Geometric and electronic structure of epitaxial iron silicides


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The geometric and electronic structure of several iron silicide phases epitaxially grown on Si(111)7×7 have been characterized by means of surface sensitive techniques including scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy, ion scattering spectroscopy (ISS), and ultraviolet photoelectron spectroscopy. The silicides were grown by solid-phase and reactive-deposition epitaxy, and their stability range was determined in situ as a function of iron coverage and annealing temperature. In particular, we have studied the phases appearing in the low-coverage low-temperature region. Additionally, the crystallites of the most important FeSi2 phases (γ-FeSi2 and β-FeSi2) have been characterized at atomic level with STM, while the surface termination was analyzed with ISS.

I. INTRODUCTION

The thermal stability and electrical properties of transition-metal silicides explain why these materials are widely used in the microelectronics industry. Most of transition-metal silicides are metallic, and some of them present a very good epitaxial growth on Si (e.g., NiSi2, CoSi2). There exists also a reduced number of semiconducting transition-metal silicides. The possibility of epitaxially growing semiconducting silicides on Si has prompted studies on several of these materials, and in particular on β-FeSi2. This compound presents a direct band gap of ~0.85 eV, a value suitable for the transmission window of optical fibers, and thus its growth could open a new avenue towards integration of optoelectronic materials in Si-based devices. At variance with CoSi2 and NiSi2 (which crystallize in the fluorite structure), β-FeSi2, the phase stable at room temperature (RT), is orthorhombic with a relatively complicated unit cell, containing 48 atoms. However, the cell can be seen as a distortion of the more simple fluorite unit cell. Theoretical calculations have shown that a hypothetical FeSi2 phase crystallizing in the fluorite structure would present a large density of states at the Fermi energy. This fact makes the fluorite unstable, and one may envisage that the actual β-FeSi2 structure could be stabilized due to a Jahn–Teller distortion. The bulk Fe-Si phase diagram presents several other phases which may appear during any epitaxial process as well. We may cite ε-FeSi (with the cubic B20 structure), α-FeSi2 (tetragonal), and Fe3Si (cubic D03 structure). α-FeSi2 is only stable at elevated temperatures, but can be retained metastable at RT when rapidly quenched. Furthermore, there exist surface stabilized phases, presenting a crystalline structure different from the bulk phases. In particular, the FeSi2 phase with the fluorite structure (γ-FeSi2) has been observed. Additionally, an FeSi phase with the CsCl structure has been recently reported. These phases are surface stabilized due to their good lattice-constant matching with the Si substrate, as compared to the more stable bulk phases. The gain in strain energy for the epitaxial film compensates (at least for thin films) the lesser stability of the structure. In this case one would expect the existence of a critical film thickness for such metastable phases. Over the critical thickness, the film should spontaneously revert into the more stable bulk phase.

In this work we set out to characterize the geometric and electronic properties of the phases appearing when solid-phase epitaxy (SPE) and reactive-deposition epitaxy (RDE) processes are performed on Si(111)7×7. In a SPE process, Fe is deposited at RT, and the surface is annealed to increasingly higher temperatures to promote the surface reaction. In a RDE process, Fe is deposited on a substrate held at elevated temperatures. To study the silicides formed, we have employed several surface sensitive techniques, including scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), ultraviolet photoelectron spectroscopy (UPS), and Auger electron spectroscopy (AES). A combination of these techniques is sensitive to the stoichiometry (XPS, AES), geometric structure (STM, LEED), electronic structure (UPS), and atomic composition of the surface (ISS), a point of interest in many cases.

II. EXPERIMENT

The experiments were carried out in two ultrahigh-vacuum (UHV) chambers (base pressure: 1×10−10 mbar). The first one is equipped with XPS, UPS, AES, ISS, and STM. The second one is equipped with an STM head, and a rear-view LEED optics, also suitable to perform AES. The substrates used for the epitaxial growth were Si wafers oriented in the [111] direction. The wafers were of n type (P-doped, 1015 and 1019 cm−3, for photoelectron spectroscopy and STM, respectively). They were introduced in the UHV chamber without previous treatments, and were cleaned by cycles of Ar+ sputtering and annealing to 900°C. A thick Si-buff layer was grown at 600°C to improve the quality of the substrate. No traces of contamination were observed within AES and XPS sensitivity. The samples always presented sharp 7×7 LEED patterns.
Iron was evaporated from a 99.998% pure Fe wire wrapped around another resistively heated W wire. The XPS spectra were taken by using the Mg Kα line (photon energy: 1253.6 eV) in the constant resolution mode of the hemispherical analyzer, while the He I line (photon energy: 21.2 eV) was employed for the angle-integrated UPS spectra. The Fermi level was determined from the emission of thick metallic films. Fe coverages were calibrated from the XPS/AES intensities of Fe and Si, following previously described procedures. In the case of ISS, a primary He⁺ beam of ~500 eV energy was used to obtain information on the atomic composition of the topmost surface layer. The scattering angle was 130°.

