July 2008
SLAC-PUB-13302

The effectiveness of HCl and HF cleaning of $Si_{0.85}Ge_{0.15}$ surface

Yun Sun,[a)] Zhi Liu, Shiyu Sun, Piero Pianetta

Stanford Synchrotron Radiation Lab, Menlo Park, CA 94025

The cleaning of $Si_{0.85}Ge_{0.15}$ surfaces using HCl and HF solutions is studied using synchrotron radiation photoelectron spectroscopy. The HF solution is found to be effective in removing both the Si oxide and the Ge oxide while the HCl solution can only remove part of the Ge oxide. For samples treated with HF, four spectral components are needed to fit the Ge 3d photoemission spectra. One is the bulk component and the other three are attributed to the surface Ge atoms with mono-hydride, di-hydride and tri-hydride terminations, respectively.

Material names: SiGe, HF, HCl

[a)] ssun@slac.stanford.edu corresponding author

Work supported in part by US Department of Energy contract DE-AC02-76SF00515
Published in the Journal of Vacuum Science and Technology A

Recently, $Si_{1-x}Ge_x$ alloys have received a lot of attention due to their potential abilities to improve the performance of very large scale integrated (VLSI) circuits independent of geometric scaling.[1, 2] The strains generated by incorporating $Si_{1-x}Ge_x$ into Si based devices allow significant enhancement of carrier mobility over bulk Si.[1] Although the electrical properties and the fabrication of devices using $Si_{1-x}Ge_x$ have been thoroughly studied, only limited research has been carried out on their surface chemical cleaning.[3-8] Wilde et al. reported the existence of hydrogen on HF cleaned $Si_{1-x}Ge_x$ surfaces,[9] but the nature of the surface after HF cleaning is still not clearly understood. In this study, we use synchrotron radiation photoelectron spectroscopy to examine $Si_{0.85}Ge_{0.15}$ surfaces cleaned by HCl and HF solutions. We found that HCl can only remove some of the Ge oxide, leaving the Si oxide on the surface almost intact, while HF is effective in removing the oxides and leaves the surface hydrogen terminated.

The $Si_{0.85}Ge_{0.15}$ sample used in this work is grown on a Si(100) substrate using molecular beam epitaxy (MBE). The thickness of the film is 150 nm and the Ge atomic concentration is 15%. The chemical treatments by 10% HCl solution or 2% HF solution are performed in a glove bag purged with Argon. Photoemission spectra are collected at beam line 8-1 ($h\nu$: 50 – 170 eV) and beam line 10-1 ($h\nu$: 180 – 1400 eV) of the Stanford Synchrotron Radiation Lab (SSRL). Unless stated otherwise, all spectra are collected at normal emission angle. Ge 3d spectra are fitted with a spin-orbit splitting of 0.585 eV and a branching ratio of 0.667 using the fitting program developed by A. Herrera-Gomez.[10]

The Ge 3d and Si 2p spectra of an as-received $Si_{0.85}Ge_{0.15}$ sample are shown as the top curves in figure 1(a) and 1(b), respectively, where the peak at 92 eV in figure 1(a) is due to the native Ge oxide and the peak at 22 eV in figure 1(b) is due to the native Si oxide. The calculated atomic ratio between the Ge and the Si in the native oxide layer is about 0.04, which is much less than 0.176 (= 15 / 85), the ratio in the $Si_{0.85}Ge_{0.15}$ bulk. This is consistent with the earlier research on the oxidation of Si_xGe_{1-x}, where it is found that the oxide layer accumulates Si.[4]

The Ge 3d and Si 2p spectra after the sample is treated by 10% HCl solution for 10 min are shown as the middle curves in figure 1(a) and 1(b), respectively. There is almost no change for the Si oxide peak while the Ge oxide peak is reduced but not completely removed. Further reduction of the Ge oxide, by extending the etch time to 30 min, is very small. This is totally different than what was observed on a Ge sample, where the oxide can be completely removed by HCl treatment and the resulting surface is Cl terminated.[11] For our $Si_{0.85}Ge_{0.15}$ sample treated by the HCl solution, no detectable Cl is found by monitoring Cl 2p core level, which indicates that there are no Cl terminated Ge atoms on the surface. This is consistent with our earlier conclusion that the native oxide layer mainly consists of Si oxide, which serves as a protection layer against HCl etching because SiO_2 is inert in HCl solutions. H^+, Cl^- and H_2O can still diffuse into the native oxide layer to etch away part of the buried Ge oxide. However, the fact that SiO_2 does not react in HCl solutions clearly excludes the treatment by HCl solutions as an effective method in $Si_{0.85}Ge_{0.15}$ surface cleaning.

