PHYSICAL REVIEW B VOLUME 29, NUMBER 10 15 MAY 1984

Samarium chemisorption on group-IV semiconductors

A. Franciosi
Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

P. Perfetti* and A. D. Katnani†
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

J. H. Weaver
Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

G. Margaritondo
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

(Received 25 July 1983; revised manuscript received 21 December 1983)

Samarium is an excellent test system with which to study the interaction between chemisorbed metallic overlayers and different kinds of substrates because the 4*f* configuration is sensitive to the Sm valence state. We used this unique feature to study the chemisorption of Sm on cleaved Ge(111) and Si(111) surfaces. In both cases, synchrotron radiation photoemission spectra exhibited only divalent Sm features at coverages below 2—3 Å and a mixture of trivalent and divalent Sm features at higher coverages. This transition was accompanied by strong adatom-substrate chemical interactions as revealed by large core-level shifts.

INTRODUCTION

The chemical and physical phenomena underlying the formation of metal overlayers on semiconducting substrates are of great fundamental and technological interest.[1] For example, the chemisorption of simple metals on Si surfaces provided the first direct test of the Bardeen model for Schottky barriers.[2] The many experiments performed since then have given increasing evidence that the adatom-substrate interaction is generally rather complicated—and at the same time is of crucial importance in determining metal-semiconductor—interface properties.[1]

The onset of a chemical reaction at an interface is difficult to observe in most cases because the changes of the chemical state of the interface components are small. However, rare-earth atoms, in general, and Sm atoms, in particular, exhibit 4*f* spectral "fingerprints" sensitive to the atomic valence configuration. These features are well known and for Sm have been used to identify the valence state in bulk compounds,[3] surfaces,[4] and clusters.[5] In this paper we use a rare-earth—atom probe to study the multistep formation process of metal-semiconductor interfaces.[6,7]

Surface-sensitive synchrotron-radiation photoemission studies have enabled us to identify the coverage-dependent valence state of Sm atoms chemisorbed on cleaved covalent semiconductor surfaces. Results for the Si(111)-Sm system have been presented elsewhere.[6] This paper focuses on the Ge(111)-Sm junction, while drawing from Ref. 6 for discussion of differences and similarities of the Ge-Sm and Si-Sm results.

We have observed several distinct chemisorption stages for Sm both on Ge and Si surfaces. For coverages below 2—3 Å, Sm appears in a purely divalent form, but, at the onset of chemical reaction, trivalent features appear and they ultimately become dominant for coverages greater than 10—15 Å. Studies of the semiconductor cores have revealed weak substrate-adatom chemical interactions at coverages for which only divalent Sm was observed. However, the appearance of the spectral features of trivalent Sm corresponded to strong chemical interactions, as revealed by large energy shifts of the metal and semiconductor core levels. The relative concentration of the trivalent to divalent species increases for coverage up to 8—12 Å on Ge (10—15 Å for Si). At higher coverages the ratio decreases toward the samarium-metal value, when unreacted Sm forms on top of the fully reacted interface region. We conclude that a qualitatively similar multistep interface-formation process takes place both for Si and Ge, although quantitative differences exist in the characteristic coverage ranges.

EXPERIMENTAL

The experiments consisted of taking photoemission spectra on cleaved (111) semiconductor surfaces before and after deposition of Sm overlayers of increasing thickness. The samples were *n*-type single crystals of Ge ($n = 2.3 \times 10^{17}$ cm^{-3}),[6] which were cleaved *in situ* at working pressures of 5×10^{-11} Torr. Sm overlayers were deposited from a tungsten crucible, and their thickness was measured by a quartz microbalance (pressure $\leq 6 \times 10^{-10}$ Torr during evaporation).

Synchrotron-radiation photoemission experiments were performed at the Wisconsin Storage Ring, Tantalus, using a grazing-incidence "grasshopper" monochromator and a 3-m toroidal-grating monochromator ($10 \leq h\nu \leq 140$ eV).

The emitted photoelectrons were energy-analyzed by a computer-controlled double-pass cylindrical mirror analyzer. The overall resolution, analyzer plus monochromator, was 300—600 meV.

