

## Substrate-dependent valency of Yb chemisorbed onto Si(111)7×7, Si(100)2×1, and *a*-Si surfaces

G. Rossi, D. Chandesris, P. Roubin, and J. Lecante

*Laboratoire pour l'Utilisation du Rayonnement Electromagnetique,  
Universite de Paris-Sud, F-94305 Orsay, France*

*and Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucleaires,  
F-91191 Gif-sur-Yvette, France*

(Received 2 December 1985)

Yb chemisorption at monolayer coverages onto Si substrates is the precursor stage of Yb/Si interface formation. Ytterbium is divalent as a metal but forms mixed-valent intermetallic compounds with silicon. *L*-edge x-ray-absorption resonance measurements show that at the early stage of the Yb/Si interface formation the Yb-Si chemisorption on different Si substrates induces mixed valency in the Yb atoms chemisorbed on the *a*-Si surface sites and a lower mixed valency in those on the Si(100) sites, but leaves purely divalent Yb ions on the Si(111) surface. This has direct consequences on the kinetics of the interface formation that develops for higher Yb coverages. Delocalization of Yb 4*f* electrons appears to be a unique electron probe of the bonding at semiconductor surfaces, and the Yb/Si interface can be viewed as a prototype case for understanding the kinetics of metal-semiconductor interface formation.

The large amount of data collected recently on metal-semiconductor interfaces<sup>1</sup> clearly indicates that the early stage of formation of metal-semiconductor contacts determines the subsequent growth mode and its kinetics. The energetics involved in the early stage of interface formation is a complex balance of the heat of condensation of the metal adatoms, the heat of formation of the chemisorption bonds and/or the heat of formation of adsorbed metal clusters, the thermal energy available at the surface, and the energy required to loosen the semiconductor surface bonds and displace atoms. Diffuse or abrupt interfaces result as a consequence of this complex energy balance for a given semiconductor-surface-metal-adsorbate system at a given temperature. Manipulation of some of these parameters can lead to dramatically different interface behaviors as was significantly shown for the rather abrupt Ag/Si(111) interface which becomes broadly interdiffused if a submonolayer of Au is chemisorbed on Si prior to Ag adsorption,<sup>2</sup> as well as in the opposite case of diffusion barrier interlayers.<sup>3</sup> Here we present a study of the growth of one-monolayer and thicker films of Yb on three atomically clean silicon substrates: Si(111)7×7, Si(100)2×1, and ion-amorphized Si (*a*-Si). Solid rare-earth (RE) elements gain energy by delocalizing one atomic 4*f* electron, becoming trivalent, as a consequence of the increase in energy of the 4*f* subshell due to Coulomb interaction with the valence charge; Yb (as well as Eu) is divalent though, and its complete 4*f*<sup>14</sup> subshell lies at very shallow energies (~1.2 eV below *E<sub>F</sub>*), overlapping the (6*s*5*d*)<sup>2</sup> delocalized states. As a consequence, the valency of Yb becomes unstable for relatively small perturbations of the local potential, as occur under pressure (fcc 2+ → hcp 3+ transition) or in most intermetallics where Yb is mixed valent with a temperature-dependent mean valency. This feature constitutes a unique probe of the local potential at chemisorption sites and allows us to discriminate between slightly different bonding configurations.

The Yb/Si(111) (2×1 and 7×7) system has been recently investigated by means of synchrotron-radiation (SR) photoelectron spectroscopy (PES) by x-ray photoelectron,<sup>4,5</sup> and