The Ge 3d and Si 2p spectra after the sample is etched in a 2% HF solution for 2 min are shown as the bottom curves in figure 1(a) and 1(b), respectively. Both Si oxide and Ge oxide are completely gone, which demonstrates that the HF solution is effective in removing the native oxide on the $Si_{0.85}Ge_{0.15}$ surface. The Ge 3d line shape is surprisingly different from that of a Ge sample treated by HF.[11] It is found that four components are needed to fit the Ge 3d spectra; otherwise the fitting is unstable and inconsistent. The result of the fitting is shown in figure 2(a), where the separation between any pair of adjacent components is 0.40 ± 0.03eV. One possible explanation for the existence of four Ge 3d components is that a Ge atom in the $Si_{0.85}Ge_{0.15}$ bulk can be surrounded by 1, 2, 3 or 4 Si atoms. However, it is doubtful that different numbers of Si neighbors can cause such a large chemical shift (0.40eV per Ge-Si bond) since the electronegativity difference between the Si (1.90) and the Ge (2.01) is very small. In addition, the intensity of the optical phonon mode for Ge-Ge bond is negligible, which indicates that most of the Ge atoms are surrounded by four Si atoms

To elucidate the origin of the four components, Ge 3d spectra are measured at different emission angles with 0^o being defined as the normal emission angle. Figure 2(b) shows the Ge 3d spectrum collected at an emission angle of 60^o. It is clear that the three components on the left become larger compared to the spectrum taken at 0^o in figure 2(a). Since the measurement at 60^o is more surface sensitive than that at 0^o, we can reach a conclusion that the three components on the left are due to the Ge atoms on the surface while the component on the right is due to subsurface Ge atoms. This conclusion is further supported by the Ge 3d spectrum taken at $h\nu = 420$ eV, which is shown in figure 2(c). In figure 2(c), the three surface components become smaller at $h\nu = 420$ eV than those at $h\nu = 80$ eV due to the smaller surface sensitivity. This reduced surface sensitivity is due to the longer escape depth of the photoelectrons excited at $h\nu = 420$ eV compared with those excited at $h\nu = 80$ eV

Because there is no detectable fluorine in the F 1s spectrum, and the oxygen coverage, calculated from the O 1s spectra, is less than 0.03 monolayers (ML) and is mostly due to adsorbed water because it is almost gone if sample is annealed at 100°C, those Ge 3d surface components are not due to the surface Ge atoms terminated by either fluorine or hydroxide. The plausible conclusion is that they are due to the surface Ge atoms terminated with hydrogen. This conclusion is consistent with the known fact that both Si and Ge samples treated with HF solutions result in hydrogen-terminated surfaces;[11] it also agrees with the reported existence of hydrogen on HF treated $Si_{1-x}Ge_x$ surfaces.[9] Therefore, the two surface components with the chemical shift of 0.40 eV and 0.80 eV relative to the bulk peak are assigned as the Ge mono-hydride and the Ge di-hydride, respectively. The leftmost component with a chemical shift of 1.20 eV is assigned as the Ge tri-hydride. However, we do not exclude the possibility that it may contain small contributions from the surface Ge atoms terminated by one hydroxyl group (<0.01ML), which has a similar chemical shift.[11] The three hydride peaks disappear when the sample is annealed at 210 °C for 30 min, indicating the complete removal of hydrogen termination at this temperature.

