Surface electronic structure of $CoSi_2$(111)

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The surface electronic structure of $CoSi_2$(111) surfaces is studied by angle-resolved photoemission using synchrotron radiation in the energy range $10 \leq \hbar\omega \leq 60$ eV. Depending on preparation technique the crystal termination is either a Co or a Si(111) plane. The $CoSi_2$(111)-Co terminated surface exhibits two surface-related features at $\bar{\Gamma}$ at -1.4 and -2.7 eV. The prominent low-lying peak is a true surface state of the Shockley type located in an absolute Si $3s3p$–Co $3d$ hybridization gap of the projected bulk band structure at $\bar{\Gamma}$ and shows an oscillating emission intensity in reciprocal space. The relevant surface-state band disperses toward the Fermi level with increasing $k_{\parallel}$ and corresponds to bonding states of surface Co atoms with a reduced coordination shell. In contrast, the -1.4-eV feature is rather a Tamm surface state or resonance derived from surface Co $3d$ nonbonding orbitals. On $CoSi_2$(111)-Si terminated surfaces only weak surface-related features can be identified.

Information on the bulk and surface electronic structure of transition-metal silicides may be very useful when dealing with interface formation of epitaxial silicide-silicon heterostructures both for fundamental reasons and technological interests. $CoSi_2$ appears to be a very interesting candidate for the fabrication of devices with numerous promising applications.[1–3] Little work on Co silicide surface properties has been reported.[4] In a previous paper[5] we have demonstrated that $CoSi_2$(111) surfaces of epitaxial $CoSi_2$ on Si(111) can be prepared in either a silicon-rich form [hereafter labeled $CoSi_2$(111)-Si] or a cobalt-rich form [hereafter labeled $CoSi_2$(111)-Co] depending on annealing conditions. It was proposed that $CoSi_2$(111)-Co obtained by low-temperature annealing (400 °C) represents a truncation of the ideal $CoSi_2$ crystal exposing a plane of Co atoms having four rather than eight Si nearest neighbors. $CoSi_2$(111)-Si surfaces were formed by annealing $CoSi_2$(111)-Co surfaces above 500 °C. About two monolayers (ML) of Si are found to segregate in these conditions. The Si-rich nature of the surface of epitaxial $CoSi_2$ crystals formed above $\sim$500 °C has been recently confirmed by angle-resolved Auger electron spectroscopy studies by Chambers *et al.*[6]

The aim of this report is to provide an analysis of the surface-related photoemission features identified in a synchrotron radiation study of both $CoSi_2$(111)-Co and $CoSi_2$(111)-Si surfaces, basically designed to investigate bulk electronic properties of $CoSi_2$ as reported elsewhere.[7] The data confirm and extend our previous conclusions.[5] Two surface-state bands, one of the Shockley type and one of the Tamm type derived from bulk bonding Si $3s3p$–Co $3d$ and nonbonding Co $3d$ states, respectively, can be unambiguously identified on the $CoSi_2$(111)-Co surface. Thus, this finding demonstrates a clear one-to-one correspondence between the bulk and surface states of $CoSi_2$(111)-Co. The situation is less clear cut for $CoSi_2$(111)-Si where definite surface-related emission is more difficult to identify.

The measurements were performed in an ultrahigh-vacuum chamber ($P \sim 10^{-10}$ Torr range) equipped with low-energy electron diffraction and Auger electron spectroscopy, a Co source, and quartz balance. Photoelectron analysis was achieved using a 180° hemispherical energy analyzer with angular and total energy resolution of $\sim$2° and $\sim$150 (300) meV at $\hbar\omega = 20$ (50) eV. The spectra were recorded using linearly polarized synchrotron radiation emitted by an undulator inserted into the ACO-LURE storage ring at Orsay. The photon energies provided by a toroidal-grating monochromator ranged from 10 to 60 eV. Typical data acquisition times per spectrum were as short as 200 s.

Epitaxial $CoSi_2$ crystals on Si(111) were grown by pure Co deposition (usually $4+4$ ML) onto clean Si(111)(7×7) surfaces prepared by standard methods and subsequent annealing in the 400–550 °C range after each deposit. This method resembles the so-called template method[8] with, however, an important difference. For Co thickness ≤ 8 ML annealing temperatures of $\sim$400 °C are found to be sufficient to get well-defined $CoSi_2$ crystals.[5,7,9] This temperature is lower than the 550 °C usually quoted in the literature. This is apparently connected with the fact that a thin $CoSi_2$-like layer is already formed at room temperature.[2,10] Crystals obtained in this way at 400 °C have a $CoSi_2$(111)-Co surface structure and the films are probably pinhole-free since recent work reporting successful preparation of continuous *B*-type films by a different method[11,12] or by coevaporation[13] uses similar temperatures. Si-rich $CoSi_2$(111)-Si surfaces were

