Surface morphology of semiconducting iron silicides grown on Si(111)

J. de la Figuera, A.L. Vázquez de Parga, J. Alvarez, J. Ibáñez 1, C. Ocal and R. Miranda
Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

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A surface roughness analysis of β-FeSi₂ films grown by solid phase epitaxy on Si(111) substrates is presented. The composition and stoichiometry of the silicides are determined by X-ray photoemission spectroscopy. Pinholes are detected in thick samples grown by the SPE method. Quantitative measurements of the roughness for different FeSi₂ thicknesses are based on scanning tunneling microscopy imaging of the films. At small lateral scale (hundreds of Ångströms) all the films present similar granular structures at their surface. Contrary, at larger lateral scale (of the order of a micrometer) an extra-roughness is developed for thicker FeSi₂ films. Scanning electron microscopy micrographs of the same samples are consistent with these results and also give the pinhole density of the grown films. Images of an as-deposited iron film on the same substrate strongly support the idea that roughness appears during the solid phase epitaxy growing procedure.

1. Introduction

The surface roughness is an important parameter controlling a variety of phenomena during heteroepitaxial growth. Interdiffusion between metal films and silicon substrates is generally believed to depend on the structural order of the starting Si surface [1]. Electromigration of Al/Si contacts is also strongly dependent on the surface perfection [1]. Preparing the substrates and the films in ultrahigh vacuum (UHV) produces metal/semiconductor interfaces that are much more abrupt than those obtained in high vacuum systems [2]. The crystalline quality during heteroepitaxial growth of Si on NiSi₂ epitaxial films grown on Si(111) is strongly dependent on the surface roughness of the silicide film [3].

Surface roughness measurements can be made based on different experimental techniques. The profilometer method has a poor lateral resolution (100 nm) dictated by the size of the stylus and moderate (1 nm) perpendicular resolution, provided that the mechanical properties of the surface are uniform. Scanning electron microscopy (SEM) can resolve lateral inhomogeneities at a scale of ~10 nm, but the perpendicular resolution is limited and the surface roughness complicated to quantify. Visible light scattering, X-ray diffraction or X-ray reflectivity are sensitive to roughness on a lateral scale difficult to determine, perhaps of the order of a few times the wavelength of the radiation. An instrument to match the performance range of the various techniques with superb lateral and perpendicular resolution is the scanning tunneling microscope (STM).

The epitaxial growth of semiconducting β-FeSi₂ on Si substrates has attracted considerable attention [4–14]. An increased knowledge about the surface topography of this material is of high importance for both understanding metal/semiconductor interfaces and for actual applications in technology. Profiles taken with a stylus instrument have shown that the surfaces of thin films of β-FeSi₂ prepared by high vacuum evaporation of Fe on Si(111) and annealing to 900°C [5–8] are very rough. It has been observed that lower temperatures of preparation (800°C) lead...
to a decrease in surface roughness [8]. In UHV, β-FeSi₂ can be grown at even lower temperatures by a variety of methods, such as solid phase epitaxy (SPE) [9–14], molecular beam epitaxy (MBE) [10], coevaporation and annealing [13] or reactive deposition epitaxy (RDE) [10,13]. It is expected, then, that the surface roughness can be improved by growing the films under UHV conditions. In order to understand and eventually improve the surface roughness of the FeSi₂ layer, we have studied the surface morphology of β-FeSi₂ grown in UHV on Si(111) as a function of the thickness of the silicide. We have used SEM and STM to characterize the surface roughness in the real space.

2. Experimental

Samples with different thicknesses of β-FeSi₂ have been grown by SPE (evaporation of Fe onto Si(111) substrates at 60°C, annealing to 600°C and cooling at 40°C/min) in a MBE chamber. The procedure used to clean the Si wafers, described in detail elsewhere [14], consisted of two stages: ex situ chemical etching and in situ desorption of the native oxide by annealing to 800°C with Si deposition onto the sample. After this treatment, the Si(111) samples always show the RHEED pattern characteristic of the 7x7 reconstruction. Fe was deposited onto the wafer surface and the samples were annealed until the formation of β-FeSi₂ was detected by RHEED [14]. The samples were removed from the growth chamber, visualized by SEM and STM in air and inserted back into another UHV chamber, where they were analyzed by XPS.