The data are presented here in the form of photoelectron energy-distribution curves (EDC's). Figure 1 shows the EDC's taken in the valence-band region of clean and Sm-covered Ge(111). The corresponding spectra for

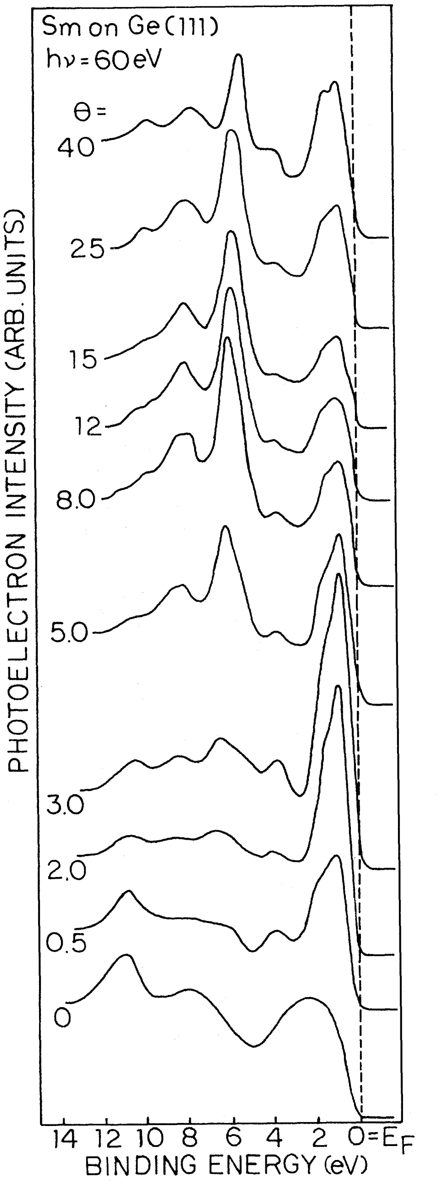

FIG. 1. Valence-band photoelectron energy-distribution curves (EDC's) for clean and Sm-covered Ge(111) showing the evolution of the divalent Sm $4f$ features and the appearance of the trivalent features for $\Theta \gtrsim 2$ Å. The Sm coverage Θ is shown at the right-hand side of each spectrum. The zero of the energy scale is referred to the Fermi level.

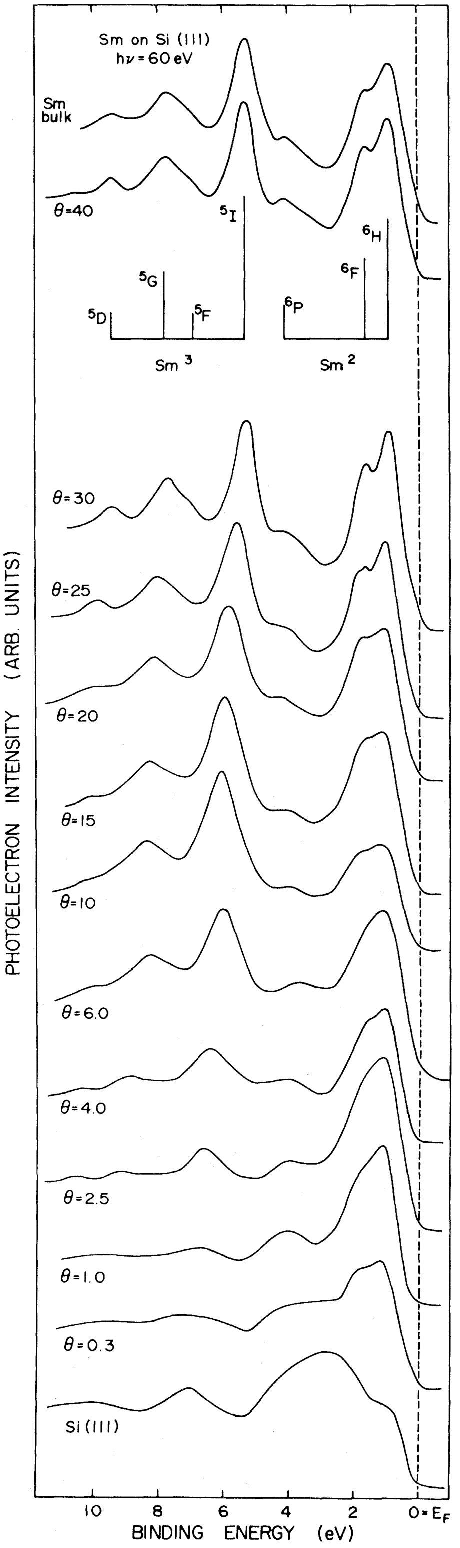

FIG. 2. EDC's for clean and Sm-covered Si(111) showing the evolution of the divalent and trivalent Sm features (from Ref. 6). The topmost curve shows the spectrum of a thick Sm film on oxidized tantalum. Also shown is the multiplet identification (vertical bars) of the final states for the Sm $4f$ excitations. The length of the bars is proportional to the relative strength of the corresponding excitation channel.

