

11-13-1992

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Chevrier, J.; Thanh Vinh, Le; and Derrien, J. (1992) "Strained and Relaxed Semiconducting Silicide Layers Heteroepitaxially Grown on Silicon," *Scanning Microscopy*: Vol. 7 : No. 2 , Article 2.

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STRAINED AND RELAXED SEMICONDUCTING SILICIDE LAYERS HETEROEPITAXIALLY GROWN ON SILICON

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(Received for publication May 13, 1992, and in revised form November 13, 1992)

Abstract

The semiconducting silicide β -FeSi₂, which can be grown epitaxially on silicon, is potentially an interesting material for integrated optoelectronic devices. Its semiconducting state stabilised by a solid state Jahn Teller effect is very unusual. Indeed the epitaxial growth of FeSi₂ on silicon (111) in a Molecular Beam Epitaxy (MBE) chamber has revealed the existence of a metallic strained FeSi₂ phase which is *the result of a simultaneous electronic and structural transition*. The stability and the relaxation of this strained phase which is specifically due to the epitaxy of FeSi₂ on the silicon (111) face will be detailed in this paper. Furthermore, depending on the kinetics of the growth, we shall show that it is possible to epitaxially grow, on silicon, any silicide existing at low temperature (bcc Fe, FeSi, β -FeSi₂) and to observe dynamical transitions from the strained FeSi₂ phase toward epitaxial β -FeSi₂ and FeSi.

Key Words: Epitaxial growth, iron silicide, silicon, metal-semiconductor transition, molecular beam epitaxy, electron diffraction, photoemission electron spectroscopy.

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Introduction

In near future, information technology will likely become an important discipline of interest for many scientists. Efficient silicon-based microprocessors with optoelectronic devices are at the roots of these widespread applications. The ability to produce optoelectronic systems on a silicon chip would combine the silicon digital technology with new optoelectronic devices based so far on III - V, II - VI and related semiconducting compounds (SiGe alloys and superlattices).

Recently, semiconducting silicides have been claimed to be an alternative and new avenue towards integration of optoelectronic and microelectronic devices on a single silicon chip (Derrien et al., 1992). Among these promising materials, β -FeSi₂ appears to be a potential candidate since its optical gap is located around 0.85 eV which nicely fits one of the transmission windows of silica optical fibers. Moreover β -FeSi₂ has been clearly demonstrated to be epitaxially grown on silicon both on the (111) face (Derrien et al., 1992, Cherief et al., 1989a, Cherief et al., 1989b) and on the (100) face (Mahan et al., 1990). Furthermore following the work done on III-V and II-VI compounds during the last few years, one may investigate another long term goal in making semiconducting silicides available for the development of a full range of novel integrated optoelectronic devices: the band gap engineering of semiconducting silicides by mixing two binary silicides to form pseudo binary compounds with controlled lattice parameters and energy band gaps (Derrien et al., 1992, Motta and Christensen, 1991).

This paper will report on an extensive study of β -FeSi₂ heteroepitaxy on silicon performed in a molecular beam epitaxy (MBE) chamber and probed with various in-situ and ex-situ surface techniques. The β -FeSi₂ phase which presents at equilibrium a very peculiar orthorhombic structure derived from a distorted fluorite structure, displays an unusual and fascinating behaviour during its epitaxial growth on

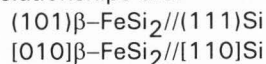
silicon (111) face. Indeed it has been recently demonstrated that a strained cubic metallic FeSi₂ phase can be stabilized by epitaxy on the silicon (111) face (Onda et al., 1992, Onda et al., 1991, Chevrier et al., 1992). The relaxation towards the orthorhombic semiconducting phase has also been observed. This structural and electronic phase transition will be described in this paper.

