

Surface Termination and Roughness of Ge(100) Cleaned by HF and HCl Solutions

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Oxide removal from Ge(100) surfaces treated by HCl and HF solutions with different concentrations are systematically studied by synchrotron radiation photoelectron spectroscopy (SR-PES). SR-PES results show that clean surfaces without any oxide can be obtained after wet chemical cleaning followed by vacuum annealing with a residual carbon contamination of less than 0.02 monolayer. HF etching leads to a hydrogen terminated Ge surface whose hydrogen coverage is a function of the HF concentration. In contrast, HCl etching yields a chlorine terminated surface. Possible etching mechanisms are discussed. Surface roughness after HF and HCl treatments is also investigated by AFM, which shows that HF treatment leaves a rougher surface than HCl.

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Germanium (Ge) is increasingly being studied for MOSFET applications to take advantage of its high intrinsic electron and hole mobility. To fabricate high performance devices on Ge, it is essential to understand Ge surface chemistry and find an effective way to clean and passivate its surface. Although Si surface cleaning and passivation have been extensively studied,¹⁻³ only recently has some research been done on Ge surfaces.⁴⁻⁷ Conventional XPS results show that HF etching removes Ge oxide and carbon contamination significantly,⁴ and HCl etching leads to a chlorine terminated Ge(111) surface, which only forms Ge monochloride.⁷ However, it is difficult to probe the details of the chemical nature of treated surfaces and quantify the surface termination and cleanness with conventional XPS, because of its limited surface sensitivity and resolution. In addition, little attention has been paid to the HF concentration, which turns out to be an important factor in the surface hydrogen passivation.

In this work, we study the Ge(100) surfaces treated by aqueous HCl and HF solutions with three different concentrations by synchrotron radiation photoelectron spectroscopy (SR-PES) at Stanford Synchrotron Radiation Laboratory (SSRL). Using SR-PES, we can tune the photon energy to achieve very high surface sensitivity and good resolution, so the chemical states of treated surfaces can be resolved unambiguously, and the surface termination and cleanness can be quantified. We find that HF treatment results in a hydrogen terminated surface, and the hydrogen coverage depends on the HF concentration. In contrast, a Cl terminated Ge(100) surface is achieved after HCl treatment. Both monochloride and dichloride are formed on the surface. The termination difference between HF etching and HCl etching can be explained by the etching

mechanism. In both cases, the residual carbon and oxygen after chemical etching can be removed by vacuum annealing.

N-type Ge(100) wafers with resistivity of 2-6 ohm.cm from Umicore were used in this study. Three concentrations of HF (49% HF:H₂O = 1:3, 1:5, and 1:25) and 10% HCl were used. All the chemical treatments were performed inside an Ar purged glove bag⁸ with the following cleaning procedure. First, samples were dipped into DI water (resistivity 18.6 MΩ.cm) for 30 seconds to dissolve the native oxide and then put into 10% H₂O₂ for 30 seconds to grow a fresh chemical oxide. Next, the samples were immersed into an HF or HCl solution, respectively, for 10 min. Finally, the samples were blown dry with Ar gas, and then immediately put into the load lock. After the load lock was pumped down by a turbo pump, the samples were transferred into the photoemission chamber with a base pressure of 1×10^{-10} torr. The photoemission experiments were conducted using Beam Lines 8-1 and 10-1 at SSRL. 80eV photon energy was selected for the Ge3d to achieve a mean free path of approximately 4Å, while the Cl2p, C1s, O1s and F1s were monitored at 300eV, 400eV, 620eV and 800eV, respectively.