In a previous study of HF cleaning of Ge samples, the average chemical shift for Ge 3d caused by one Ge-H bond is around 0.20 eV,[12] slightly smaller than the 0.25 eV shift for Si 2p caused by each Si-H bond on a hydrogen terminated Si surface.[13, 14] For our $Si_{0.85}Ge_{0.15}$ sample, the chemical shift of Ge 3d caused by each Ge-H bond is 0.40 eV, which seems too large. However, we have to keep in mind that this chemical shift is referenced to the Ge 3d position of bulk $Si_{0.85}Ge_{0.15}$, not the Ge 3d position of bulk Ge. By comparing the Ge 3d bulk peak positions, we found that the binding energy of Ge 3d of the $Si_{0.85}Ge_{0.15}$ sample is 0.40 eV smaller than that of a pure Ge sample. This is consistent with the fact that the Ge atoms in SiGe alloys are negatively charged.[15] Using the Ge 3d of pure Ge as a common reference, the average chemical shift caused by each Ge-Si bond is about 0.1 eV in $Si_{0.85}Ge_{0.15}$ with Ge negatively charged, and the average chemical shift caused by each Ge-H bond is about 0.2 eV with Ge positively charged. Therefore, for the $Si_{0.85}Ge_{0.15}$ sample, if we replace one Ge-Si bond by one Ge-H bond, we will get a chemical shift of 0.3 eV. This rough analysis qualitatively explains why the Ge 3d chemical shift caused by each Ge-H bond for $Si_{0.85}Ge_{0.15}$ sample should be larger than that for a pure Ge sample, but quantitatively, this empirically estimated chemical shift of 0.3 eV is still smaller than the 0.40 eV chemical shift observed experimentally. More careful study in the future is needed to fully explain such large chemical shifts on a hydrogen-terminated $Si_{0.85}Ge_{0.15}$ surface.

The ratios of the three Ge 3d surface components to the bulk component at different emission angles are plotted in figure 3(a). Based on those ratios, the calculated coverages of the Ge hydrides are plotted in figure 3(b). We can see that the coverages calculated from the data at different emissions angles are reasonably consistent. The average coverages for Ge-H, Ge-H_2 and Ge-H_3 are 0.20 ML, 0.09 ML and 0.06 ML, respectively. The combined coverage of the three hydrogen terminated Ge atoms is much larger than 0.15 ML, the expected coverage of Ge on a perfectly truncated $Si_{0.85}Ge_{0.15}$ surface. This is probably due to the roughness of the HF treated surface, which has a rms value of 0.5 ± 0.1 nm, much larger than the rms of 0.29 ± 0.05 nm for the as-received sample. This increased roughness may partly caused by the possible different etching rate of Si and Ge in HF solution.

The chemical cleaning study of $Si_{0.85}Ge_{0.15}$ surface shows that HCl solution is not effective in removing the native oxide. HF treatment can remove all the surface oxide and leaves the surface hydrogen terminated. The Ge 3d chemical shifts caused by the hydrogen termination on $Si_{0.85}Ge_{0.15}$ surfaces are much larger than those found on pure Ge surfaces. Part of the reason is due to the fact that the Ge atoms in $Si_{0.85}Ge_{0.15}$ are slightly negatively charged.

The research is partially funded by NSF through the SiWEDS and was carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The authors would like to thank SSRL staff for their support.

References

[1] M. L. Lee, E. A. Fitzgerald, M. T. Bulsara, M. T. Currie, and A. Lochtefeld, J. Appl. Phys. **97**, 011101 (2005).

[2] F. Schaffler, Semicond. Sci. Technol. **12**, 1515 (1997).

[3] K. Koyama, M. Hiroi, T. Tatsumi, and H. Hirayama, Appl. Phys. Lett. **57**, 2202 (1990)

[4] E. Martinez, A. Abbadie, O. Renault, I. Cayrefourcq, and S. Quiais-Marthon, Surf. Interface Anal. **38**, 437 (2006).

[5] M. S. Carroll, J. C. Sturm, and M. Yang, J. Electrochem. Soc. **147**, 4652 (2000).

[6] A. Abbadie, J. Hartmann, C. Di Nardo, T. Billon, Y. Campidelli, and P. Besson, Microelectronic Engineering **83**, 1986 (2006)

[7] B. Xie, G. Montano-Miranda, C. C. Finstad, and A. J. Muscat, Materials Science in Semiconductor Processing **8**, 231 (2005).

[8] J. Ku, and R. J. Nemanich, Phys. Rev. B **54**, 14103 (1996)

[9] M. Wilde, K. Fukutani, S. Koh, K. Sawano, and Y. Shiraki, J. Appl. Phys. **98**, 023503 (2005).