Si(111) are shown for comparison in Fig. 2 (from Ref. 6). The photoemission spectrum of bulk Sm is also shown in this figure (top curve).

DISCUSSION

A crucial point in the use of a rare-earth adatom (Sm) to probe the evolving chemistry of an interface is to identify the divalent and trivalent Sm $4f$ features in the valence-band region. The ground-state configuration of trivalent Sm is $4f^5$ and the photoexcitation to a $4f^4$ configuration gives rise to atomic multiplet states in the region 5×10 eV below E_F, as shown for bulk Sm in Fig. 2, where vertical bars indicate the final-state identification and the relative strength of each channel.[4,8] The ground-state configuration of divalent Sm is $4f^6$ and the corresponding $4f^5$ final-state multiplet states appear within 5 eV of E_F, as shown in Fig. 2.

Comparison of the Sm-coverage spectra of Figs. 1 and 2 with the bulk-Sm EDC establishes the following points for both Ge and Si substrates. First, at coverages above $\sim$25 Å for Si and above $\sim$40 Å for Ge, the valence-band spectra exhibit both divalent and trivalent multiplets and the spectra are indistinguishable from those of bulk Sm. The semiconductor core-level spectra in this coverage range indicate very small amounts of Si and Ge still present at the film surface, but this is not visible in the valence-band spectra. We propose that the high-metal-coverage regime of interface formation for Ge-Sm involves the formation of a largely unreacted metal film, as proposed in the Si-Sm case (Ref. 6). We note, however, that this situation is reached on Ge at higher coverage (40 Å) than on Si ($\sim$25 Å). Secondly, we observe (both on Ge and on Si) that only divalent Sm features are present for coverages below 2—3 Å. This suggests that a quantitatively similar first chemisorption stage exists for Sm on Ge(111) *and* Si(111) surfaces.

For intermediate coverages there are spectral contributions from both divalent and trivalent samarium, with relative strengths different from those of metallic samarium. The relative intensity of the trivalent and divalent contributions varies in a strikingly nonmonotonic fashion in this coverage range. The intensity ratio increases for coverages up to 8—12 Å (Fig. 1) and then *decreases* slowly toward the bulk-Sm value obtained for coverages of $\sim$40 Å. This result indicates that the interface-formation process has three different stages which correspond to different valence states for the adatoms. The existence of three different regimes (clearly indicated by the semiconductor core-level data we will discuss next) is pointed out in Fig. 1 by the fact that the spectra for coverages of 8—12 Å cannot be obtained simply as a superposition of purely divalent (stage-1) and metallic Sm (stage-3) spectra, since such a superposition cannot yield a trivalent-to-divalent intensity ratio *above* the metallic Sm value.

To gain additional insight into the evolving character of the interface, we examined the coverage-dependent emission from the Ge $3d$ core levels (Fig. 3). Inspection indicates that as the Sm coverage (Θ) increases the original Ge $3d$ doublet is rapidly attenuated, but a second doublet appears at lower binding energy (higher kinetic energy) and becomes dominant for $\Theta\sim$8—12 Å.

