RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 6 15 FEBRUARY 1989-II

Ultraviolet photoemission study of the initial adsorption of Pb on Si(100)2×1

G. Le Lay*
Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Centre National de la Recherche Scientifique, Campus de Luminy, Case Postale No. 913, 13288 Marseille CEDEX 09, France

K. Hricovini and J. E. Bonnet
Laboratoire pour l'Utilisation du Rayonnement Électromagnétique, Bâtiment No. 209D, 91405 Orsay CEDEX, France

(Received 14 October 1988)

Using monochromatized synchrotron radiation ($30\ \text{eV} \leq h\nu \leq 52\ \text{eV}$) we have measured uv photoemission of the valence bands and shallow core levels of the Pb/Si(100)2×1 system during the initial stages of interface formation at ~280 °C. We have analyzed the shape of the spectra and the intensity of the Pb 5d emission which we compare with Auger electron spectroscopy data. The results show that the system is unreactive and the growth proceeds according to a layer-plus-islands mode. We show also evidence of the metallization of the surface beyond monolayer coverage.

I. INTRODUCTION

There have been relatively few studies of the initial adsorption of metals on Si(100) when compared with the extensive literature on Si(111) surfaces. Recent synchrotron radiation studies concern reactive systems: Au/Si(100) (Refs. 1 and 2), Cu/Si(100) (Ref. 3) which show intermixing at low metal coverages. The analysis of the data, in this context, is quite involved. Thus, unreactive systems are of basic interest because they may provide a good meduium in which to study coverage-dependent structural arrangements, bonding characteristics, growth modes, and development of the electronic properties in a more straightforward way. In this respect lead monolayers on Ge and Si are very good examples because the phase diagrams do not show the presence of any chemical compound and the mutual solubilities are negligibly small at the Pb melting point.[4]

In the last period we have carried out extensive studies of the Pb/Ge(111) and Pb/Si(111) system using in parallel different surface-sensitive techniques [low-energy-electron diffraction (LEED), Auger electron spectroscopy[5] (AES), ellipsometry,[6] uv, and soft-x-ray photoelectron spectroscopy[7]] to probe complementary aspects of the physical properties of the interface in the course of its formation. Simultaneously another group[8] has taken the advantage of the high atomic number of the overlayers, which leads to large scattering amplitudes, to perform surface x-ray scattering experiments to determine the atomic geometries. However, to our knowledge, no study of the adsorption of lead on (100) surfaces of group-IV semiconductors has been undertaken until now. Thus, it is the aim of this paper to present the first adsorption study of Pb on Si(100)2×1. In addition to the evolution of the electronic states, followed by synchrotron radiation uv photoemission, we study in detail the morphology of the growing interface using *in situ* LEED and AES data and *ex situ* scanning electron microscopy (SEM) observations.

II. EXPERIMENT

The LEED, AES experiments, and SEM observations were carried out in Marseille and a series of photoemission measurements has been performed at the Anneau de Collision d'Orsay storage ring of the Orsay Synchrotron Radiation Facility (LURE) in the photon energy range 39–52 eV. Silicon single crystals (n-type, ~100 Ω) oriented along the (100) direction were in both cases cleaned by heating at 1100 °C; the cleanliness of the surface was controlled by LEED and AES. During lead evaporations (using a Knudsen cell) the pressure remained in the low 10^{-9}-Torr range. The Pb deposition was monitored with a quartz-crystal oscillator. The monolayer (ML) scale is referred to the density of Si atoms on the ideal Si(100) surface (1 ML Pb: $\Theta = 1$ is equivalent to 6.8×10^{14} atoms/cm^2). In the photoemission experiments, the incidence angle of the photon beam was 45°. Photoelectrons were collected at normal emission with a hemispherical analyzer (2° acceptance angle) with a typical resolution of 0.2 eV.