Figure 1 shows Ge3d core level spectra taken at a photon energy of 80eV. All the curves are normalized to the height of the bulk peak in order to emphasize the peak shape differences, and the inset shows the O1s peak taken at 620eV. Both Ge3d and O1s show that HF etching removes Ge oxide significantly, and the amount of residual oxygen depends on the HF concentration. After HF (1:25) etching, there is a clear shoulder on the low kinetic energy side of Ge3d, which implies a noticeable oxide-like component. On the other hand, after HF (1:3) or HF (1:5) etching, no obvious oxide component can be seen for Ge3d. In addition, the intensity of the O1s is much smaller than that of the HF

(1:25) case, indicating that only a small amount of oxide is left on the surface. To identify the chemical states of treated surfaces, the Ge3d peaks are carefully fitted as shown in Fig. 2. Voigt line shapes (Gaussian broadened Lorentzian) are applied during the least-squares fitting. Key fitting parameters are 170 meV Lorentzian width, 280 meV Gaussian width, 0.585 eV spin-orbit splitting, and 0.667 branching ratio. Two doublet peaks are used in the peak fitting. One is the Ge3d bulk peak (Ge^{0+}), and the other has a chemical shift of 1.1eV. This component, mentioned earlier as oxide, is most likely due to Ge surface atoms terminated by OH (Ge^{1+}). From the peak area ratios, we can calculate the hydroxide (OH^-) coverage⁹ i.e. 0.10 ± 0.02 monolayer (ML) for HF (1:3), 0.11 ± 0.02 ML for HF(1:5), and 0.20 ± 0.04 ML for HF(1:25). The hydroxide can be removed by 30 min annealing at 400°C in our ultrahigh vacuum chamber. This HF concentration effect can be explained by understanding the HF etching mechanism.

To understand the HF etching mechanism on Ge surfaces, we can begin by referring to the extensive work on Si surfaces. Although from the thermodynamic point of view, a F passivated Si surface is more stable,¹⁰ research shows that kinetics plays a more important role in the surface hydrogen passivation.^{11,12} Since Ge is next to Si in the same column, and has electronegativity very close to that of Si,¹³ similar arguments can be applied to Ge, yielding a hydrogen passivated surface. During the etching process, H^+ etches the oxide and passivates the Ge surfaces. With increasing HF concentration, the H^+ concentration is higher, so the HF concentration plays a key role in determining the hydrogen coverage. However, a perfect hydrogen terminated Ge(100) surface can not be achieved, even by solutions with very high HF concentrations, which could be due to the nature of the Ge(100) surface itself. This concentration effect is not observed in the Si

case, which can be explained as follows. Since the electronegativity difference between Si and F is greater than that between Ge and F (the electronegativity of Si, Ge, F is 1.90, 2.01, 3.98, respectively), and Si-F bonds are stronger and shorter than Ge-F bonds (the bond strength: Si-F 553 KJ/mol, Ge-F 485 KJ/mol; the bond length: Si-F 1.58 Å, Ge-F 1.73 Å),¹³ Si-Si back bonds are polarized more, making it easier for them to be further attacked by HF, so it is expected that HF concentration is less critical in the Si case than in the Ge case.

In addition to the hydroxide contamination, carbon contamination after cleaning also needs to be considered from the device application point of view. Survey scans show that O1s and C1s are reduced substantially after HF etching. We can estimate the carbon coverage: 0.08 ± 0.02 ML for HF (1:3), 0.08 ± 0.02 ML for HF (1:5), and 0.15 ± 0.04 ML for HF (1:25). The residual carbon can be reduced further by vacuum annealing. Our results show that for all three cases, the carbon coverage is below 0.02 ML after 30 min vacuum annealing at 400°C.

10% HCl solutions were also used to clean the Ge(100) surfaces. Figure 3 shows the Ge3d spectrum taken at 80eV after HCl etching, and the inset depicts the Cl2p of the same sample. Three peaks are used to fit the Ge3d spectrum. The peak with the highest kinetic energy is the Ge bulk peak, and the other two peaks have chemical shifts of 0.60eV and 1.15eV, respectively, towards lower kinetic energy. Because of the existence of a strong Cl2p signal and relatively smaller chemical shifts compared with those of Ge oxides and hydroxides, we can conclude that these two shifted peaks are Cl induced peaks. One is Ge monochloride with a chemical shift of 0.60eV, and the other is Ge dichloride with a chemical shift of 1.15eV. Calculations⁹ show that the monochloride