**III. RESULTS AND DISCUSSION**

In a previous work we have characterized the phase diagram obtained when RDE and SPE processes are performed on Si(111)7×7,15 following analogous procedures as in the case of Si(100)2×1.13 The phase diagram is reproduced in Fig. 1 for convenience. SPE processes can be represented as vertical lines in Fig. 1 (for a fixed initial Fe coverage, different phases are obtained when the annealing temperature is increased). RDE processes correspond to horizontal lines (the iron amount is increased at fixed temperature). For a detailed exposure on the way the different phases were identified, we refer the reader to Refs. 13 and 15. In short, in the case of films thicker than XPS escape depth (~30 Å), quantitative XPS was used to determine the stoichiometry. Simultaneously, the characteristic density of states was measured with UPS, and the Fe LVV plasmon-loss energy was also determined. The value of this energy depends significantly on the nature of the silicide, and thus it can be used to identify some phases. The results obtained with these techniques for the epitaxial films were compared in some cases to standards measured for single crystalline silicides [ε-FeSi(100), α-FeSi₂(100)] under identical conditions. In the case of thin films, a comparison with UPS data obtained for thicker films was useful. Additionally, AES was used to determine the stoichiometry, although the error was larger than for the stoichiometries determined by XPS in thicker films.

We note that the detailed analysis of the low-coverage region in the case of Si(111)7×7 allowed us to determine the appearance of several phases, not clearly observed on Si(100): γ-FeSi₂, FeSi₁₋ₓ, and FeSi₂. The stoichiometry of Fe₂Si₁₋ₓ was determined with a larger error than for other phases, and thus the identification is only tentative. γ-FeSi₂ and FeSi₁₋ₓ correspond to surface stabilized phases.\(^{11,12}\)

Figures 2 and 3 present photoemission spectra corresponding to two different SPE processes (for initial Fe coverages of 1.9 and 19 ML, respectively). These values have been marked as dashed lines in Fig. 1. The two pro-
cesses comprise an almost complete overview of the electronic structure of the different phases appearing, as seen by UPS. The two bottom spectra of Fig. 2 present the clean Si(111) 7×7 features, and the density of states after deposition of 1.9 ML Fe at RT, respectively. For this coverage, immediate reaction takes place after deposition, resulting in an amorphous overlayer of FeSi, followed by growth of Fe crystallites with Si interdiffused. The average composition of the film corresponds to Fe$_3$Si$_{1-x}$ on the basis of AES measurements. A sharp Fermi edge is observed, together with emissions at 0.5 and 1.4 eV, and a shallow feature at ~3.2 eV. After a mild annealing at 145 °C, two strong peaks at 0.7 and 2.8 eV appear, and a much-broader less-intense Fermi edge is observed. We attribute this spectrum to Fe$_3$Si on the basis of the stoichiometry determined by XPS in the case of thicker films presenting the same UPS spectrum (see next paragraph). When the initial Fe coverage is over 2 ML, only the UPS spectrum of metallic Fe is detected at RT. This fact does not exclude that a reaction takes place at the interface, due to the considerable surface sensitivity of UPS. Nevertheless, Fe$_3$Si$_{1-x}$ is not observed over ~6 ML Fe for any annealing temperature (see Fig. 1). This behavior confirms that it corresponds to a reactive phase associated with the initial stages of growth, and is not observed for thick films. On the contrary, stoichiometric Fe$_3$Si appears in the whole coverage range analyzed, and over ~7 ML is the first phase to nucleate (see Fig. 1). Further annealing up to 270 °C gives rise to a progressive weakening of the Fe$_3$Si features. In the temperature range from 350 to ~600 °C, epitaxial γ-FeSi$_2$(111) appears. The phase was identified on the basis of the UPS features, and STM results (see below). A typical spectrum is presented in Fig. 2 for an annealing temperature of 395 °C. The step height determined by STM for the γ phase (3.2 Å, see below) is in agreement with the fluorite structure. In a narrow temperature range before the formation of γ-FeSi$_2$ (220–300 °C) we have found UPS spectra which may be attributed to FeSi$_{1+x,1}$ (111), the...
ClCs-structure phase of FeSi. A step height of 1.6 Å as determined by STM further supports this assignment. Both γ-FeSi$_2$(111) and FeSi$_{1-x}$(111) present a 2×2 LEED pattern, although the spots are much sharper in the case of γ-FeSi$_2$. Above 650 °C, a 7×7 pattern reappears, and concomitantly the features of clean Si(111)7×7 are observed in UPS, as shown in Fig. 2 for an annealing temperature of 830 °C.

