Surface characterization of epitaxial, semiconducting, FeSi$_2$ grown on Si(100)

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We have identified the composition and range of thermal stability of FeSi and FeSi$_2$ films grown on Si(100) by solid phase epitaxy and reactive deposition epitaxy. Evidence for the semiconducting character of FeSi$_2$ is obtained from photoemission measurements giving a low density of states at the Fermi level. Si enrichment at the outer surface of the silicides at temperatures much lower than previously thought has been found by depth profiling. Scanning tunneling microscopy reveals a rather inhomogeneous growth with a tendency towards epitaxial growth favored by the presence of surface steps on the Si substrate.

Narrow-gap semiconducting silicides can represent a new avenue towards integration of opto- and microelectronic devices on a single chip. Since the pioneering work of Mahan and coworkers, $\beta$-FeSi$_2$ (with a direct gap of 0.87 eV) has established itself as a promising candidate. Very recently epitaxial films of $\beta$-FeSi$_2$ have been grown on Si(111) and Si(100) by solid phase epitaxy (SPE), molecular beam epitaxy (MBE), and reactive deposition epitaxy (RDE). The films have been characterized by x-ray diffraction, reflection high-energy electron diffraction, and transmission electron microscopy. The evidence for semiconducting behavior comes from resistivity measurements.

In this letter we provide, for the first time, spectroscopic evidence for the semiconducting character of $\beta$-FeSi$_2$ grown on Si(100) and the presence of Si at the external surface of the disilicide film. The latter result may have a profound impact on the capability to further grow epitaxial Si on FeSi$_2$. Preliminary evidence obtained with scanning tunneling microscopy (STM) points to an important role of the steps in the nucleation of epitaxial $\beta$-FeSi$_2$ on Si(100).

The experiments have been carried out in three different ultrahigh-vacuum chambers. The first one was equipped with Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), and low-energy electron diffraction (LEED). The second had capabilities for performing x-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), ion scattering spectroscopy (ISS) and AES. The third one had AES and STM.

The samples were cut from Si wafers oriented to within 1° of the (100) direction and cleaned by Ar sputtering and annealing. No contaminants were detected with AES and/or XPS. Fe was deposited onto the samples by sublimation of a thin Fe wire. The deposited amount has been calibrated by AES. Identical results were obtained in all three chambers. The temperature of the samples was measured by means of an infrared and optical pyrometer calibrated at high (>700°C) temperature against a Pt/Pt-13% Rh thermocouple.

Iron silicides have been formed by SPE following closely the recipes described by Cherief et al. The composition of the resulting phases has been identified by AES, EELS, and XPS. In agreement with the thermodynamic predictions of the Ben show the first silicide formed (at 430–580°C) is FeSi, and FeSi$_2$ is stable from 600 to 800°C. We have verified the accuracy of our determination of the chemical composition by measuring, under the same conditions, single crystals of FeSi(100), $\alpha$-FeSi$_2$(100), and a thick (>100 Å) film of $\beta$-FeSi$_2$.

Evidence for the semiconducting character of the iron disilicide can be obtained from UPS measurements. Figure 1 shows angle integrated UPS spectra of the valence band for clean Si(100), a 20-monolayer (ML)-thick Fe film deposited on Si(100) at room temperature (RT) and annealed at 600°C, where XPS has revealed the formation of FeSi$_2$. Clean Si shows the well-known surface state band at 0.9 eV below the Fermi level, $E_F$, and the bulk derived state at 3 eV. The Fe spectrum shows a high density of states (DOS) at $E_F$ and $d$-derived peaks at 0.7 and 3 eV, in agreement with spectra for bulk Fe. The FeSi$_2$ spectrum shows peaks at 0.8 and 1.5 eV below $E_F$, in accordance with the DOS derived from an $ab$ initio band structure calculation for $\beta$-FeSi$_2$. They are attributed to nonbonding Fe 3d states and bonding Fe 3d-Si sp states, respectively. Furthermore, the density of states at $E_F$ is negligible (an order of magnitude smaller than for metallic, $\alpha$-FeSi$_2$(100)), confirming that the disilicide grown on Si(100) is indeed the semiconducting $\beta$ phase.

