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Room-temperature growth of Er films on Si(111): A photoelectron spectroscopy investigation

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The Er-Si interaction at the Er/Si(111) interface formed at room temperature is investigated by core-level and valence-band photoemission spectroscopy as well as by work-function measurements. The valence-band spectra are dominated by Er 4*f* emission detected in the 4–11-eV binding-energy range and by emission from Er 5*d* conduction-band states near the Fermi edge. The change in binding energy and shape of the Er 4*f*, Er 5*d*, and Si 2*p* structures is discussed in connection with the photoemission data measured on amorphous Er_xSi_{1-x} $(0<x<1)$ silicides and on a monocrystalline $ErSi_{1.7}$ layer epitaxially grown on Si(111). As expected, it appears that the Er 5*d* valence states hybridize with the Si 3*sp* states, while the Er 4*f* states, although located in the valence-band region, behave like atomiclike states. At low Er coverage [<2 monolayers (ML)], the Er atoms react readily with the substrate, giving rise to Si-rich silicidelike features. It appears that a thin amorphous silicide layer grows up to about 6–8 ML. Its Er concentration is found to increase with the deposited Er thickness, as evidenced by the valence band and Si 2*p* core-level evolution from Si-rich to Er-rich silicide signatures. We also find that the total amount of reacted Si remains quite constant for Er coverages above 3 ML. Furthermore, the valence-band data clearly reveal a heterogeneous growth involving a mixture of pure Er clusters and silicide patches at coverages as low as 3 ML. The reaction stops above 6–8 ML with the formation of a pure Er-metal overlayer.

I. INTRODUCTION

A great deal of effort has recently been devoted to determining the mechanism of rare-earth (R)/Si interface formation, the resulting silicide formation, and the height of the Schottky barrier (SB). These materials are very interesting from a fundamental point of view as from a technological one.$^{1-5}$ In particular, R metals form silicides with the lowest SB height on *n*-type Si with potential applications in infrared detectors and as Ohmic contacts. Thus the electronic properties of R silicide/Si interfaces and their dependence on compositional changes are of great interest in a quantitative understanding of the SB formation. For these reasons photoemission studies of R/Si interfaces have been the subject of many recent investigations.$^{6-14}$ The Er/Si(111) interface is especially attractive since Er silicide $ErSi_{1.7}$ can be epitaxially grown on Si(111).

In this paper we present the first spectroscopic investigation of the interaction of Er atoms with Si(111) at room temperature (RT) by means of Si 2*p*, Er 4*f*, and valence-band photoemission measurements carried out under ultrahigh-vacuum conditions. The change in shape and binding energy of the Si 2*p*, Er 4*f*, and Er 5*d* structures upon Er deposition are followed and compared with the relevant data from amorphous Er_xSi_{1-x} silicides formed by codeposition of Er and Si species onto a RT Si(111) substrate. This experimental procedure is expected to allow a good characterization of the interface reaction products which are most likely disordered for the Er/Si(111) interface formed at RT. The Er-metal ground-state configuration is $4f^{11}$ and the photoemission processes lead to a $4f^{10}$ configuration giving rise to 4*f* multiplet states which are localized and corelike even though their binding energies are shallow and degenerate with valence-band states. We take advantage of their large photoionization cross section and favorable location in the 4–11-eV binding-energy range in using He II photoemission to investigate the change in their binding energy versus Er coverage with a very good energy resolution. Nevertheless there remains a window at least 4 eV wide in which the electron states directly involved in the Er—Si chemical bonds (Er 5*d*–Si 3*sp*) are easily observed without interference with Er 4*f* atomiclike states.