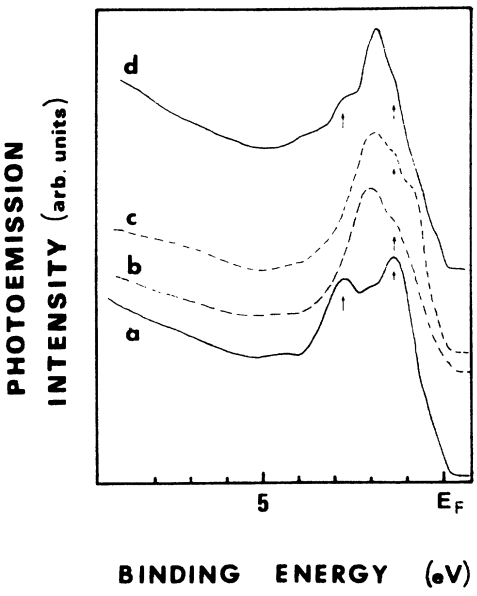

FIG. 1. Energy distribution curves (EDC's) of $CoSi_2$(111)-Co surfaces at $\hbar\omega=21$ eV: curves *a* and *d*. Normal emission ($\theta=0°$) for a $CoSi_2$ film thickness of 9 and 25 Å, respectively; curves *b* and *c*, $\theta=15°$ and $\theta=20°$, respectively, for a 9-Å $CoSi_2$ film. The peaks at -2.7 and -1.4 eV are due to surface states (arrows).

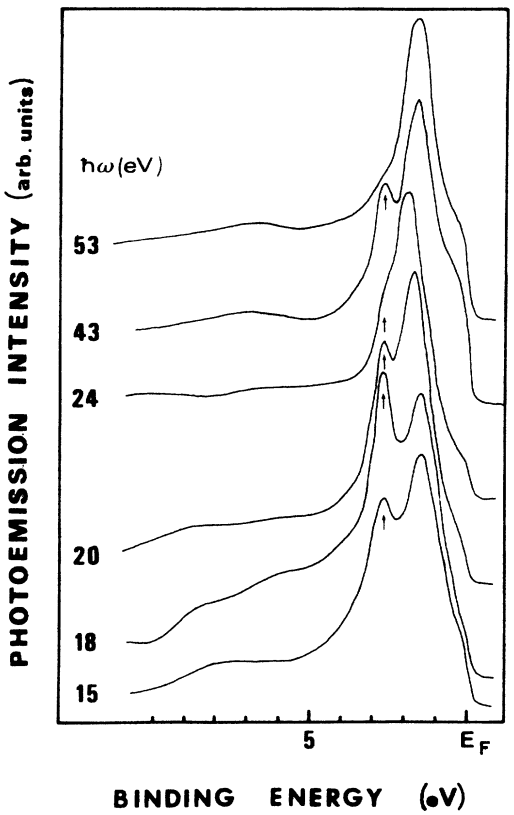

FIG. 2. EDC's at normal emission of $CoSi_2$(111)-Co for photon energies in the 10–60-eV range. The $CoSi_2$ film thickness is ~25 Å.

prepared by annealing at 550 °C.[5] Though pinholes are probably formed at this temperature this has no noticeable effect on photoemission. Actually we find that evaporating ~2 ML of Si on $CoSi_2$(111)-Co surface at 400 °C also yields $CoSi_2$(111)-Si surfaces with the same photoemission properties.[14] A further 1-ML Co deposit on a $CoSi_2$(111)-Si surface at 400 °C results again in a $CoSi_2$(111)-Co surface.[5] Repeated application of this procedure makes possible the formation of new $CoSi_2$ layers with a very good crystallinity even at temperatures <400 °C.[14]

Most data concern $CoSi_2$(111)-Co surfaces. Figure 1 presents photoemission spectra for two $CoSi_2$ film thicknesses of 9 and 25 Å, respectively. The -1.8-eV feature reflects emission from bulk bands.[5,7] Let us concentrate here on the prominent peaks at -1.4 and -2.7 eV visible in the 9-Å spectrum at normal emission. These peaks must be connected with the surface electronic structure since their intensities normalized to the -1.8-eV bulk feature intensity decrease progressively to a limiting value with increasing film thickness near 15–20 Å, i.e., at thicknesses where the bulk emission intensity reaches a maximum because of the limited mean free path of the photoelectrons. Thus in the 25-Å spectrum the -2.7-eV feature is only visible as a shoulder and the -1.4-eV peak can hardly be detected. This original argument for the surface-related nature of these features was developed in a previous study.[5]

