Co/Si(111) interface investigated by bremsstrahlung isochromat spectroscopy and x-ray-induced photoemission spectroscopy

J. Y. Veuillen, T. T. A. Nguyên, and R. Cinti

*Laboratoire d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique,
Boîte Postale No. 166x, 38042 Grenoble CEDEX, France*

M. De Crescenzi* and J. Derrien

*Centre de Recherches sur les Mécanismes de la Croissance Cristalline, Centre National de la Recherche Scientifique,
Case Postale No. 913, 13288 Marseille CEDEX 9, France*

Bremsstrahlung isochromat spectroscopy and x-ray-induced photoemission spectroscopy have been applied to probe the density of empty and occupied electronic states at the Co/Si(111) interface. Experimental results are compared to theoretical calculations. The results confirm that at very low coverage (2–3 Å of Co), Co and Si atoms interdiffuse to form a $CoSi_2$-like phase at the interface.

In the past few years bremsstrahlung isochromat spectroscopy (BIS) has provided detailed information on the empty states above the Fermi level E_F of condensed matter.[1] With this technique one excites the solid with incident electrons of varying energies (> 1 keV). Measuring the intensity of the x rays emitted by the excited solids at a fixed frequency, one obtains information on the number and position of unoccupied states. An attractive feature of this technique is that one can use the same x-ray monochromator usually employed to perform monochromatized x-ray photoemission spectroscopy (XPS). The combination of the two techniques, XPS and BIS, provides us with a powerful probe to describe the electronic density of states of condensed matter and facilitate comparison with theoretical band-structure calculations.

Up to now, most BIS work has concentrated on bulk materials and metallic alloys in order to test electronic-structure calculations.[1,2] BIS spectra of surfaces and interfaces have received relatively less attention probably because of the low count rate in the x-ray energy range and the high mean free path of the incident high-energy electrons. Moreover it is more difficult to probe empty states of condensed matter than occupied states because of their lower density of states (DOS) (~ 1 order of magnitude).

The aim of this work is to demonstrate the potential of BIS to investigate interface formation. We apply this technique to the Co/Si(111) interface which has already been extensively studied by several groups with various surface-sensitive techniques, because of its technological and fundamental interest.[3] Earlier investigations concluded that at room temperature (RT), Co-Si interdiffusion yields formation of a $CoSi_2$-like phase on top of the Si substrate in the very-low-Co-coverage range (2–3 Å). With increasing coverage the interfacial layer composition becomes richer in cobalt and then a nearly pure Co film is formed on top of the transition boundary layer. Annealing a thick Co deposit (> 30 Å), one increases Co-Si interdiffusion, allowing sequential formation of Co_2Si, $CoSi$, and finally of epitaxial $CoSi_2$ at ~ 250 °C,

~ 400 °C, and ~ 600 °C, respectively.

This paper examines for the first time the RT Co/Si(111) interface by means of BIS. We compare BIS spectra of the RT Co/Si(111) to those recorded for a $CoSi_2$ sample and confirm the formation of a $CoSi_2$-like phase at low coverage at RT, in agreement with parallel XPS and Auger electron spectroscopy of the same interface.

All experiments have been carried out in a new Vacuum Scientific Workshop customer-designed multitechnique apparatus. The system is comprised of an analysis chamber with ultraviolet photoemission spectroscopy (UPS), XPS, Auger electron spectroscopy (AES), depth-profiling and imaging techniques, using a large hemispherical electron analyzer (150 mm). The analysis chamber is connected to a preparation chamber with substrate cleaning, cooling, and heating, metal evaporation and diffraction facilities, including a fast entry system. The base pressure of the two chambers is in the ultrahigh vacuum range (UHV) ($\sim 10^{-10}$ Torr). The Si substrates (n-type 10^2 Ω cm) were cleaned with conventional ion etching and annealing cycles to obtain the well-known (7×7)Si(111) reconstructed surfaces. AES did not reveal any contaminant. Co atoms were then deposited with a miniature home made electron beam evaporator, especially designed to work under UHV conditions with low power (~ 20 W), in order to avoid an increase in base pressure (less than 10^{-9} Torr during evaporation) and Si-surface heating by irradiation. The evaporation rate used for BIS experiment was ~ 0.7 Å/min as measured *in situ* from the XPS Co core-level intensity. It was also checked *a posteriori* in another UHV system equipped with a quartz microbalance with identical geometrical conditions. In this case the accuracy of the Co coverage calibration could be estimated at $\pm 30\%$. After each Co deposition XPS, Auger, and BIS spectra were recorded. BIS spectra have been detected with a VSW x-ray monochromator (diffractor size $\sim 200 \times 200$ mm^2, acceptance angle ~ 0.1 steradian, Rowland circle diameter ~ 700 mm) equipped with a multichannel plate as x-ray detec-

