Surface electronic structure of metastable FeSi(CsCl)(111) epitaxially grown on Si(111)

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We report an investigation on the electronic structure of metastable, epitaxial FeSi films grown on Si(111). The electronic structure of the metastable silicides was probed with angle-resolved photoemission, and compared with theoretical calculations. We identify the silicide as FeSi crystallizing in the CsCl structure. Its surface is Fe terminated, and presents a prominent, strongly dispersing surface state at a binding energy of -3.5 eV in $\bar{\Gamma}$. Its origin lies in the truncation of Fe bonds at the surface, and thus it has a major Fe d_{z^2} content. [S0163-1829(97)50424-3]

Iron silicides have been investigated during the last years due to their interesting properties, both from fundamental and applied points of view.¹⁻⁹ One of the most relevant features of these materials is that, in addition to bulk phases,¹⁰ metastable phases can be stabilized through epitaxial growth on a Si substrate.⁴ The stabilization of metastable phases is due to their better lattice matching with the substrate. This reduces the interface energy, and favors an otherwise unstable crystalline structure. Obviously, these phases may exhibit interesting properties not found in the bulk compounds. Growth of FeSi crystallizing in a CsCl lattice,⁴ and of FeSi₂ in a fluorite structure (γ -FeSi₂),^{5,6} have been reported. The lattice mismatch of FeSi (CsCl) with Si(111) is $\sim 2\%$,⁷ and this structure appears in a wide range of Fe concentrations (from FeSi to FeSi₂). The crystalline structure of FeSi (CsCl) is very close to the DO₃ structure of Fe₃Si, which is ferromagnetic. This feature, and the use of iron silicides as spacers in Fe multilayers exhibiting magnetic ordering,⁸ have prompted a great interest on the electronic and/or magnetic properties of this and other metastable phases.⁹ In addition to interesting properties, metastable epitaxial phases have the basic interest of being crystallographically simpler than the bulk phases. They often represent ideal phases prior to instability driven deformations.

In this paper we study the electronic structure of metastable iron silicides grown epitaxially on Si(111). We identify a 1×1 phase as quasi-stoichiometric FeSi (CsCl). 1×1 -FeSi (CsCl) films are Fe terminated, and present electronic states which agree well with theoretical calculations for this compound. A band gap of the projected bulk band structure is predicted between 2.5- and 4.0-eV binding energy (BE), in agreement with the experiment. In this area we observe a strongly dispersing surface state, which can also be

well reproduced in the theoretical calculation. The surface state has a major Fe- d_{z^2} content, in agreement with the Fe surface termination found.

The experiments have been carried out in an ultrahigh vacuum (UHV) chamber permanently located at the exit of a Seya-Im monochromator receiving synchrotron light from the DORIS III storage ring of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronensynchrotron. It was equipped with facilities for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and angle-resolved ultraviolet-photoemission spectroscopy (ARUPS). The ARUPS spectra were recorded with a hemispherical analyzer mounted on an UHV goniometer. The base pressure of the system was 2×10^{-10} Torr. The Si(111) n -doped, mirror-polished single-crystalline samples (resistivity $0.2 \Omega \text{ cm}$) were cleaned by annealing at 1150°C after long-time degassing at lower temperatures. All surfaces prepared as described above consistently displayed intense surface states¹¹ and a sharp 7×7 LEED pattern. Iron silicide films were prepared by solid-phase epitaxy. Fe coverages were measured with a quartz balance, and cross checked by AES.¹² All cited coverages are subject to an estimated error of $\pm 20\%$. Ion scattering spectroscopy (ISS) experiments were performed using an angle-integrating hemispherical analyzer for a He⁺ energy of 500 eV. We estimate a $\sim 90\%$ sensitivity to the topmost surface layer under our experimental conditions.

The electronic structures of FeSi (CsCl) and γ -FeSi₂ were calculated using a first-principles method based on the local-density approximation (LDA) to density-functional theory.¹³ The core electrons are replaced by norm-conserving pseudopotentials.¹⁴ One-electron wave-functions are expanded in the nonorthogonal basis given by finite-range pseudoatomic orbitals,¹⁵ including s , p , and d orbitals, both

for Si and Fe. The matrix elements of the Hamiltonian were computed with two different schemes: (i) using a direct linear combination of atomic orbitals computation within the Harris approximation to LDA,^{15,16} and (ii) from a full self-consistent plane-wave LDA calculation, obtaining the matrix elements by projecting the plane-wave Hamiltonian into the space spanned by the atomic-orbital basis, as in Ref. 17. Both techniques were used and compared in FeSi (CsCl) and γ -FeSi₂, showing satisfactory agreement. A detailed comparison will be presented elsewhere.¹⁸ The approximation implied by the choice of basis set, introduces a deviation in the bands as compared with other LDA calculations.¹⁹ In the energy region studied, it represents a shift of a few tenths of an eV. For example, at the lower edge of the band gap at $\bar{\Gamma}$ relevant to this work, the shift is of 0.4 eV to lower binding energies, indicating that the deviations of the theory with respect to experiment could be partially due to finite basis effects. The use of atomic orbitals is, however, justified by their suitability for the surface calculations described below.