We present now compelling evidence that the -2.7-eV peak is a true surface state. Figure 2 shows normal emission spectra for various photon energies. The first test is that a surface state must not disperse with the component of momentum normal to the surface $k_\perp$. This is strictly the case within experimental accuracy (~0.1 eV). In Fig. 3(a) the measured binding energies of surface-related transitions are plotted versus $k_\perp$ along with the experimental bulk bands along ΓL.[7] According to Ref. 7, using a free-electron final band,

$$k_\perp=\left[\frac{2m}{\hbar^2}(\hbar\omega+E_i-\phi+V_0)\right]^{1/2} \quad (1)$$

where E_i is the initial-state energy, $\phi=4.90$ eV the work function, and $V_0=14.8$ eV the inner potential. These data also demonstrate that the -2.7-eV surface state is located in a large gap of the projected bulk band structure at $\bar{\Gamma}$. This absolute gap in the energy range $-3.50<E_i<-2.05$ eV is a hybridizational gap which results from crossing of two Λ_1 bands (dashed lines) near the midpoint of ΓL. One of these bands is derived from Si $3s3p$ orbitals and exhibits strongly dispersive free-electron-like character. The other band is built up from Co $3d$ states. Hybridization results in an upper and a lower Λ_1 band (solid lines) separated by a large gap. The surface state is almost exactly located at midgap. These observations indicate that the -2.7-eV surface state is of the Shockley-state type[15] in contrast to Tamm states usually found in nonhybridizational energy gaps of the projected bulk band structure in close proximity to a bulk band edge.

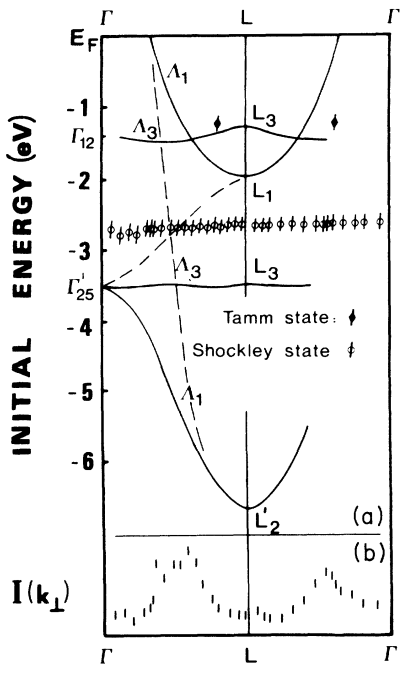

FIG. 3. (a) Measured binding energies of the surface-related peaks on $CoSi_2$(111)-Co vs $k_\perp$ calculated using a direct transition model with a free-electron-like final band dispersion. Continuous lines represent the experimental bulk bands along $\Gamma L \Gamma$ taken from Ref. 7. Dashed lines are schematic bands of Λ_1 symmetry before hybridization around their crossing point at $k_\perp \approx \Gamma L/2$. (b) Variation of the -2.7 eV surface-state intensity I_s vs $k_\perp$ along $\Gamma L \Gamma$. I_s is normalized with respect to bulk emission near the Fermi level.

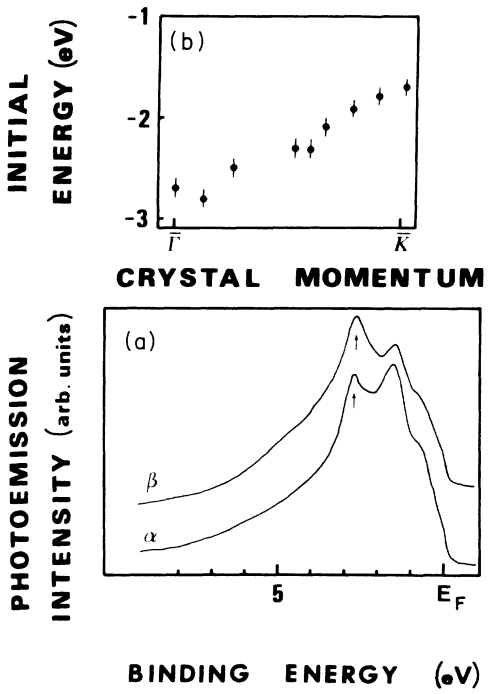

FIG. 4. (a) EDC's of $CoSi_2$(111)-Co at normal emission for $\hbar\omega = 14$ eV: α, mainly s polarization and β, mainly p polarization. The surface state (arrow) is essentially excited with p-polarized light. (b) Dispersion behavior of the surface state along the $\bar{\Gamma}\bar{K}$ line of the surface Brillouin zone measured at $\hbar\omega = 18$ eV.

The symmetry of the surface state is inferred from experiments with s- or p-polarized light. In Fig. 4 it appears that the -2.7-eV emission is predominantly excited by the normal component of the light electric field, corresponding to an initial state with Λ_1 symmetry at normal emission. This also confirms the close connection of the -2.7-eV surface state with the upper and lower Λ_1 bulk bands. However, a closer examination of the data indicates that about 20% of the peak intensity would still be excited with pure s polarization. The reason for that is not yet clear.