II. EXPERIMENT

All experiments were performed *in situ* in an ultrahigh-vacuum system, consisting of a molecular-beam epitaxy (MBE) chamber and an analysis chamber equipped with low-energy electron diffraction and angle-resolved ultraviolet (ARUPS) and x-ray (ARXPS) photoemission measurements. XPS measurements were made using an unmonochromatized Mg cathode source ($\hbar\omega=1253.6$ eV) while for all UPS works He II ($\hbar\omega=40.8$ eV) radiation was used because at lower photon energy the 4*f* emission is rather weak. For that photon energy ($\hbar\omega=40.8$ eV) the Er 4*f* photoionization cross section is sufficiently large to ensure a signal-to-noise ratio of the order 50:1. This high Er 4*f* photoionization cross section along with a very good energy resolution (0.2 eV) make these spectra very sensitive to minute changes in the local environment of the Er atoms. Evaporations of high-purity erbium (99.9%) and silicon (99.9%) were performed in the MBE chamber at base pressure of about 2×10^{-10} Torr from thoroughly degassed homemade electron bombardment sources. After evaporation the pressure always dropped to 7×10^{-11} Torr in less than one minute. The deposited amounts were monitored with quartz thickness monitors and all Er coverages are given in terms of the Si(111) atomic density: 1 monolayer (ML) for 7.8×10^{14} atoms cm^{-2}. The Er and Si deposition rates are typically in the 0.5–1 ML min^{-1} range. Due to the high reactivity of the Er/Si(111) interface formed at RT, each layer is condensed onto the clean Si(111) substrate by single step deposition. 100-Å-thick amorphous $\mathrm{Er}_x\mathrm{Si}_{1-x}$ silicide films were prepared *in situ* by simultaneous evaporation of Si and Er species with the desired flux ratio onto a clean Si(111) substrate maintained at RT. For both RT interfaces and amorphous silicides, the XPS spectra were collected at grazing, electron emergence ($\theta=80°$ with respect to the normal to the sample) to be very surface sensitive. All photoelectron spectra were obtained by a Leybold-Heraus spectrometer equipped with an EA 10 energy analyzer. The energy resolution was set to about 0.2 and 1 eV for UPS and XPS, respectively.

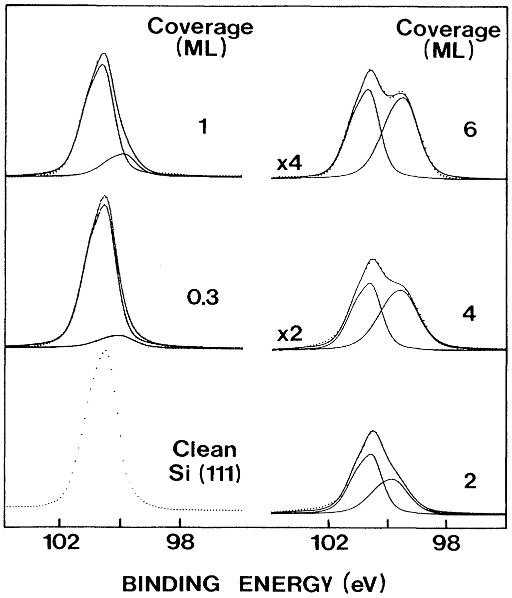

FIG. 1. Selected Si 2*p* core lines from the RT Er/Si(111) interface taken with 1253.6-eV photons collected at grazing electron emergence ($\theta=80°$). These lines are displayed after background subtraction and are decomposed into a pair of spin-orbit doublets. The solid line is the resulting fit.

III. RESULTS AND DISCUSSIONS

When Er is deposited onto a clean Si(111) surface at RT the 7×7 pattern gradually evolves into a strong diffuse background over the 0–1-ML coverage range indicating the formation of either amorphous or polycrystalline layers.

A. Si 2*p* core line measurements

In a preliminary investigation[15] we examined the RT Er/Si(111) interface formation using Si 2*p* core-level photoemission spectroscopy. Two chemically shifted Si 2*p* components were identified, one related to the Si substrate contribution and the other to a reacted phase at lower binging energies. Each component comprises a $\mathrm{Si}\,2p_{1/2,3/2}$ doublet with a branching ratio of 2:1 and a spin-orbit splitting of 0.61 eV. The evolution of the reacted component intensity and binding energy was studied versus coverage. Figure 1 shows selected Si 2*p* lines measured for 0.3, 1 , 2, 4 , and 6 ML. The ratio of reacted to unreacted components grows progressively up to 3 ML and then levels off. The absolute intensity of both components, however, steadily decreases and they completely disappear for about 20 ML.

