of each oxidation factor in the oxidation process.

N-type Ge(111) wafers with resistivity of 5-15 Ω.cm from Umicore are used in this study. HF (49% HF:H_2O =1:5), 10% HCl and 10% HBr are used to clean and passivate the surface. The experimental setup and the cleaning procedure are described in ref. 4. A bottle of research grade oxygen and a tube of deionized (DI) water (resistivity 18.6 MΩ.cm) are attached to the load lock for the oxygen and moisture dosing, respectively. To study the effect of pure moisture, the DI water is deoxygenated by sparging 99.9998% argon through it for 1 hour, reducing the dissolved O_2 content to 0.3 ppm, while the air saturated DI water contains 3.4 ppm of dissolved oxygen.[12] Before dosing oxygen or moisture, the load lock has base pressure below $1\text{x}10^{-7}$ torr. During the oxygen dosing, the oxygen pressure is kept at around 160 torr, which is the oxygen partial pressure in air. As for the moisture dosing, the moisture pressure is kept at about 9.5 torr. After dosing, the load lock is pumped down immediately by a turbo pump, and then the sample is transferred into the analysis chamber to take spectra. Throughout the whole process, the system does not break the vacuum, so the contamination is minimized. During the experiments without room light, all the viewports of the load lock and the analysis chamber are covered by aluminum foils to avoid room light.

HF, HCl and HBr etching clean the Ge(111) surface and terminate the surface with hydrogen (H), chlorine (Cl) and bromine (Br), respectively. In general, the wet chemical (HF, HCl, and HBr) cleaned Ge(111) surface has less carbon and oxygen compared with the treated Ge(100) surface.[6] Figure 1 shows Ge3d taken at 80eV right after etching with careful peak fitting.[4,18] For the HF etched surface, two doublet peaks are used in the peak fitting. One is the Ge bulk peak, and the other has a chemical shift of 0.64eV towards the lower kinetic energy side and a calculated coverage of 0.36 ± 0.09

monolayer (ML), which is assigned as Ge tri-hydride, since HF etched Ge surfaces are atomically rough and Ge mono-hydride, di-hydride and tri-hydride all exist.[5,13] The chemical shifts of Ge mono-hydride and di-hydride are very small and beyond the experimental resolution. As for the HCl and HBr cleaned surfaces, Ge mono-chloride and mono-bromide are formed. The chemical shifts of Ge mono-chloride and mono-bromide are 0.59eV and 0.52eV, and the coverage is 0.95 ± 0.24 ML and 1.02 ± 0.25 ML, respectively, so a complete Cl or Br termination layer is formed.

Controlled oxidation experiments are performed after wet chemical cleaning. First, we dose the cleaned surface with dry O_2 in dark conditions. Figure 2(a) depicts Ge3d taken at 80eV after each dosing step for both H terminated and Cl terminated surfaces. The oxygen dosage shown in the legend is accumulated dosage, and the same for both surfaces. The total dosage is $9.4\text{x}10^{11}$ Langmuir (L), which is equivalent to dosing the surface at the oxygen partial pressure in air, i.e. 160 torr, for 98 minutes. From the Ge3d of the H terminated surface, we can see the H passivated Ge surface is not stable in dry O_2, and oxide grow significantly, which is also confirmed by O1s peaks taken at 620eV.[6] After the final dosing, peak fitting shows the total oxide coverage is 0.73 ± 0.18 ML, and the coverage of tri-hydride is 0.31 ± 0.08 ML, almost the same as that before oxidation, so dry O_2 does not replace the hydride, but breaks Ge-Ge back bonds and grows oxide. The same conclusions were also drawn from the Si case.[9] However, it is difficult for dry O_2 to fully oxidize the surface in dark conditions, because according to the peak fitting, the Ge oxide grown is not GeO_2, but suboxide with Ge oxidation states of 1+, 2+, and 3+. And their chemical shifts are 0.9eV, 1.7eV, and 2.5eV, respectively, consistent with the literature.[15,16].