VEUILLEN, NGUYÊN, CINTI, DE CRESCENZI, AND DERRIEN

tor. A LaB_6-filament electron gun provides electrons with energy varying in the 1470–1500 eV range and beam current density $\sim 10 \mu A/mm^2$. In these conditions BIS spectra with good signal-to-noise ratio have been collected within few minutes. The total energy resolution of BIS spectra has been estimated by measuring the full width at half maximum (FWHM) of the elastic peak of the incident electrons which is of about 0.8 eV for 1500-eV incident electrons. Several BIS studies were performed at sequential times in order to check the effect of electron irradiation on interface formation. No dramatic change was observed after several sequential experiments on the same interface. No noticeable increase of the sample temperature under electron beam exposure was observed with a thermocouple attached to the sample.

Figure 1 shows BIS spectra recorded on Si substrates at various metal coverages. All experimental conditions (geometry and electronics) were kept constant during spectra recording. The spectra in Fig. 1 are normalized in intensity to the incident-beam current. For bulk Si and Co our BIS spectra agree with previously published results,[1,4] except for the absence of the empty surface states around ~ 0.5 eV above E_F usually observed on clean Si surfaces with inverse photoemission spectroscopy (IPE).[4] This is likely to be due to the high mean free path of the high-energy electrons used here, and also to the low-energy resolution of the BIS experiments since on the same surface we observed with UPS all surface states below E_F, characteristic of clean (7×7) Si surface. The bulk Si spectrum shows a bump around ~ 3 eV above E_F which corresponds mainly to contribution from Si $3p$ states. The Co spectrum shows a prominent peak at ~ 1 eV which corresponds to the main Co $3d$ contribution.
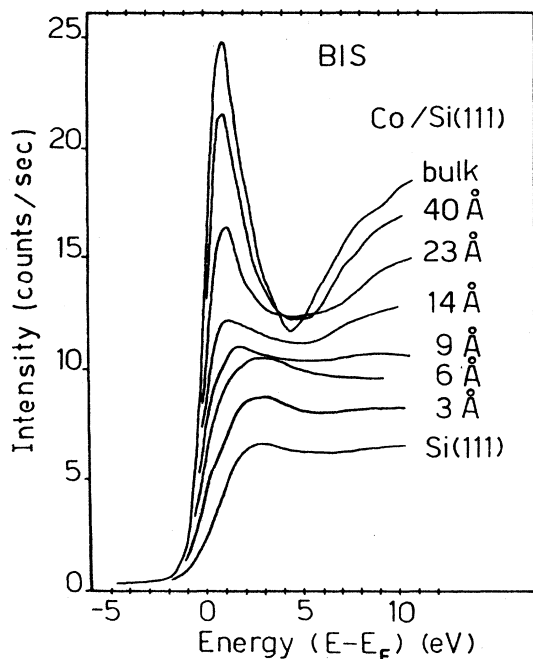
With Co evaporation on Si(111) at RT, all BIS spectra increase in overall intensity. A small shoulder appears at low coverage $(\sim 3 \text{ Å})$ close to E_F $(\sim 0.3 \text{ eV})$, while the initial Si $3p$ peak $(\sim 3 \text{ eV})$ remains unchanged. With increasing coverage, the feature close to E_F $(\sim 0.3 \text{ eV})$ disappears and a broad feature grows at ~ 1.5 eV and evolves toward the Co 1-eV peak at high coverage $(> 10 \text{ Å})$.