Figure 2(a) shows the binding-energy shift versus Er coverage: this chemical shift, about 0.5 eV for 0.3 ML, increases up to ~0.7 eV for 1 ML and then remains rather constant in the 1–2-ML range suggesting the formation of a thin silicide layer in which the Si atoms have a constant definite chemical environment. Upon further Er deposits this shift increases again reaching its maximum value of 1.3 eV for 6 ML. Note that such largely shifted Si 2*p* components are observed for all rare-earth/Si interfaces[6–14] and that they have been interpreted as due to the charge transfer from the rare earth to Si atoms.[16] Figure 2(b) displays the Si 2*p* core-level shift, with respect to clean Si, measured within the same experimental conditions on 100-Å-thick $\mathrm{Er}_x\mathrm{Si}_{1-x}$ silicides of various *x* concentrations. This figure also reports the Si 2*p* line

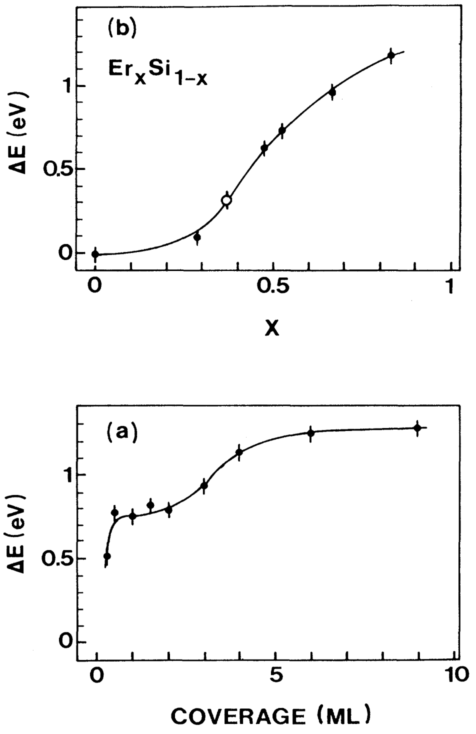

FIG. 2. (a) Evolution of the reacted Si 2*p* component binding-energy shift vs Er coverage for the RT interface. (b) Si 2*p* line binding-energy shift measured on amorphous $\mathrm{Er}_x\mathrm{Si}_{1-x}$ compounds as a function of *x* and on crystalline $\mathrm{ErSi}_{1.7}$ (ϕ). All these shifts are measured with respect to the substrate Si 2*p* line.

shift measured on an $\mathrm{ErSi_{1.7}}$ layer epitaxially grown on Si(111). This layer is achieved by deposition of 30 Å Er onto a Si(111) substrate followed by annealing at ~600 °C.[2] Figure 2(b) shows that the Si $2p$ line shift, about 0.1 eV for the silicide with low Er content, i.e., $x=0.28$, increases up to a value as large as 1.3 eV for the most Er-rich silicide we have formed, i.e., $x=0.83$. The continuous Si $2p$ shift towards lower binding energies versus Er content demonstrates a one-to-one relationship between stoichiometry and Si $2p$ binding energy in these amorphous compounds. This permits a more quantitative characterization of the chemical environment of Si atoms in the reacted layer formed at the Er/Si(111) interface. The comparison between Si $2p$ shifts reported in Figs. 2(a) and 2(b) mainly suggests that a Si-rich silicide is first formed at low coverage (<2 ML), the stoichiometry of which lies between $\mathrm{ErSi_{1.7}}$ and ErSi. Upon further Er deposition, the reacted silicide stoichiometry evolves towards Er-rich compounds apparently by the diffusion of the incoming Er atoms (or at least a part of them) into the interfacial silicide or alternatively by Si out diffusion from the already formed silicide. Above 6–8 ML the reaction stops; both reacted and unreacted Si $2p$ lines decrease monotonically without any change in their binding energy or intensity ratio as shown in Fig. 2(a). This means that an unreacted Er overlayer progressively covers the interfacial silicide layer.

A close examination of the reacted component shape in Fig. 1 reveals that its full width at half maximum (FWHM) is not constant versus Er coverage as would be expected for a silicide film with a definite Si environment and stoichiometry. The reacted Si $2p$ FWHM is plotted as a function of Er coverage in Fig. 3(a). One can observe that the FWHM, about 1.35 eV for 1 ML, increases up to ~1.65 eV for 3–4 ML and then decreases again to ~1.40 eV for 6 ML. This would suggest that for coverages near 3–4 ML the experimental Si $2p$ line involves more than two contributions so that, for example, silicide clusters of different Er concentrations could be formed. We have tried to decompose these experimental lines into three or four components but each attempt has failed: the best fit, for any coverage, is always obtained allowing only two Si $2p$ components. A detailed description of the decomposition is given in Ref. 15. In order to get more insight into the origin of the reacted component FWHM, we have also measured the Si $2p$ FWHM for the amorphous $\mathrm{Er_xSi_{1-x}}$ silicides: these data are reported in Fig. 3(b). This figure demonstrates that the FWHM also passes through a maximum when x is about 0.5. Yet for RT codeposited amorphous layers the diffusion length of the Si or Er species is so short (a few angstroms) that it is reasonable to assume a simple binomial distribution of the probability of finding n nearest neighbors surrounding a given Si atom:

