Study of interface formation on Co/Si(111)-7×7 using angle-resolved photoemission

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The electronic structure of epitaxial layers of $CoSi_2$ on Si(111) substrates is of intense scientific interest both because these structures offer the possibility of novel high-speed electronic devices and because they are excellent model systems for understanding the systematics of epitaxial growth and of Schottky barrier formation. We have studied electronic structure using angle-resolved UV photoemission on three types of silicon–silicide samples: a thick $CoSi_2$ layer with $CoSi_2$–Si termination, thinner layers with $CoSi_2$–Co termination, and unannealed submonolayer deposits of Co on Si(111). The $CoSi_2$–Si sample shows electronic states in very close agreement with the energy bands for bulk $CoSi_2$ computed by Mattheiss and Hamann. The $CoSi_2$–Co samples have similar bulk states, but their outermost layers show a shift by 0.5 eV toward E_F of the Co($3d$) states, apparently because the outermost Co atoms are less strongly reacted with Si. A state at -3 eV is found and attributed tentatively to an interface state of the Si(111)/$CoSi_2$ interface formed at 450 °C. The electronic structure of unannealed deposits indicate a strong reaction between Co and Si. This suggests similarities between the bonding environment of the deposited Co and that of the outermost Co on the $CoSi_2$–Co surface.

I. INTRODUCTION

The high structural quality that can be obtained with epitaxial thin films of silicides on silicon has aroused considerable interest. Of particular interest are the silicides $NiSi_2$ and $CoSi_2$, which have the CaF_2 structure with lattice parameters only 0.4% and 1.3% smaller than that of Si, respectively. Two orientations with respect to the Si(111) substrate, denoted as type A and type B, are known to be possible for a film with the CaF_2 structure. Type-A films share the orientation of the silicon substrate, while a type-B film differs from the substrate by a 180° rotation about the surface normal. With proper recipes of Ni deposition and annealing, one can grow a $NiSi_2$ film of either type A or type B,[1] whereas $CoSi_2$ generally grows as type B.[2] It is possible, however, to grow films with mixtures of type-A and type-B orientations.[3,4]

It has been observed that different preparations of epitaxial $CoSi_2$ on Si(111) produce different terminal surfaces.[3,5] For deposition of ~ 1 monolayer (ML; 1 ML $= 7.8\times 10^{14}$ cm^{-2}) Co on $CoSi_2$(111), a low-temperature (420 °C) anneal produces a more cobalt-rich "$CoSi_2$–Co" surface while annealing above 550 °C yields the silicon-rich "$CoSi_2$–Si" surface. Hellman and Tung[3] propose that $CoSi_2$–Co is bulk $CoSi_2$ truncated between Si–Co–Si trilayers, and that $CoSi_2$–Si is $CoSi_2$–Co with an additional Si bilayer. Tung and Batstone[6] have proposed that the formation of pinholes often observed for high-temperature annealing is associated with Si atoms being supplied from the substrate to form the $CoSi_2$–Si surface.

An understanding of the electronic structure of cobalt-modified Si(111) surfaces is important to the scientific and technological interest in epitaxial silicides. As noted in a recent theoretical study[7] of the electronic structure of bulk $CoSi_2$, good conduction through a heterojunction requires matching of electronic states between substrate and overlayer; the authors find no such match for $CoSi_2$(111) on n-Si(111).[7] It is important to test this calculated band structure experimentally. Furthermore, the states observed by angle resolved ultraviolet photoemission spectroscopy (ARUPS), especially those identified as surface states, are used as an indicator of surface atomic structure.

We have studied valence-band electronic structure of the Si(111)–epitaxial $CoSi_2$ system in three types of samples: (i) thick $CoSi_2$ films to examine its bulklike dispersion; (ii) deposits of 0.5, 1.0, and 2.0 ML of Co annealed to form $CoSi_2$, to emphasize the effect of surfaces; and (iii) unannealed deposits up to 0.5 ML to study the initial reaction of Co on Si(111).

II. EXPERIMENTAL PROCEDURE

Lightly-doped n-type Si(111) substrates were cleaned by cycles of Ne^+ bombardment (1 keV) and annealing at 900 °C measured by an infrared pyrometer, followed by slow cooling. This yielded samples with sharp, strong 7×7 low-energy electron diffraction (LEED) patterns and an Auger electron spectroscopy (AES) peak height ratio C (272 eV):Si (92 eV) of typically 0.002. No measurable oxygen AES signal was detected [O (510):Si (92 eV) <0.0003] using a single-pass cylindrical mirror analyzer (CMA). ARUPS spectra for substrates cleaned in this way showed the three surface states characteristic of a clean Si(111)-7×7 surface.