The STM used in this work corresponds to the design of Zeglinski et al. [15]. The x-y-z scanning head consists of two concentric cylindrical piezotubes epoxied to a rigid mounting block. The external piezo provides the sample–tip coarse approach and offset. The internal piezo holds and scans the tip. An excellent compensation of thermal drifts can be achieved with this design. Positioning of the sample was carried out by means of a micropositioner based on a stick-slip mechanism. The microscope head was calibrated in air with atomic-resolution images of graphite and on the large scale by Michelson interferometry (z drive) and images of a CD stamper (x and y drives). The calibration factors were 43 Å/V (x and y) and 35 Å/V (z drive), within 10% of the specifications of the supplier. The maximum lateral range in a single image is 2.1 μm. Several micrometer-wide images can be taken piecewise and matched by the computer due to minimum thermal drift. The size of these composed images overlaps those taken by the SEM. The tunneling tip was made by electrolytically etching a 0.8 mm diam tungsten wire. The STM control electronics was supplied by RHK Technology. Image acquisition and processing software of our own were employed. Images of 256×256 pixels have been taken in the constant current mode in a typical time of 2.5 min. A layer of SiO₂ grown at the surface during exposure to air (see below) precludes the achievement of atomic resolution. For the present purpose, the microscope has been used with a large field of view at moderate resolution. The STM images had not been corrected for drifts, piezoelectric creep, nor treated in any way (except for the subtraction of an average plane).

3. Results

Fe deposited at about 60°C has been reported [14] to grow epitaxially with a bcc structure on Si(111), in agreement with earlier LEED/AES studies [16,17]. On the other hand, previous reports for Fe growth at RT on Si(100) have found layer-by-layer growth, but only polycrystalline films without LEED pattern [11]. SEM micrographs indicate that the surface morphology of the as-prepared Fe films was indeed rather smooth. Fig. la reproduces a STM image of an Fe overlayer 3 nm thick taken in air. Platelet-like crystallites of Fe epitaxially aligned with the terraces of the Si substrate are observed. The crystallites are, on the average, 600 nm long, 100 nm wide and 6 nm high. Their surface roughness is very small (less than 0.3 nm). The flatness of the crystallites and the orientation of their edges suggest that they are (111) oriented. As shown in
the large STM image reproduced in fig. 1b, the Fe platelets cover large epitaxial islands of Si, which are probably produced during the cleaning procedure [18]. The shape of these Si islands is hexagonal or triangular with the edges parallel to the \(\langle 11\bar{2}\rangle\) directions of the Si substrate. Ho-

Fig. 1. (a) STM image (1.92 \(\mu m \times 1.87 \mu m\)) of 30 \(\AA\) of Fe evaporated at 60°C on Si(111); (b) composed STM image (4.5 \(\mu m \times 4.5\) \(\mu m\)). The tunneling bias was 1.62 V (sample positive) and the tunneling current was 1 nA. The total grey scale is 295 \(\AA\).
moepitaxial growth of Si on Si(111) in UHV at elevated temperature – the same procedure used here to prepare and clean the Si(111) substrate – has been shown by STM to result in triangular epitaxial islands with bilayer (0.31 nm) height [19].

Following the SPE method, Si samples covered with Fe films of various thicknesses were annealed in UHV to the appropriate temperature to get β-FeSi₂ films [14]. The completion of the reaction can be determined by RHEED as well as by AES, ELS and XPS [11–13]. The β-FeSi₂ film is believed to be oriented with the ⟨101⟩ plane parallel to the Si(111) surface [9]. The lower symmetry of the rectangular unit cell of the silicide allows the formation of three domains. For silicide thickness below 20 nm the samples actually display the three-domain RHEED pattern characteristic of β-FeSi₂. For thicker silicides, no RHEED pattern was observed [14].

The composition and stoichiometry of the deposited films can be obtained from the quantitative XPS formalism developed for homogeneous alloys [20] with a proper calibration of the intensities of bulk Si and Fe. Fig. 2a shows the ratio of the intensities of the Fe 3p/Si 2p core levels in XPS, which gives 0.43 ± 0.02 for FeSi₂ samples prepared by SPE in situ. The accuracy of the XPS calibration was verified by our comparing to an XPS analysis of a single crystal of metallic α-FeSi₂(100). The same ratio for FeSi samples, either (100) single crystal or grown by SPE on Si(100), gives a higher value of the order of 0.9. The plasma losses appearing at lower kinetic energy of the (X-ray excited) Fe LVV Auger peak (see the inset in fig. 2b) can also be used to identify the chemical identity of the silicide [12], as shown by the data reproduced in fig. 2b.

After preparing the samples in the MBE chamber, they were removed from the vacuum system and STM images were taken in air (see below). In order to check the modifications introduced in the surface composition of the samples by exposure to the air they were inserted back into the UHV chamber and XPS analyzed. Wide-scan XPS spectra of the samples after going through the STM indicate only C and O contamination. Additionally, the Si 2p core level displays a chemically shifted component, whose intensity changes with the angle of detection measured from the surface plane, Θθ, as shown in fig. 3. The shifted peak corresponds to a SiO₂ overlayer 1.1 nm thick (as estimated from the angular dependence of its intensity) covering the silicide. The SiO₂ overlayer is produced by oxidation of the silicide upon exposure to air. There is no sign of oxidation of Fe. In this context it should be mentioned that β-FeSi₂ has been shown to be Si-terminated [12].