$$p(n)=x^n(1-x)^{N-n}\frac{N!}{(N-n)!n!}$$

where N is the number of nearest neighbors. Thus we suggested that the Si $2p$ FWHM variation versus x can be understood in terms of a statistical distribution of the various possible Si environments comprising $1,2,\ldots,N$ Er nearest neighbors. The width of this distribution $\Delta n=[Nx(1-x)]^{1/2}$ remains unchanged when x is changed into $1-x$ and reaches a maximum at $x=0.5$. Thus, in this model, the inhomogeneous contribution of the various local configurations to the Si $2p$ linewidth exhibits a maximum at $x\approx0.5$. As can be seen, this is indeed observed experimentally.

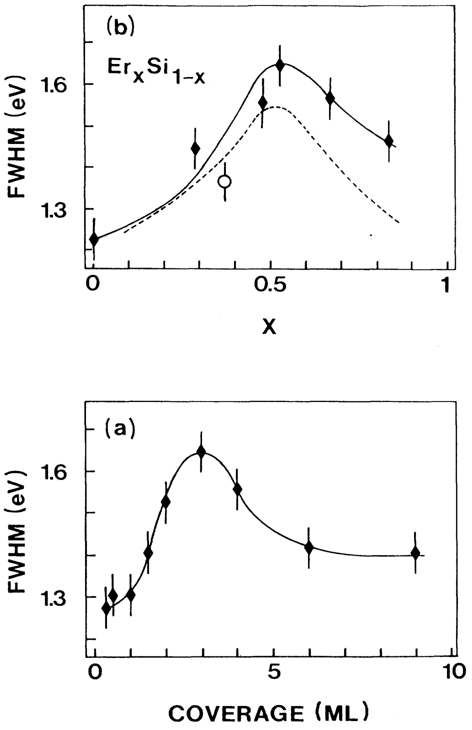

FIG. 3. (a) Evolution of the Si $2p$ full width at half maximum (FWHM) as a function of Er coverages on Si(111). (b) Si $2p$ FWHM measured on amorphous $\mathrm{Er_xSi_{1-x}}$ silicides (♦), on epitaxially grown $\mathrm{ErSi_{1.7}}$ (ϕ) and calculated Si $2p$ FWHM for these silicides (dotted line) as a function of x.

To give a more quantitative comparison between the experimental and theoretically expected Si $2p$ FWHM evolution versus x, we have simulated the Si $2p$ line assuming a dense packing of 12 nearest neighbors around a Si atom and a random environment distribution. For each atomic configuration, the Si $2p$ binding energy is deduced from Fig. 2(b) and its FWHM was supposed to be 1.25 eV, which is the value measured for crystalline Si(111) at $\theta=0°$. The calculated Si $2p$ FWHM's are reported in Fig. 3(b) (dotted line) versus Er concentration x. One observes a fairly good qualitative as well as quantitative agreement between calculated and experimental data. This confirms the present interpretation in terms of an inhomogeneous reacted Si $2p$ line. The mean stoichiometry of the interface silicide evolves from a Si-rich to an Er-rich one but the limited diffusion at RT results in a variety of local Si environments whose distribution depends on Er coverage or mean stoichiometry. Finally Fig. 3 shows that the Si $2p$ FWHM from crystalline $\mathrm{ErSi_{1.7}}$ is 0.1 eV larger than the one measured on pure Si(111). Arnaud d'Avitaya *et al.*[2] have recently shown that Er silicide films epitaxially grown on Si(111) have a hexagonal AlB_2 structure with Si deficiency up to 20% giving rise to an $ErSi_{1.7}$ stoichiometry. These vacancies are found to be periodically distributed in the whole silicide film and then at least two inequivalent Si sites are expected. Thus the slightly increased experimental Si 2*p* FWHM for crystalline $ErSi_{1.7}$ could also be explained by the presence of two or more Si 2*p* components corresponding to the inequivalent Si sites. However, this is a small second-order effect since the local Si environments only differ in their second coordination shells. Within the model considered above the Si 2*p* line for crystalline $ErSi_{1.7}$ is essentially homogeneous with the same FWHM as for Si substrate. Many other effects, such as differences in crystalline perfection, phonon contributions, etc. could explain the observed difference of 0.1 eV.