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Cobalt was deposited on Si(111)-7×7 substrates from a Co pellet heated by electron bombardment and surrounded by a shuttered collimating shroud cooled with liquid nitrogen. Typical Co deposition occurred at a rate of 0.4 ML/min; the rate was checked using a quartz-crystal thickness monitor. The sample Co coverage was determined by AES with the total accumulated coverage calibrated using Rutherford backscattering spectroscopy (RBS). A 5-min deposition caused a pressure rise of $<3\times10^{-10}$ Torr. A small increase in carbon contamination (to an AES ratio C:Si of 0.006) was observed after 2 ML of Co deposition, with no oxygen contamination.

$CoSi_2$ films were grown *in situ* by depositing Co onto a substrate heated at 450° ± 30 °C by combined radiative and electron-bombardment heating from behind. Co coverages of 0.5, 1, 2, and 10 ML Co were used to produce 1.6, 3.1, 6.3, and 31 Å of $CoSi_2$. Below ~525 °C the Si samples were transparent at the infrared (IR) wavelength used by the pyrometer (1.1 μm) so the temperature was estimated by extrapolating sample temperture as a function of heating power. The ratio of the low-energy Auger peak heights, Co(*MMV*)/Si(*LVV*), was measured for each $CoSi_2$ film using a single-pass CMA at a modulation amplitude of 2 eV p.-p. The value for 31 Å agrees with that for $CoSi_2$–Co on bulk $CoSi_2$,[3] while the ratios for 1.6, 3.1, and 6.3 Å are consistent with layer-by-layer growth of $CoSi_2$–Co.[8]

Additional studies on $CoSi_2$ were done using a thick (~100-Å $CoSi_2$) layer grown epitaxially on Si(111) in a separate molecular-beam epitaxy (MBE) system by deposition of both Co and Si. This layer was capped with amorphous Si, which was sputtered off after transfer into our sample preparation chamber. Sputtering was stopped when the $CoSi_2$ layer was reached, to avoid depletion of Si at the surface. This was followed by annealing at 600 °C to produce a $CoSi_2$–Si termination.

Prepared samples were transferred *in vacuo* into a separate chamber, with a typical pressure of 1×10^{-10} Torr, for ARUPS measurements using linearly polarized synchrotron radiation at the National Synchrotron Light Source. A toroidal-grating monochromator[9] was used in the photon-energy range 12–80 eV, at a resolution of $\Delta h\nu \leqslant 0.05$ eV. The hemispherical electron energy analyzer[9] was typically operated to give an overall energy resolution of $\Delta E \leqslant 0.1$ eV full width at half-maximum (FWHM) height and angle resolution of $\Delta\theta \approx 1°$ FWHM. Electron energies are initial-state energies with respect to $E_F = 0$.

III. RESULTS AND DISCUSSION

A. Annealed $CoSi_2$ films

Figure 1 shows photoemission spectra taken at normal emission from the MBE-grown $CoSi_2$(111) sample, which show dispersion of bulk states with respect to photon energy variation. They are dominated by a band of Λ_1 symmetry, which disperses upward from $E_i = -2.1$ eV at $h\nu = 25.5$ eV and crosses E_F at $h\nu \approx 14$ and 50 eV, and a Λ_3 band which disperses between −1.55 eV at $h\nu = 25.5$ eV and −1.9 eV at $h\nu = 60$ eV. There also appears to be another weak feature dispersing toward the Fermi energy for $h\nu = 30$–40 eV; its origin is undetermined. This dispersion with photon energy has been interpreted[10] as dispersion with respect to $k_\perp$, which we estimate by assuming a free-electron final-state band, so that