coverage is 0.29 ± 0.06 ML, and the dichloride coverage is 0.50 ± 0.1 ML. In addition, estimates based on the Cl2p and Ge3d peaks taken at 300eV show the coverage of absorbed Cl atoms is 1.5 ± 0.3 ML. These results are consistent, since one Ge monochloride has one Cl atom while one Ge dichloride has two Cl atoms. The total chloride coverage is approximately 0.80 ML, implying that a chlorine terminated surface is achieved. A similar conclusion has been drawn by Lu for Ge(111) surfaces.⁷ However, unlike Ge(111) surfaces which only form Ge monochloride,⁷ Ge(100) surfaces in our study have both monochloride and dichloride, which is not very surprising since each Ge(100) surface atom has two dangling bonds. These Ge chlorides can be completely removed by 30 min vacuum annealing at 400°C. The surface termination difference between HF etching and HCl etching can also be explained by the etching mechanism. The key point is that the Ge back bonds are less weakened during HCl etching than during HF etching. In both HF and HCl treatments, the initial surface upon oxide removal is similar, i.e. F termination (HF case) or Cl termination (HCl case) of Ge dangling bonds. However, the electronegativity difference between Ge and Cl (electronegativity difference is 1.15) is much smaller than that between Ge and F (electronegativity difference is 1.97). Furthermore, compared with Ge-F bonds, Ge-Cl bonds have a weaker bond strength and a longer bond length.¹³ All the factors make Ge back bonds less polarized during HCl etching, and resistant to further attacking of HCl, so Cl atoms can remain on the surface and terminate the surface.

We want to point out that neither aqueous HF nor HCl etching alone can lead to an oxygen free or low carbon coverage surface; therefore, final vacuum annealing is needed. Our results show that after 10% HCl cleaning, there is 0.15 ± 0.05 ML oxygen and $0.20 \pm$

0.05 ML carbon left on the surface. After vacuum annealing at 480°C for 30 min, the oxygen is totally removed, and only a tiny amount of carbon is left. Then the same sample is taken out of the photoemission chamber and dipped into a fresh 10% HCl solution for 10 min, and similar amounts of oxygen and carbon appear again. Similar results are also obtained from the HF cleaning case. Since all the treatment was done in an Ar environment to avoid contamination from air, we believe the residual carbon and oxygen on the surface after wet chemical treatments come from the solutions. Comparing the spectra taken after HF treatment with those taken after HCl treatment, we notice that the amount of carbon and oxygen left on the surface after HF cleaning is smaller than that after HCl cleaning, which is due to the nature of treated surfaces. After HCl treatment, the surface is hydrophilic. In contrast, the HF treated surface is hydrophobic, which helps reduce contamination from aqueous solutions. A similar result has also been found on InP.⁸

To fully understand the Ge(100) surface cleaning, surface roughness after HF and HCl treatment was also investigated by atomic force microscopy (AFM). The AFM analysis used a scan area of $1\mu\text{m}^2$. At least three different spots on each treated surface were scanned to better reflect the surface roughness. The average Root Mean Square (RMS) value of the HCl treated surface is 0.29 ± 0.02 nm, close to that of the sample as received (0.23 ± 0.02 nm), implying the original morphology is preserved. On the other hand, the HF treated surface is rougher with a roughly doubled RMS value (0.6 ± 0.1 nm) for all three HF concentrations, which is consistent with the Ge back bond breaking during HF etching.

In summary, we systematically study the Ge(100) surface cleaning by aqueous HF and HCl solutions. A clean surface with little oxygen and less than 0.02 ML carbon can be achieved after our chemical cleaning and vacuum annealing process. HF etching leads to a hydrogen terminated surface, and the hydrogen coverage is a function of the HF concentrations. In contrast, HCl etching results in a chlorine terminated surface with more carbon and oxygen, but smaller roughness. The surface termination differences and the HF concentration effect can be explained by the etching mechanisms.

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Figure Captions

Figure 1. Ge3d core level peaks taken at a photon energy of 80eV for samples both as received and after treated by three different concentrations of HF. All four curves are normalized to the height of the bulk peak to emphasize the peak shape differences. The inset shows O1s peaks taken at 620eV, which are normalized to the area of the Ge3d peaks taken at 620eV.