III. RESULTS AND DISCUSSION

A. Si(100)2×1

Following the cleaning procedure, sharp 2×1 LEED patterns [consisting of (2×1) domains in two orientations 90° apart] appeared. Figure 1 shows a set of normal-emission spectra. The binding energy is referred to the Fermi level E_F measured on a polycrystalline Au foil in electrical contact with the sample. The energy distribution curves (EDC's) are characterized by the well-known surface state (SS) at the upper edge (~ −0.8 eV) of the valence band.[9] We note that because of our rather good resolution this SS is clearly resolved in the 30–52 eV photon energy range, this was not the case in previous studies.[10] Other distinct features (B, C, and D) are apparent

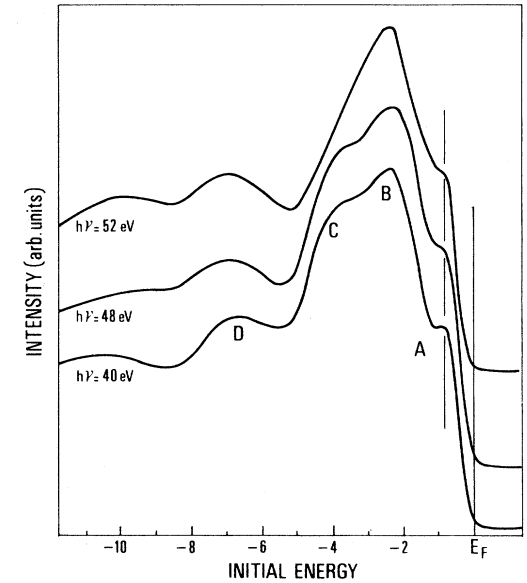

FIG. 1. Normal-emission spectra for Si(100)2×1 taken with the indicated photon energies. The binding-energy scale is referred to the Fermi level at E_F. The nondispersive peak *A* is assigned to SS emission. Peaks *C* and *D* were interpreted by emission from bulk Si states (Ref. 10).

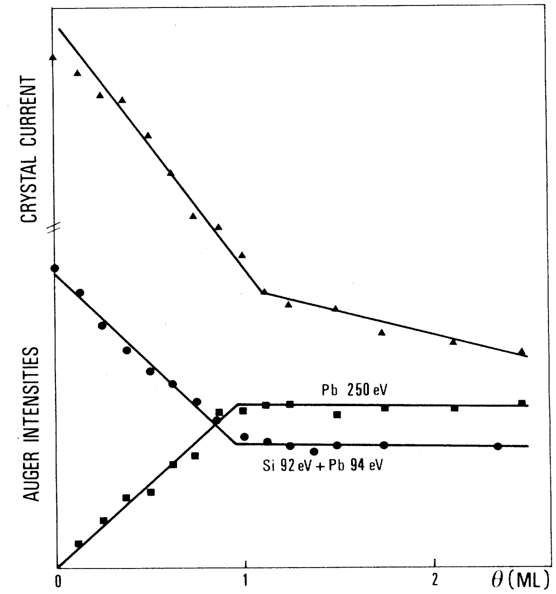

FIG. 2. Variations of the crystal current and Auger amplitudes [Si(92 eV) + Pb(94 eV); Pb(250 eV)] vs lead coverage at RT; similar curves are obtained at higher temperatures.

in the spectra; the broad-emission feature *D* as well as peak *C* could be interpreted as emission from bulk Si states.[10]

B. Geometric structure

From room temperature (RT) to the desorption region ($T \gtrsim 400\,°\mathrm{C}$) the initial (a few ML's) adsorption of lead on Si(100) preserves the original 2×1 reconstruction of the clean surface. The patterns are sharper after annealing (at ~300 °C of a RT deposit) or upon deposition at high temperatures ($T \gtrsim 200\,°\mathrm{C}$). The variations of the Auger intensities, measured with a cylindrical mirror analyzer (CMA) as well as of the crystal current to ground, as displayed for a RT deposition in Fig. 2, testify to a Stranski-Krastanov (SK or layer plus islands) growth mode. Note that because the two main Auger peaks of Si and Pb (Si *LVV* at 92 eV, Pb *NOO* at 94 eV) are too close to be resolved, we have chosen to record their joint decaying intensity and, in addition, the increasing intensity of the Pb peak at 250 eV. All signals vary fairly linearly in the submonolayer region up to a clear-cut break at 1 ML followed by very little variations, called hereafter for simplicity plateaus. We underline the fact that these linear variations, especially that of the Pb + Si decreasing amplitude, indicate the unreactivity of the two components which yield a linear variation (decay for Si, increase for Pb) of each of them (but with different rates) and also of their measured superposition.

