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Roles of Oxygen and Water Vapor in the Oxidation of Halogen Terminated Ge(111) Surfaces

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The initial stage of the oxidation of Cl and Br terminated Ge(111) surfaces is studied using photoelectron spectroscopy. The authors perform controlled experiments to differentiate the effects of different factors in oxidation, and find that water vapor and oxygen play different roles. Water vapor effectively replaces the halogen termination layers with the hydroxyl group, but does not oxidize the surfaces further. In contrast, little oxidation is observed for Cl and Br terminated surfaces with dry oxygen alone. However, with the help of water vapor, oxygen oxidizes the surface by breaking the Ge–Ge back bonds instead of changing the termination layer.

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 hydrogen and halogen passivation layers formed during etching are not stable in the air.[5,6] Therefore, it is crucial to understand the mechanism of the initial oxidation of the treated Ge surfaces in the air. Since Ge(111) surfaces are structurally simple and halogen terminated surfaces are more stable than hydrogen terminated surfaces,[7] the halogen terminated Ge(111) surface can serve as a model system to investigate the oxidation mechanism, and help to understand the Ge(100) surface, which is technologically more important.

In this work, we study the initial stage of the oxidation of Ge(111) surfaces treated by HCl and HBr solutions using synchrotron radiation photoelectron spectroscopy at Stanford Synchrotron Radiation Laboratory. Initial oxidation of hydrogen (H) terminated Ge(111) surfaces is also studied and will be discussed elsewhere.[6] The oxidation experiments are performed at room temperature. It is well known that the oxidation in the air is complicated, since oxygen, water vapor, trace oxidants such as ozone, etc., and illumination conditions can all affect the oxidation process.[8–12] Therefore, controlled experiments are performed to differentiate the effects of different oxidation factors. First, we perform the oxidation experiments in dark conditions, and then we repeat all the experiments with room light to study the effect of the room light illumination. Under either illumination condition, we study the oxidation with water vapor alone, dry O_2 alone, water vapor followed by dry O_2, combination of water vapor and O_2, and room air to understand the role of each oxidation factor in the oxidation process.

n-type Ge(111) wafers with resistivity of $5-15\ \Omega\,\mathrm{cm}$ from Umicore are used in this study. 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 de-ionized (DI) water (resistivity of $18.6\ \mathrm{M}\Omega\,\mathrm{cm}$) are attached to the load lock for oxygen and water vapor dosing. To study the effect of pure water vapor, the DI water is deoxygenated by sparging 99.9998% argon for 1 h, reducing the dissolved O_2 content to 0.3 ppm, while the air saturated DI water contains 3.4 ppm of dissolved O_2.[13] Before dosing with oxygen, water vapor or room air, the load lock is pumped to a pressure below 1×10^{-7} Torr. During the oxygen dosing, the O_2 pressure is kept at around 160 Torr (the oxygen partial pressure in room air), during the water vapor dosing, the water vapor pressure is kept at about 9.0 Torr (the water vapor pressure in room air with relative humidity of approximately 30%), and during dosing with room air, the load lock is completely vented to room air. After dosing, the load lock is pumped down immediately by a turbo pump, and then the sample is transferred into the analysis chamber to be analyzed. During all the experiments under dark conditions, the samples are kept in the load lock with the viewports covered. As for the experiments with room air and room light, samples are taken out of the load lock, and exposed to the light from normal fluorescent lamps.

Chlorine (Cl) and bromine (Br) terminated surfaces are achieved by etching Ge surfaces with HCl and HBr solutions, respectively. Figure 1 shows the Ge 3*d* core level taken at 80 eV right after etching. For the HCl etched surface, two doublet peaks are used in the peak fitting.[4,14] One is the Ge bulk peak, and the other has a chemical shift of 0.59 eV towards the lower kinetic energy side and a calculated coverage of 0.95 ± 0.24 ML (monolayer),[15] which is assigned as Ge monochloride. As for the HBr cleaned surface, Ge monobromide is formed. The chemical shift of Ge monobromide is 0.52 eV, and the coverage is 1.02 ± 0.25 ML. Clearly, a complete Cl (Br) termination layer is formed after etching.

