Nucleation of a two-dimensional compound during epitaxial growth of CoSi₂ on Si(111)

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The epitaxial growth of thin $CoSi_2$ films on Si(111) surface has been achieved under ultrahigh vacuum conditions using sensitive surface techniques such as low-energy electron-diffraction, angle-resolved ultraviolet photoemission, and core-level photoemission spectroscopies. During the course of the $CoSi_2$ formation, we observed the presence of an intermediate silicide phase displaying two-dimensional characteristics. It seems to control the kinetics and mechanisms of the $CoSi_2$ formation.

Recently, special attention has been devoted to the $CoSi_2$-Si(111) interface for both technological and fundamental reasons.[1-4] The $CoSi_2$ film has the particular advantage that it grows epitaxially on the Si(111) surface (lattice parameter mismatch $\sim 1.2\%$) and is an ideal system for calculations of structural and electronic properties of solid-solid interfaces (abrupt interface, interfacial reaction, chemical bonding and band structures, Schottky-barrier modeling, . . .).[5] Moreover, it is possible to epitaxially grow Si(111) on top of the $CoSi_2$-Si interface, giving rise to heterostructures such as Si-$CoSi_2$-Si, therefore opening the way to semiconductor-metal–semiconductor devices.

During the course of the $CoSi_2$ formation on the Si(111) surface under ultrahigh vacuum conditions (UHV), we find the presence of an ultrathin two-dimensional (2D) silicide compound film that seems to govern the $CoSi_2$ formation mechanisms. This "2D silicide membrane" has been investigated with low-energy electron diffraction (LEED) and angle-resolved ultraviolet photoemission spectroscopy (AR-UPS), and we present here the results concerning this 2D compound.

Experimental details can be found in Ref. 3. Usually, various coverages θ of cobalt atoms were evaporated onto the (7×7) Si(111) surfaces maintained at room temperature and the systems were then annealed under UHV at various temperatures T_A (up to ~ 750 °C) for various durations t (up to 1 h). The kinetics of the silicide formation were monitored *in situ* with LEED, ARUPS, and XPS (x-ray photoemission spectroscopy).

For the annealing conditions $T_A \geq 550$ °C, $t \geq 5$ min, and high coverages ($\theta \geq 3$ monolayers—a monolayer, ML, corresponds to 7.8×10^{14} Co atoms/cm²), the final product is always a quasiperfect flat and continuous $CoSi_2$ film. An increase in the annealing temperature ($T_A \geq 700$ °C) produces a disruption of the $CoSi_2$ film which agglomerates into $CoSi_2$ islands.[6] The ARUPS spectra obtained on $CoSi_2$ film are reproduced in Fig. 1, curve e. They essentially show two features at normal emission (electron analyzer axis normal to the sample surface). The first one is located at ~ 1.7 eV with fine structure at ~ 1.2 eV. It is assigned to the nonbonding Co d states. These states do not participate to the

Co–Si bonds due to their mutually unfavorable symmetry. Their energy positions and widths increase continuously (towards the Fermi level E_F) along the series $CoSi_2$, CoSi, Co_2Si, Co. This behavior can be understood in terms of a rigid-band model and tight-binding approximation as discussed in Refs. 5 and 7. The second characteristic feature of $CoSi_2$ is located at 3.7 eV below E_F. It is attributed to the bonding states of mixed Si p–Co d orbitals of corresponding symmetry. The ARUPS experiments we carried out on $CoSi_2$ show no significant energy dispersion of these features when angle and photon energy are varied. The photoemission features reflect emission from the essentially flat d bands due to the large Co-Co distance in $CoSi_2$ compound. The ARUPS spectra at normal emission in Fig. 1 thus can be compared to the $CoSi_2$ density of states as observed with angle integrated UPS (Refs. 8 and 9) or theoretically calculated in Ref. 5. This comparison has been stressed in Ref. 3 and the agreement was excellent. It is worth mentioning that experiments other than ARUPS have also confirmed the existence of a true $CoSi_2$ phase under the same annealing condition observed here. In particular, LEED observations show a (1×1) pattern with a threefold symmetry characteristic of $CoSi_2$; the work function of the film coincides exactly with that of bulk $CoSi_2$ (Ref. 10) and core-level spectroscopy gives identical results as on bulk $CoSi_2$.[10] Moreover, films prepared under identical conditions have been examined *ex situ* with electron diffraction (TEM) and Rutherford backscattering technique (RBS), when possible, and all results confirm the final $CoSi_2$ formation.[6]