A stringent test for the surface-state nature of this feature comes from the resonant behavior of the peak intensity near $\hbar\omega = 17$ and 40 eV visible in Fig. 2. In Fig. 3(b) the relative peak intensity to that of the bulk near the Fermi level is plotted against $k_\perp$. The data show oscillations in reciprocal space with maxima near the ΓL midpoint. Similar oscillations have been observed previously for Cu (Refs. 16 and 17) and Al (Ref. 18) surface states. According to Ref. 16 this behavior reflects the fact that the surface-state wave function oscillates as it decays evanescently into the bulk with a dominant spatial frequency about a particular value of $k_\perp$. In other words, an expansion of the surface state ϕ_s in terms of bulk states $\phi_B(k_\perp)$,

$$\phi_s = \sum_{k_\perp, n} \alpha_{k_\perp, n} \phi_B^n(k_\perp) \tag{2}$$

where $k_\perp$ runs over the first Brillouin zone and n over all bands of appropriate symmetry has the $|\alpha_{k_\perp, n}|$'s strongly peaked near a particular value of $k_\perp$. Thus in a direct transition model the surface-state emission is expected to show maxima at $\hbar\omega$ corresponding to the relevant $k_\perp$. In simple cases for Tamm-like states only bulk states from one band appear in Eq. (2), namely those closest to the surface-state energy around a particular $k_\perp$ at a band extremum.[16] In the present case, however, it appears that two bands (the upper and lower Λ_1 bands) must be involved in the expansion of Eq. (2). The data indicate that the -2.7-eV surface state shows a dominant oscillation period into the bulk corresponding to $k_\perp \approx \Gamma L/2$. That the surface state should actually be constructed from bulk states with this translation symmetry may become apparent if one considers the expansion of Eq. (2) in terms of bulk Λ_1 bands before rather than after hybridization. The crossing of these bands schematically drawn in Fig. 3(a) shows that the bulk states closest in energy have $k_\perp$ vectors near $\Gamma L/2$.

Off-normal spectra at $\hbar\omega = 18$ eV indicate that this surface state corresponds to a surface band which can be followed over most parts of the surface Brillouin zone. The dispersion behavior is consistent with the translational symmetry of the surface[5] and the data along $\bar{\Gamma}\bar{K}$ are shown in the inset of Fig. 4.

Let us now consider the -1.4-eV peak at normal emission, which is another surface-state candidate. Since the state's intensity is weak except on samples with a very thin $CoSi_2$ film (~ 9 Å) only limited experimental data are available. Figure 1 shows that this feature shows no dispersion with polar angle of emission. Also the energy location is found to be the same at $\hbar\omega = 16.8$, 21.2, and 40.8 eV and the symmetry is Λ_3. Yet, from our data [Fig. 3(a)] it is difficult to decide whether or not this state is split off from the upper bulk band of Λ_3 symmetry. We assign this peak either to a Tamm state very close in energy to the bulk states at L_3 or to a surface resonance.

From all these properties, interesting conclusions about the origin of these surface bands can be drawn. Since the low-lying surface band states are closely related to Si $3s3p$–Co $3d$ hybridization they should result from cutting of Si–Co bonds at the surface. On the other hand, the Tamm surface band near -1.4 eV may be interpreted as Co $3d$ nonbonding states in the surface Co layer split off from the neighboring bulk band with similar nonbonding character by the surface potential. Finally, considering the $CoSi_2(111)$-Si surface, the major observation is that both surface bands discussed above are completely suppressed. A search for well-characterized surface states on $CoSi_2(111)$-Si was not successful for the $CoSi_2$ film thicknesses mainly investigated in this study (~ 25 Å). Possible surface states are most likely connected with Si rather than Co-derived states. Thus the situation is not favorable since the underlying Co has a much higher photoionization cross section than Si. A feature observed at 4.2 eV in spectra probing the bulk electronic structure at L (Ref. 7) is possibly related to the surface electronic structure since it is not observed on $CoSi_2(111)$-Co and cannot be explained in terms of bulk electronic structure. A search for surface states on $CoSi_2(111)$-Si using very thin $CoSi_2$ films in order to minimize the intensity from bulk features is presently underway.[14]

In summary we have identified and characterized surface-related photoemission features on epitaxial $CoSi_2$ layers on Si(111). In particular, for $CoSi_2(111)$-Co terminated surfaces it is shown that two surface states, a Shockley state and a Tamm state, originate from the surface perturbation of the bulk Si $3p$–Co $3d$ bonding states and Co $3d$ nonbonding states, respectively. This simple relationship between bulk and surface electronic structure is observed for the first time on a silicide surface.

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