B. Work function

Figure 4 summarizes the work-function data (ϕ) measured on the RT interface as a function of Er coverage. The arrows indicate the ϕ values measured on several amorphous Er_xSi_{1-x} silicides. For the RT Er/Si(111) interface, ϕ decreases rapidly from the initial value of 4.50 eV for clean Si(111) 7×7 surface down to ~3.80 eV for 1 ML. At this stage, in agreement with the Si 2*p* core-level analysis, work-function data suggest that the interfacial silicide has a stoichiometry close to ErSi. A small plateau is observed in the 1–2-ML range. Upon further Er deposition ϕ gradually drops down to about 3.00 eV above 5 ML, which is the value measured on a pure Er film. It can be seen that the work-function evolution is quite consistent with the conclusions drawn from Si 2*p* core-level analysis. It confirms the one-to-one correspondence between the interfacial film stoichiometry and the Er coverage inferred from Si 2*p* data.

C. Er_xSi_{1-x} silicide valence bands

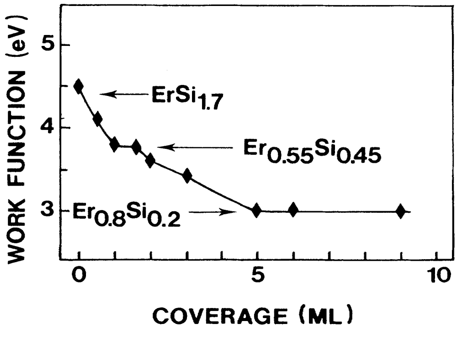

FIG. 4. Work-function variation at the Er/Si(111) interface as a function of Er coverage. The work-function values measured on amorphous Er_xSi_{1-x} silicides and on epitaxially grown $ErSi_{1.7}$ are indicated by arrows.

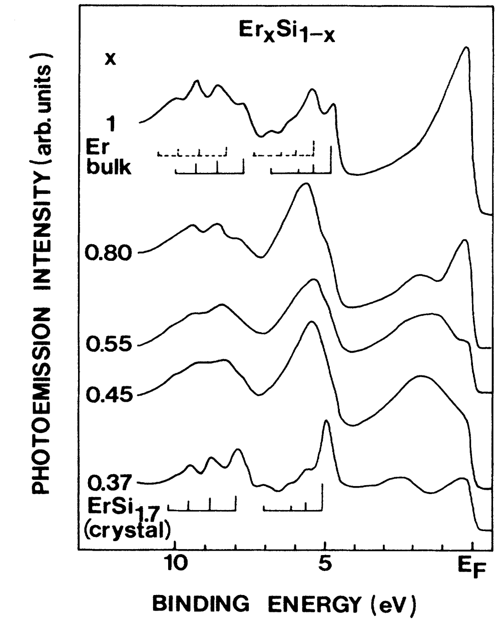

FIG. 5. Valence-band spectra for Er_xSi_{1-x} amorphous layers, epitaxial $ErSi_{1.7}$, and pure Er layer taken with He II ($\hbar\omega=40.8$ eV) radiation, collected at normal electron emergence ($\theta=0°$). Also shown is the identification of the bulk (solid line vertical bars) and surface (dashed line bars) 4*f* multiplets components.

Figure 5 exhibits the valence-band spectra recorded with He II radiation at normal emission ($\theta=0°$) for three stoichiometries, $x=0.45$, 0.55, and 0.8. This figure also shows the valence-band spectra measured on a 30-Å-thick epitaxial $ErSi_{1.7}$ layer grown on Si(111) (bottommost curve) and on a 50-Å-thick polycrystalline erbium film (topmost curve). The pure Er-metal film was evaporated onto a tantalum substrate. Our spectrum related to pure erbium is in good agreement with the data published by Lang *et al.*[17] The prominent emission close to the Fermi level is associated with the Er 5*d* derived states while the emission in the 4–11-eV binding-energy window reflects the various 4*f* multiplet states. As commonly observed for rare-earth surfaces, the 4*f* multiplet structure is strongly affected by the reduced coordination of the surface atoms.[18,19] Gerken *et al.*[18] have identified both bulk and surface Er 4*f* emission by fitting the experimental spectra with calculated 4*f* spectra obtained by adding a surface shifted multiplet structure to the bulk one. The energy separation and fractional parentage intensities of the final-state 4*f* multiplet lines were calculated from an atomic model using the intermediate coupling scheme.[19] The surface components are broadened and shifted by 0.7 eV towards higher binding energies with respect to the bulk ones. In Fig. 5 the solid line vertical bars illustrate the bulk 4*f* multiplets whereas the dashed line bars are related to the surface components. One should note that the spectra displayed in Fig. 5 are characteristic of very clean films and show an extreme sensitivity to contamination. Indeed, chemisorption of hydrogen or oxygen leads to a depletion of the 5*d* states near the Fermi level and to the appearance of new features at ~3.8 and ~6.1 eV binding energy for hydrogen and at ~6.0 eV for oxygen.[20] Both silicide and pure erbium layers must therefore be prepared under very clean conditions since impurity contributions to the photoemission spectra are strong and would be superimposed on the 4f structures, thus obscuring the valence-band spectra interpretation.