Given the Hamiltonian matrix elements, the electronic structure of the surface is obtained for the actual semiinfinite geometry, neither finite-size nor slab approximations being used. This is accomplished using Green's functions techniques.²⁰ As an approximation in obtaining the surface electronic structure, the Hamiltonian matrix elements are taken unchanged from the corresponding ones in the bulk of the material. The nonorthogonal character of the basis set used is known to improve the transferability of the calculated interactions.²⁰ The electronic structure of the ideal 1×1 surface of FeSi (CsCl)(111) has been calculated using this procedure. A more detailed theoretical characterization of the surface electronic structure requires proper account of the change of the Hamiltonian matrix elements due to the presence of the surface. However, for the very qualitative conclusions of this paper, the used approximation is perfectly sufficient.

A variety of different coverages and preparation conditions were analyzed to produce epitaxial films of the bulk and the metastable phases.²¹ In this paper we concentrate in the experiments performed on silicides characterized by 1×1 LEED pattern (see below). They were grown on different, freshly-prepared Si(111) surfaces, and are stable within a coverage range of 2-6 ML, and a temperature range between 280 and 350 °C. For a deposited Fe coverage of 4 ML, the 1×1 pattern appears around 300 °C, showing a strong asymmetry between the two sets of three 120° symmetrical spots. Annealing to higher temperatures gives rise to the formation of a 2×2 reconstruction, which will be discussed elsewhere.²² The actual stoichiometry of the 1×1 phase deviates slightly from a perfect 1:1 FeSi. Quantitative x-ray-photoemission spectroscopy (Ref. 3) provides a composition for this temperature and coverage range of FeSi_{1-x} ($x \leq 0.1$), i.e., the 1×1 structure corresponds to a slightly defective iron monosilicide, with excess Fe, the actual value of x depending on the annealing temperature and on the initial Fe coverage (for a particular temperature).

The observation of a 1×1 LEED pattern is associated with characteristic features in the valence band. Figure 1 [left, trace (a)] shows a normal-emission photoemission spectrum of a 1×1 surface, taken with an angle of incidence of the light of 75° with respect to the surface normal (p

FIG. 1. Left: normal-emission ARUPS spectra before (a) and after (b) exposing the surface to 20-L CO. Note the quenching of S_1 after CO adsorption. Right: surface termination as probed by ISS. Spectrum (a) corresponds to a clean Si(111) surface, spectrum (b) corresponds to a 1×1 -FeSi (CsCl) surface.

polarization geometry). The 1×1 pattern is characterized in ARUPS by intense emission close to the Fermi level (B_1) and a prominent peak labeled S_1 at -3.5 eV BE in $\bar{\Gamma}$. S_1 is enhanced under p polarization geometry. Trace (b) shows the effect of saturating the surface with CO at room temperature. A strong (but not total) quenching of S_1 is observed, suggesting that this peak is related to a surface state sensitive to CO. The remaining intensity probably is due to a partial bulk contribution at an energy close to the surface-related band S_1 . CO molecules have a very low sticking coefficient on Si atoms, which may be present at the top silicide surface layer.²³ Thus, the adsorption of CO (evidenced by the prominent CO molecular orbitals in Fig. 1, left) demonstrates that the surface top layer contains Fe atoms. In view of the observed quenching, S_1 should contain a significant percentage of Fe orbitals. ISS experiments were performed in order to probe directly the surface termination. Figure 1 (right) shows the results. Spectrum (a) corresponds to a clean Si(111) surface. Spectrum (b) corresponds to a 1×1 FeSi surface. The Fe peak detected in this case demonstrates the presence of Fe in the topmost layer.

The assignment of S_1 to a surface state is reinforced by the results shown in Fig. 2(a). The photon energy was changed in the range from 11 to 27 eV, both for s - (not shown) and p -polarization geometries, while normal-emission spectra were recorded. Note the lack of dispersion of S_1 with $k_{\perp}$, a further support for the assignment to a surface state. A strong intensity dependence of S_1 with the photon energy is also observed in Fig. 2(a). In fact, S_1 intensity resonates for a photon energy of ~ 21 eV. This corresponds to $k_{\perp} \approx 3 \text{ \AA}^{-1}$. This value was calculated assuming a free-electron-like final-state band with an inner potential of $V_0 = 15$ eV. Intensity oscillations of this type have been observed previously for surface states of Cu,^{24,25} Al,²⁵ and epitaxial CoSi₂.²⁶ Following Refs. 24 and 26 this behavior reflects that the surface state wave function oscillates as it decays evanescently into the bulk with a dominant spatial

FIG. 2. Panel (a): normal-emission ARUPS spectra as a function of photon energy. Note the lack of dispersion for S_1 . Panel (b): ARUPS spectra ($h\nu=21.1$ eV) as a function of emission angle along the $\bar{\Gamma}K$ line. Note the strong dispersion of surface peak S_1 . B_1 is a bulk related peak.