The Ge $3d$ core-level peaks were analyzed in terms of a best fit by the sum of two different components.[9] Each component was a doublet with line shape represented by the sum of two Gaussians fit to the Ge $3d$ cores of the clean surface where the relative intensity of the two was 0.68 and the spin-orbit splitting was 0.61 eV. Typical results of the fitting procedure are shown in Fig. 4 for several Sm coverages. One component of the Ge $3d$ line (kinetic energies of 24.97 and 25.58 eV for the spin-orbit doublet) did not change in energy position during the interface formation and corresponds to Ge atoms in a Ge-like environment. The fact that it did not shift indicates that Sm chemisorption did not change the substrate band bending. The second component exhibits a variable chemical shift with respect to the initial Ge $3d$ line, and therefore corresponds to Ge atoms in a chemical environment different from that of the Ge surface. The magnitude of this line was negligible for coverages up to 2 Å, and it increased monotonically with coverage until it became the *only* component of the Ge $3d$ peak at coverages above 20 Å. Furthermore, this component exhibited an increasing shift in energy with respect to the $3d$ substrate line as the coverage increases, as shown in Fig. 5. At $\Theta=3$ Å, the shift was $\sim$0.6 eV to lower binding energy, and it ulti-

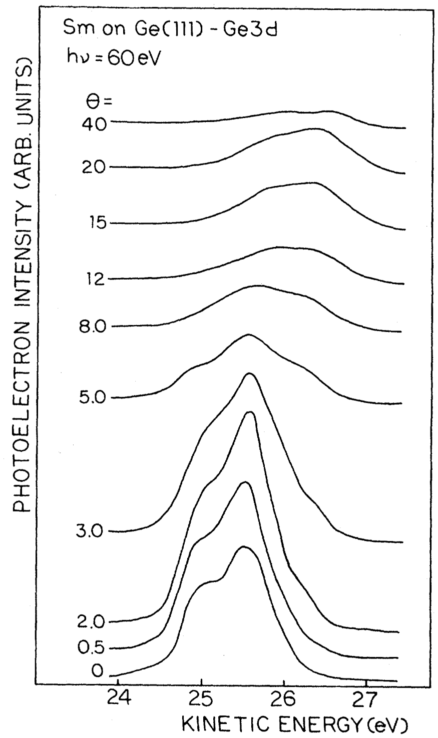

FIG. 3. EDC's showing the Ge $3d$ core emission as a function of Sm coverage. These spectra have been normalized to the intensity of the monochromatized synchrotron-radiation beam. The doublet centered around 25.3 eV reflects Ge in a bulk-Ge configuration. As Sm-Ge reaction starts to occur, a chemically shifted doublet appears at higher kinetic energy, and this shifts with Sm coverage.

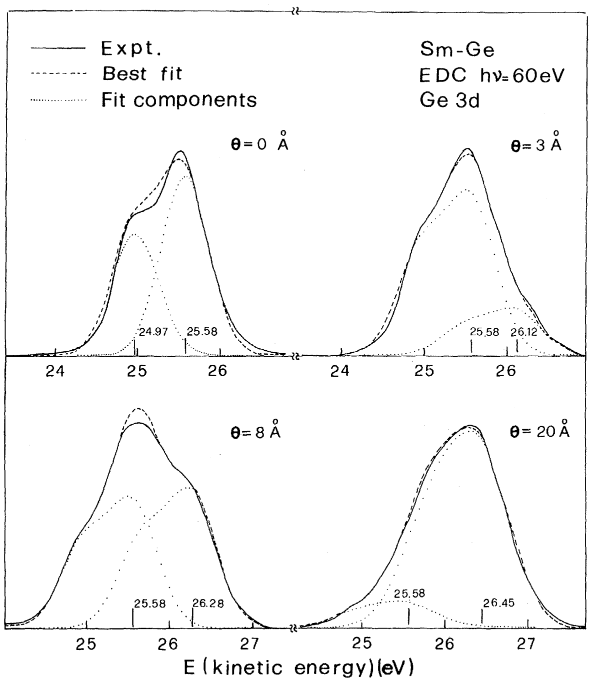

FIG. 4. Examples of best-fit results for the Ge 3*d* spectra. The top left-hand spectrum shows the two-Gaussian fit for the clean Ge surface. For the Sm-covered surfaces another set of Gaussians was introduced with a line shape equal to that of clean Ge 3*d*, and their intensities and positions were the fitting parameters. Note the effect in the shift of energy scale.