$$k_\perp = [(2m/\hbar^2)(h\nu + E_i - \Phi + V_0)]^{1/2}.$$

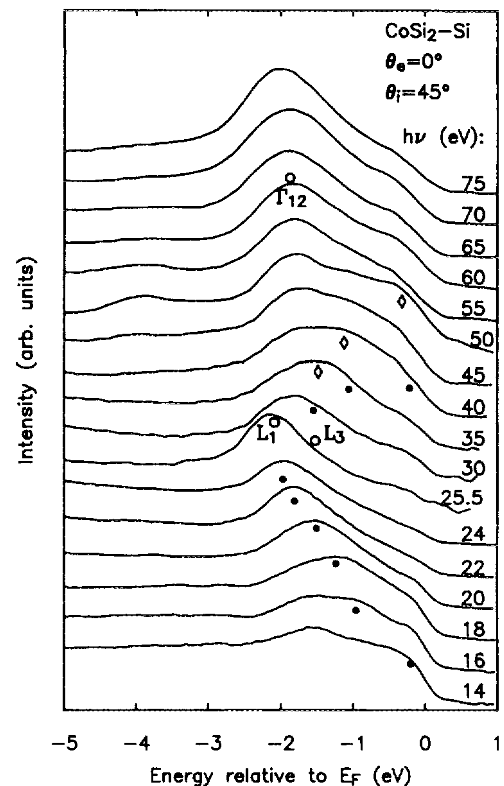


FIG. 1. Normal-emission photoemission spectra for a $CoSi_2$–Si sample. Open circles mark features at symmetry points, with binding energies −1.9 eV for Γ_{12}, −2.1 eV for L_1, and −1.6 eV for L_3. (Γ'_{25} is too weak in these spectra for a reliable energy determination). Filled circles show dispersion of Λ_1 band. Diamonds indicate dispersive state of unidentified origin. Incidence angle is 45° from normal.

The parameter $\Phi = 4.75$ eV is the work function for $CoSi_2$–Si[5] and $V_0 = 14.8$ eV is the assumed value of the inner potential measured with respect to the vacuum level.[10] The initial-state energy at symmetry points is then −1.9 eV for Γ_{12}, −2.1 eV for L_1, and −1.6 eV for L_3. These agree very closely with the calculated values presented in Fig. 1 of Ref. 7. As photon energy increases above $h\nu = 50$ eV, the photoelectron escape depth decreases to one or two lattice constants, and the corresponding uncertainty in $k_\perp$ becomes a large fraction of the Brillouin-zone size. The spectra are thus dominated by a $k_\parallel$-selective surface density of states (DOS) emphasizing Co (3*d*) states because of their higher cross section. The maximum for $h\nu = 60$ eV lies at −1.9 eV, which coincides with the peak in calculated DOS for bulk $CoSi_2$ in Fig. 5(a) of Ref. 7.

Figure 2 shows off-normal spectra for the same sample at $h\nu = 60$ eV in the $(1\bar{1}0)$ mirror plane, with polarization that selects even-parity states. At this photon energy, $\theta_e = 0°$ corresponds to Γ in the extended-zone scheme for a free-electron final state, and angle sweeps 0° to −32° and 0° to +20° correspond approximately to Γ–*L*–Γ and to Γ–*K* in the bulk Brillouin zone. For the most part the peaks observed can be

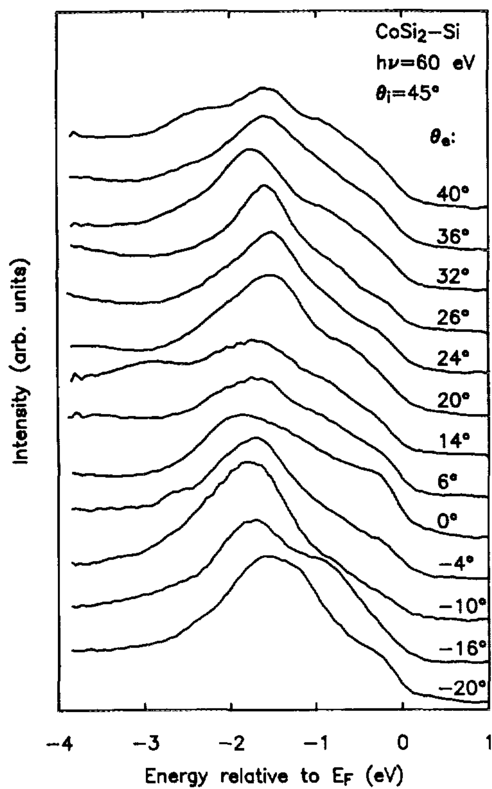
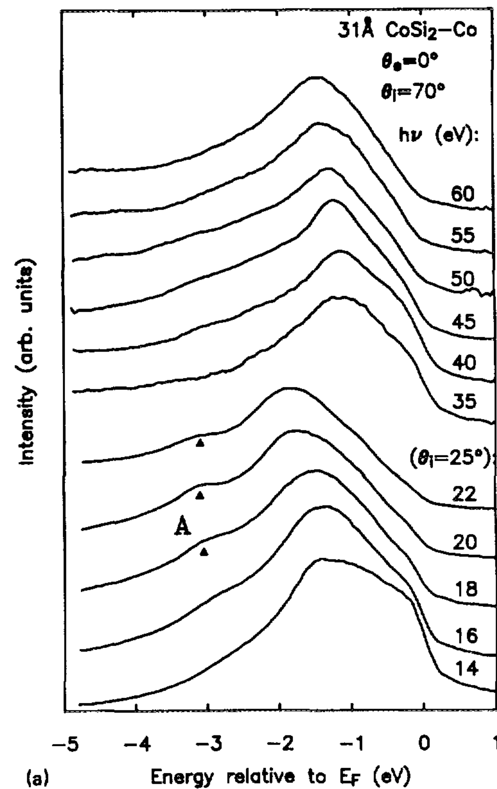