Controlled oxidation experiments are performed after the wet chemical treatments. First, we dose the treated surface with water vapor alone in dark conditions. Figure 2 shows the Ge 3*d* core level taken at 80 eV after 6.17×10^{10} L dosing with water vapor for the Cl terminated surface, and the inset shows Cl 2*p* taken at 300 eV after each dosing step. As shown in the inset, the intensity of the Cl 2*p* drops with each

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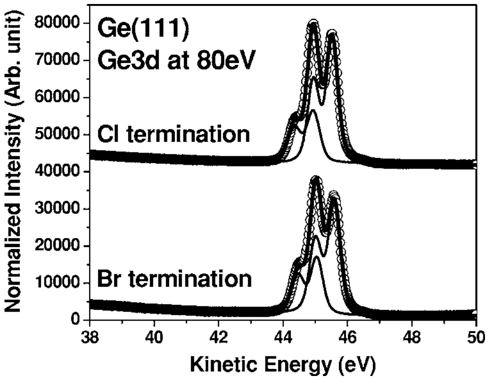

FIG. 1. Ge 3*d* core level peaks with peak fitting taken at a photon energy of 80 eV for samples treated by HCl (10%) and HBr (10%). The open dots are experimental data and the solid lines are fitting curves.

step, implying that the Cl termination layer is modified and some Cl atoms are replaced. After the largest dose (6.17×10^{10} L), i.e., dosing the surface at 9.0 Torr for 114 min, the intensity of the Cl 2*p* peak decreases to 49% of that before dosing. At the same time, peak fitting of the Ge 3*d* shows that the coverage of the Ge monochloride drops to 0.45 ± 0.11 ML, and a third peak with a chemical shift of 0.83 eV towards the lower kinetic energy side and coverage of 0.20 ± 0.05 ML is needed for a good fit. The third peak is assigned as Ge hydroxide, which indicates that the Cl termination layer is replaced by the hydroxyl group (OH) according to the most plausible chemical reaction: $\mathrm{Ge{-}Cl + H_2O = Ge{-}OH + HCl}$. The intensity of the remaining Ge monochloride peak is 47% of that before water vapor dosing, which is in agreement with the reduction of the Cl 2*p*. However, the calculated hydroxide coverage is less than expected since the replacement of Cl by OH should be one to one. This discrepancy is still under investigation. In addition, higher Ge oxidation states, i.e.. $\mathrm{Ge^{2+}}$, $\mathrm{Ge^{3+}}$, and $\mathrm{Ge^{4+}}$ with chemical shifts of 1.8, 2.6, and 3.4 eV,[16] respectively, are not observed in the Ge 3*d* spectra, which suggests that water vapor did not further oxidize the substrate in dark conditions aside from replacing Cl with OH. Similar results are observed on the Br terminated surface. Our work on the initial oxidation of the hydrogen terminated Ge(111) surface with water vapor alone also confirms that water vapor dosing replaces the H termination layer with OH, but does not oxidize the surface further in dark conditions. In addition, the replacement rate of the H termination layer is larger than that of the Cl (Br) termination layer, which is due to the smaller bond strength of Ge–H bonds.[17]

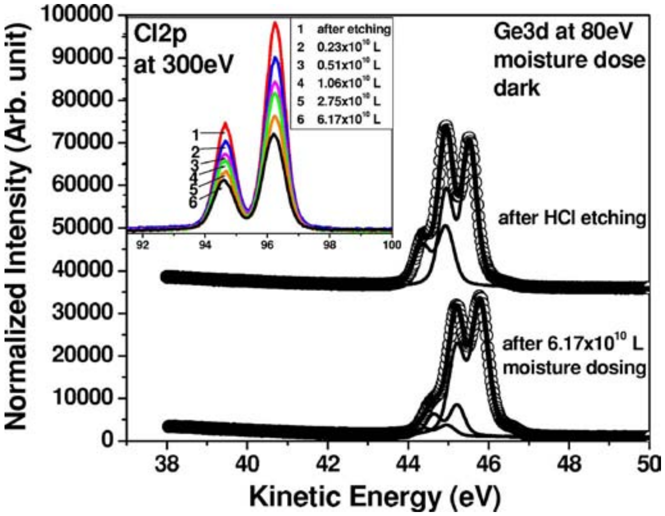

FIG. 2. (Color online) Ge 3*d* core level peaks with peak fitting taken at 80 eV for the Cl terminated surface right after etching and after 6.17×10^{10} L water vapor dosing in dark conditions. The open dots are experimental data and the solid lines are fitting curves. The inset shows Cl 2*p* core level peaks taken at 300 eV after water vapor dosing with accumulated dosages of 0, 0.23×10^{10}, 0.51×10^{10}, 1.06×10^{10}, 2.75×10^{10}, and 6.17×10^{10} L in dark conditions.