Auger electron spectroscopies,<sup>4</sup> and by photoionization-cross-section measurements around the Yb 5*p* energy.<sup>6,7</sup> All the results indicate reactivity at low Yb coverages, saturation of Yb-Si intermixing for coverages exceeding four monolayers (ML), and subsequent overgrowth of metallic divalent Yb. 4*f*<sup>13</sup> final-state photoemission shifts of ~1 eV towards the Fermi level have been measured for 1-ML Yb on Si(111) surfaces, indicating that the energy barrier for delocalization of one 4*f* electron is reduced to a few hundred millivolts. Silicon 2*p* core levels for Si atoms bound to Yb start to display a large (1.5 eV) chemical shift above 1-ML coverage. Ambiguity remained, after PES experiments, as to the valency of Yb atoms in the narrow intermixed region because of the tentative recognition of the 4*f*<sup>12</sup> (Yb<sup>3+</sup>) peaks from the plasmon structures of the intense 4*f*<sup>13</sup> (Yb<sup>2+</sup>) peaks. In fact, pure Yb divalency was proposed.<sup>4</sup> X-ray absorption resonance spectroscopy (XARS) on rare-earth *L*<sub>2</sub> and *L*<sub>3</sub> edges is a very sensitive probe of valency.<sup>8-10</sup> The threshold transitions arise from resonant 2*p*-5*d* dipole coupling of the excited state with the empty 5*d* density of states (DOS) above *E<sub>F</sub>*.<sup>11</sup> The intense *L*<sub>3</sub> white line for divalent fcc Yb is given in Fig. 1. Double white lines are measured for multiple or mixed-valent intermetallics corresponding to the delayed absorption edge of the more tightly bound Yb<sup>3+</sup> vs Yb<sup>2+</sup> ion configurations.<sup>7-11</sup> The line shape of *L*<sub>2,3</sub>-edge resonances for Yb intermetallics is easily decomposed into two white lines shifted typically by the 6.5-eV chemical shift.<sup>11</sup> The *L*<sub>2,3</sub> resonance intensity and widths are most sensitive to chemical changes of the relative 5*d*-6*s* empty density of states. The x-ray absorption new-edge-structure (XANES) region is also much influenced by the absorbing-atom environment. Owing to these considerations, the decomposition procedure for the *L*<sub>2,3</sub> resonances of this study consists of subtracting from the spectra the experimental Yb<sup>2+</sup> line shape obtained for 1-ML Yb on Si(111) (see below) rather than fitting mathematical line shapes or bulk Yb resonances.

The present results were, therefore, born out of experimental difference spectra and the estimate of the Yb<sup>3+</sup> and Yb<sup>2+</sup> contributions rests on the hypothesis of equal pho-

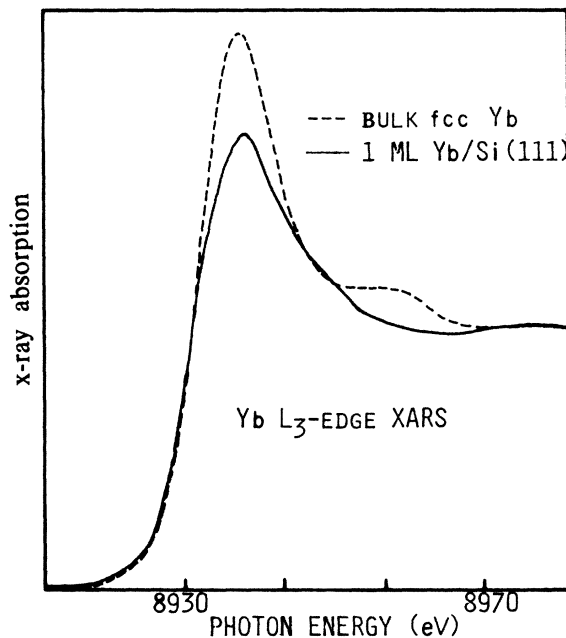


FIG. 1. Yb  $L_3$ -edge absorption resonance for divalent fcc Yb (dashed) and 1-ML Yb adsorbed onto the Si(111)7 $\times$ 7 surface at room temperature (solid line).