Figure 3 presents a similar process for an initial Fe coverage of 19 ML deposited at RT (bottom spectrum of Fig. 3). The spectrum is typical of metallic polycrystalline Fe, without signs of reaction. For this thickness range, XPS can be used to determine the stoichiometry of the film. A mild annealing to 370 °C produces the formation of FeSi. Further heating in the range from 400 to 550 °C gives rise to e-FeSi formation. e-FeSi does not present any sharp LEED pattern for our growth conditions. The spectrum is characterized by a relatively broad emission centered at ~0.5 eV, and a shallow hump at ~1.8 eV. Further annealing to 830 °C promotes the formation of β-FeSi$_2$. The corresponding UPS spectrum has been previously described in detail. Annealing above ~900 °C destroys the silicide crystallites and the 7×7 LEED pattern reappears. The spectra of β-FeSi$_2$ present a semiconducting character (lack of emission at the Fermi energy), at variance with the metallic γ-FeSi$_2$ ones. In view of Fig. 1, an initial Fe coverage of ~4 ML Fe is enough to produce a silicide layer over the critical coverage for the γ-FeSi$_2$ to β-FeSi$_2$ transformation. Nevertheless, thicker values have been reported for films grown by coevaporation of Fe and Si, which might indicate that kinetic limitations strongly influence the nucleation process of each phase.

Since the γ- and β-FeSi$_2$ phases present characteristic LEED patterns (see Fig. 4), thus indicating long-range ordering, they have been studied in more detail. Figure 4(a) shows a γ-FeSi$_2$(111) 2×2 LEED pattern. The surface is composed of triangular crystallites with the same orientation (not shown, see also Ref. 17). The upper surface of the crystallites [see Fig. 5(a)] presents a hexagonal array of protrusions separated 7.6±0.1 Å, i.e., a distance which will give rise to a 2×2 pattern in the reciprocal space [as in Fig. 4(a)]. Their corrugation is 1.2 Å when empty states are observed, and 0.6 Å in the case of occupied states. The lateral position of the protrusions remains constant when the tunneling bias is inverted and when the absolute value of the bias is changed. This fact, together with the observation of a Fermi level cutoff in photoemission spectra taken under identical conditions (Fig. 2 at 395 °C), suggests that γ-FeSi$_2$ is metallic. The crystallites have the shape of truncated pyramids [see Fig. 5(b)]. The sides of the pyramids present an angle of 108°±5° with the flat top surface, and show the same hexagonal arrangement. A profile along one of these crystallites is shown in Fig. 5(c). The angle expected for two [111] planes in the...
Fig. 7. STM pictures of $\beta$-FeSi$_2$ (110) or (101) taken at different voltages [(a) for $I_e = 0.5$ nA, $V_r = -1.2$ V, and (b) for $I_e = 0.5$ nA, $V_r = 0.64$ V]. The images have been selected from a large series covering positive and negative voltages, and correspond to the same $140 \times 140$ Å region of the surface (the arrow marks the same defect site observed in all the images of the series).

The step height is $3.2 \pm 0.1$ Å, as previously mentioned. Figure 6 presents the information on the surface termination obtained from ISS. The corresponding $\gamma$-FeSi$_2 (111)$ $2 \times 2$ ISS spectrum shows a very small amount of Fe at the surface, which indicates that the surface reconstruction is basically due to Si atoms. A detailed model for the reconstruction has been exposed elsewhere. In short, we propose that the $2 \times 2$ reconstruction is associated with Si adatom reordering at the surface, forming a $2 \times 2$ pattern, similar to the one observed at each half of the $7 \times 7$ reconstruction.

Figure 7 shows two STM pictures of the same surface region of $\beta$-FeSi$_2$, taken at different polarities ($V_r = 0.64$ V, and $V_r = -1.2$ V). In this case, a semiconducting UPS spectrum is observed, as well as a strong variation in the STM pictures as a function of the bias voltage. The LEED pattern belonging to the $\beta$-FeSi$_2$ face of Fig. 7 is shown in Fig. 4(b). The pattern can be interpreted as being due to three different domains of the epitaxy of $\beta$-FeSi$_2$ with the [101] plane parallel to the surface of the Si substrate. The corresponding images in the real space (see Fig. 7) reveal a periodic structure with complex subunits. A detailed interpretation at atomic level of these pictures will be the subject of a forthcoming publication. Finally, the ISS spectrum of the $\beta$-FeSi$_2$ phase (Fig. 6) reveals a certain amount of Fe at the surface. A rough estimation of the surface Fe/Si ratio provides a value of Fe/Si = (0.11 ± 20\%).

IV. CONCLUSIONS

The iron silicide phases appearing during SPE and RDE processes on Si(111)7×7 have been characterized. The metastable $\gamma$-FeSi$_2 (111)$ phase presents structural parameters in agreement with a fluorite structure. The phase is metallic, and the crystallites are Si terminated. The bulk phase $\beta$-FeSi$_2 (101)$ presents a worse epitaxial growth, with three equivalent domains. The crystallites are terminated with a Fe/Si = 0.11 ratio, and a complex atomic arrangement. A new phase has been observed in the low-temperature low-coverage region of the phase diagram. It has been attributed to Fe$_3$Si.

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