Specific Properties of β-FeSi₂

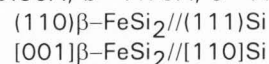
Contrary to closely related transition metal silicides like CoSi₂ and NiSi₂, β-FeSi₂, the compound in equilibrium with silicon at low temperature, is not a metal with a cubic structure but a semiconductor with an orthorhombic structure. The origin of this semiconducting state must be investigated in some detail in order to understand the behaviour of this material. Indeed β-FeSi₂ cannot easily be compared to the common semiconductors (Si, Ge, GaAs...) as its electronic structure is not based on the sp³ hybridisation but on a solid state Jahn Teller effect (Birkholz and Schelm, 1968). This effect is simultaneously the cause of a lattice distortion and a band gap opening at the Fermi level as compared to the metallic state of the fluorite structure of CoSi₂ and NiSi₂. From a general point of view, the occurrence of a solid state Jahn Teller effect in transition metal alloys has been described many years ago (Friedel, 1969, Adler and Brooks, 1967). Recently, a detailed theoretical study of FeSi₂ has shown that a fluorite FeSi₂ phase would be metallic with the Fermi level pinned in a peak of the non bonding d states of iron in the FeSi₂ electronic density of states (Christensen, 1990). Compared to the actual orthorhombic phase, this leads to an instability of the fluorite structure. Therefore the system lowers its energy by undergoing a lattice distortion to relax toward the more stable orthorhombic and semiconducting β-FeSi₂. A cubic FeSi₂ phase does not exist in the equilibrium Fe-Si phase diagram. If the α-FeSi₂ phase found at high temperature (T > 940°C) is metallic, its tetragonal structure has no evident relationship with the fluorite structure.

Epitaxy on (111) Silicon Face

The epitaxial relationships of β-FeSi₂ on the (111) silicon surface have been clearly identified by many techniques (RHEED (Chevrier et al., 1992), LEED (Cherief et al., 1989a), TEM (Cherief et al., 1989b), grazing incidence X ray diffraction (Gay et al., 1993) and also on the (100) silicon surface (RHEED (Mahan et al., 1990)). For the (111) silicon surface which we shall be mostly concerned with in this paper, these epitaxial relationships are:



or as β-FeSi₂ presents an orthorhombic structure with only a small difference in between the b and the c axis (a = 9.86 Å, b = 7.79 Å, c = 7.83 Å):



The differences in lattice parameters are respectively -5.3% (-5.5%) along the [112] azimuth of silicon and +1.4% (+2%) along the [110] azimuth for the (101) ((110)) epitaxy of FeSi₂ on silicon (111). From X ray measurements (Scarinsi et al., 1992), the (101) plane of epitaxy is preferentially found in epitaxial films grown by the SPE techniques, even though local analysis by Transmission Electron Microscopy usually reveals the existence of both orientations (Cherief et al., 1989b). The (101) and (110) faces of β-FeSi₂ have a rectangular symmetry. Together with the hexagonal symmetry of the (111) face of silicon, this rectangular symmetry is at the origin of three equivalent domains formed during the growth. These three domains have been repeatedly identified during the epitaxial growth by RHEED (Chevrier et al., 1992) and by X ray diffraction at grazing incidence (Gay et al., 1993). They are with their boundaries, a source of intrinsic defects in the grown films. Single domain growth of FeSi₂ is certainly an important issue to be achieved for the growth of high quality β-FeSi₂ on silicon.

Current Techniques for Silicide Heteroepitaxy

The most widely used routes to grow epitaxial silicides on silicon are the Solid Phase Epitaxy (SPE) and the Reactive Deposition Epitaxy (RDE) techniques. In SPE, the transition metal film is first deposited on a silicon substrate and during a subsequent annealing, intermixing finally leads to the formation of the compound in equilibrium with silicon (β-FeSi₂ for the Fe/Si system). In RDE, a flux of transition metal atoms is sent on a hot silicon surface. The intermixing takes place readily because the atomic diffusion is well activated. In both SPE and RDE growth techniques, a common feature is that all the silicon found in the epitaxial silicide film is extracted from the silicon substrate. The intermixing and the epitaxial growth are then controlled by the thermodynamics which determine the compound in equilibrium with the silicon and by the atomic diffusion which determines together with nucleation processes, the kinetics of the phase formation.

The major limitations of these two techniques lie in the limited thickness of epitaxial films one can grow and their poor morphology and large roughness. Mechanisms which limit the epitaxial thickness (at about 300 Å for SPE) are not understood in detail. However the huge transport of silicon across the whole film during the growth is definitely at the root of these problems.