For annealing temperature greater than 700 °C, the kinetics of formation are rather rapid for these thin films and we did not succeed in following *in situ* the dynamics of the interfacial formation, or the distinguishing of the various silicide phases, at least with the photoemission technique.

However, upon mild annealing ($T_A \lesssim 400$ °C and brief annealing times), it is possible to observe, step by step, the $CoSi_2$ formation starting from the Co-Si interface. Depending on the Co coverage, the temperature T_A and the annealing time t, we found that several phases ($CoSi_2$, CoSi, and Co_2Si) coexisted during the course of the formation of the
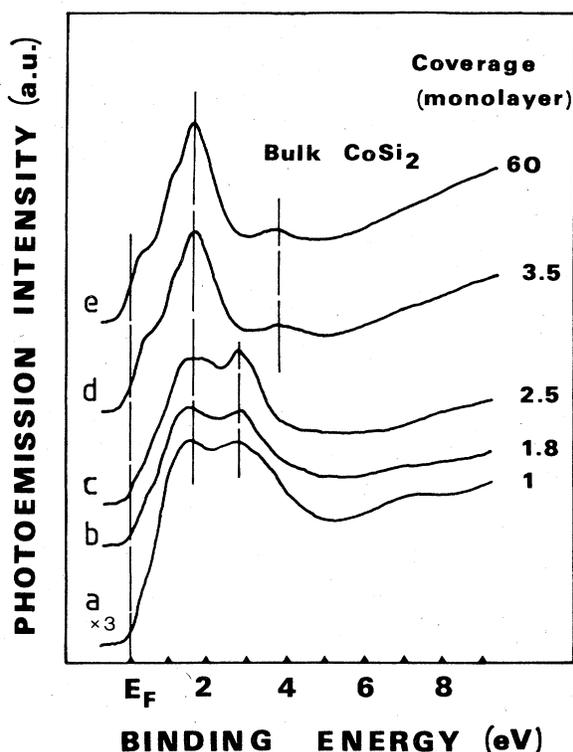
FIG. 1. Photoelectron distribution $N(E)$ recorded at normal emission for various thicknesses of $CoSi_2$ on Si. $h\nu = 21.2$ eV. The incident photon angle at the surface was 45°. Curves a–c reflect the "2D silicide" spectra. Curves d and e do not show any difference with that of bulk $CoSi_2$. Note the very sharp transition between curve c ($\theta = 2.5$ monolayers) and curve d ($\theta = 3.5$ monolayers). This fact testifies a very sharp interface between $CoSi_2$ epitaxially grown on Si.

interface and also the presence of a kind of "membrane." This membrane displays only 2D characters, as described below, and will be referred to as 2D silicide. It always existed prior to the final $CoSi_2$ formation. We prepared a Co-Si interface at room temperature, annealed it at T_A less than 400 °C and probed the vacuum-Co interface with ARUPS. The technique sampled the surface region (≤ 20 Å) and we observed the successive arrival of various silicide phases at the probed region. The typical sequential growth was as follows (with sufficient Co thickness), $Co-Co_2Si-CoSi-2D$ silicide-$CoSi_2$. The 2D silicide seems to play the role of a precursor state to the $CoSi_2$ formation and more details will be published elsewhere[11] on the formation of $CoSi_2$ thin films on Si.

Let us focus on this 2D silicide. Although its composition is very close to $CoSi_2$, its photoemission "signature" is quite distinct from that of $CoSi_2$, $CoSi$, and Co_2Si.