[10] A. Herrera-Gomez, F. S. Aguirre-Tostado, Y. Sun, P. Pianetta, Z. Yu, D. Marshall, R. Droopad, and W. E. Spicer, J. Appl. Phys. **90**, 6070 (2001)

[11] S. Sun, Y. Sun, Z. Liu, D. Lee, S. Peterson, and P. Pianetta, Appl. Phys. Lett. **88**, 021903 (2006)

[12] S. Sun, *Germanium surface cleaning, passivation, and initial oxidation,* Ph. D. dissertation, Stanford University, p. 42 (2007)

[13] K. Yamamoto and M. Hasegawa, J. Vac. Sci. Technol. B **12**, 2493 (1994)

[14] C.H. Bjorkman, J.L. Alay, H. Nishimura, M. Fukuda, T. Yamazaki, and M. Hirose, Appl. Phys. Lett. **67**, 2049 (1995)

[15] T. Sengstag, N. Binggeli, and A. Baldereschi, Phys. Rev. B **15**, 8613 (1005)

Figure Captions:

Figure 1. (a) Ge 3d and (b) Si 2p spectra for $Si_{0.85}Ge_{0.15}$ at hν = 130 eV. Top: as received; middle: etched in 10% HCl for 10 min; bottom: etched in 2% HF for 2 min. Spectra are normalized by the bulk peak intensity to show the line shape change.

Figure 2. Ge 3d spectra for $Si_{0.85}Ge_{0.15}$ etched in 2% HF for 2 min with numerical fitting. (a) hν = 80 eV, normal (0^o) emission angle; (b) hν = 80 eV, 60^o emission angle; (c) hν = 420 eV, normal emission angle. Ge mono-hydride, di-hydride and tri-hydride are labeled as Ge-H_1, Ge-H_2, and Ge-H_3, respectively.

Figure 3. (a) The ratios of the Ge 3d (hν = 80 eV) intensities for Ge-H_1, Ge-H_2, and Ge-H_3 peaks over bulk peak at different emission angles. (b) The calculated surface coverages of Ge-H_1, Ge-H_2, and Ge-H_3 at different emission angles.