Concerning the silicide valence-band structure, recent work performed on rare-earth silicide electronic structure has pointed out the importance of covalent mixing between R 5d and Si 3sp states in the chemical bond.[21] In this work Braicovich *et al.* have shown that the valence band extends over several eV below the Fermi level E_F with increasing 5d content near E_F. In our spectrum for crystalline ErSi$_{1.7}$ taken at $\hbar\omega = 40.8$ eV, these Er 5d–Si 3sp hybridized states are reflected by two broad structures at ~2.55 and 0.4 eV. The 4f related multiplet structure is located in the 4–11-eV binding-energy window. It reveals a main well-resolved peak at 4.95 eV dominating the low-binding-energy part of the 4f structure while the high-binding-energy region comprises a series of incompletely resolved peaks. We observe that the 4f related multiplet structure shape for ErSi$_{1.7}$ looks different from that observed on a pure Er layer which involves both surface and bulk related 4f multiplet structures. This suggests that in crystalline ErSi$_{1.7}$ all Er atoms are in the same bulklike atomic environment. We have compared the 4f multiplet structure observed in crystalline ErSi$_{1.7}$ with that recorded with bulk sensitive photoemission using a monochromatized x-ray source on pure Er.[17] The latter reflects essentially Er atoms in a bulk environment giving rise to a single 4f multiplet structure. The very good agreement, as far as the number and relative intensities of 4f multiplets are concerned, between the spectrum recorded on epitaxial ErSi$_{1.7}$ with $\hbar\omega = 40.8$ eV and the spectrum collected on pure Er with $\hbar\omega = 1486.6$ eV leads us to conclude that in ErSi$_{1.7}$ all Er atoms have indeed a single atomic environment. Thus in contrast with pure Er, there is apparently no surface related 4f component for crystalline ErSi$_{1.7}$.

Let us now discuss the electronic structure of the amorphous Er$_x$Si$_{1-x}$ silicides for three stoichiometries, i.e., $x = 0.45$, 0.55, and 0.8. The 5d related features are strongly affected by the silicide stoichiometry. For Er$_{0.45}$Si$_{0.55}$ the valence-band spectrum displays only a broad feature at 1.8 eV below E_F. When x increases, the relative density of states increases at the Fermi level, and the broad structure at ~1.8 eV becomes more structured showing two components at ~1.2 and 2.3 eV for Er$_{0.55}$Si$_{0.45}$. These features shift towards the Fermi level with increasing Er content and are located at ~0.30 and 1.8 eV for Er$_{0.8}$Si$_{0.2}$. Similar modifications of the 5d related states are also observed by Braicovich *et al.*[21] for Gd silicides. In the higher binding energy region of the UPS spectra, one can observe that the 4f emission is much less structured than the one for crystalline ErSi$_{1.7}$ or even for pure Er. This is clearly visible for the low-binding-energy 4f peak, located at 4.95 eV in crystalline ErSi$_{1.7}$. This feature is only 0.4 eV wide in crystalline ErSi$_{1.7}$ while in all amorphous compounds it evolves into a very broad structure as wide as 1.5 eV. The centroid of this feature as well as the whole 4f structure shifts towards higher binding energies when Er concentration x increases. The centroid is located at 5.30 eV for $x = 0.45$, at 5.40 eV for $x = 0.55$ eV, and at 5.80 eV for $x = 0.8$. In the latter case, however, a small shoulder grows at 4.75 eV which is attributed to the 4f emission from Er atoms in a pure bulk Er environment. This indicates the presence of local Er-metal configurations and suggests an inhomogeneous nature of the broad Er 4f structure and/or the formation of pure metal clusters at large x values.