Figure 2 shows a few selected XPS results obtained from the same interface. The recorded Si valence-band spectrum displays the three well-known features from Si orbitals $(3s, 3s\text{-}3p,$ and $3p$ states located at ~ -10, -7, and -3 eV below E_F, respectively). At low Co coverage, d emission appears at ~ -1.7 eV and weakly at ~ -3.7 eV in agreement with previous UPS results[5] and recent synchrotron radiation experiments.[6] With increasing coverage the d emission increases in intensity and shifts towards the bulk Co d band position at ~ -0.4 eV below E_F.

For a detailed comparison between the 3-Å Co/Si(111) interface and a thick $CoSi_2$ sample, the corresponding XPS valence bands are reproduced in Fig. 3. The 3-Å Co/Si(111) plot (mid curve, Fig. 3) is in fact obtained by subtracting from the clean Si(111) spectrum the as-recorded 3-Å Co/Si(111) spectrum (in Fig. 2). This subtraction should emphasize the changes occurring on the Si substrate upon 3-Å Co deposition. The $CoSi_2$ sample was obtained by annealing, under UHV at $\sim 600\,^\circ C$ for a few minutes, a Co layer $(\sim 30 \text{ Å of thickness})$ previously deposited at room temperature on a (7×7)Si(111) surface. It has been demonstrated[3] that this procedure provides one with a $CoSi_2$ layer $(\sim 100 \text{ Å of thickness})$ epitaxially grown on Si(111). The surface of this $CoSi_2$ sample was in that case richer in Si (Ref. 6) although for the XPS experiment the "surface" contribution to the collected signal is rather small as compared to the "bulk" one.

In Fig. 3, we also show results from calculations of the total $CoSi_2$ DOS (solid line).[7] The dotted line is obtained by convoluting the as-calculated DOS with an instrumental Gaussian broadening function with FWHM of ~ 1 eV.

FIG. 1. BIS spectra recorded from the Si(111) surface at increasing Co coverages.
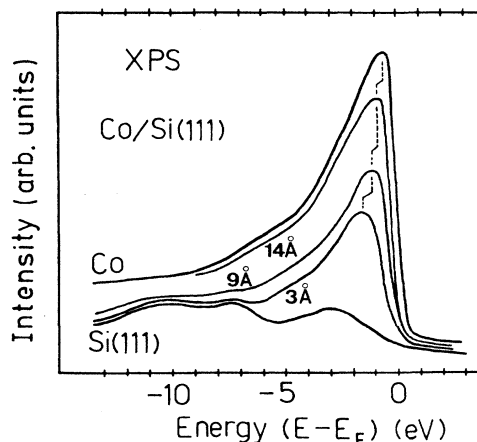

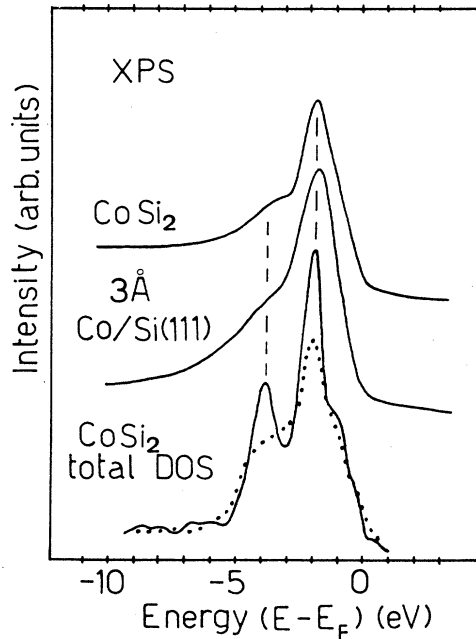FIG. 2. XPS spectra from the Si(111) surface at increasing Co coverages.

FIG. 3. Comparison of XPS spectra for a thick $CoSi_2$ layer obtained by annealing a 30 Å Co/Si(111) interface at 600 °C (topmost curve), a 3-Å Co/Si(111) interface (mid-section) and the results of a total DOS calculation for $CoSi_2$ (bottom-most curves) from Ref. 7.