The atomic geometry of the clean Si(100)2×1 surface reconstruction is now established. The building block, as observed in scanning tunneling microscopy[11] (STM), is a surface dimer formed by dangling-bond pairing of adjacent atoms in the top-most layer. The Auger experiments and LEED observations reveal that two Pb atoms are adsorbed in the reconstructed 2×1 unit cell, most probably keeping the dimer rows, a further indication of a very gentle adsorption process. As a matter of fact, a variety of adsorbates (As, Cl, H_2O) form 2×1 structures on Si(100). In some cases, the adsorbate replaces a dimer atom[12] (As) in other cases it bonds to it via the remaining broken bond[13,14] (Cl, H_2O). With As and Cl, all dimers found are symmetric while they are asymmetric with H_2O. Detailed Si 2*p* core-level studies (to be undertaken soon), should permit us to assign the dimer formed with lead either to the symmetric or to the asymmetric geometry. The breaks at 1 ML followed by the plateaus indicate the onset of three-dimensional (3D) nucleation of lead islands. Indeed our *ex situ* observations with SEM reveal the presence of a low-density (~$2\times10^5\,\mathrm{cm}^{-2}$) of 3D lead crystallites that cover only a very small fraction of the surface.

C. uv photoemission studies

1. Pb 5d core levels

Figure 3(a) displays a set of lead core levels taken at $h\nu = 48$ eV while Fig. 3(b) shows their intensity variation versus coverage. For this, the data have been reduced to a constant photon flux by taking into account the intensity variations of the electron current in the storage ring.

Lead disposition was performed at 280 °C to obtain a well-ordered surface (sharp 2×1 LEED patterns). The Pb 5*d* intensity variation is analogous to the AES one (cf. Fig. 2) and confirms the SK growth mode. Regarding the overall shape of the core-level peaks one should only men-

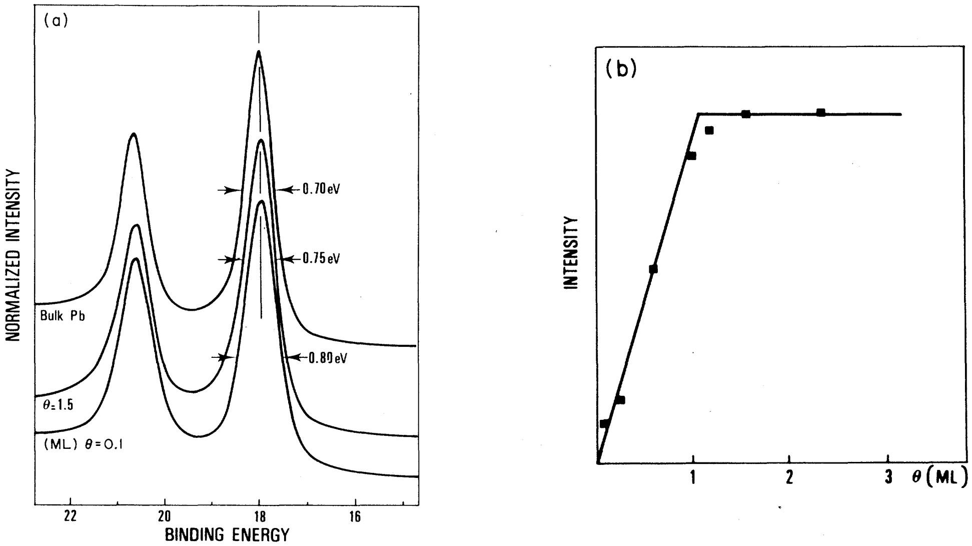

FIG. 3. (a) Pb 5d core-level spectra ($h\nu$=48 eV, normal emission) at increasing coverages. For clarity the spectra are displayed with equal maximal amplitudes. (b) Intensity variation of the Pb 5d lines at increasing coverages normalized to the incident photon flux.

tion an ~5% decrease of the full width at half maximum (FWHM) beyond 1 ML, a slight increase of the branching ratio $I(5d_{5/2})/I(5d_{3/2})$ from ~1.3 below $\Theta=1$ to ~1.5, the statistical value $(l+1/l=\frac{3}{2})$ beyond $\Theta=1$. These small changes reflect the turning on from two-dimensional atomic adsorption to 3D crystalline overgrowth. The spin-orbit splitting remains fairly constant at ~2.65 eV, as well as the binding energy (Pb $5d_{5/2}$: 18.0±0.05 eV). A major point of interest regarding Fig. 3(a) is that the Pb 5d core-level spectra exhibit narrow linewidths for all coverages, i.e., in all cases observed linewidths (FWHM) are ~0.7 and 0.8 eV to be com-