In the present work, STM images have been taken with large gap resistance.
Fig. 4 reproduces a composed STM image (4 μm × 4 μm) of a 25 nm thick β-FeSi₂ sample taken in air. The image is representative of silicides of smaller thicknesses, in the sense that all the silicide films have a rough surface. The surface mainly consists of grains with a lateral size of 100–150 nm and irregular shape. Since, although oxidized when viewed in air, the as-deposited Fe films are composed of atomically flat crystallites, the surface roughness in the silicides must appear during annealing, probably related to Si interdiffusion through the iron layer. Furthermore, the STM and SEM images prove that the roughness changes systematically with the β-FeSi₂ thickness. For the thinner silicides, the grains could rarely be found forming larger structures similar in shape to the crystallites of the original Fe overlayer.

A quantitative measurement of the surface roughness in STM images can be obtained by computing the root-mean-square (RMS) deviation from the mean surface height:

$$\text{RMS}^2 = \frac{1}{L} \int_0^L [z(x, y) - \bar{z}(x, y)] \, dl$$

where $L$ is the profile length, $z(x, y)$ the actual profile and $\bar{z}(x, y)$ the mean value of the profile. The surface roughness of the silicides is shown in fig. 5 as a function of the profile length, $L$. For a 3 nm-thick β-FeSi₂ film, which looks essentially flat in SEM micrographs, the RMS increases with $L$ until it reaches saturation at a final value of ~4 nm for $L \approx 0.5$ μm. In fig. 5a a typical profile of this surface is reproduced. It shows the grains and indicates that the mean surface is flat, i.e., it maintains a constant ($L$-independent) mean value.

The RMS measurements from a 14 nm thick β-FeSi₂ sample are plotted in fig. 5b. The RMS saturates at a final value (3.5 nm) similar, within the error, to the one corresponding to the thinner silicide. The saturation is reached for profile lengths of the order of 1 μm. Note that, contrary to the thinner silicide, the typical profile now reveals a non-flat mean value. The surface seems to be “modulated” by an extra roughness with long (1 μm) wavelength in the lateral scale. That is what we call large-scale roughness. In general the STM images indicate that now the structure of the initial Fe film is completely lost. Fig. 6 reproduces SEM micrographs of this sample. The images show a number of pinholes. The density of pinholes is $\left(6-7\right) \times 10^6$ cm⁻². Around each of the pinholes a circularly shaped, dark region, can be observed. When the dark circles collide, lighter regions of increased surface roughness are detected. The formation of β-FeSi₂ has been described to occur by transformation of FeSi to FeSi₂ in columns perpendicular to the Si surface, rather than by layers parallel to the surface [8]. These dark regions could be associated to the surface of such columns. The average size of the dark columns is consistent with the long-wavelength modulation seen by STM. Holes were rarely seen in STM images. They seem to correspond to the smallest pinholes seen in SEM.
Samples prepared with a thicker silicide film (~ 25 nm) yield SEM micrographs, reproduced in fig. 7, showing a larger density of pinholes, of the order of (1.6–1.8) × 10^7 cm^-2. The pinholes are larger, while the dark regions around each pinhole have a smaller lateral size than before. Furthermore, the surface roughness due to the coalescence of the dark patches ascribed to FeSi₂ is visually increased with respect to the sample of 14 nm (see lighter regions of fig. 6 for details). The roughness analysis of the STM images corresponding to this surface (fig. 4c) reveals two regimes with different cutoffs: whereas the RMS gets a first saturation value (4 nm) similar to those of figs. 4a and 4b for \( L \leq 1 \) μm, the final RMS saturation reached at large profile lengths (\( L \approx 1.5 \) μm) is nearly twice as large (7.5 nm). A typical profile (fig. 4c) shows that the mean surface is modulated by the large-scale roughness with larger amplitude than in the 14 nm case, but smaller wavelength (0.5 μm). These findings are consistent with the average size of the dark columns and the rougher light regions seen in the SEM micrographs.