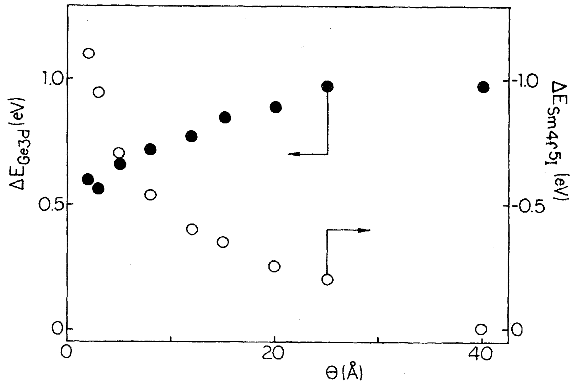

FIG. 5. Position in energy of the chemically shifted Ge 3*d* component and the Sm 4*f* ^5I multiplet feature for Sm-covered Ge(111) as a function of Sm overlayer thickness. The position of the Ge 3*d* peak is referred to that on the clean Ge(111) surface. The Ge 3*d* points were deduced from best fits such as those shown in Fig. 4. The position of the trivalent Sm 4*f* feature is referred to that in metal Sm. The two energy scales are in opposite directions to simplify the comparisons of the two behaviors.

mately saturated for large coverages at $\sim$1.0 eV. The shift in energy of the Sm ^5I multiplet component is also shown in Fig. 5. At low coverage the energy of this state appeared shifted by 0.95 eV to higher binding energies with respect to its position in Sm metal, but this shift was progressively reduced as the Sm coverage increased. For thick coverage, the position was indistinguishable from that of Sm metal.

The correlation of the core data of Figs. 4 and 5 with the valence-band data of Fig. 1 suggests a number of conclusions. Since at coverages below 2–3 Å only divalent Sm features are observed and only one unshifted component is visible in the Ge 3*d* spectrum, we conclude that an identical first chemisorption stage exists for Sm on Ge(111) and on Si(111). In Ref. 6 we proposed that this chemisorption stage on Si would involve a relatively weak adatom-substrate interaction and a low-coordination chemisorption geometry for Sm, and we are extending these considerations to the Sm-Ge(111) interface.

By increasing the metal coverage above 3 Å, trivalent Sm features and a 0.6-eV–shifted Ge 3*d* line appears in Figs. 1 and 4. The intensity ratio between trivalent and divalent Sm features reaches a maximum for $\Theta = 8$–10 Å when the Ge 3*d* chemically shifted line (Fig. 4) becomes dominant. The coverage range for $3 < \Theta < 8$–12 Å also corresponds to the largest variation of the binding energy of the Sm ^5I and of the chemically shifted Ge 3*d* components (see Fig. 5). We propose that this second interface-formation stage, characterized by the increase of the trivalent Sm signal, corresponds to a strong chemical interaction between Sm adatoms and Ge atoms, and therefore to reactive interdiffusion at the interface. In particular, the core-shift direction suggests charge transfer from Sm to the semiconductor, consistent with the difference in electronegativity between Sm and Ge and with the formation of germanidelike phases during this interface-formation stage. The depth of the reacted-interface region, roughly estimated from the saturation coverage of 8–10 Å, is somewhat smaller than for the Si-Sm case (10–15 Å, from Ref. 6). There is, however, remarkable symmetric behavior of the two interfaces during the second stage, since an analogous symmetry seems absent, for instance, for the Si-Au and Ge-Au systems.[10]

For coverages above 10–12 Å the Ge 3*d* shift saturates, and the ratio between trivalent divalent Sm decreases toward the bulk Sm value. No further evolution of the Ge 3*d* line shape and binding energy is seen for $\Theta > 20$ Å, a coverage at which the interface valence emission is already very similar to the bulk-Sm emission. In this third stage the valence spectra *are* consistent with a superposition of bulklike-Sm and reacted-Sm (stage two) spectra, if allowance is made for a residual shift of about 0.2 eV of the Sm 4*f* features as compared with Sm metal. While we maintain that this third interface-formation stage does correspond to the presence of largely unreacted Sm on top of the reacted-interface region, the presence of a residual Sm 4*f* shift and of a Ge 3*d* signal persistent at the highest coverages explored, requires a few words of explanation. The residual Ge 3*d* signal could be explained by an island morphology of the unreacted-Sm film or by some segregation of Ge in a largely metallic Sm film. We favor this latter explanation because it is consistent with the residual shift of the Sm 4*f* features. In fact, a Stranski-Krastanov or Volmer-Weber growth of an *elemental* Sm film cannot account for the rigid shift of the sharp Sm $4f$ features in this coverage range. This shift corresponds instead to the presence of residual small amounts of Ge in the Sm matrix. A comparison with the results of Ref. 6 for Sm-Si shows that a true bulklike-Sm emission is obtained for $\Theta \gtrsim 25$ Å on Si and $\Theta \gtrsim 40$ Å on Ge, and argues for larger segregation phenomena in the Ge-Sm case than in the Si-Sm system.