toionization cross sections for Yb<sup>2+</sup> and Yb<sup>3+</sup>  $L_{2,3}$  resonances.<sup>8,9,12</sup> The fact that the difference curves systematically show Yb<sup>2+</sup>-like line shapes and a chemical shift of 6.5 eV as in homogeneously mixed-valent YbPd<sub>2</sub>Si<sub>2</sub> (Ref. 12) supports our choice. Only  $L_3$ -edge curves are shown in the figures since  $L_2$  analysis results were identical. The experiment was done in an ultrahigh-vacuum surface extended x-ray-absorption fine-structure (SEXAFS) apparatus which exploits synchrotron radiation from a double Si(311) crystal monochromator on the DCI storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE) at the Université de Paris-Sud in Orsay. Variations of the absorption coefficient were measured in the total-electron-yield mode. Yb was evaporated from 99.9% pure Yb samples by Ohmic heating, in a 10<sup>-10</sup>-torr-range environment, onto atomically clean (Ar<sup>+</sup>-sputtered and annealed) Si(111)7 $\times$ 7 and Si(100)2 $\times$ 1 surfaces and onto an

Ar<sup>+</sup>-ion-amorphized Si sample. The crystalline Si surfaces displayed clear standard low-energy electron diffraction patterns whilst only a diffused background was observed for the amorphized Si sample. Auger analysis showed traces of implanted Ar in the  $\alpha$ -Si. All evaporations were done by exposing simultaneously the three clean surfaces to the Yb beam, at a deposition rate of 0.3 ML/min.

The XARS result for 1-ML Yb on Si(111)7 $\times$ 7 is shown in Fig. 1 where it is compared to the fcc Yb  $L_3$  white line. It appears that the Yb ML on Si(111) is basically divalent; apart from the different XANES region no structural differences appear between the two peaks. It is noteworthy, though, that the white-line intensity for the Yb monolayer on Si(111) is lower and broader than that for fcc Yb which accounts for the redistribution of the Yb 5*d* band in the bonding with Si. This is consistent with the decrease of the Yb 5*d* density of states close to  $E_F$  inferred from photoionization cross-section experiments.<sup>13</sup> The results for 1-ML Yb on the three Si substrates are compared in Fig. 2. The Yb  $L_3$  white line for the Si(100) substrate shows a clear shoulder towards higher photon energies, and the peak shape for the  $\alpha$ -Si substrate has a resolved second white-line peak corresponding to Yb<sup>3+</sup> ions. Shadowed areas under the spectra are the difference between the spectra and the spectrum of 1-ML Yb on Si(111)7 $\times$ 7. The valency for 1 ML on Si(100)2 $\times$ 1 is 2.09 and valency for 1-ML Yb on  $\alpha$ -Si is 2.15. The homogeneity of the surface Yb monolayers cannot be strongly assessed since a SEXAFS determination of the bonding geometry turned out to be unreliable due to the unfavorable Debye temperature of Yb (120 K) which determines a smearing out of the EXAFS and the presence of unavoidable Bragg diffractions in the Si substrate. The divalency of submonolayer (see Table I) and monolayer coverage of Yb on Si(111) and the corresponding Yb 4*f* and Si 2*p* photoemission results<sup>4,15</sup> strongly suggest that most surface Yb sites are equivalent. Furthermore, metal atoms at semiconductor surfaces have been shown to chemisorb systematically in the high-symmetry-high-coordination sites available. From the results of Fig. 2 it follows that the local potential for chemisorbed Yb atoms on the three substrates is drastically different, inducing instability of the 4*f* subshell population for Yb on Si(100), where fourfold sites are available with six Si neighboring atoms per each adsorbed Yb atom, and on  $\alpha$ -Si, where high coordination sites are possible, or leaving Yb divalent on Si(111),