FIG. 2. Off-normal emission-angle scan for a $CoSi_2$–Si sample at photon energy 60 eV. Positive emission angles lie near Γ–K in the bulk Brillouin zone while negative angles correspond approximately to Γ–L–Γ.

explained in terms of the calculated band structure in Ref. 7.

The $CoSi_2$ layers grown *in situ*, with $CoSi_2$–Co terminations, are significantly different from $CoSi_2$–Si, as we see in Fig. 3(a) for a 31-Å $CoSi_2$ layer. Particularly at higher, more surface-sensitive photon energies, the shapes of the spectra are different, with the positions of the maxima shifted toward E_F. At $h\nu = 60$ eV the maximum is at -1.5 eV, shifted by 0.4 eV toward E_F compared with $CoSi_2$–Si (Fig. 1) and with calculated bulk DOS.[7] At lower photon energies, which mostly reflect dispersion of bulk states, the spectra are much more similar between $CoSi_2$–Co and $CoSi_2$–Si. The features have the same shape, and while there is still some apparent shift due to increased DOS intensity around -1.5 eV, it is much smaller. This indicates that the shift at higher photon energies denotes a change in surface electronic structure, probably because Co atoms have fewer Si neighbors at the $CoSi_2$–Co surface than in bulk $CoSi_2$. The peak in surface DOS lies at the same energy as the surface resonance/Tamm state at -1.4 eV reported by Pirri *et al.*[11]

Thinner $CoSi_2$ films also display a shift of the surface DOS peak toward E_F, but for both a 6.3-Å layer [Fig. 3(b)] and for a 3.1-Å layer (not shown) the shift is smaller than for the 31-Å film. One explanation for this may be that part of the DOS peak at -1.5 eV is associated with defect sites in the films grown by Co deposition and annealing. If limited mobility of Si at the annealing temperature causes films to have regions that are, say, slightly Si deficient, then thicker films will have a greater incidence of these defects. The $CoSi_2$–Si film of Fig. 1, on the other hand, was grown by deposition of both Co and Si and would not have defects associated with



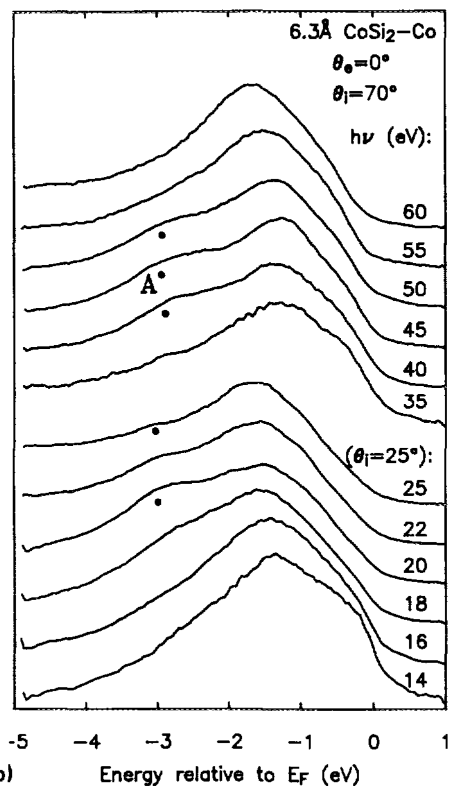


FIG. 3. (a) Normal-emission spectra for 31-Å $CoSi_2$–Co film. Incidence angle is 25° off normal for low photon energies ($h\nu \leqslant 25$ eV) and 70° for $h\nu \geqslant 35$ eV. For $h\nu \leqslant 25$ eV, the spectra are similar to those in Fig. 1, but the bulk features are shifted 0.15 eV toward E_F. For $h\nu \geqslant 35$ eV the dominant intensity is shifted toward E_F by ~ 0.5 eV. An additional feature A is seen at -3.0 eV for low photon energies. (b) Comparable spectra for 6.2-Å $CoSi_2$–Co. Feature A is now strong at high photon energies as well. The apparent shift toward E_F of the Co DOS feature as compared to Fig. 1 is ~ 0.3 eV.