In contrast, Ge3d of the Cl terminated surface does not change in dry O_2. In addition, figure 2(b) shows that Cl2p taken at 300eV remains almost the same, which confirms that dry O_2 does not interrupt the termination layer. Different from the H terminated surface, the Cl terminated surface is quite inert to dry O_2 and little oxide grows. One reason of the good stability of the Cl passivation layer is that the Cl termination layer is almost complete (0.95 ML), and the other reason is that the Cl atoms are much larger than the H atoms, so that the Cl termination layer serves as a good physical barrier to prevent dry O_2 molecules reaching the Ge surface. Similarly, the Br terminated surface is also stable in dry O_2, and little oxide grows.[6]

In order to study the role of moisture during oxidation, we dose the cleaned surfaces with only moisture in dark conditions. Figure 3(a) shows Ge3d after each dosing step for both H terminated and Cl terminated surfaces. The moisture dosage shown in the legend is accumulated dosage, and the same for both surfaces. Ge3d of the H terminated surface gets broader at the lower kinetic energy side with moisture dosing, indicating new components grow. And at a certain point, the intensity of the new components gets saturated. However, it is not straightforward to know what the new components are. Since we can observe the Cl peak, the Cl terminated surface can serve as a model system to understand the role of moisture in the oxidation. Figure 3(b) shows that the intensity of Cl2p drops with moisture dosing, implying that the Cl termination layer is interrupted and some Cl atoms are replaced. After the largest moisture dosing ($6.17\text{x}10^{10}$ L), i.e. dosing the surface at 9.5 torr for 108 min, the intensity of the Cl2p peak decreases to 49% of that before moisture dosing. At the same time, Ge3d of the Cl terminated surface also gets broader, and careful peak fitting shows that the Ge3d spectrum needs three peaks to fit well. One is the Ge bulk peak, and another is Ge mono-chloride with a chemical shift of 0.59eV towards the lower kinetic energy side and coverage of 0.53 ± 0.13 ML. The third peak has a chemical shift of 0.88eV to the lower kinetic energy side and coverage of 0.20 ± 0.05 ML, which is assigned as Ge hydroxide (OH). The intensity of the remaining Ge mono-chloride peak is 56% of that before moisture dosing, which is in agreement with the reduction of the intensity of Cl2p. After the final moisture dosing, the total coverage of chloride and hydroxide is around 0.73 ML, and the rest of the surface could be terminated by hydride, most likely mono-hydride which can not be resolved by our experiments, and by carbon contaminants, which is supported by the fact that the carbon signal increases after moisture dosing. As for the Br terminated surface, it has similar results. In summary, the appearance of hydroxide and the reduction of Cl2p show that moisture replaces the hydrogen and halogen termination layers with hydroxide, which has been observed in the Si case.[9,10] But the saturation of hydroxide indicates that moisture alone hardly oxidizes the surface further.

To simulate the oxidation of room air and derive the mechanism of the initial oxidation in air, we also dose the cleaned surface with O_2 and moisture together in dark conditions. The moisture partial pressure is 9.0 torr and the oxygen partial pressure is 160 torr. Both Ge3d and O1s spectra show that the surface grows oxide faster with O_2 and moisture together than with O_2 alone or moisture alone, especially for the Cl and Br terminated surfaces. This means the coexistence of O_2 and moisture enhances the oxidation rate. We also compare the oxidation rates in the following three oxidation conditions: O_2 and moisture together in dark conditions, room air in dark conditions and room air with room light. As shown in figure 4, in dark conditions, the oxidation rate with O_2 and moisture together is similar to that with room air, although room air has trace oxidant species such as nitrogen oxides, hydrocarbon radicals etc. The similarity of the oxidation rates indicates that in dark conditions, room air oxidation follows the same mechanism we derive above, i.e. moisture assists O_2 to attack the Ge-Ge back bonds and oxidize the surface, and the trace oxidant species in air do not affect the oxidation rate greatly. However, the oxidation rate increases dramatically with room light illumination, which is believed to be due to the ultraviolet (UV) components of the room light.[17]

In conclusions, we perform controlled experiments to systematically study the mechanism of the initial oxidation of the H and halogen terminated Ge(111) surface in air. The mechanism can be summarized as follows: moisture in air replaces the H and halogen termination layer with hydroxide, and then assist the oxygen in air to attack the Ge-Ge back bonds and oxidize the surface. The trace oxidant species do not play an important role in the oxidation, but the UV components in room light accelerate the oxidation process substantially.