Simultaneous deposition of both species from atomic beams is highly desirable to circumvent these effects due to long range diffusion of atoms. It has been used only in few cases for the growth of silicides. A reason for that may be the limited control of the chemical composition during deposition compared to the narrow domain of stoichiometry of disilicides. This is basically due to the use of electron gun evaporators for both the transition metal and the silicon. It remains that the precisely controlled codeposition of both species is a major challenge for the growth of high quality silicide films in MBE machine compared to the SPE and RDE techniques. Indeed during stoichiometric codeposition, exchanges of atoms with the substrate should be avoided. One may then think that surface effects should become the important parameters controlling the epitaxial growth (in the case of RDE or SPE, the whole film is involved at any stage of the growth due to the massive diffusion of silicon across the film).

In the following sections, we shall present studies of epitaxial growth of Fe/Si alloys by two different techniques: a detailed analysis of RDE in the temperature range of 300°C-600°C and preliminary results on codeposition of iron and silicon which clearly show the large difference between the two procedures.

Experimental

Growth on (111) oriented silicon wafers (two-inch diameter) was performed in a MBE machine equipped with silicon and iron evaporation cells. The base pressure of the MBE chamber at room temperature was between 1×10^{-10} and 2×10^{-10} torr. The silicon source was an evaporation cell using a thermally heated graphite crucible. During silicon evaporation, the cell temperature was kept at 1300°C. Deposition of silicon atoms on a silicon surface at low temperature ($T = 200^\circ\text{C}$) enabled us to measure RHEED intensity oscillations during layer by layer growth and therefore the silicon flux (about one atomic layer per 40 sec). The iron flux that we have used was about $1 \text{ \AA}/\text{min}$ and it has been kept constant for all experiments presented in this article. Cleaning of the silicon was based on two stages: i) an ex situ chemical etching following the classical Shiraki procedure ii) a desorption of the protective oxide by heating the wafer at 800°C associated with an atomic beam of silicon directed onto the surface. Such a treatment resulted in a reproducible, clear 7×7 reconstructed silicon surface.

Results presented here mainly come from in situ RHEED and photoemission spectroscopy experiments, our MBE apparatus being equipped with a 10keV electron gun and connected to a multitechnique analysis chamber with UPS (ultra

violet photoemission spectroscopy) and XPS (X ray photoemission spectroscopy) facilities. For RHEED experiments, the grazing angle of the electron beam with the surface was about one degree. A camera periodically took pictures of the RHEED patterns (the acquisition period could be changed from 10 pictures/sec up to 1 picture/day) which were stored in a computer. Image analysis was then performed. Intensities of diffraction spots were extracted from the RHEED pattern. The temperature control was better than 1°C for both the substrate and the evaporation cells as it was measured on their own thermocouple. The accuracy of the temperature measurement was controlled on the crystallisation of amorphous silicon and on the $7 \times 7 \leftrightarrow 1 \times 1$ transition at the silicon surface: the temperature shift should not be larger than 10°C - 20°C . After the epitaxial growth in the MBE chamber, samples were transferred to the analysis chamber. During sample transfer, the vacuum was about 10^{-9} torr. UPS and XPS measurements were performed using the Helium I radiation at 21.2 eV and the Al K α radiation at 1486.6 eV, respectively. During the UPS measurements, the base pressure in the analysis chamber was 3×10^{-8} torr of helium. Spectra have been recorded for both UPS and XPS using a hemispherical V.S.W. analyser with a diameter of 150mm. The energy resolution determined at the Fermi level of a clean silver foil was about 100 meV. We have used XPS to determine the chemical composition at the surface and UPS to characterise the electronic properties of the grown film.

Results

Iron flux on a heated silicon surface: RDE between RT and 600°C

At room temperature or slightly above ($T < 80^\circ\text{C}$), we observed the growth of an epitaxial film of pure iron. The thickness of this epitaxial film had been extended to 2400Å. It is not an upper limit, probably larger thicknesses could be obtained. During the growth of this film, the RHEED pattern of the iron surface slowly became typical of a transmission diffraction pattern. This is what is usually observed for a rough surface. This gradual change from a flat iron surface to a rough surface during the growth has been analysed as the signature of kinetic roughening. An analysis of this effect which is of some importance for the MBE growth can be found in reference (Chevrier et al., 1991).