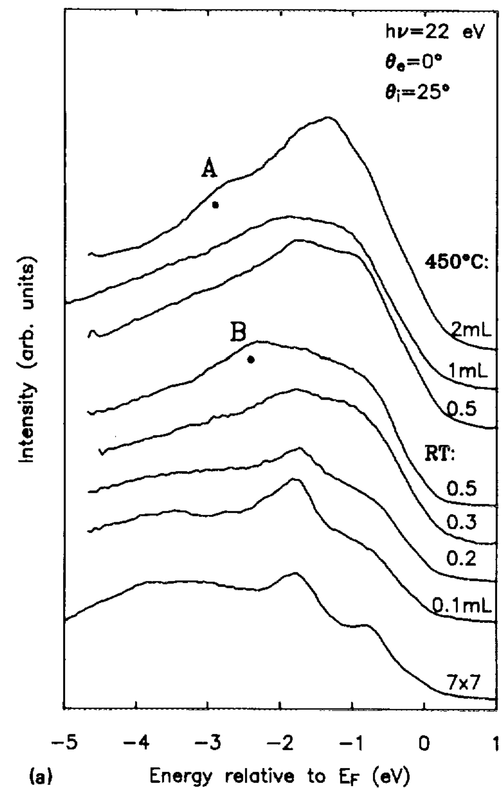
incomplete transport of Si. It should also be noted that a small part of the apparent peak shift, <0.1 eV, is an artifact of different photon incidence angles used for the spectra of Fig. 1 (45° from normal) and those of Fig. 3 (70°): in the latter case, an increased proportion of $\epsilon_\perp$ in the linear photon polarization enhances emission from the Λ_1 states, which lie closer to E_F than the Λ_3 states along most of the Γ-L line.

The $CoSi_2$–Co surfaces also display a new peak A with $E_i = -3.0$ eV. This peak is more apparent for the 6.3-Å film than for the 31-Å film, particularly at the more surface-sensitive photon energies. While this feature is close to the surface state on the $CoSi_2$–Co surface at -2.7 eV reported by Pirri *et al.*,[11] it is not the same: the sample used for Fig. 3(b) also displays the -2.7-eV surface state at proper photon energy and incidence angle, and feature A shows the opposite incidence-angle dependence. Feature A is not accounted for by the bulk band structure of $CoSi_2$ nor is it seen in comparable spectra for clean Si(111). It thus seems to be a state specific to the surface or interface. Off-normal polar-angle scans reveal dispersion qualitatively similar to Pirri's surface state.[11] We note also that thinner $CoSi_2$ films (3.1 Å) show peak A only weakly and at a different energy; this is not surprising since these films consist for the most part of a single $CoSi_2$ trilayer, which should be electronically different from a surface layer on bulk $CoSi_2$ or even on a two-trilayer film. An intriguing possibility is that peak A is actually a state like Pirri's surface state but localized at the Si/$CoSi_2$ interface rather than at the surface. This hypothesis is suggested by our data, since peak A appears in our more surface-sensitive spectra only when the $CoSi_2$ layer is thin; but further experimental tests are necessary.

B. Unannealed Co deposits

Figure 4 compares photoemission spectra at normal emission for unannealed deposits of 0.1, 0.2, 0.3, and 0.5 ML Co on Si(111) with corresponding results for annealed deposits of 0.5, 1.0, and 2.0 ML (i.e., $CoSi_2$ films). We note first that at low coverage there is increased intensity in the peak near -1.8 eV, where the S_3 surface state of Si(111)-7×7 appears. Upon Co deposition, the S_3 surface state peak is probably quenched and is replaced by emission from Co(3*d*) states; a slight change in peak shape suggests this. Since this energy corresponds to the DOS peak in bulk $CoSi_2$, growth of this peak suggests that the initial 0.1 ML of deposited Co is strongly bonded to Si, in an environment similar to that in $CoSi_2$. It would be interesting to perform surface EXAFS measurements as a function of Co coverage to see if there are the expected differences from the early stages of Si/$NiSi_2$ interface formation.[12]