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Figure Captions

Figure 1. Ge3d core level peaks with peak fitting taken at a photon energy of 80eV for samples treated by HF (1:5), HCl (10%) and HBr (10%). The open dots are experimental data, and the solid lines are fitting curves.

Figure 2. (a) Ge3d core level peaks taken at a photon energy of 80eV after dry oxygen dosing step by step in dark conditions for both H terminated and Cl terminated surfaces. The oxygen dosage shown in the legend is accumulated dosage, and the same for both surfaces. (b) Cl2p core level peaks taken at a photon energy of 300eV after dry oxygen dosing step by step in dark conditions for the Cl terminated surface.

Figure 3. (a) Ge3d core level peaks taken at a photon energy of 80eV after moisture dosing step by step in dark conditions for both H terminated and Cl terminated surfaces. The moisture dosage shown in the legend is accumulated dosage, and the same for both surfaces. (b) Cl2p core level peaks taken at a photon energy of 300eV after moisture dosing step by step in dark conditions for the Cl terminated surface.

Figure 4. (upper curves) Ge3d core level peaks taken at a photon energy of 80eV after 2.8 hours dosing with O_2 and moisture together in dark conditions, room air in dark conditions and room air with room light, respectively, for H terminated surfaces, and (lower curves) after 2 hours dosing with O_2 and moisture together in dark conditions, room air in dark conditions and room air with room light, respectively, for Br terminated surfaces.

