RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

Core-level shifts of the Ge(100)-(2×1) surface and their origins

R. Cao, X. Yang, J. Terry, and P. Pianetta
Stanford Synchrotron Radiation Laboratory, P.O. Box 4349, Bin 69, Stanford, California 94309-0210

(Received 3 February 1992)

The surface shifts of the Ge 3*d* core level from the clean Ge(100)-(2×1) surface have been investigated using Si epitaxial layers grown with Sb as a surfactant. We are able to obtain a line shape close to that of the natural line shape of the Ge 3*d* and, in turn, we have resolved two surface-related components in the core-level spectrum of the clean surface, in contrast to previously observed single component. The origin of these shifts is addressed: one comes from the top layer and the other from the layer below the surface. A comparison with the Si(100)-(2×1) surface is also presented.

The Si(100)-(2×1) and Ge(100)-(2×1) surfaces have been extensively studied for decades due to their practical importance and fundamental interest. Despite much progress, a number of questions regarding these reconstructed surfaces remain unanswered. For instance, there is no concensus about how many surface-related components are present in the core-level photoemission spectra. For Si(100)-(2×1), some studies have shown only one surface component but others reported two surface components.[1-5] For Ge(100)-(2×1), only one surface component has been observed.[6-8] The nature of these surface components also remains controversial. A number of theoretical calculations and experimental studies have attributed the observed surface core-level components to the contribution from the top-layer surface atoms, which then favors strong charge transfer between the two atoms within the dimer.[1-4,9,10] On the contrary, other suggest that the observed surface components may arise from different layers, implying that the charge transfer between the two dimer atoms may not be significant.[5,11] Much of the controversy stems from the lack of direct experimental determination of the surface shifts and the lack of convincing evidence of the origination of these surfaces.

The key to accurately resolve the surface shift in the core-level spectrum is to employ a core-level line shape that is close to the nature line shape to fit the experimental spectrum. In order to achieve such a goal, adsorbates that occupy the epitaxial sites of the surface are used to relax the surface and to make the substrate better approximate the bulk environment. In this case, one hopes to get rid of the surface shift(s) from the spectrum and take the remaining as the bulk component. Moreover, it is desired to have neither adsorbate-induced core-level shifts nor interference in the spectrum from the adsorbates themselves. The epitaxially grown adsorbate, Sb, has been successfully applied to the III-V(110) surfaces to resolve surface core-level shifts.[12] For some semiconductors, thick epitaxial layers were required to turn the substrate into a true bulk environment.[13] This has also been experimentally demonstrated in the case of Si(100).[5] For Ge(100), an epitaxial Si overlayer is probably the best candidate because Si and Ge are similar in many aspects, including electronic and chemical properties. Furthermore, with the help of the recently emerging surfactant-assisted growth technique one is able to achieve uniform and epitaxial growth of multilayer SI on the Ge(100) substrate, which has not been realized by other growth techniques.[14,15] In this work, we used Sb as a surfactant in Si, Ge epitaxial growth, and our results show that uniform layers can indeed be grown with good epitaxy.[16] We demonstrate that more than two epitaxial layers are required to yield the narrowest line shape in the core-level photoemission spectrum. With the obtained line shape, we are able to directly determine the core-level shifts, their positions, and amplitude. These data as well as their changes with epitaxial growth provide unambiguous evidence about the origin of these shifts.

The experiment was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line I-2 with a 6-m toroidal grating monochromator. A VG ADES400 angle-resolved system equipped with a hemispherical analyzer was used. The combined resolution was about 0.2 eV, including contributions from both the analyzer and the monochromator. In this particular study, photon energy was fixed. Thus, we eliminate potential complication in data analysis due to variation in monochromator resolution at different photon energies and in probing depth at different photoelectron kinetic energies. The *n*-type Ge(100) wafers with less than 1° miscut were cleaned by thermal annealing at ∼800 °C. A sharp (2×1) diffraction pattern with two domains from these surfaces was observed from the low-energy electron-diffraction (LEED) optics. Sb was evaporated from a tungsten filament evaporator, and Si was evaporated with an electron-beam evaporator. Thorough outgassing was performed prior to deposition, and no trace of contamination was found within the sensitivity of photoemission. The pressure was kept in the 10^{-10} torr range during evaporation with a base pressure around 1×10^{-10} torr.