Further deposition causes more growth near -1.4 eV and above, as seen in the difference curves of Fig. 4(b). This is indicative of Co less strongly reacted with Si. More significant is the growth of a definite peak B at ~ -2.6 eV for 0.5-ML deposition; this is also visible as a weak shoulder for 0.3 ML. Peak B appears very similar to the surface state found by Pirri *et al.*[11] It is easily quenched by contamination, and for 0.5-ML coverage is not visible after ~ 1 h at 1×10^{-10} Torr. At normal emission it appears stronger in spectra with glancing photon incidence (70° off normal) than for near-



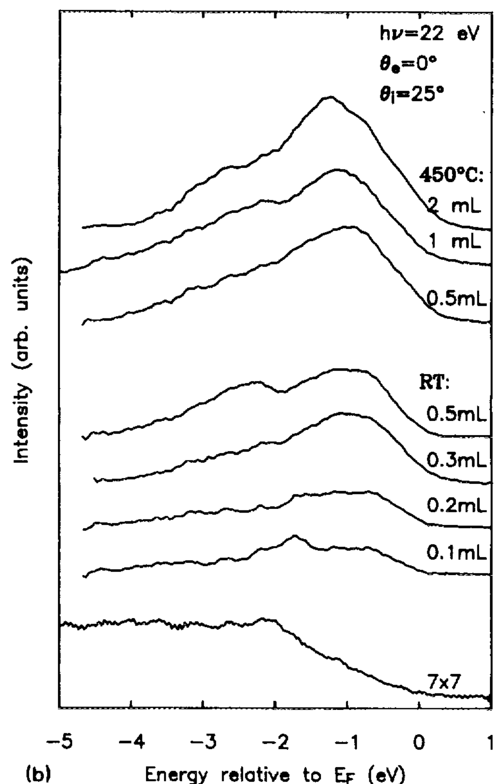


FIG. 4. (a) Normal-emission spectra at $h\nu = 22$ eV for clean Si(111)-7×7, Co deposits of 0.1, 0.2, 0.3, and 0.5 ML at room temperature (RT), and several deposits with substrate at 450 °C to form $CoSi_2$. (b) Spectra of Fig. 4(a) with "bulk Si(111)" background spectrum subtracted. Subtracted spectrum, shown at bottom, is from a slightly contaminated Si(111)-7×7 sample so that sharp surface state peaks do not distort difference curves. With increasing deposits at RT the intensity increases first at ~ -1.8 eV, then at -1.4 eV and above, and, for 0.5 ML, at -2.6 eV.

normal (25°) incidence; this is true also for Pirri's surface state, which has Λ_1 symmetry. It apparently does not disperse with variations in photon energy; although below 18 eV the changes in the bulk-Si contribution to the spectra make this difficult to test.

IV. CONCLUSIONS

There is a clear electronic difference between the Si- and Co-rich surfaces of $CoSi_2$. In $CoSi_2$–Si even the outermost Co atoms are in an essentially bulklike electronic environment; the states we observe agree well with the calculated bulk band structure.[7] In $CoSi_2$–Co the outermost Co atoms are in a different environment that pushes the $(3d)$ states upward toward the Fermi level. Some of the Co$(3d)$ shift may also be due to incomplete Co bonding in defected regions of the films. In addition to altered Co$(3d)$ behavior at the surface, our results also suggest the possibility of an interface state A that consists of a Co$(3d)$–Si$(3p)$ hybrid near the Si/$CoSi_2$ boundary as formed at 450 °C. More detailed examination of the behavior of this state should be a fruitful step toward understanding the structure of this interface.

Valence-band studies of unannealed deposits of submonolayer Co coverage help to confirm and refine the conclusions of previous core-level studies[13] that initially deposited Co (<0.5 ML) occupies $CoSi_2$-like sites. It appears that roughly 0.1–0.2 ML of deposited Co on Si(111)-7×7 occupies an almost bulklike environment, while further deposited Co reacts less strongly. Some of this less-reacted Co seems to be in an environment similar to that of the outermost Co in $CoSi_2$–Co, with a photoemission peak at -1.4 eV. This conclusion is also supported by the presence of a state B similar to the surface state at -2.7 eV reported by Pirri *et al.*, for the $CoSi_2$–Co surface.[11] Further studies of this interface formation will focus on the properties of Co/Si hybrid states in this energy range.

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