As the **substrate temperature** is increased ($T \sim 300$ - 350°C), thermal diffusion of silicon is activated. During deposition of iron on a silicon (111) face, at temperatures between 300°C and 350°C, RHEED patterns recorded as the growth proceeded, displayed completely different features: at the beginning of the iron deposition until the

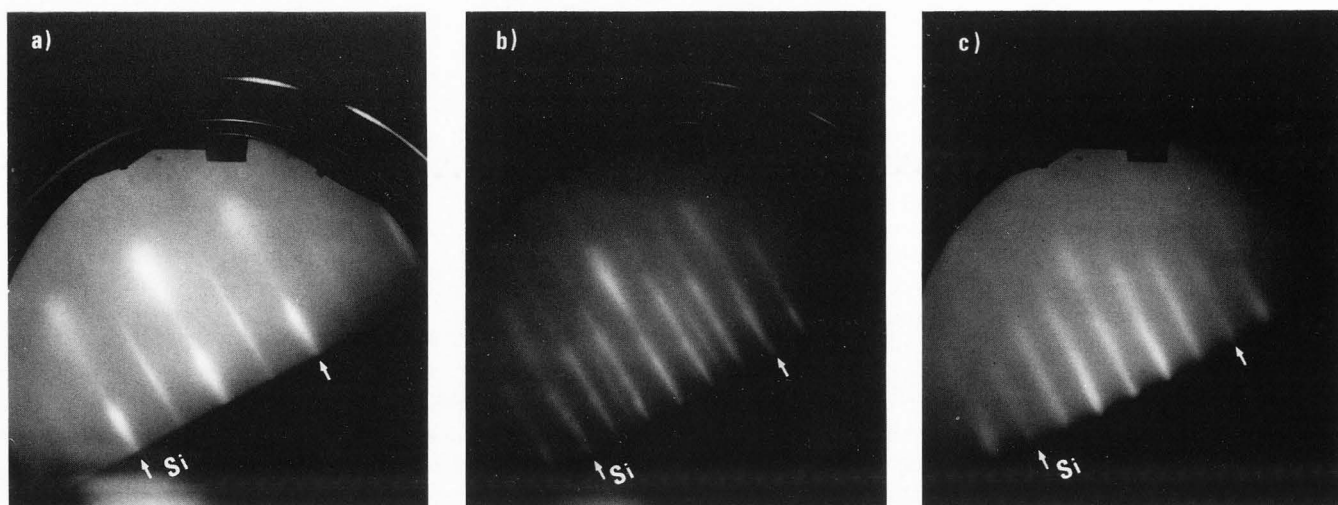


Figure 1: RHEED patterns along the [112] silicon azimuth during iron deposition on a silicon substrate at $T=350^{\circ}\text{C}$: a) the initial strained FeSi_2 evidenced by a 2×2 surface structure; b) coexistence on the RHEED pattern of the 2×2 and the $\sqrt{3} \times \sqrt{3}$ $R30^{\circ}$ surface structures; c) after completing the transition from the strained FeSi_2 to FeSi : the $\sqrt{3} \times \sqrt{3}$ $R30^{\circ}$ surface structure

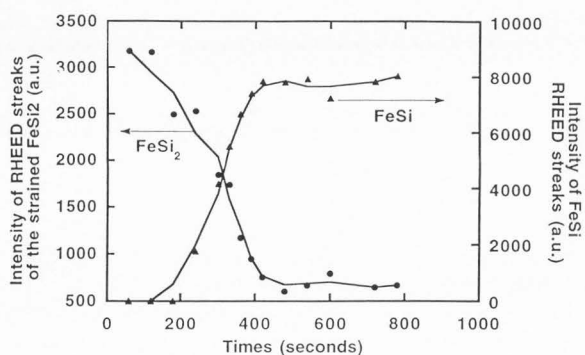


Figure 3: Plot of intensities of characteristic RHEED peaks of the strained FeSi_2 phase (half order peak) and of the FeSi phase (peak located at $1/3$ in the RHEED pattern).

equivalent thickness of a pure iron film of about 5\AA , the epitaxial growth of iron was no longer observed but instead a 2×2 surface structure was seen. At the precision of the RHEED, the lattice parameter of this structure measured parallel to the surface is equal to the one of silicon: it is a strained thin film. Furthermore, the RHEED streaks observed on the electron diffraction pattern (Figure 1a) exhibit remarkable features. Streaks which are at the location of 1×1 silicon diffraction streaks display localised spots at positions which form on the whole screen, a rectangular lattice. Along the [112]