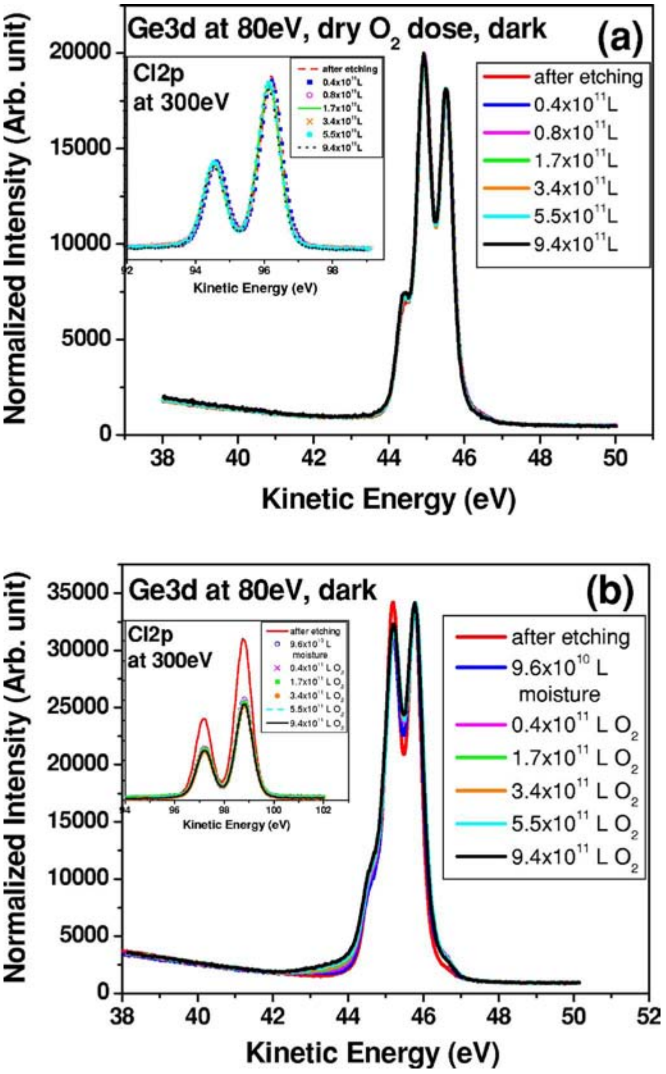

FIG. 3. (Color online) (a) Ge 3*d* core level peaks of the Cl terminated surface taken at 80 eV after dry oxygen dosing in dark conditions. The accumulated dosages are 0, 0.04×10^{11}, 0.08×10^{11}, 1.7×10^{11}, 3.4×10^{11}, 5.5×10^{11}, and 9.4×10^{11} L. All Ge 3*d* curves are essentially the same and overlap with each other. The inset shows Cl 2*p* taken at 300 eV after the same treatment. (b) Ge 3*d* core level peaks taken at 80 eV after one step water vapor dosing followed by dry oxygen dosing in dark conditions for the Cl terminated surface. The accumulated dosage is 0, 9.6×10^{10} (water vapor), $0.4 \times 10^{11}(\mathrm{O_2})$, $1.7 \times 10^{11}(\mathrm{O_2})$, $3.4 \times 10^{11}(\mathrm{O_2})$, $5.5 \times 10^{11}(\mathrm{O_2})$, and $9.4 \times 10^{11}(\mathrm{O_2})$. All the curves are normalized to the height of the bulk peak to emphasize the peak shape differences. The lower kinetic energy side grows as the oxygen dosage increases. The inset shows Cl 2*p* core level peaks taken at 300 eV accordingly.