After the Ge(100) surface was thermally cleaned, a couple of monolayers (ML) of Sb (1 ML=6.27×10^{-14} atom/cm^2) were deposited on this surface. After deposition thermal annealing up to ∼500 °C leads to the formation of 1 ML of Sb on the surface.[17] This layer is ordered, as indicated by an observed (2×1) LEED pattern with weak and diffuse half-order spots. Further evidence for a single-ordered Sb monolayer is found in the observed dispersive features in angle-resolved photoemission (ARPES) valence-band spectra (not shown here). It is known that the Sb atoms occupy the epitaxial sites of the Si(100) surfaces and saturate the surface dangling bonds resulting from the surface dimers.[18] The similar behavior has been proposed at the As/Si(100) and As/Ge(100) interfaces.[19,20] In view of the analogous topographic and spectroscopic behavior of the Sb/Ge(100) compared with the above interfaces (for instance, the ARPES spectra), we propose that Sb forms dimers on the Ge(100) surface, as would a Ge epitaxial layer be in its place. As will be shown later, this Sb layer saturates the Ge(100) surface dangling bonds. Such a structure also provides an excellent base for Si epitaxial growth on the Ge(100) surface.[14,15] The epitaxial growth is achieved by depositing Si on this structure at room temperature followed by thermal annealing to ~500 °C or by depositing Si at elevated temperatures (~500 °C). The key to this growth process is the reduction of the surface energy induced by the ordered Sb overlayer. Consequently, uniform epitaxial growth occurs. This is in sharp contrast to the nonuniform growth of Si on a bare Ge surface using other techniques. We have characterized the entire growth process by several techniques and our results reveal the presence of a uniform and epitaxial Si film on the Ge surface with Sb atoms that had segregated to the top surface and formed another ordered layer.[16]

Figure 1 shows the Ge 3*d* spectra for various surfaces taken at a photon energy of 62.5 eV. The spectra have been moved to correct for the band bending of the substrate induced by either the Sb or Si overlayer. The spectrum from the clean Ge(100)-(2×1) surface has an obvious shoulder to the low binding-energy direction relative to the main peak. This has been observed and attributed to the surface core-level shift previously.[17] When the surface is covered by an ordered Sb monolayer this shoulder vanishes from the spectrum, indicating that this surface component has been removed. Previously, it was suggested that Sb fully relaxes the Ge lattice and that the remaining spectral feature represents the bulk contribution of Ge. However, after a Si layer was epitaxially grown on the Ge(100) surface [notice that in this case Sb atoms move away from the interface and form an ordered layer on the top of Si (Ref. 16)], the Ge 3*d* core level was even sharper than that obtained from the Sb/Ge(100) interface. This is evidenced by an increase of the intensity ratio between the Ge $3d_{5/2}$ peak and the valley from 2 in spectrum (B) to 3 in spectrum (C). The fact that this line shape is narrower means that it is closer to the Ge 3*d* nature of the line shape, and the substrate is closer to its bulk environment. Although curve (C) may not represent the ultimate bulk component, this certainly sets an upper limit of the linewidth of the bulk component. The narrowing of the Ge 3*d* line shape is not surprising, given the fact that Si and Ge are similar in electronic and chemical properties. The Ge atoms will not feel much of a difference when the neighboring Ge atoms are replaced by Si atoms.