$\beta$-FeSi$_2$ has also been grown by RDE at 350°C. As Fig. 2 shows, depositing Fe on a heated Si substrate leads to a ratio of the low energy Fe$_{3d}$/Si$_{3p}$ Auger peaks which increases quickly to a constant value of 0.24. During the rise of the AES ratio the LEED pattern was $2 \times 1$ and the (electron excited) EELS spectrum shows the coexistence of plasma losses from Si at (14 and 11 eV, bulk and surface plasmon, respectively) and FeSi$_2$ (see inset in Fig. 2). These results indicate that, during the early stages of the RDE growth, large patches of the surface are clean Si, while FeSi$_2$ grows as islands without lateral continuity. Above an evaporated thickness of 8 ML of Fe (equivalent), the Fe/Si AES ratio stays constant reflecting the
Fig. 1. Angle-integrated ultraviolet photoemission spectra of (a) a clean Si(100) surface, (b) 20 ML of Fe deposited at room temperature on the Si substrate, and (c) annealed to 650 °C for 5 min. The spectra have been taken at room temperature with a photon energy of 21.2 eV.

Formation of a Fe–Si compound of well-defined stoichiometry. The LEED pattern disappears and the EELS spectrum shows only the characteristic losses of FeSi₂ at 20.4 and 13.9 eV. In these conditions a continuous film of FeSi₂ has formed by coalescence of the islands. The constant value of the AES ratio (0.24) corresponds to a FeSi₂ film covered with a Si bilayer.

Other silicides (CoSi₂, NiSi₂) have Si excess at the external surface when epitaxially grown on Si substrates.

Fig. 2. Ratio of the peak-to-peak amplitude of the Auger transitions of Fe at 47 eV and Si at 92 eV measured during (a) evaporation of Fe on a Si(100) substrate maintained at 350 °C (open dots). The evaporation rate was 1 ML/min. (b) Sputtering with Ar ions (1.5 keV, 17 μA). The continuous line shows the Auger ratio expected for a bulk sample of FeSi₂. The inset reproduces EELS spectra, excited with electrons of 100 eV of kinetic energy, for selected (see the arrows) Fe evaporation times. The known plasma losses from Si and FeSi₂ are indicated in the figure.

Fig. 3. Scanning tunneling microscopy images of FeSi₂ grown epitaxially on Si(100). The images have been obtained with sample bias of +4.55 V (right) and +0.6 V (left), respectively, and 1.4 nA of tunneling current. The lateral dimension of the images is 2400 Å x 2400 Å. Auger spectroscopy performed in situ prior to transfer to the STM, indicates that the Fe/Si ratio corresponds to FeSi₂.

We have verified this possibility in the case of FeSi₂ by means of depth profiling and ISS. The full dots in Fig. 2 reproduce the Fe/Si AES ratio measured during depth profiling of the FeSi₂ overlayer grown by RDE. The Fe/Si ratio increases to a value of 0.4 close to the theoretical value for a bulk FeSi₂ sample (0.44). Since the reported effect of preferential sputtering of Si is negligible in our conditions, the depth profiling experiments confirm both the identification of the silicide and the presence of Si excess at the external surface. Similar findings have been obtained with FeSi₂ layers prepared by SPE at 540 °C. The surface enrichment of Si is expected in silicides in view of the respective surface energies.

STM topographic measurements suggest a possible role of ordered surface steps in favoring the nucleation of the epitaxial β-FeSi₂ phase on (100) substrates. Thin layers of Fe were evaporated at RT on Si(100) surfaces, annealed until AES detected the formation of FeSi₂ and the sample was transferred under UHV to the STM head. In order to check the epitaxial character over selected extended areas, the STM was employed with a large field of view at moderate resolution. Figure 3 reproduces STM images of the in situ grown silicides. The 2400 Å x 2400 Å images show sets of parallel terraces, ≈ 80 Å wide, running along the [110] direction, separated by steps ≈ 10 Å high. The size of the terraces is what one would expect due to the miscutting of the wafer (misalignment of 1° produces terraces of ≈ 78 Å on the average, separated by single-layer steps). Although these images were by no means the general situation—a rather heterogeneous growth has been observed instead—there were portions of the sample where this kind of structure was repeatedly found. The fact that the step density (not the step height) is equal to that of clean Si(100) (not shown), suggests that (at least in these regions of the surface) β-FeSi₂ has grown epitaxially reproducing the surface topography (albeit changing the local slope) of the Si substrate. As there is already some experimental evidence, this points to a crucial role of...
surface steps in achieving epitaxial growth of large grains.

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