A representative spectrum of this 2D silicide is shown in Fig. 1, curve c. If the coverage θ is ≤ 3 ML, one obtains the 2D silicide. With $\theta \gtrsim 3$ ML, the sequential growth described above occurs and in order to record the 2D silicide spectrum, one must stop the thermal reaction exactly at its appearance. Figure 1, curve c shows a large difference between the 2D silicide spectrum and that of $CoSi_2$ (Fig. 1, curve e). In particular, if the nonbonding states of the Co $3d$ electrons appear as expected in a slightly less structured

broad peak at ~ 1–1.7 eV, nearly similar to that observed on $CoSi_2$, the bonding states between Co $3d$ and Si $3p$ electrons do not occur anymore at 3.7 eV as on $CoSi_2$, but at 2.8 eV. This clearly shows a different atomic environment between Co and Si atoms in this 2D silicide. Moreover, the ARUPS spectra exhibit a strong angle dispersive behavior in contrast with the $CoSi_2$ ones. Figure 2 shows ARUPS spectra recorded with different collection angles (normal and off-normal emission) along the [01$\bar{1}$] axis probing wave vectors $\vec{k}$ parallel to the surface, along the ΓK directions of the (1×1) surface Brillouin zone (SBZ). The axis is referenced by means of the (1×1) LEED pattern of the 2D silicide. It is worth stressing that this (1×1) pattern does not display the threefold character of the $CoSi_2$ layer, emphasizing again the difference between the two compounds.

ARUPS spectra recorded with normal emission and various photon energies (i.e., probing various wave vectors $\vec{k}$ perpendicular to the surface) display the same energy location for the two observed features (nonbonding and bonding states), asserting the two-dimensional character of the compound.

In Fig. 3, the energy positions of the main peaks are plotted versus the wave vector $\vec{k}$ parallel to the surface, along high-symmetry lines of the SBZ. These dispersion curves display a (1×1) periodicity in the $\vec{k}$ space. Note the peak energy location at equivalent Γ points of the extended Brillouin zone scheme.
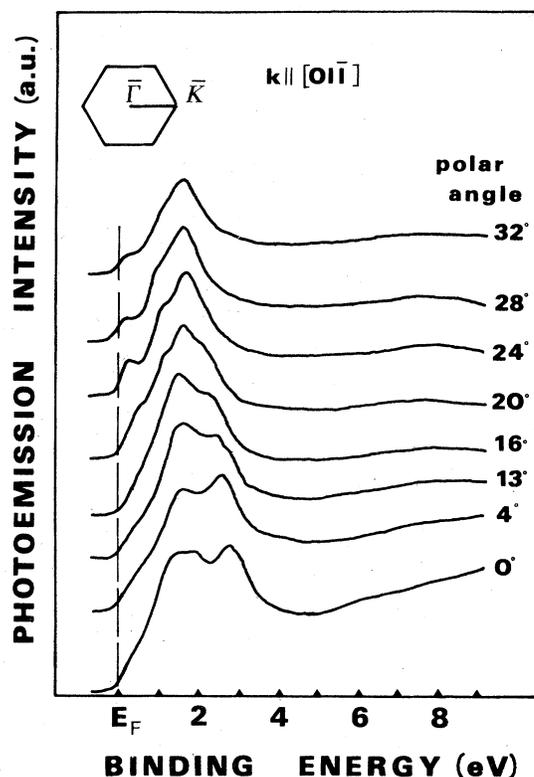