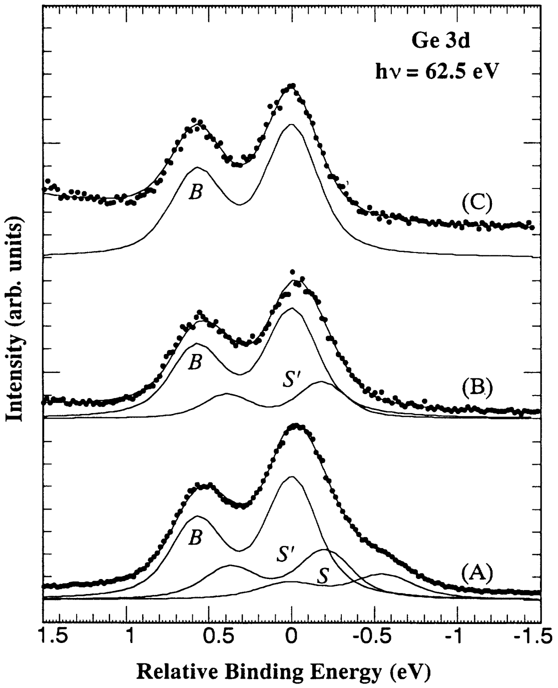

FIG. 1. Experimental and the least-squares fits of the Ge 3*d* spectra from (A) Ge(100)-(2×1) clean surface, (B) Sb/Ge(100), and (C) Sb/Si/Ge(100) interfaces.

Based on the previous argument, we assume that there is only a single doublet in spectrum (C). Voigt line shapes (convolution of a Gaussian and a Lorentzian) were applied during the least-squares fitting, and a Gaussian width equal to 0.24 eV and a Lorentzian width of 0.12 eV were obtained. Other fitting parameters are as follows: spin-orbit splitting, 0.58 eV; and branching ratio of $d_{3/2}/d_{5/2}$, 0.67. Using these parameters, we fit the other two spectra in Fig. 1. During the fitting, both Gaussian (instrumentation broadening) and Lorentzian (lifetime of the core hole) were kept fixed. This assumes that all the surface components have the same line shape as the bulk component. No asymmetric line shape was used, although the introduction of an asymmetric line shape for certain components does not appear to affect the final result in quality. The fits are indicated by the solid curves overlapping the experimental data points. The differences between the data and the fits are small and indicate that the quality of the fitting is good. The results from the computer fitting were rather interesting. On the clean Ge(100) surface, we observed two surface components (indicated by *S* and *S*′) in addition to the bulk component (*B*) for the clean surface spectrum. The shifts of the surface components relative to the bulk component are −0.54 and −0.19±0.02 eV for *S* and *S*′, respectively. *S* corresponds to the shoulder seen in the spectrum that had been observed previously.[17] The presence of *S*′ is evidenced by the filling in of the valley between the two spin-orbit split peaks of the bulk component. This is the first time that two surface components have been resolved on the Ge(100) clean surface.

It is clear that there are two distinct core-level shifts in addition to the bulk component in the Ge 3*d* spectrum of the clean Ge(100) surface. Now we attempt to elucidate the nature of these components. Let us study the Ge(100) surface covered by one ordered Sb monolayer first. Here, the *S* component disappears, while the *S*′ component remains virtually intact. It clearly demonstrates that the *S* component is the contribution from the atoms on the top surface. Sb on the Ge(100) surface behaves, to a large extent, similar to Sb on the Si(100) surface. That is, Sb atoms occupy the epitaxial sites of the Ge(100) surface and form dimers themselves. As a result, the original top layer is relaxed to some extent, and the contribution associated with the Ge dangling bonds of the Ge(100) surface are eliminated from the spectrum. This is in accordance with previous studies. The major difference between the current work and the previous work is that previous photoemission studies of this interface assumed a total relaxation of the substrate beneath the Sb layer and failed to reveal the existence of the *S′* component. Then, a much larger linewidth of the bulk component was used in order to achieve a reasonable fit. The key reason was that there were no means to obtain a narrower line shape (close to that of the natural line shape) in these studies. On the contrary, in our work we were able to obtain a narrower Ge 3*d* spectrum and as a result the existence of *S′* becomes obvious. The fact that the *S′* component remains virtually unchanged, particularly that the *B*/*S′* intensity ratio is roughly the same, suggests that this component does not come from the top-layer Ge atoms, but instead is the contribution from the atoms below the surface (notice that in case of the Sb/Ge(100) the original Ge(100) top layer is now the second layer of the system). The observed little shift of the *S′* feature from 0.19 to 0.17 eV relative to the main peak may result from a slight change of the environment due to certain differences in the electronegativity and size between Ge and Sb atoms. When more than one epitaxial layer of Si is grown on the Ge(100) surface with Sb remaining on the top surface (notice that this Sb layer also occupies the epitaxial sites so that the Ge surface is covered by more than two epitaxial layers) the *S′* component also disappears from the spectrum, indicating that the *S′* component is mainly a contribution from the second layer.