The broadening of the 4f main peak might be understood in the same way as that of the reacted Si 2p component. It reflects different Er atomic environments giving rise to a distribution of 4f lines with different energy locations according to the statistical fluctuations of local Er environments in the disordered Er$_x$Si$_{1-x}$ compounds. Indeed the 4f states also behave like atomic states and thus we expect a broadening of the 4f main line with respect to monocrystalline ErSi$_{1.7}$ in the same way as discussed above for Si 2p. In this respect we have measured the 4f related peaks shift versus Er concentration x using an x-ray source ($\hbar\omega = 1253.6$ eV). The spectra excited with this high photon energy are essentially bulk sensitive. We find that the largest 4f line shift with respect to ErSi$_{1.7}$ is about 0.5 eV. This shift is of the same order of magnitude as those measured for the Si 2p line. Thus one would expect for $x = 0.5$ a broadening of the 4f related peaks of about 25–30% with respect to crystalline ErSi$_{1.7}$. However, the main 4f line FWHM is enhanced by a factor 4 which cannot be explained only by a bulk environment distribution for the Er atoms. If we keep in mind that the valence-band spectra are recorded using a photon energy of 40.8 eV, i.e., under surface sensitive conditions, we must consider the contribution of surface Er environment. Thus we believe that the 4f line broadening reflects both bulk and surface statistical distribution of Si nearest neighbors around an Er atom. Since in pure Er layers the surface related 4f lines are shifted by 0.7 eV towards higher binding energies with respect to the bulk one, it is reasonable to assume that a similar shift would occur for amorphous silicides. Clearly this explains, for instance, the large apparent shift by about 1 eV towards higher binding energies of the 4f main line in Er$_{0.8}$Si$_{0.2}$ with respect to crystalline ErSi$_{1.7}$. In fact according to XPS the relevant shift is only about 0.3 eV for bulk related 4f features. The presence of surface related Er 4f features therefore considerably complicates the spectral interpretation in the 4f region.

D. Valence-band results for the RT Er/Si(111) interface

In Fig. 6 we display the valence-band spectra measured after deposition of Er onto a clean Si(111) substrate versus Er coverage. They were collected at normal emission ($\theta = 0°$) with He II radiation. Included in Fig. 6 is also the valence-band spectrum of clean Si(111) 7×7 surface (bottom-most spectrum). This spectrum is essentially dominated by intrinsic bulk related features at ~3.4 and 7.5 eV below E_F along with surface states at 0.2, 0.85, and 1.8 eV. For the photon energy used in these experiments, the 0.2- and 1.8-eV surface-state cross section is small and so they appear only as shoulders. The uppermost spectrum shows the emission from a 50-Å-thick polycrystalline Er film and has been discussed in Sec. III C.

At submonolayer coverages ($\Theta=0.5$ ML), Fig. 6 shows that both bulk and surface Si(111) structures are strongly attenuated whereas three structures appear, two structures at 5.8 and 9.0 eV binding energy associated with Er $4f$ states and a broad one at $\sim 1.5-2$ eV arising from Er $5d$–Si $3sp$ hybridized states. We have shown in Sec. III A (Fig. 1) that for such a low Er coverage, a chemically shifted Si $2p$ line is detected, the shift being of the order of 0.5 eV. It indicates the chemical interaction between the incoming Er atoms and the Si(111) substrate with a charge transfer from Er to Si species. This is qualitatively different from the results from other rare-earth/Si(111) interfaces[22] where the reacted Si species could only be detected for coverages of about 1 ML [0.8 ML for the Ce/Si(111) interface, for example[9,10]] with more surface sensitive and highly energy resolved techniques. Furthermore the UPS spectrum recorded for 0.5 ML shows no distinct Fermi edge and only poorly resolved $4f$ structures. In particular, this spectrum shows that the main Er $4f$ structure FWHM (located at ~ 5.8 eV) is at least twice as large as the one measured on pure Er (uppermost spectrum). If only pure Er clusters would be formed at this stage, as it is observed for many other rare-earth/Si(111) interfaces,[22] one might expect the appearance of well-resolved Er $4f$ lines arising from Er atoms in a definite atomic environment as it was found by Grioni *et al.* in Refs. 9 and 10. These results suggest that a large part of the deposited Er atoms are probably chemically bound to Si atoms with a statistical distribution of local environments onto (or beneath) the Si(111) surface rather than agglomerated in pure Er clusters. However, this point cannot be settled unambiguously on the basis of the present data since the photoemission signals, especially in XPS, are rather small. Further experiments, probably with other techniques, are needed and it remains an open and interesting problem for the future.