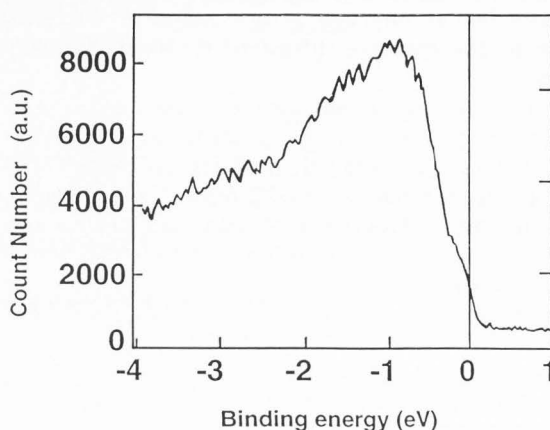


Figure 2: UPS spectrum measured on a thin film of the FeSi_2 strained phase.

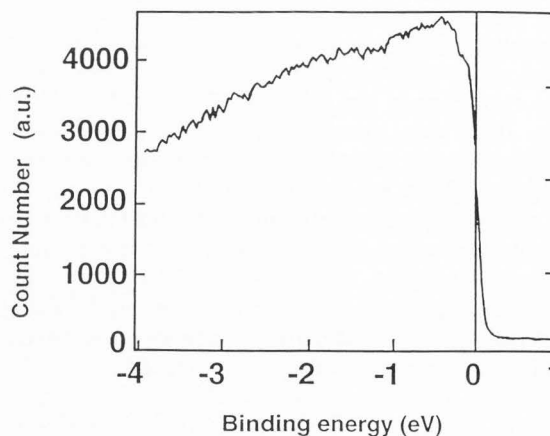


Figure 4: UPS spectrum measured on a thin film of the FeSi phase.

azimuth of silicon, this can be analysed as the electron diffraction of a rough surface of a cubic crystal. Analysis of the RHEED pattern on the [110] azimuth leads to the same conclusion. The RHEED streaks on this phase are consistent with a cubic phase and a 2×2 surface reconstruction. One can notice that this result has been repeatedly reported for silicides with a fluorite structure like CoSi_2 (Derrien and Arnaud d'Avitaya, 1987, von Kanel et al., 1987). Taking into account only the phases described in the Fe-Si equilibrium phase diagram, no clear analysis has been found to describe this phase and its epitaxial relationships with silicon. XPS and UPS measurements have been performed on this phase. The ratio measured by XPS between Fe3p and Si2p peaks is quite close to what has been measured for $\beta\text{-FeSi}_2$. As it can be seen in figure 2, the measured UPS spectrum clearly exhibits an important peak at energies just below the Fermi level (at about 1.5 eV below it). This is expected for a Fe-Si compound with an important d-band character due to iron atom non bonding states. A more detailed analysis shows that the curve presents a clearly defined bump right at the Fermi level energy. This is a strong indication of a metallic character as also noticed in (Onda et al., 1992). As the film thickness increased beyond 5 \AA equivalent iron, an important and gradual structural change is observed by RHEED. At this stage of the growth, the 2×2 diffraction pattern is gradually disappearing and instead the characteristic diffraction patterns of $\sqrt{3} \times \sqrt{3} \cdot R30^\circ$ surface structure emerged (figure 1. b-c). This is an irreversible transformation from the growth of the strained phase characterised by a 2×2 surface structure to the growth of the FeSi compound characterised by the $\sqrt{3} \times \sqrt{3} \cdot R30^\circ$ pattern. This transition is quantitatively described in figure 3. During the growth, no experimental parameters we can control were changed. Therefore such a transformation is a dynamical change occurring during the growth. UPS measurements performed on this FeSi phase (figure 4) are quite different from the results obtained on the previous phase and they present the characteristic shape of FeSi as it is reported in reference (Egert and Panzner, 1984). In some references, FeSi is reported to have a narrow gap at the Fermi level (Aronsson et al., 1965). If this gap exists, its width is not large enough so that we could measure it taking into account the resolution of our spectrometer. In our measurements, FeSi is found to have a strong metallic character.