The qualitatively similar picture of the evolution of these interfaces does not include the Schottky-barrier—formation process. In Ref. 6 we indicated, without discussion, that during the first stage of Si(111)-Sm interface formation the divalent Sm $4f$ features and the Si $2p$ line showed a rigid shift of the order of 0.2 eV to lower binding energies. These shifts were observed at the lowest coverage explored (0.2—0.4 Å) and no further evolution was visible during the first stage of interface formation ($\Theta < 2$—3 Å). Such a behavior can be explained by a change in the substrate band bending of the order of 0.2 eV for submonolayer coverage. Since the surface position of the top of the valence band of our clean, cleaved Si surfaces is 0.5 eV below the Fermi level, after the band-bending change we estimate the Schottky barrier at (0.9 ± 0.1) eV. For the Ge(111)-Sm interface, instead, no shift in energy of the Ge $3d$ substrate component was observed, indicating no band-bending change. Since we found the top of the clean Ge valence band to be 0.2 eV below the Fermi level, we estimate a Schottky-barrier height of (0.47 ± 0.1) eV.

The high value of the Schottky barrier on silicon and the different barrier behavior for germanium and silicon are intriguing phenomena that should stimulate transport studies of these interfaces. To our knowledge no transport results have been published for the Sm-Si and Sm-Ge junctions. Transport studies of interfaces between silicon and silicides of several other rare earths[11,12] argue for smaller (0.35-eV) Schottky-barrier values. Preliminary results for Sm-Si seem to agree with this trend.[13] If the transport investigations now in progress[13] will confirm these apparent discrepancies, it will be of paramount importance to obtain transport and photoemission results for samples as close as possible in composition and thermal history. A first approximation could involve photoemission work on annealed interfaces at submonolayer metal coverage as well as transport studies of unannealed metal overlayers deposited on atomically clean substrates.[14]

CONCLUSIONS

In summary, we have shown that the Ge(111)-Sm interface exhibits a three-stage interface-formation process qualitatively similar to the one observed for the Si(111)-Sm interface.[6] In the first weak chemisorption stage only divalent Sm atoms are observed. In the second stage reactive interdiffusion takes place with the formation of Ge-Sm intermixed phases involving predominantly trivalent Sm atoms. In the third stage, a largely unreacted Sm overlayer forms on top of the intermixed layer, and substantial Ge segregation is seen at the highest coverages explored. Quantitative differences with respect to the Si-Sm system exist in the depth of the intermixed layer, in the importance of segregation phenomena, and in the evolution with metal coverage of the Schottky-barrier height. An important common point is, instead, the correlation between the Sm adatom valence and the strength of the adatom-substrate interaction. The divalent and trivalent states of Sm are nearly degenerate in energy since the energy Δ_+ required to promote a d conduction electron from E_F to an empty $4f$ state is small, about 0.2 eV.[15] When the coordination of Sm atoms is reduced with respect to the bulk, the largely empty Sm $5d$ bands narrow about their center, raising the Fermi level with respect to the $4f$ level.[4] This results in a stabilization of the divalent $4f^6$ configuration. Therefore, the reduction of the Sm coordination is linked to the stability of the divalent configuration. Likewise, in our present case the stability of the low-coverage, purely divalent phase is linked to a weak adatom-substrate interaction.

Conversely, the trivalent Sm configuration is stabilized during the second chemisorption stage by the strong hybridization of metal d states with Ge and Si p states and by the corresponding charge transfer. The formation of germanidelike or silicidelike bonds results in an effective broadening of the $5d$ bands because of the formation of bonding and antibonding d-p hybrids that straddle the "nonbonding" d states.[16—19] The corresponding large chemical shifts of the core levels indicate a substantial electron transfer from the metal to the semiconductor atoms. Both the $5d$ broadening and the charge depletion lower the Fermi level with respect to the metal $4f$ states. The result is a predominant $4f^5$ configuration during the second state of interface formation.