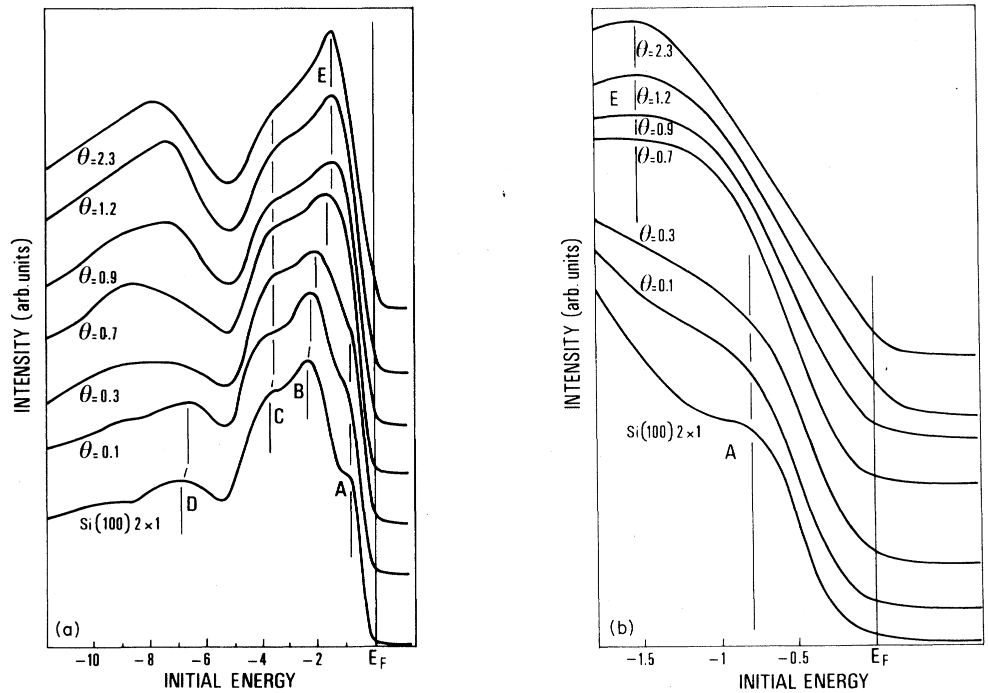

FIG. 4. (a) Valence-band photoemission spectra ($h\nu$=48 eV, normal emission) referred to E_F, at increasing lead coverages. (b) A zoom on the corresponding VB edge region showing the decay of the clean SS A, the growing of a new extrinsic SS E and the increased density of states at E_F beyond 1 ML.

pared with the ~0.67 eV FWHM of the $5d_{5/2}$ line of a thick (~100-Å) Pb film deposited on Si at RT. This is indicative of a simple interface without multiple binding sites, intermixing, etc.

2. *Valence-band spectra*

Figure 4(a) shows a set of valence-band (VB) spectra taken at a photon energy of $h\nu = 48$ eV at increasing coverages, in Fig. 4(b) the corresponding VB edge regions are magnified; as previously stated, deposition was performed at 280 °C. As as matter of fact, some of these spectra correspond to the same deposit used in Fig. 3. At the smallest coverage ratio $\Theta \sim \frac{1}{10}$, one already notices a strong damping of the clean Si SS emission (peak *A*) and a small (~0.1-eV) rigid shift of the other features towards lower binding energies (BE's) which points to a slight band-bending change. However, in the absence of substrate core-level studies (Si 2*p*) cautions must be taken: The development of the broad *sp* valence band of Pb might possibly mask a larger band-bending shift. At $\Theta \sim 0.3$ this SS peak has already nearly disappeared, peak *B* is also strongly damped. Upon further deposition a new peak "*E*" develops. This peak remains at fixed binding energy (~1.5 eV) beyond 1 ML. Moreover, this peak does not disperse with energy in the photon energy range 30 eV $\le h\nu \le$ 52 eV and it is not related to bulk lead as clearly seen in Fig. 5. We thus assign it to a new extrinsic surface state originating in the ordered two-dimensional adsorption of Pb atoms in the 2×1 reconstructed cell below 1 ML. Beyond 1 ML one notices a marked increase of the emission at the Fermi level; this metallization is correlated with the onset of 3D nucleation and the development of metallic Pb clusters.