At higher temperatures of the silicon substrate, between 400°C and 450°C , a new régime has been observed. Still at the beginning of the growth, RHEED patterns were again characteristic of the 2×2 surface structure. Again during the growth, a gradual change occurred in the same range of thicknesses. But the appearing phase is no longer an epitaxial

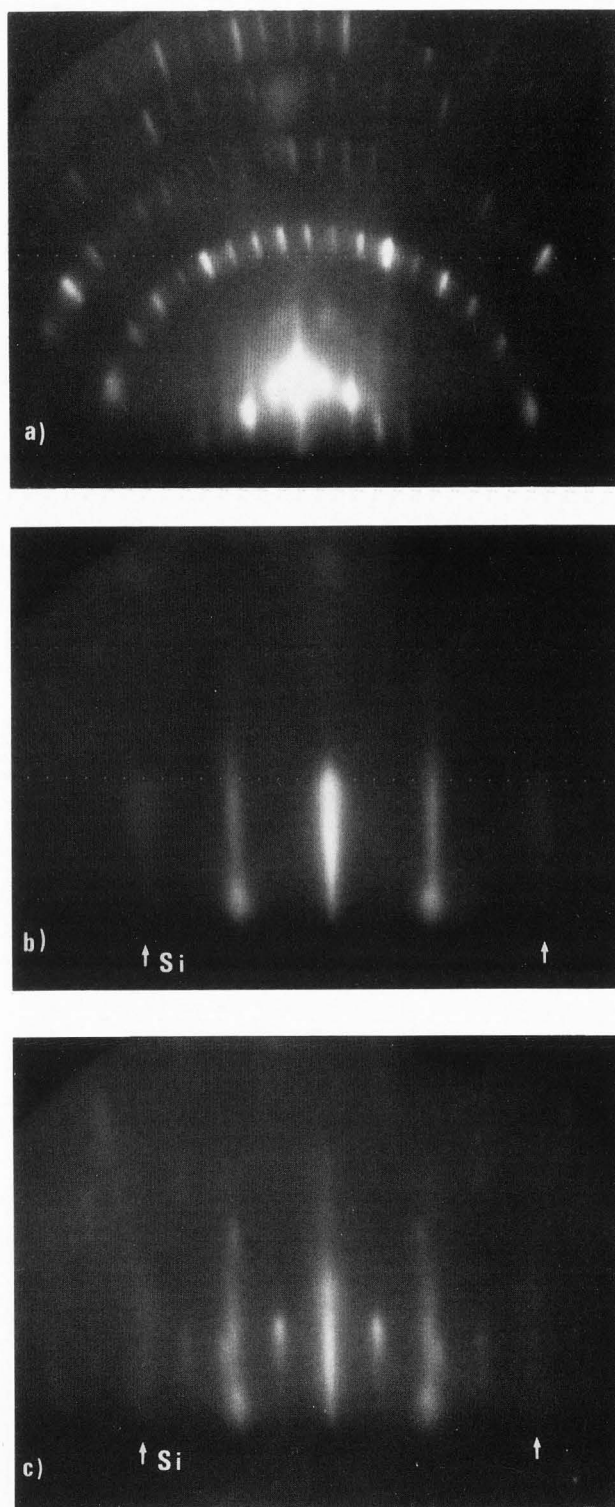


Figure 5: RHEED patterns along the [112] silicon azimuth during iron deposition on a silicon substrate at $T=450^\circ\text{C}$; a) original silicon diffraction pattern; b) the strained FeSi_2 evidenced by a 2×2 surface structure; c) after the transition, the relaxed $\beta\text{-FeSi}_2$ phase.

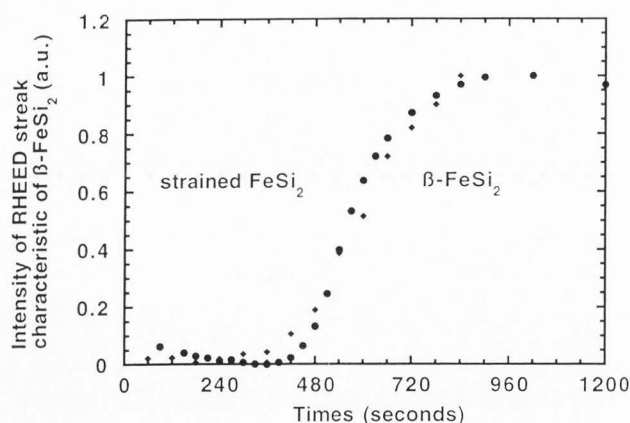


Figure 6: Plot of the intensity of the 1/4 peak characteristic of β -FeSi₂ versus the deposition time. Two different experiments are reported to show how reproducible are the results. The critical thickness for the relaxation can be directly determined: $e_c(\text{FeSi}_2) \sim 30\text{\AA}-40\text{\AA}$.