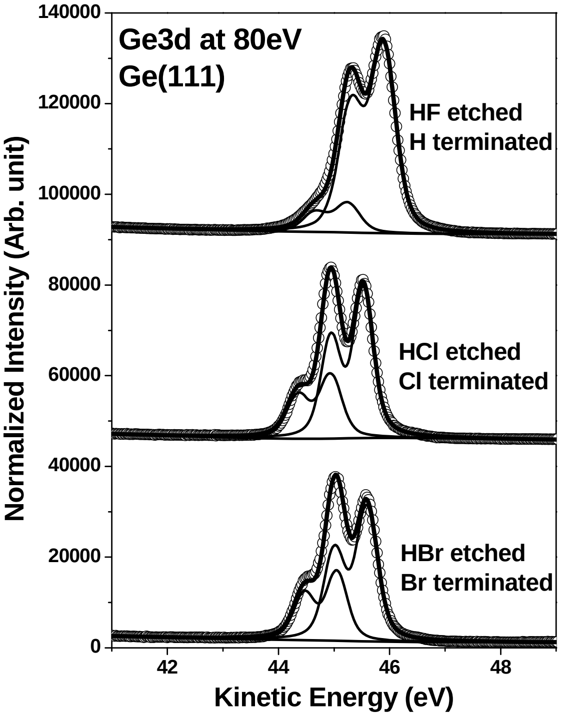

Figure 1 Shiyu Sun *et al.*

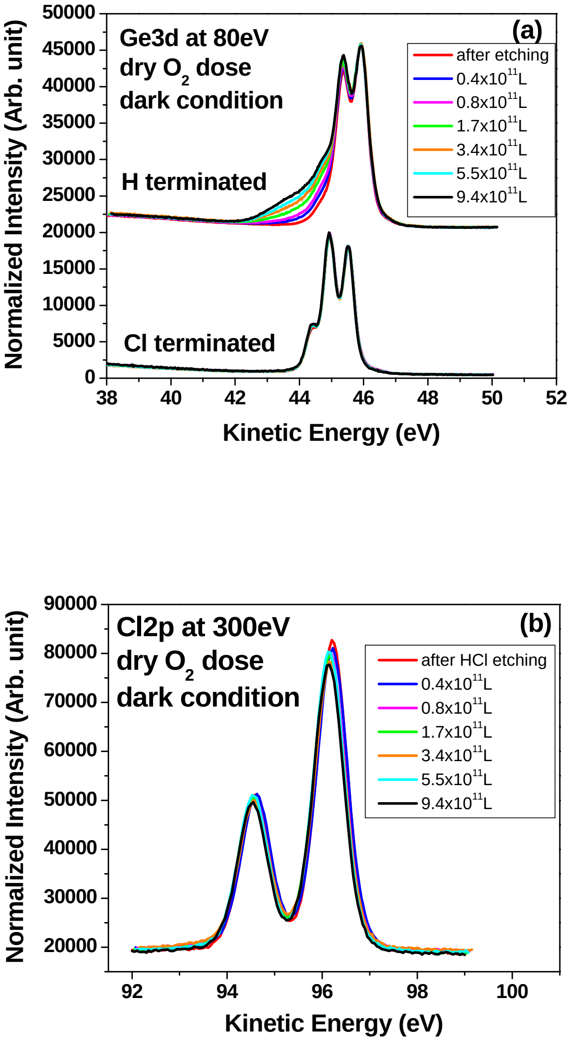

Figure 2 Shiyu Sun *et al.*

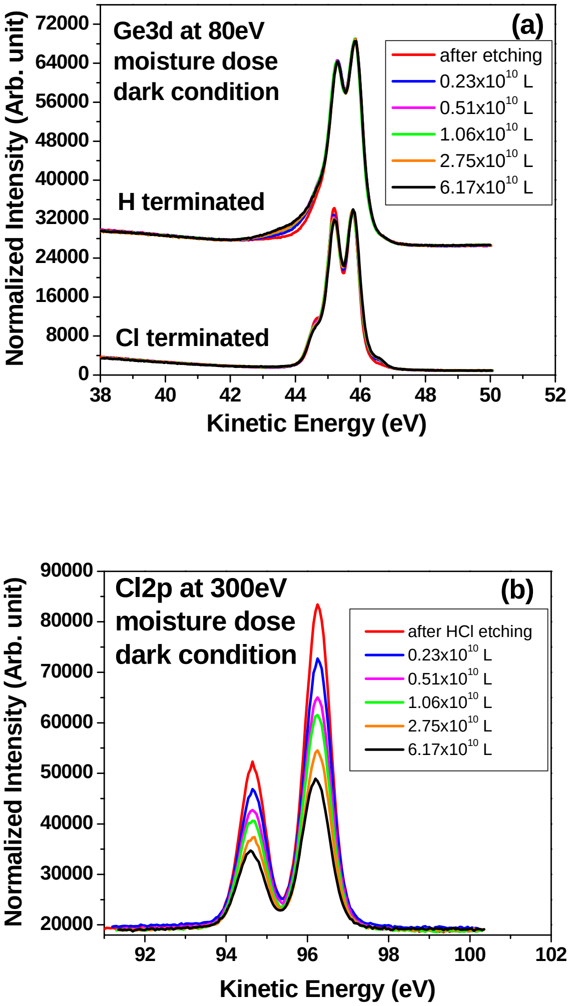

Figure 3 Shiyu Sun *et al.*

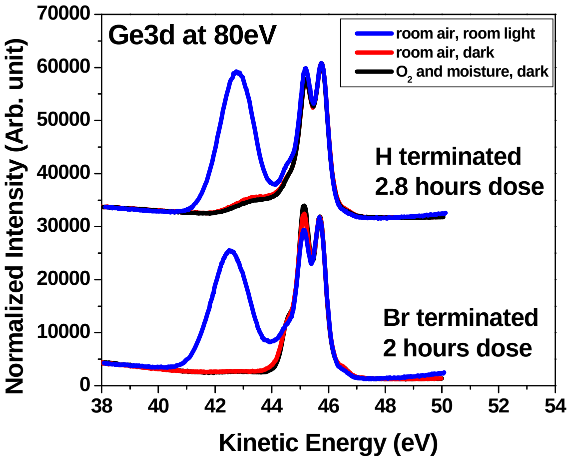

Figure 4 Shiyu Sun *et al.*