Using a similar method, we also studied the surface core-level shifts of the clean Si(100)-(2×1) surface.[21] In this case, an epitaxial Ge overlayer was grown using Sb as a surfactant. The Si 2*p* core-level spectra from various surfaces and the least-squares fits (dotted curves) are shown in Fig. 2. Here, two surface components are resolved with the shifts of -0.46 and 0.26 ± 0.02 eV relative to the bulk component for the *S* and *S′* components, respectively. They agree well with the results reported by Lin, Miller, and Chiang, where a Ge film was grown on the Si(100) surface directly.[5] Again, we observe the *S′* component at the Sb/Si(100) interface that others have not been able to resolve.[22]

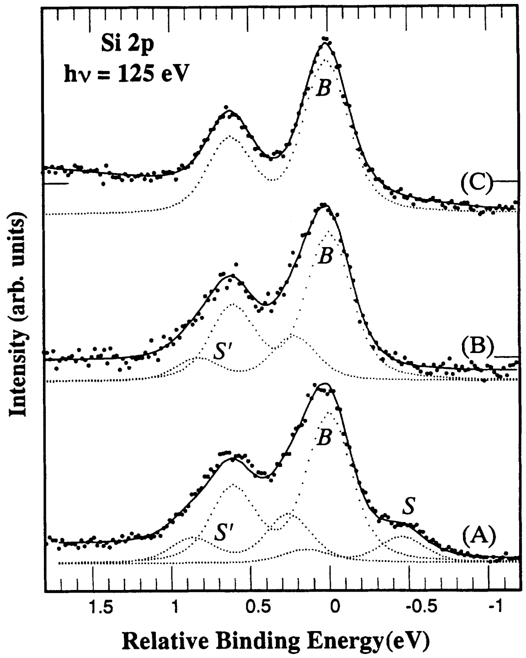

FIG. 2. Experimental and the least-squares fits of the Si 2*p* spectra from (A) Si(100)-(2×1) clean surface, (B) Sb/Si(100), and (C) Sb/Ge/Si(100) interfaces. The spectra were taken using the second-order light from the 62.5-eV primary source.

We have established two points in this work. First, we demonstrate that both the clean Ge(100) and Si(100)-(2×1) surfaces have two surface components instead of one. Second, our results show strong evidence that the two surface components have different origins. For both surfaces, the *S* component is the contribution from the top-layer atoms, while the *S′* component is associated with the submonolayer atoms. This work, together with the work of Lin, Miller, and Chiang, implies that although asymmetric dimers exist on the Si(100) and Ge(100) surfaces charge transfer between the two atoms in the same dimer may be much less than previously suggested[4,9] since for both Si and Ge one expects to observe an approximate 2-eV core-level shift when one electron charge transfer occurs.[2,23] On the other hand, the fact that the *S* component is located on the lower binding-energy side with respect to the *S′* component implies that there is a considerable amount of charge transfer from the top surface layer to the sublayer.

Although the Ge(100) and Si(100) surfaces behave very similar to each other, there is an interesting difference between them. For the Si(100) surface, two surface components straddle the bulk component, while for Ge(100), the two surface components are both shifted to lower binding energy relative to the bulk component. Our results also differ from those reported by Lin, Miller, and Chiang,[5] where a large separation of the two surface components implies that the configuration of the epitaxially grown Ge layer is close to that of the Si(100) surface but different from the Ge(100) surface. It is interesting to compare our findings with those from other Si and Ge surfaces, where one always sees different arrangements of *S′* relative to the bulk component for the Si surface as compared to the Ge surface.[24,25] As yet, there is no theory that can successfully explain such a striking difference but it is almost certain that this has little to do with different surface reconstructions. A plausible explanation may involve the role of initial- and final-state effects on the surface core-level shifts. As for the initial-state effect, one can consider the surface dipole moment induced by the charge density accumulated on the surface atoms. The final-state effect includes a screening effect from the surface electrons. A strong screening effect can, indeed, induce drastic alternation of the measured binding energy of the surface atoms.[10] The role of lattice size also cannot be overlooked.