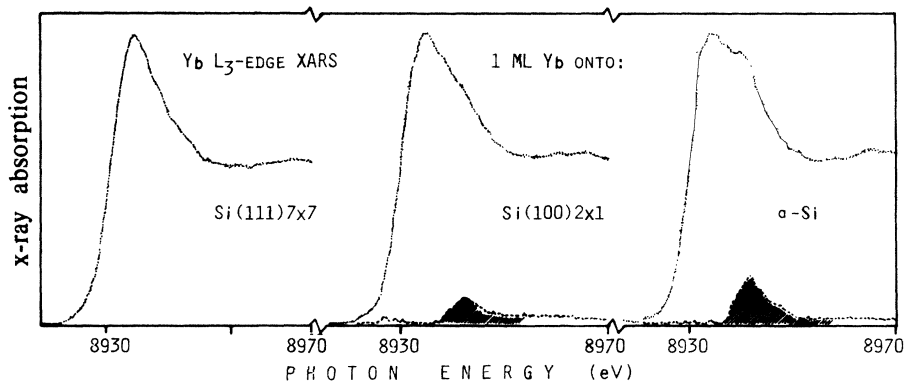


FIG. 2. Yb  $L_3$ -edge absorption resonances for 1-ML Yb adsorbed onto Si(111)7 $\times$ 7 (left), onto Si(100)2 $\times$ 1 (center), and onto  $\alpha$ -Si (right) surfaces. The dashed areas are the difference spectra with respect to the divalent Yb/Si(111) line shape; see Fig. 1 and text.

TABLE I. Mean valency of Yb at the various stages of growth of Yb/Si interfaces on the different Si substrates at room temperature. The estimates of the valency are obtained by decomposing the Yb  $L_3$ -edge spectra by means of divalent Yb experimental line shapes from the (1-ML Yb)/Si(111) interface, as shown in the last panel of Fig. 3. The values obtained from magnetic susceptibility for  $\text{YbSi}_{1.8}$  and  $\text{Yb}_3\text{Si}_5$  are 2.35 and 2.45, respectively (Ref. 17).

Yb coverage (ML)	Si(111)	Si(100)	<i>a</i> -Si
0.2	2		
1	2	2.09	2.15
2	2.11	2.15	2.29
4	2.11		2.31

where threefold hollow and atop sites with three Si neighboring atoms per chemisorbed Yb atom are available. Bulk Yb silicides of known stoichiometries have Yb—Si bond lengths ranging from 2.92 Å and  $\text{Yb}_3\text{Si}_5$  with eight neighboring Si atoms (plus two more Si atoms at 3.24 Å) and a mean valency at 300 K of  $\sim 2.45$ , to 2.99 Å in disordered  $\text{YbSi}_{1.8}$  with less than 12 neighboring atoms and a mean valency of  $\sim 2.35$ .<sup>17</sup> Lower surface Yb valency is a general case in RE intermetallics<sup>14</sup> and divalency of Yb surface atoms was measured for annealed Yb/Si interfaces<sup>5,15</sup> and for  $\text{Yb}_3\text{Si}_5$ ,<sup>16</sup> being related to the reduced Yb—Si coordination and relative bond length changes at the surface. The small number of Yb—Si bonds attainable for adsorption in the threefold sites of the Si(111) surface is the likely explanation of the measured divalency. The sixfold coordination possible at the Si(100) surface for silicidelike bond lengths and adsorption in the fourfold sites determines 4*f* instability and a higher mixed valency is bound to the high-coordination bonding at the bombarded silicon surface. XARS results for 2- and 4-ML Yb are summarized in Fig. 3

and Table I. The Yb/*a*-Si interface shows a quick increase of the mean valency which reaches the value of 2.31, typical of a silicidelike electronic structure indicating the occurrence of intermixing and silicidelike coordination [to be compared to 2.35 valency for  $\text{YbSi}_{1.8}$  (Ref. 17)]. The Yb/Si(100) interface also presents atomic mixing with an increase of the average Yb valency. The Yb/Si(111) interface starts, at 2 ML, to show traces of trivalency indicating that diffusion through the interface has started.