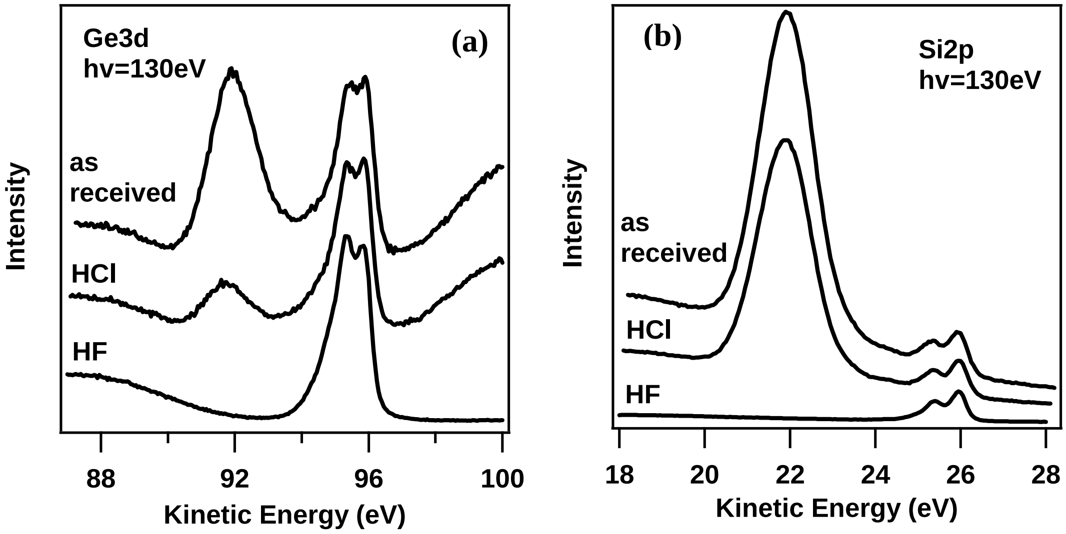

Figure 1

Y. Sun, et al. JVST

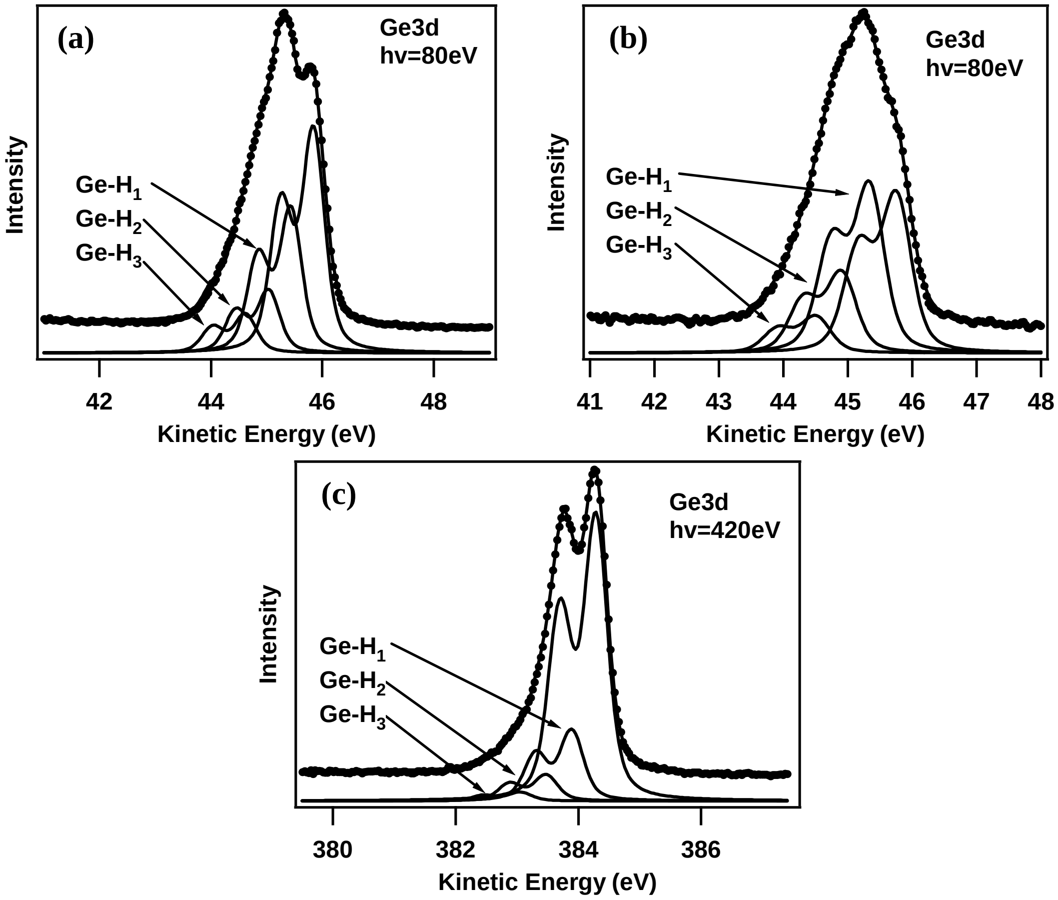

Figure 2

Y. Sun, et al. JVST

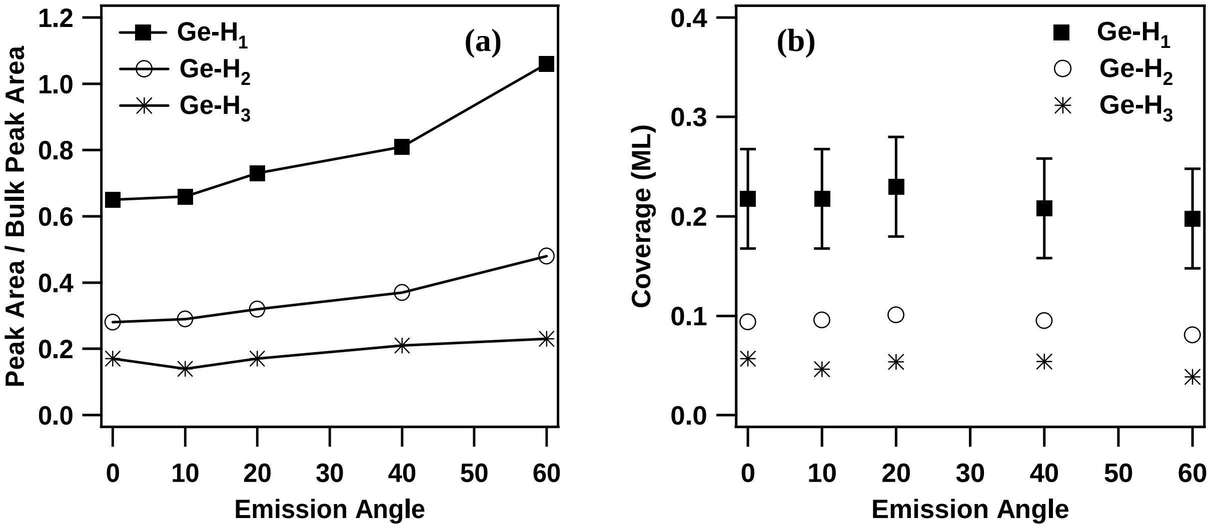

Figure 3

Y. Sun, et al. JVST