frequency about a particular value of $k_{\perp}$. A surface state lying in an hybridization gap is constructed from the bulk wave functions closest in energy. Thus, the surface state has a maximum intensity for a photon energy corresponding to the value of $k_{\perp}$ at which the nonhybridized bands would cross each other.²⁶ The resonance value of $k_{\perp}$ corresponds to $k_{\perp} = \Gamma R/2$ for a CsCl structure, i.e., halfway between Γ and R points. This agrees well with the crossing point of the bands spanning the hybridization band gap. Note that a different crystalline structure of the film is not compatible with this result. In the case of a fluorite structure, the peak would lie within a hybridization gap of the projected bulk band structure, but the maximum would be located close to the L point, because the lattice parameter is double than for FeSi (CsCl). This would be in disagreement with the intensity resonance found, because the bands spanning the gap in a fluorite structure would also cross each other halfway between Γ and L points.

Figure 2(b) presents an overview of selected ARUPS spectra as a function of the emission angle along the $\bar{\Gamma}K$ direction for p polarization geometry. S_1 presents strong dispersion vs the emission angle. Figure 3 shows the projection of the calculated bulk bands along the surface Brillouin zone for FeSi (CsCl). S_1 nicely fits within bulk band gaps of FeSi (CsCl).²⁷ It can be followed along most of the zone, and, as shown in Fig. 3, it displays a 1×1 periodicity, with a strong parabolic dispersion along both the $\bar{\Gamma}M$ and the $\bar{\Gamma}K$ direc-

FIG. 3. Shaded area: projection of the bulk bands along the surface unit cell symmetry lines for FeSi (CsCl). Open circles correspond to experimental points. The calculated surface states are represented by dots for an Fe-terminated surface, and by crosses for a Si-terminated surface.

tions. The symmetry of S_1 is mostly Λ_1 at $\bar{\Gamma}$, with a residual Λ_3 contribution, in view of its dependence with the angle of incidence of light (not shown).

Electronic structure calculations performed for the FeSi (CsCl)(111) surface are shown in Fig. 3. The surface states obtained in the gap between 2.5 and 4 eV below E_F are displayed for both bulklike Si-terminated and Fe-terminated surfaces, together with the experimental results. The Si-terminated surface states exhibit a binding energy and dispersion which do not agree with the experiment. The Fe-terminated surface presents at $\bar{\Gamma}$ two very close surface states of symmetries Λ_1 and Λ_3 , at ~ 4 eV below E_F . Away from $\bar{\Gamma}$ the Λ_3 degenerate states split. One band merges into the bulk states at lower energies, and the other band disperses up in energy, relatively close to the band coming from the Λ_1 state, staying both within the gap. The origin of S_1 can be traced back from the theoretical calculation. It has a major d_{z^2} content, and thus it can be interpreted as being due to the loss of periodicity along the (111) direction, which leaves unsaturated Fe bonds at the surface.

The bulk band structure of FeSi (CsCl) shown in Fig. 3 was calculated assuming a perfect epitaxy (i.e., a lattice constant determined by the Si substrate). However, there are some experimental evidence that suggest that a larger lattice parameter could be preferred for the CsCl structure. To investigate the effects of a possible structural relaxation we have calculated the electronic structure of bulk FeSi (CsCl) with a lattice constant of $2.77 \text{ \AA}$,⁷ 2% larger than the lattice parameter imposed by the Si substrate. The general picture is not modified. The projection of the bulk band structure presents the same shape and band gaps. A general shift of ~ 0.2 eV to lower binding energies and the tendency of the band gaps to become narrower by an amount of $\sim 10\%$ are the most remarkable changes. More precisely, in the energy region shown in Fig. 3, the lower edge of the band gap at $\bar{\Gamma}$ is shifted by 0.39 eV, while the upper edge of this gap is shifted by 0.17 eV. For the $\bar{K}$ point there are two band gaps of interest. For the gap around -3 eV, the shifts are 0.29 and 0.23 eV for the lower and upper edges, respectively, and for

the gap in the neighborhood of -2 eV these shifts are 0.23 and 0.17 eV. All the shifts are toward lower binding energy. From these data we can conclude that the possible increment of the lattice parameter by relaxation of the structure does not modify the validity of the our results, but improves the agreement between the experimental findings and the theoretical calculations by shifting the latter toward lower binding energies. This information can be used as an indication that the real structure could have partially relaxed laterally in addition to vertically. This indication, however, cannot be taken as conclusive, since other effects not included in the calculations could also be the origin of those shifts (for example, the vertical relaxation of the surface and/or the whole film).

In summary, the electronic structure of metastable, epitaxial, 1×1 -terminated, quasistoichiometric FeSi films has been

probed with ARUPS. The results have been compared with first-principles electronic-structure calculations. We conclude that the experiments are compatible only with a CsCl structure. The surface is Fe terminated. The truncation of the Fe bonds gives rise to a prominent and strongly dispersing surface peak located in a band gap of the bulk band structure. Both the overall features of the valence band and the surface state observed are in good agreement with theoretical calculations.

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