FeSi phase but instead the β -FeSi₂ phase, the compound which is normally in equilibrium with silicon. The relaxation of the strained phase toward an epitaxial β -FeSi₂ film is well identified. The usual epitaxial plane of β -FeSi₂ on the silicon (111) face with the three domains are definitely observed. In figure 5c, for the [112] azimuth of silicon, the RHEED patterns of β -FeSi₂ is shown. The 1/4 and 3/4 diffraction streaks observed in this figure are the signature of the transformation of the strained phase into the three domain structure of the relaxed β -FeSi₂. A quantitative analysis can be performed by following the RHEED intensity of the 1/4 peak. It is presented in figure 6. This is a direct measurement of the structural transition of the strained phase toward the relaxed phase. It enables us to determine the critical thickness of the strained phase FeSi₂ at 450°C for a RDE growth.

UPS spectrum on β -FeSi₂ is presented in figure 7. Our UPS measurements on β -FeSi₂ are consistent with already published results (Onda et al., 1992). At lower energy than the Fermi level (about 1 eV below), like in other Fe-Si compounds, the strong d band character is present. At the Fermi level, the curve presents a very low intensity which appears as the tail of a decreasing signal. Taking into account the energy resolution of our spectrometer, this result indicates that β -FeSi₂ presents a semiconducting character. It should be emphasized that the measured signal for β -FeSi₂ and for the strained FeSi₂ phase are clearly different even though the chemical compositions of both phases are experimentally identical.

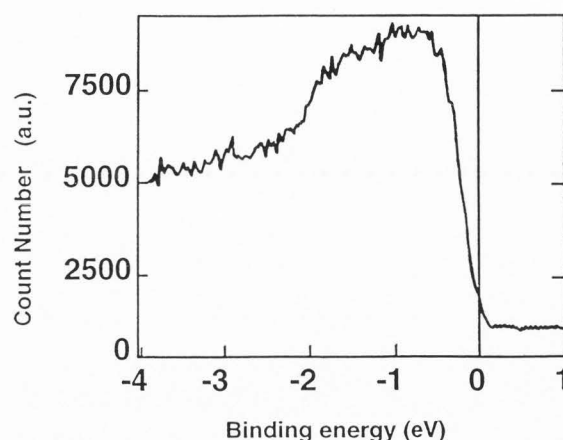


Figure 7: UPS spectrum measured on a thin film of the β -FeSi₂ phase

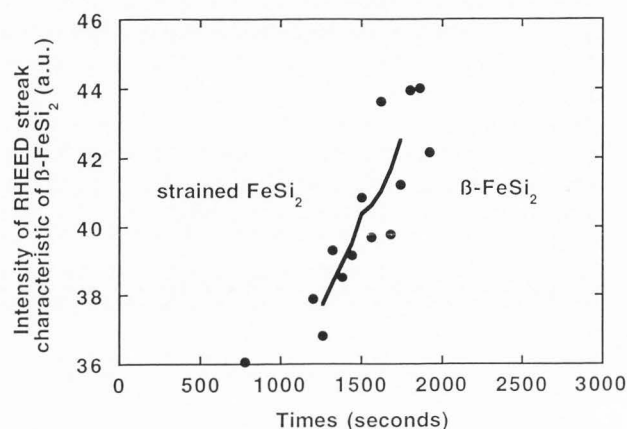


Figure 8: Plot of the intensity of the 1/4 peak characteristic of β -FeSi₂ versus the deposition time during codeposition at 300°C. This critical thickness can be compared with figure 6.

Codeposition of iron and silicon.