Upon further Er deposits the $4f$ peaks increase and move rapidly towards lower binding energies at 5.50 eV for 1 ML. At this stage both bulk and surface Si(111) states are swept out and only a broad structure is observed at ~ 2 eV. Concomitantly the broad $4f$ structure centered at ~ 9 eV for 0.5 ML evolves into a more structured feature. Between 1 and 2 ML, the UPS spectrum remains quite unchanged and is very similar to the one recorded on $Er_{0.45}Si_{0.55}$ in Fig. 5. Again this is in good agreement with the stoichiometry deduced from the Si $2p$ line analysis in Sec. III A.

Higher Er deposition up to ~ 6 ML results essentially in a general broadening of the $4f$ line shape for the lower- as well as higher-binding-energy parts. To a large extent this broadening results from the evolution of the interfacial silicide stoichiometry towards a more Er-rich silicide with a larger distribution of local surface and bulk Er environments as explained in Sec. III C for the amorphous Er_xSi_{1-x} compounds. Furthermore, on the low-binding-energy side, a feature appears at 4.75 eV first as a shoulder for 3 ML and then develops rapidly with increasing Er coverage. This reveals that unreacted Er clusters form at coverages as low as 3 ML. This conclusion is also supported by an increasing emission at the Fermi level which characterizes the growth of essentially pure Er. Note that at this stage, the thin reacted silicide layer has not yet reached its maximum Er content since its stoichiometry inferred from Si $2p$ data is about $Er_{0.65}Si_{0.35}$. Clearly this implies a heterogeneous growth mode for Er/Si(111) formed at RT.

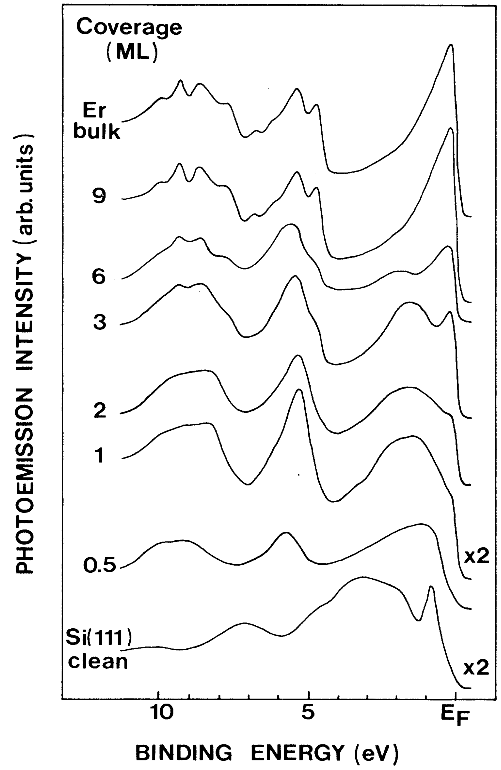

FIG. 6. Valence-band spectra for the RT Er/Si(111) interface taken with He II ($\hbar\omega=40.8$ eV) collected at normal electron emergence ($\theta=0°$).

Finally, according to the results of Sec. III A, the spectrum displayed for 6 ML is quite identical to that measured on the $Er_{0.8}Si_{0.2}$ amorphous silicide. At 9 ML coverage, the spectrum is indistinguishable from that relevant to a pure Er layer indicating the formation of largely unreacted Er overlayer on top of the intermixed region.

IV. CONCLUSION

The complementarity of the information extracted from XPS and UPS spectra has permitted a rather detailed description of the Er/Si(111) interface formation which can be summarized as follows: the reaction at the Er/Si(111) interface forms silicide patches whose stoichiometry evolves with Er coverage. Above 3 ML they coexist with pure Er clusters. These clusters are observed before the reacted thin silicide layer has reached its maximum Er content. From a spectroscopic point of view it is apparent that the presence of the shallow atomiclike $4f$ levels somewhat complicates the interpretation of the valence-band spectra. However, a detailed and careful analysis of the $4f$ data reveals numerous interesting features. In particular we find no evidence for the presence of surface Er sites on well-defined crystalline $ErSi_{1.7}$ whereas amorphous RT codeposited Er silicides or pure Er show prominent surface related Er $4f$ features.

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