4. Discussion

Since the first demonstration of the capability of STM to image technical surfaces in air [21], the quantitative evaluation of surface roughness by STM has remained an unsolved problem. Si surfaces transported in air, where a native oxide layer develops, have been studied by STM frequently [22–25]. For imaging in vacuum, the main tunnel barrier is between the conduction bands of Si and SiO₂ (3.25 eV) with the barrier from the conduction band of SiO₂ to the vacuum (0.9 eV) playing only a minor role. Considering the different tunnel barriers involved (3.2 versus 4.5 eV), the constant-current topographic images are dominated by the Si/SiO₂ interface and not by the SiO₂ surface topography [24]. Larger features are thought to be intrinsic to the surface. Now,
imaging a thin layer of SiO₂ in air, adds the problems derived from the low tunnel barriers commonly found in air and attributed to contamination layers [26]. The barrier heights of these layers range from 1 to 0.2 eV [26].

In the present case, tunneling proceeds through a silicon/silicide/silicon oxide/air barrier. We assume that the SiO₂ layer found by XPS is homogeneous over the sample surface and that the silicide/SiO₂ tunnel barrier, being similar to the Si/SiO₂ barrier, provides the relevant barrier for tunneling. A variation of the location of the silicide/SiO₂ interface (or oxide thickness) by \( d \) changes the tunneling probability by \( \exp[-d(3.2)/2] \). In order to maintain a constant current the tip retracts by \( z = (3.2/0.2)^{1/2}d \). This transforms thickness variations into apparent topographic height changes \( z = 4d \). Since we consider that variations of the oxide thickness larger than 0.3 nm are not reasonable for an average thickness of 1.1 nm, we assume that tip height changes larger than 1–1.5 nm represent topographic features of the imaged surface.

A second problem when imaging rough surfaces is that the STM images are a convolution of structural (and electronic) features of both tip and surface. If the radius of curvature of the tip is smaller than the surface protrusions, the image reflects basically the surface topography. On the contrary, when the radius of curvature of the tip is larger than that of the protrusions, the STM image is determined by the tip structure and may actually consists of a set of identical ghost images of the tip. In fact, ghost images of the tip have been frequently reported [27]. Here, the completely different surface topographies of Fe deposits and silicide films visualized in the same conditions by the same tip allow us to assign the measured profiles essentially to the imaged surfaces and not to the tip.

In conclusion, the absolute values of RMS reported here may be somewhat larger than the “true” surface roughness. The relative values and the long wavelength roughness, however, are significant.

We have found that the surface roughness for \( \beta \)-FeSi₂ films grown in UHV is much smaller (4–7.5 nm) than those grown in high vacuum (15–30 nm). This is due to the lowering of the temperature needed to form \( \beta \)-FeSi₂ under UHV conditions. The surface roughness may depend on the growth temperature because of the wide difference between the thermal expansion coefficients of Si (3 ppm/°C) and silicides (13 ppm/°C) producing tensile stress at room temperature. In this sense, lower temperatures of growth are expected to produce smaller roughness.

We have found that the surface roughness of the \( \beta \)-FeSi₂ film increases with increasing thickness for films grown at the same temperature (600°C). This is due to the appearance of a large-scale roughness with a (thickness-dependent) wavelength of the order of 1 μm. Actually, there are two kinds of roughness at different lateral scale. The small-scale roughness, which is inde-
Fig. 6. SEM micrographs of \(~140\ \AA\) thick FeSi\textsubscript{2} grown by SPE on Si(111) at two different magnifications. The micrograph has been taken with 5 keV of primary energy and detection of secondaries to maximize the surface sensitivity.

dependent of the film thickness, is due to the grains formed at the surface, which have the same size for all the silicides. These grains make them to be essentially identical from the morphological point of view at small scale (less than 1 \(\mu\)m\textsuperscript{2}). The size of the grains is probably determined by the temperature at which the Fe film was annealed to complete the solid-state reaction.

On the other hand, the large-scale roughness, which increases with the film thickness, could be related to the mechanism of formation of \(\beta\)-FeSi\textsubscript{2} by SPE. The reaction produces first FeSi [12],
and then $\beta$-FeSi$_2$ seems to nucleate in columns perpendicular to the Si surface that later grow laterally [8]. Collision of these columns results in a modulated surface with an additional large-scale roughness. Each column surrounds a pinhole in such a way that the increase in the density of pinholes (that occurs as the thickness of the initial Fe overlayer becomes larger) is responsible of the increase in the large-scale roughness after completion of the SPE process. This kind of roughness limits the maximum thickness of epitaxial silicide that can be grown by SPE [14].

Most of these problems may be circumvented by growing $\beta$-FeSi$_2$ by alternate methods such as
coevaporation or RDE. We are presently trying to improve the surface roughness of β-FeSi₂ following this approach. Anyhow, much work still needs to be done in order to find conditions that optimize the surface roughness of these materials.

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References

[18] Since the size of these islands is 2 μm, i.e., much larger than the cut-off in the surface roughness, they do not contribute to the RMS values given below.