Figure 2. Peak fitting of Ge3d taken at 80eV for Ge sample treated by HF solutions. The open dots are experimental data, and the solid lines are fitting curves.

Figure 3. The Ge3d peak with peak fitting taken at a photon energy of 80eV after 10% HCl etching. The open dots are experimental data, and the solid lines are fitting curves. The inset shows a Cl2p peak taken at a photon energy of 300eV.

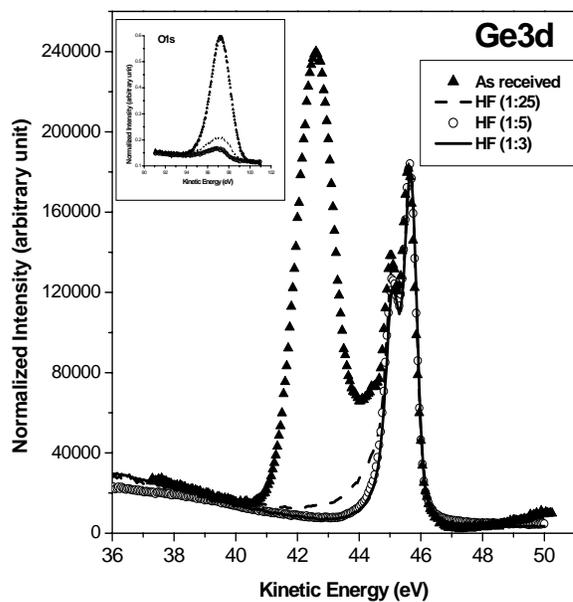


Figure 1. Shiyu Sun *et al.*

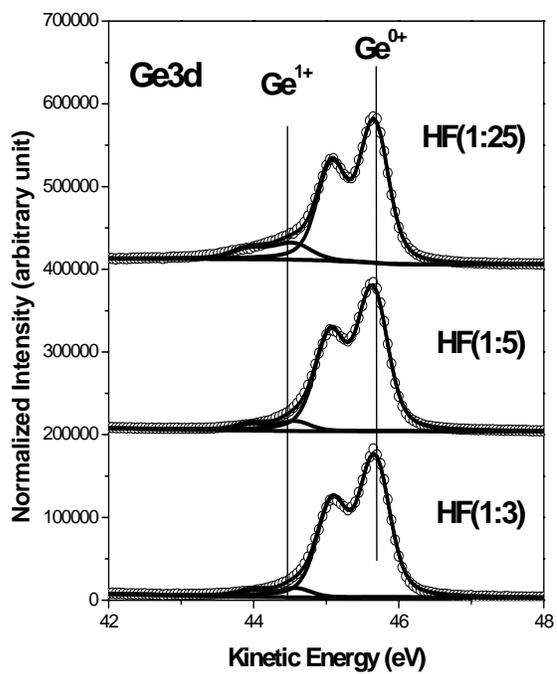


Figure 2. Shiyu Sun *et al.*

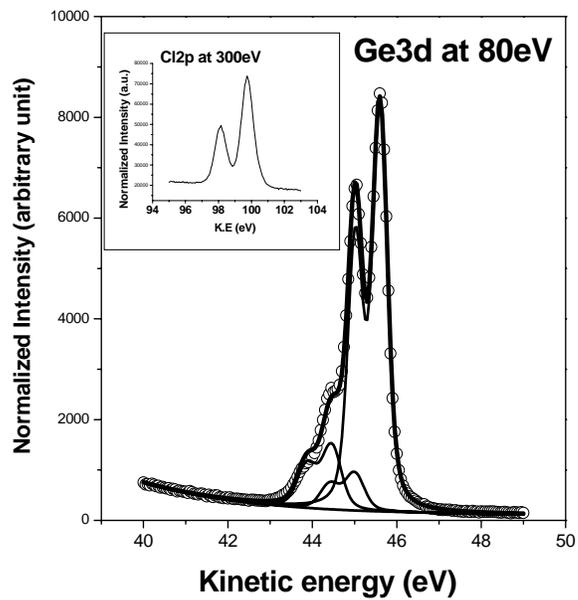


Figure 3. Shiyu Sun *et al.*