The Yb/Si(111) results are well complemented by the photoemission results; it is relevant to remark that the divalency of the 1-ML stage is directly confirmed as well as the small perturbation of the Si(111) substrate; only at 2 ML do photoemission Si 2*p* chemical shifts start as well as do the mixed valency of the first intermixed Yb atoms. There appears a direct correlation between interface growth kinetics and chemisorption stage bonding. The Yb/*a*-Si interface shows a precursor silicidelike behavior at 1-ML coverage and develops a silicidelike valency very quickly. The Yb/Si(111) appears “sharp” with only low-coordinated divalent Yb at the monolayer stage; adsorption of a second layer is needed to promote atomic transport through the interface. The Yb/Si(100) interface grows consistently with a kinetics intermediate between the other two cases for all investigated coverages. The number of Yb—Si bonds formed at the monolayer stage and the relative energy released appear to be the key parameter for promoting the interdiffusion and ultimately the interface reaction. This could indeed be a result of broad generality for metal-semiconductor interfaces. In this sense the Yb/Si system can be viewed as a prototype case of metal-semiconductor interface growth. In fact, the prototypical cases of critical thickness for interdiffusion, diffusion-limited reaction kinetics, and ready nucleation of interface compounds are found in the Yb/Si system, respectively, for Yb/Si(111)7×7, Yb/Si(100)2×1, and Yb/*a*-Si. The unique advantage of having an easily measurable, extremely sensitive electronic observable (the 4*f* population instability or mixed valency)

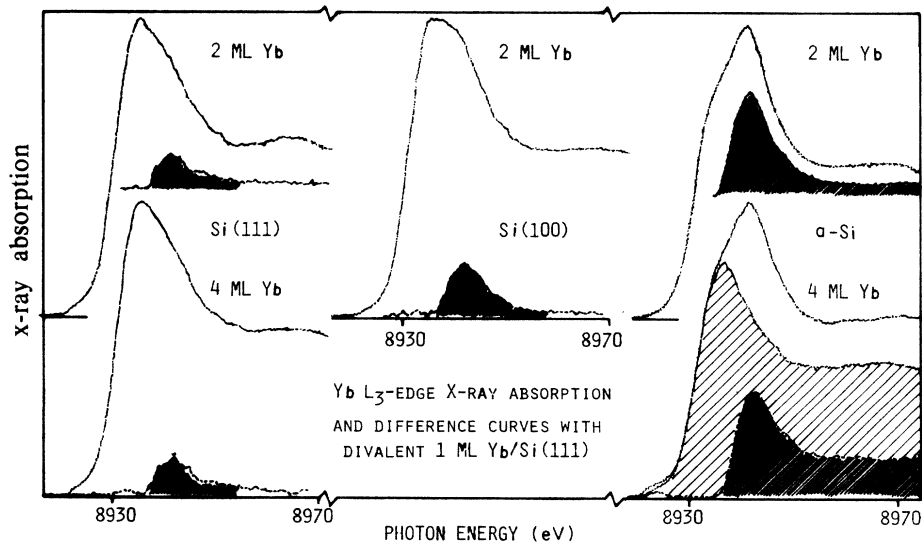


FIG. 3. Yb  $L_3$ -edge spectra for 2 and 4 ML of Yb deposited onto Si(111) (left), Si(100) (center), and *a*-Si (right). The dashed areas correspond to the trivalent Yb contribution to the spectra obtained as shown in the bottom-right panel by subtracting the line shape of the  $\text{Yb}^{2+}$  component.

allows one, for the Yb/Si system, to distinguish the different chemisorption energetics that lead to different interface behaviors. We also note that metallurgical data on the growth of  $RSi_{2-n}$  silicides by interdiffusion of thick layers of a RE metal  $R$  (Y, Tb, Er)<sup>18</sup> on Si substrates show that the formation of the compounds on Si(111) substrates requires annealing temperatures 100°C higher than on Si(100) substrates. The present data provide a nice microscopic corroboration of this observation.

In summary, we have shown, on the basis of XARS measurements, that Yb monolayer chemisorption on different Si surfaces is such that the Yb valency is 2 for Si(111)7×7, 2.09 for Si(100)2×1, and 2.15 for amorphized Si and that

the kinetics of subsequent growth at room temperature of the Yb/Si interface is greatly influenced by this early chemisorption stage. We propose that the different Yb—Si bonding attained at the monolayer stage on different Si substrates has a major role in the weakening of the diffusion barrier through the surface (surface disruption) and that these results may be of value for understanding the energetics of other metal-semiconductor interface systems.

We thank R. Karnatak for providing the Yb samples and the technical staff at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique for operating the DCI storage ring.