FIG. 2. Angle-resolved photoemission distribution of the "2D silicide." The thickness was 2.5 monolayers. $h\nu = 21.2$ eV. The incident photon angle was 45° and the spectra were recorded at various emission angles (normal and off-normal emission) probing the [01$\bar{1}$] direction of the surface Brillouin zone. Strong dispersive behavior is found.
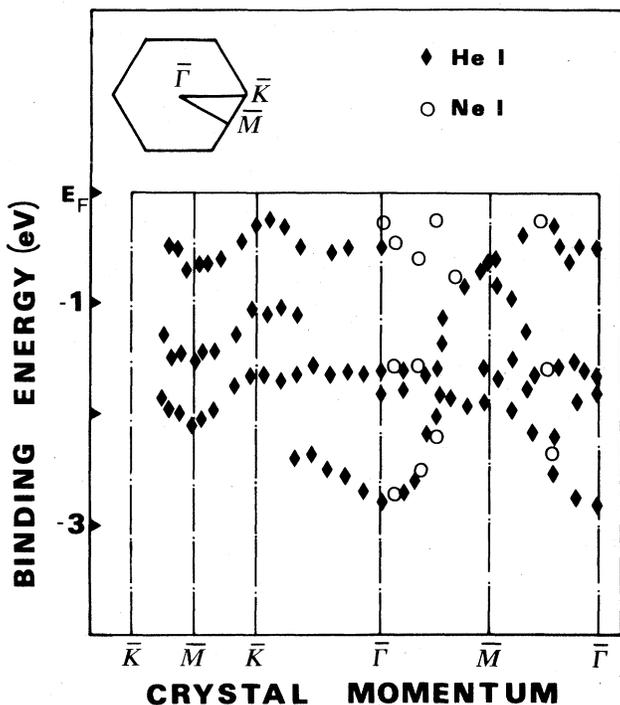
FIG. 3. Energy-dispersion curves for the main features of the "2D silicide" plotted along high-symmetry lines of the surface Brillouin zone. The curves are deduced from ARUPS data performed with various photon energies (21.2-eV He I and 16.8-eV Ne I) and at various emission angles.

For the 2D silicide, the nonbonding Co $3d$ states are located at $\sim$ 1–1.7 eV as observed on $CoSi_2$. This similitude implies that the first Co atoms coordination shell is composed of mostly Si atoms likely in $CoSi_2$. However, since the bonding states between Co $3d$ and Si $3p$ orbitals are located at $\sim$ 2.8 eV (instead of 3.7 eV in $CoSi_2$) one must

conclude that in the 2D silicide the Co atoms have still not exactly occupied the sites they occupy usually in $CoSi_2$. These facts can be explained if one assumes that Co atoms are stabilized at interstitial sites of a silicon matrix. The two interstitial sites available for this incorporation are the sixfold coordination location between the first and second Si(111) planes and a eightfold coordination location between the second and the third Si(111) planes. In both cases, the local environment of the Co atoms is Si rich and reflects the observed ARUPS spectra. With our present techniques, we cannot unambiguously assert which is the effective interstitial void. It is noteworthy that the sixfold symmetry might be a good model for the final $CoSi_2$ formation. Indeed, by expanding outwards the first plane, intercalating a plane of Co atoms between the first and second Si planes without breaking the Si–Si bonds between the second and the third planes, one can achieve the epitaxial growth of $CoSi_2$ on Si(111) that is effectively observed.[1-3] This model is identical to that proposed in order to explain the $NiSi_2$ formation on Si.[12] Furthermore, this 2D silicide model can explain the location of the bonding states at $\sim$ 2.8 eV rather than 3.7 eV (in $CoSi_2$) as a result of the lower number N of Si atoms surrounding a Co atom ($N = 8$ in $CoSi_2$). In addition, there is essentially no coupling between d states of Co atoms located in the sixfold sites between the first and second Si planes and those located between the third and fourth Si planes when the Si–Si bonds between the second and the third planes remain unaffected. Hence, such a structure is expected to show a pronounced 2D character for the Co $3d$ derived states such as we observed with ARUPS experiments.

In summary, we have revealed for the first time the presence of a 2D silicide compound appearing during the $CoSi_2$ epitaxial growth on Si(111). This 2D silicide displays significant structural and electronic properties as compared with $CoSi_2$. It corresponds to a layer, where Co atoms still occupy interstitial sites between Si atoms and it plays a precursor state prior to the final $CoSi_2$ formation.

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