ACKNOWLEDGMENTS

This work was supported by the U.S. Navy Office of Naval Research. The Frascati-Wisconsin international collaboration is supported by the Italian National Research Council and by the National Science Foundation Grant No. INT-81-22013. The expert assistance of the staff of the Synchrotron Radiation Center is gratefully acknowledged.

---

[*] On leave from PULS, Istituto Nazionale di Fisica Nucleare—Gruppo Nazionale di Struttura della Materia, Frascati National Laboratory, Italy.

[†] Present address: Xerox Palo Alto Research Center, Palo Alto, CA 94304.

[1] G. Margaritondo, Solid State Electron. 26, 499 (1983); L. J. Brillson, Surf. Sci. Rep. 2, 123 (1982), and references therein.

[2] G. Margaritondo, S. B. Christman, and J. E. Rowe, J. Vac. Sci. Technol. 13, 329 (1976); G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B 14, 5396 (1976).

[3] M. Campagna, G. K. Wertheim, and Y. Baer, in *Photoemission in Solids II—Case Studies,* edited by L. Ley and M. Cardona (Springer, Berlin, 1979), Chap. 4, and references therein.

[4] G. K. Wertheim and C. Crecelius, Phys. Rev. Lett. 40, 313 (1978).

[5] M. G. Mason, S.-T. Lee, G. Apai, R. F. Davis, D. A. Shirley, A. Franciosi, and J. H. Weaver, Phys. Rev. Lett. 47, 730 (1981).

[6] A brief report on our results for Sm-Si (n-type Si with $n=10^{15}$ cm^{-3}) appeared in A. Franciosi, J. H. Weaver, P. Perfetti, A. D. Katnani, and G. Margaritondo, Solid State Commun. 47, 427 (1983); the discussion of Schottky-barrier formation for Si(111)-Sm is presented here instead for comparison with the Ge(111)-Sm case.

[7] For related work on ytterbium chemisorption, see G. Rossi, J. Nogami, I. Lindau, L. Braicovich, I. Abbati, U. del Pennino, and S. Nannarone (unpublished).

[8] J. W. Allen, L. I. Johansson, I. Lindau, and S. B. Hagstrom, Phys. Rev. B 31, 1335 (1980).

[9] We did not perform a quantitative analysis of this kind for the Si $2p$ line shape since qualitative analysis (presented in Ref. 6) yielded conclusions similar to the present ones.

[10] L. Braicovich, C. M. Garner, P. R. Skeath, C. Y. Su, P. W. Chye, I. Lindau, and W. E. Spicer, Phys. Rev. B 20, 5131 (1979); P. Perfetti, A. D. Katnani, Te-Xiu Zhao, G. Margaritondo, O. Bisi, and C. Calandra, J. Vac. Sci. Technol. 21, 628 (1982).

[11] K. N. Tu, R. D. Thompson, and B. Y. Tsaur, Appl. Phys. Lett. 38, 626 (1981).

[12] S. S. Lau, C. S. Pai, C. S. Wu, T. F. Kuech, and B. X. Liu, Appl. Phys. Lett. 41, 77 (1982).

[13] K. N. Tu (private communication).

[14] Photoemission spectroscopy is obviously better suited for studies of the Schottky-barrier evolution at low overlayer thicknesses. Transport data in the literature are usually obtained on chemically cleaned semiconductor surfaces, following thick-film deposition and annealing.

[15] J. F. Herbst, D. N. Long, and R. E. Watson, Phys. Rev. B 6, 1913 (1972); J. F. Herbst, R. E. Watson, and J. W. Wilkins, *ibid.* 13, 1439 (1976).

[16] O. Bisi and C. Calandra, J. Phys. C 14, 5479 (1981); O. Bisi and L. W. Chiao, Phys. Rev. B 25, 4943 (1982).

[17] P. S. Ho, G. W. Rubloff, J. E. Lewis, V. L. Moruzzi, and A. R. Williams, Phys. Rev. B 22, 4784 (1980).

[18] A. Franciosi and J. H. Weaver, Physica (Utrecht) 117&118B, 846 (1983), and references therein.

[19] P. Perfetti, A. D. Katnani, Te-Xiu Zhao, G. Margaritondo, O. Bisi, and C. Calandra, J. Vac. Sci. Technol. 21, 628 (1982).