<sup>1</sup>See, for example, the recent reviews: C. Calandra, O. Bisi, and G. Ottaviani, *Surf. Sci. Rep.* **4**, 271 (1984); L. Brillson, *ibid.* **2**, 123, (1982).

<sup>2</sup>A. Cros, F. Salvan, and J. Derrien, *J. Appl. Phys.* **52**, 4757 (1981).

<sup>3</sup>A. Franciosi, J. Weaver, and D. O'Neill, *Phys. Rev. B* **28**, 4889 (1983).

<sup>4</sup>G. Rossi, J. Nogami, I. Lindau, L. Braicovich, I. Abbati, U. Del Pennino, and S. Nannarone, *J. Vac. Sci. Technol. A* **1**, 781 (1983); G. Rossi, J. Nogami, J. J. Yeh, and I. Lindau, *ibid.* **B 1**, 530 (1983).

<sup>5</sup>I. Chorkendorff, J. Kofoed, and J. Onsgaard, *Surf. Sci.* **152/153**, 749 (1985).

<sup>6</sup>G. Rossi, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors*, edited by J. Chadi and W. Harrison (Springer, New York, 1985), p. 149.

<sup>7</sup>Recent SR photoemission reports on rare-earth-metal—Si interfaces can be found for Ce/Si: M. Grioni, J. Joyce, S. Chambers, D. O'Neill, M. del Giudice, and J. Weaver, *Phys. Rev. Lett.* **53**, 2331 (1984); *Phys. Rev. B* **30**, 7370 (1984); for Sm/Si,Ge: A. Franciosi, J. Weaver, P. Perfetti, A. Katnani, and G. Margaritondo, *Solid State Commun.* **47**, 427 (1983); *Phys. Rev. B* **29**, 5611 (1984); for Eu/Si: G. Rossi, J. Nogami, I. Lindau, and J. J. Yeh, *Surf. Sci.* **152/153**, 1247 (1985).

<sup>8</sup>R. Martin, J. Boyce, J. Allen, and F. Holtzberg, *Phys. Rev. Lett.*

**44**, 1275 (1980).

<sup>9</sup>M. Croft, R. Neifeld, C. U. Segre, S. Raaen, and R. Parks, *Phys. Rev. B* **30**, 4164 (1984).

<sup>10</sup>G. Rossi, D. Chandresris, P. Roubin, and J. Lecante, *Surf. Sci.* (to be published).

<sup>11</sup>G. Materlik, J. E. Muller, and J. W. Wilkins, *Phys. Rev. Lett.* **50**, 267 (1983).

<sup>12</sup>E. V. Sampathkumaran, K. Frank, G. Kalkowski, G. Kaindl, M. Domke, and G. Wortmann, *Phys. Rev. B* **29**, 5702 (1984).

<sup>13</sup>G. Rossi and A. Barski, *Phys. Rev. B* **32**, 5492 (1985).

<sup>14</sup>See, for example, G. K. Wertheim, J. H. Wernick, and G. Crocellius, *Phys. Rev. B* **18**, 875 (1978); G. Kaindl, B. Rehil, D. Eastman, R. Pollak, N. Martenssen, B. Barbara, T. Penney, and T. Plaskett, *Solid State Commun.* **41**, 157 (1982).

<sup>15</sup>G. Rossi, These d'Etat, Paris, 1985 (unpublished).

<sup>16</sup>I. Abbati, L. Braicovich, U. del Pennino, A. Iandelli, G. Olcese, A. Palenzona, C. Carbone, J. Nogami, J. J. Yeh, and I. Lindau, in *Proceedings of the International Conference on Rare Earths, Zurich, 1985* [*Physica B* **130**, 141 (1985)].

<sup>17</sup>A. Iandelli, A. Palenzona, and G. Olcese, *J. Less-Common Met.* **64**, 213 (1979).

<sup>18</sup>J. Baglin, F. d'Heurle, and C. Peterson, *Appl. Phys. Lett.* **36**, 594 (1980); *J. Appl. Phys.* **52**, 2841 (1981).