In summary, we have provided a positive identification of the Ge(100) surface states using the epitaxial layer (Sb and Si) method. Two surface states, S and S', have been observed, and they are the contributions from the top-layer and submonolayer atoms, respectively. Although the Ge(100) surface is similar to the Si(100) surface, the two surface components shift to one direction relative to the bulk component as opposed to the Si(100) surface, where the shifted surface component straddle the bulk component.

This work was performed at SSRL, which is supported by Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences. The authors would also like to acknowledge the support of the office's Division of Material Science for this research.

---

[1] F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).

[2] F. J. Himpsel, B. S. Meyerson, F. R. McFreely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in *Chemical Physics of Atomic and Molecular Clusters,* Proceedings of the International School of Physics, "Enrico Fermi," Course CVII, edited by G. Scoles [Nuovo Cimento (special issue), p. 203 (1990)].

[3] D. H. Rich, T. Miller, and T.-C. Chiang, Phys. Rev. B **37**, 3124 (1988)

[4] G. K. Wertheim, D. M. Riffe, J. E. Rowe, and P. H. Citrin, Phys. Rev. Lett. **67**, 120 (1991).

[5] D.-S. Lin, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **67**, 2187 (1991).

[6] R. D. Schnell, F. J. Himpsel, A. Bogen, D. Rieger, and W. Steinmann, Phys. Rev. B **32**, 8052 (1985).

[7] T. Weser, A. Bogen, B. Konrad, R. D. Schnell, C. A. Schug, and W. Steinmann, Phys. Rev. B **35**, 8184 (1987).

[8] D. H. Rich, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **60**, 357 (1988).

[9] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[10] T. Yamazaki and K. Cho, Surf. Sci. **242**, 260 (1991).

[11] E. Artacho and F. Yndurain, Phys. Rev. Lett. **62**, 2491 (1989).

[12] T. Kendelewicz, K. Miyano, R. Cao, J. C. Woicik, I. Lindau, and W. E. Spicer, Surf. Sci. **220**, L726 (1989).

[13] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **13**, 826 (1976).

[14] M. Copel, M. C. Reuter, and R. M. Tromp, Phys. Rev. Lett. **62**, 632 (1989).

[15] J. M. C. Thornton, A. A. Williams, J. E. Macdonald, R. G. van Silfhout, J. F. van der Veen, M. Finney, and C. Norris, J. Vac. Sci. Technol. B **9**, 2146 (1991).

[16] R. Cao, X. Yang, J. Terry, and P. Pianetta (unpublished).

[17] R. H. Rich, T. Miller, and T.-C. Chiang, Phys. Rev. B **41**, 3004 (1990).

[18] J. Nogami, A. A. Baski, and C. F. Quate, Phys. Rev. B **44**, 1415 (1991).

[19] R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).

[20] J. F. Morar, U. O. Karlsson, R. I. G. Uhrberg, J. Kanski, P. O. Nilsson, and H. Qu, Appl. Surf. Sci. **41/42**, 312 (1989).

[21] X. Yang, R. Cao, J. Terry, and P. Pianetta (unpublished).

[22] R. H. Rich, G. E. Franklin, F. M. Leibsle, T. Miller, and T.-C. Chiang, Phys. Rev. B **40**, 11 804 (1989).

[23] D. Schmeisser, R. D. Schnell, A. Borgen, F. J. Himpsel, D. Rieger, G. Landgren, and J. F. Morar, Surf. Sci. **172**, 455 (1986).

[24] T. Miller, T. C. Hsieh, and T.-C. Chiang, Phys. Rev. B **33**, 6983 (1986).

[25] S. B. DiCenzo, P. A. Bennett, D. Tribula, P. Thiry, G. K. Wertheim, and J. E. Rowe, Phys. Rev. B **31**, 2330 (1985).