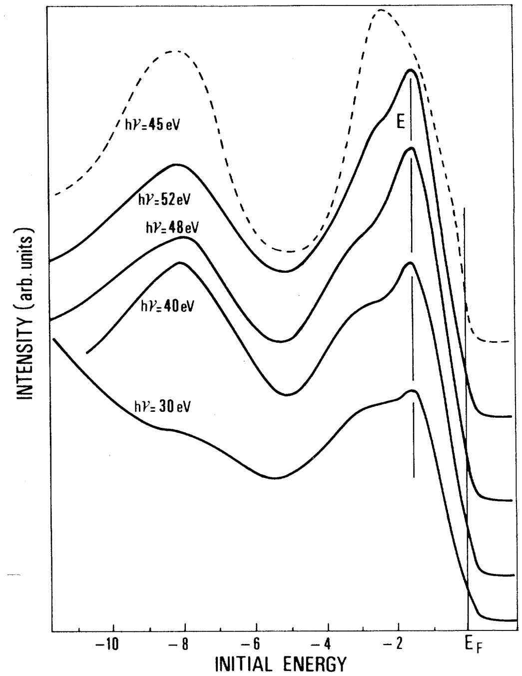

FIG. 5. Normal-emission spectra (solid lines) for Pb/Si(100) ($\Theta \sim 6$; deposition at 280 °C) as well as for a thick (~100-Å) lead film deposited at RT (dashed line).

IV. SUMMARY

We have performed AES measurements, LEED and SEM observations, and angle-resolved photoemission experiments in a normal emission geometry over a broad range of photon energies during the initial stages of adsorption of lead on Si(100)2×1 surfaces. The interface is unreactive and grows according to a layer plus islands mode. The adlayer is completed at 1 ML and keeps the initial 2×1 reconstructed unit cell. In the submonolayer range the intrinsic SS disappears below $\Theta \sim 0.5$ and a new extrinsic SS develops at ~1.5-eV binding energy. Only a slight movement (~0.1 eV) of the Fermi level is noticed in the band-bending region. Metallization of the surface is correlated to the onset of 3D overgrowth.

ACKNOWLEDGMENTS

The technical assistance of A. Ranguis is greatly acknowledged.

---

[*] Also at Unité de Formation et de Recherche Sciences de la Matière, Université de Provence, Marseille, France.

[1] B. Carrière, J. P. Deville, M. Hanbucken, and G. Le Lay, in *The Structure of Surfaces II*, edited by J. F. Van der Veen and M. A. Van Hore, Springer Series in Surface Science, Vol. 11 (Springer, New York, 1988), p. 368.

[2] K. Hricovini, J. E. Bonnet, B. Carrière, J. P. Deville, G. Le Lay, and M. Hanbucken, Surf. Sci. (to be published).

[3] W. Radlik and H. Neddermeyer, Surf. Sci. **195**, 195 (1988).

[4] R. P. Elliott, *Constitution of Binary Alloys* (McGraw Hill, New York, 1965), 1st Suppl.

[5] G. Le Lay, J. Peretti, M. Hanbucken, and W. S. Yang, Surf. Sci. **204**, 57 (1988).

[6] G. Quentel, M. Gauch, A. Degiovanni, W. S. Yang, J. Peretti, M. Hanbucken, and G. Le Lay, Phys. Scr. **38**, 169 (1988); G. Quentel, M. Gauch, and A. Degiovanni, Surf. Sci. **193**, 212 (1988).

[7] G. Le Lay, K. Hricovini, and J. E. Bonnet, *Physics of Solid Surfaces 1987*, edited by J. Koukal, Studies in Surface Science and Catalysis 36 (Elsevier, New York, 1988), p. 210.

[8] J. S. Pedersen, R. Feidenhans'l, M. Nielsen, K. Kjaer, F. Grey, and R. L. Johnson, Surf. Sci. **189/190**, 1047 (1987).

[9] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. B **24**, 4684 (1981).

[10] A. L. Wachs, T. Miller, T. C. Hsieh, A. P. Shapiro, and T. C. Chiang, Phys. Rev. B **32**, 2326 (1985).

[11] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[12] R. D. Bringans, R. I. G. Uhrberg, M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup, Phys. Scr. T **17**, 7 (1987).

[13] R. D. Schnell, D. Rieger, A. Bogen, F. J. Himpsel, K. Wandelt, and W. Steinmann, Phys. Rev. B **32**, 8057 (1985).

[14] D. Schmeisser, F. J. Himpsel, and G. Hollinger, Phys. Rev. B **27**, 7813 (1983).