In order to study the role of oxygen during oxidation, we dose the treated surfaces with dry oxygen only in dark conditions. Figure 3(a) shows Ge 3*d* after each dosing step for the Cl terminated surface, and the inset shows the Cl 2*p* after the same treatment. The $\mathrm{O_2}$ dosage shown in the legend is the accumulated dosage. The total dosage is 9.4×10^{11} L, which is equivalent to dosing the surface at 160 Torr for 98 min. As shown in Fig. 3(a), the Ge 3*d* of the Cl terminated surface does not seem to change with dry O_2 dosing, indicating that the Cl terminated surface is quite inert to dry O_2 and little oxide grows in dark conditions. This is also supported by the lack of change in the valence band (VB) spectra. At the same time, the Cl 2*p*, as shown in the inset, remains almost the same, which confirms that dry O_2 does not change the termination layer. Similarly, the Br terminated surface is also stable in dry O_2, and little oxide grows. As a comparison, the hydrogen terminated Ge(111) surface undergoes significant oxidation with dry O_2 dosing in dark conditions. Among the reasons for the better stability of the Cl and Br terminated surfaces in dry O_2 are that the surface Ge atoms are completely passivated by Cl (Br) atoms, and Cl (Br) atoms are much larger than H atoms, so the Cl (Br) termination layer serves as a better steric barrier for preventing O_2 molecules reaching the Ge surface.

To further understand the role of oxygen in oxidation, we dose the treated surface with water vapor followed by dry oxygen in dark conditions. Figure 3(b) shows the Ge 3*d* after each dosing step for the Cl terminated surface, and the inset shows the Cl 2*p* accordingly. As shown in the inset, the intensity of the Cl 2*p* drops after the first step of water vapor dosing, and then keeps the same intensity during the subsequent dry O_2 dosing, which confirms that water vapor, instead of O_2, affects the Cl termination layer. At the same time, the Ge 3*d* gets broader at the lower kinetic energy side with dry O_2 dosing after the first step of water vapor dosing, which indicates new components appear and grow with dry O_2 dosing. Peak fitting shows that the new components are Ge oxide with oxidation states of Ge^{2+} and Ge^{3+}. Since O_2 does not alter the surface termination layer, the most plausible way for this oxidation to happen is to break the Ge–Ge back bonds. One of the reasons for this oxidation enhancement after water vapor dosing is due to the smaller size of the OH compared with that of Cl, so O_2 can approach the Ge–Ge back bonds much more easily. Br terminated surfaces show the same results. The oxidation rate can also be enhanced by dosing the surface with water vapor and O_2 together. Both the Ge 3*d* and VB spectra demonstrate that the surface grows oxide faster with water vapor and O_2 together than with O_2 alone or water vapor alone.

To understand the roles of other factors in oxidation, we compare the oxidation rates in the following three oxidation conditions: water vapor (9.0 Torr) and O_2 (160 Torr) together in dark conditions, room air in dark conditions, and room air with room light. As shown in Fig. 4, for Br terminated surfaces in dark conditions, the oxidation rate with water vapor and O_2 together is similar to that with room air, although room air has trace oxidant species such as nitrogen oxides, hydrocarbon radicals, etc. This similarity of the oxidation rates indicates that in dark conditions, room air oxidation follows the same mechanism discussed above. We also observed that the trace oxidant species in the air affect the oxidation rate negligibly under dark conditions. However, the oxidation rate increases dramatically with room light illumination, which could be due to the ultraviolet (UV) components of the room light.[12] H and Cl terminated surfaces give the same results.

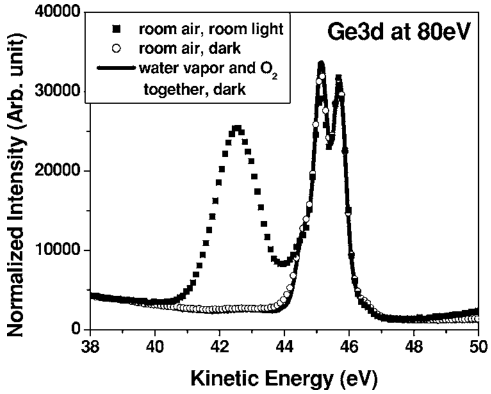

FIG. 4. Ge 3*d* core level peaks of Br terminated surfaces taken at 80 eV after 2 h dosing in the following three conditions: water vapor and O_2 together in dark conditions, room air in dark conditions, and room air with room light. All the curves are normalized to the height of the bulk peak to emphasize the peak shape differences.

To summarize the oxidation mechanism, water vapor in the air replaces the halogen termination layer with the hydroxyl group, and then assists the oxygen in the 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, under dark conditions, but room light accelerates the oxidation process substantially.

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