FIG. 4. Comparison of BIS spectra for a thick $CoSi_2$ layer (topmost curve), a 3-Å Co/Si(111) interface (mid-section) and the results of a total DOS calculation for $CoSi_2$ (bottom-most curves) from Ref. 7.

This curve will be used for a comparison with the data. There is a good agreement, on the one hand, between theory and experiment, and on the other hand, between the $CoSi_2$ and the Co/Si(111) spectrum. All of the spectra in the Fig. 3. display a prominent peak at ~ -1.7 eV corresponding to nonbonding Co d states in a cobalt disilicide and a shoulder at ~ -3.7 eV corresponding to bonding states involving Si $3s$-$3p$ and Co $3d$ electrons in cobalt disilicide.[7,8]

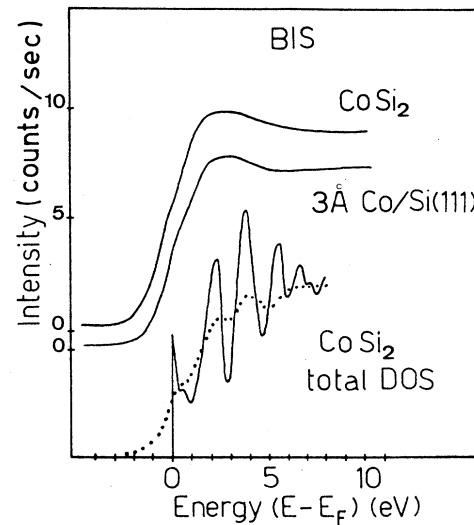Figure 4 displays the BIS spectra for the empty states which are the counterparts of the occupied states in Fig. 3.

The spectrum from the 3-Å Co/Si(111) interface resembles closely to the $CoSi_2$ spectrum. In particular, the shoulder at ~ 0.3 eV above E_F (which originates from the high-energy tail of the Co nonbonding states around E_F) is observed concurrently with the broad feature at ~ 3 eV, which originates from the empty antibonding states involving Si $3s$-$3p$ and Co $3d$ orbitals with a larger Si character. The experimental curves are in good agreement with theoretical results.[9,10]

In summary, BIS measurements can be successfully performed on evolving metal semiconductor interfaces, even at the early stages of metal deposition. The information gathered by this technique concerns mainly the empty total DOS of the interface and can be used to identify the different nucleation phases present at the interface.

*Permanent address: Dipartimento di Fisica, Università di Roma II, Rome, Italy.

[1]See, for example, W. Speier, J. C. Fuggle, R. Zeller, B. Ackermann, K. Szot, F. V. Hillerbrecht, and M. Campagna, Phys. Rev. B 30, 6921 (1984), and references therein.

[2]D. D. Sarma, F. U. Hillebrecht, M. Campagna, C. Carbone, J. Nogami, I. Lindau, J. W. Barbee, L. Braicovich, I. Abbati, and B. De Michelis, Z. Phys. B 59, 159 (1985).

[3]See a review paper by J. Derrien and F. Arnaud d'Avitaya, J. Vac. Sci. Technol. A 5, 2111 (1987), and references therein.

[4]T. Fauster and F. J. Himpsel, J. Vac. Sci. Technol. A 1, 1111 (1983).

[5]C. Pirri, J. C. Peruchetti, G. Gewinner, and J. Derrien, Phys. Rev. B 29, 3391 (1984).

[6]G. Gewinner, C. Pirri, J. C. Peruchetti, D. Bolmont, J. Derrien, and P. Thiry, Phys. Rev. B 38, 1879 (1988).

[7]J. Tersoff and D. R. Hamann, Phys. Rev. B 28, 1168 (1983).

[8]W. R. L. Lambrecht, N. E. Christensen, and P. Blöchl, Phys. Rev. B 36, 2493 (1987).

[9]C. Calandra, O. Bisi, and O. Ottaviani, Surf. Sci. Rep. 4, 271 (1985).

[10]O. Bisi, O. Jepsen, and O. K. Andersen, Phys. Rev. B 36, 9439 (1987); see also A. Franciosi, D. J. Peterman, J. H. Weaver, and V. L. Moruzzi, ibid. 25, 4981 (1982).