The experimental results presented in this section are based on alternated deposition of iron and silicon. Within the precision of our atomic fluxes, we have tried to deposit periodically one layer of iron and two layers of silicon. The aim of these experiments compared to the RDE technique is to obtain an epitaxial growth of β -FeSi₂ without exchange of atoms with the substrate. In these preliminary results, the lack of precision on the fluxes makes the growth of a stoichiometric alloy without any contribution of the substrate rather questionable. We have then performed the codeposition at $T=300^\circ\text{C}$, a temperature at which the diffusion of silicon is already efficient as shown by RDE. However the silicon atoms added in the growing film by means of the silicon atomic beam

completely change the growth characteristics. At the beginning of the growth, the 2×2 reconstruction characteristic of the strained FeSi_2 is observed on the RHEED screen as it is the case for RDE growth. But as the film is becoming thicker, the behaviour is completely changed. At the typical thickness of the $\text{FeSi}_2 \rightarrow \text{FeSi}$ chemical transition seen during a RDE growth and at a temperature of the substrate about $T=300^\circ\text{C}$, no large change is now observed with codeposition. It is only at a thickness about 5 times larger that another structural transition is definitely observed. In these codeposition experiments, the transition was the relaxation of the strained FeSi_2 toward the relaxed $\beta\text{-FeSi}_2$. This result which is reported in figure 8 shows the great influence of the silicon diffusion in RDE growth on the stability of the strained phase. In the case of RDE, the thermal limitation of the silicon diffusion across the film was an effect strong enough at $T=300^\circ\text{C}$ to induce a chemical transformation of the growing film. During codeposition at $T=300^\circ\text{C}$ of both species, silicon and iron, this chemical transformation does not occur any more in the thickness range we have investigated and only a limited exchange of silicon with the substrate is presumably used only to lock the chemical composition at the stoichiometry. We then have an experimental evidence for the relaxation of the strained phase FeSi_2 toward the $\beta\text{-FeSi}_2$ in a case where the silicon diffusion is very much limited. It is then noticeable that the critical thickness measured during codeposition is larger than the one measured at the same temperature during an RDE experiment.

Conclusions

The study of the growth of iron silicides on silicon has shown that all the low temperature phases found in the equilibrium Fe-Si phase diagram (bcc Fe, FeSi, $\beta\text{-FeSi}_2$) can be grown epitaxially on silicon (111). The Reactive Deposition Epitaxy has enabled us to describe the transition between a strained phase of FeSi_2 and the two silicides FeSi and $\beta\text{-FeSi}_2$ during the growth. These transitions are controlled by the kinetics of intermixing and the silicon diffusion across the growing film. This is further demonstrated by the fact that during codeposition, the large chemical change seen on the surface during the RDE growth can be prevented. Only the transition between strained $\text{FeSi}_2 \rightarrow \beta\text{-FeSi}_2$ remains during simultaneous deposition of iron and silicon at 300°C .

However to analyse all the experimental results presented above, two experimental parameters have to be taken into account. First the RHEED technique is a highly surface sensitive technique. This means that we have a limited information on the final structure of the grown film. It remains to determine

if the structure of the film is homogeneous despite apparent change in the epitaxial growth or if it is a *layered* structure. Also the critical thickness measured could be quantitatively dependent upon the iron flux coming on the surface. This dependence as the iron flux is changing remains to be investigated.

Within the framework of this conference, a special emphasis must be put on the nature of the strained phase. From the electron diffraction and the spectroscopic experiments together with structural analysis of reference (Grimaldi et al., 1992), this strained phase is inferred to be metallic and cubic. This is a specific effect of the epitaxy on the silicon (111) face. Due to the difference in lattice parameters between Si and $\beta\text{-FeSi}_2$, a thin growing film is submitted to a tensile strain. Experimentally this strain effect is strong enough to induce both a structural and an electronic transition from the orthorhombic semiconducting state stabilised by a Jahn Teller effect toward this metallic and cubic phase. The relaxation clearly observed during growth defines a critical thickness above which $\beta\text{-FeSi}_2$ is stabilised. To our knowledge, this is quite a unique effect and it appears very unlikely that classical theories of strain relaxation in epitaxial growth are going to apply to this case where the relaxation couples both an electronic and a structural transformation.

Indeed epitaxial growth is not known to induce any electronic transition in conventional semiconductors. This emphasizes the difference in stability between these semiconducting materials and $\beta\text{-FeSi}_2$. On the other side, the stabilisation of this strained phase by the epitaxial growth opens a new way for metallurgical studies on nanometer scale of materials submitted to epitaxial strain.

Acknowledgements

We thank S. Calisti and J.P. Dussaulcy for technical assistance. This work has been supported by the European Community through the Esprit Basic Research Action Project no. 3026. Grants from the French Ministère de la Recherche et de la Technologie (Contrat n. 88R0973 and 90S0249) and from the PIRMAT-CNRS are also gratefully acknowledged.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.