Epitaxial films of semiconducting $FeSi_2$ on (001) silicon

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Epitaxial thin films of the semiconducting transition metal silicide, beta-$FeSi_2$, were grown on (001) silicon wafers. The observed matching face relationship is $FeSi_2(100)/Si(001)$, with the azimuthal orientation being $FeSi_2[010]||Si\langle 110\rangle$. This heteroepitaxial relationship has a common unit mesh of 59 $Å^2$ area, with a mismatch of 2.1%. There is a strong tendency toward island formation within this heteroepitaxial system.

Beta-$FeSi_2$ is a direct, narrow-band-gap semiconductor[1] that offers the possibility of epitaxial growth on (001) oriented silicon substrates. The material is of considerable interest for the development of near-infrared light sources and detectors within the silicon microelectronics technology. Its development for optoelectronic applications will depend, in all probability, upon the availability of epitaxial films on silicon. Although the Bravais lattice is orthorhombic and there is no close lattice parameter match to silicon in the conventional sense, an acceptable "lattice matching"[2,3] is still achievable via the formation of a coincidence net with a small mismatch and a reasonably sized unit mesh common to the matching crystallographic faces of the two materials.

For growth on (111) oriented silicon substrates, the epitaxial tendencies of beta-$FeSi_2$ were first noted by Cheng *et al.*[4] and interfaces of impressive quality have been recently reported.[5] For growth on (001) oriented silicon substrates, epitaxy has been reported only for very thin films (corresponding to less than 25 Å of deposited metal).[6] A milestone will be reached with the growth of films of a structural quality and thickness meeting the needs of optoelectronic device development. We report here the growth on (001) silicon of what appear to be large-area single-crystal beta-$FeSi_2$ films of several hundred angstroms thickness.

Beta-$FeSi_2$ possesses an end-centered (on the *a*-face) orthorhombic Bravais lattice, with lattice parameters $a = 9.863$ Å, $b = 7.791$ Å, and $c = 7.833$ Å.[7] The silicide unit cell's "*a* face" itself offers a reasonable prospect for a common unit mesh with the silicon (001) face. Oriented with $FeSi_2[010]$ parallel to a $Si\langle 110\rangle$ direction, this common unit mesh is of 59 $Å^2$ area. One example of the proposed heteroepitaxial relationship, and its common unit mesh, are illustrated in Fig. 1. Along the $FeSi_2[010]$ direction the room-temperature mismatch is 1.6% and along [001], it is 2.1%.

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Since the bulk Si(001) face is of fourfold symmetry, there are two distinct but equivalent azimuthal orientations for $FeSi_2(100)$ on Si(001). These may be represented by $FeSi_2[010]||Si[110]$ or $Si[\bar{1}10]$. This fact may be problematical because it should lead to the formation of rotation twins. The relative crystallographic azimuthal orientations of the expected twins differ by a rotation of 90° about the $FeSi_2$ [100] direction. Twins of each orientation should be equally probable unless special steps are taken during film growth. In one study, the rotation twins were reported to be not observed with low-energy electron diffraction.[6]

We grew $FeSi_2$ films on (001) silicon wafers, obtaining similar results with both reactive deposition epitaxy (RDE—deposition of metal onto a hot silicon substrate), and molecular beam epitaxy (MBE—codeposition of iron and silicon in stoichimetric proportion at high temperature) if the same growth temperature were used. The iron and silicon were deposited using electron beam evaporation

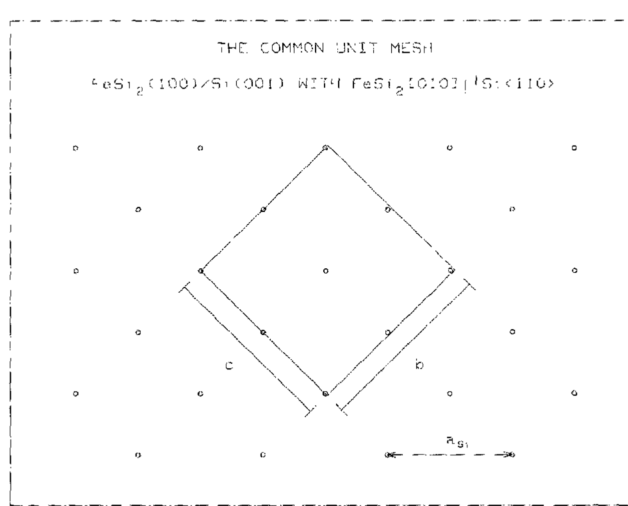


FIG. 1. Proposed heteroepitaxial relationship and common unit mesh for beta-$FeSi_2$ and the (001) silicon face. It is the relative orientation that is suggested; the relative position is merely assumed.

sources, with the iron deposition rate being typically 0.5 Å/s. The selected substrate temperature was maintained with a graphite heater, a feedback controller, and a tungsten-rhenium thermocouple near to or in contact with the back side of the rotating substrate. Although the base pressure of the growth system is in the 10^{-11} Torr range, the pressure was typically in the mid 10^{-9} Torr range during growth.

The substrate surface was prepared as follows: First, the wafer was removed from its box, etched for 30 s in buffered HF solution, and loaded immediately into the sample introduction chamber of the growth system. The wafer was then transferred to the growth chamber and brought to 200 °C over approximately a 3 min period. Next, the wafer temperature was raised to 400 °C as quickly as possible and held there for 15 min. During this time there was a sharpening of the silicon 2×2 reflection high-energy electron diffraction (RHEED) pattern (which typically appeared at ~250 °C), and the Kikuchi lines (visible initially at room temperature). The substrate preparation was concluded with a "silicon beam clean"[8] (the exposure of the surface to a silicon flux corresponding to a deposition rate of 0.2 Å/s for 250 s at 700 °C). The silicon beam clean resulted in sharper and brighter RHEED and Kikuchi patterns, suggesting that a smooth and atomically clean surface existed for the film growth.

We observed a variety of matching face relationships and azimuthal orientations among the films we grew.[9] We will describe the results for films typically of several hundred angstroms thickness (except for samples grown for x-ray diffraction analysis, which typically requires films of several thousand angstroms thickness), grown at 450–550 °C. Within this growth temperature range, we found with Bragg–Brentano x-ray diffraction a strong preference for the matching face relationship of Fig. 1. This diffraction technique samples the crystalline planes which are parallel to the substrate's surface. The patterns of numerous samples were quite similar to that of Fig. 2 (which was obtained from a ~5000-Å-thick film grown at 450 °C by MBE).

One observes, in Fig. 2, three diffraction peaks at angles corresponding to silicide (h00) planes. The peak positions which are given in the figure were calculated from the above lattice parameters. One also observes reflections from the

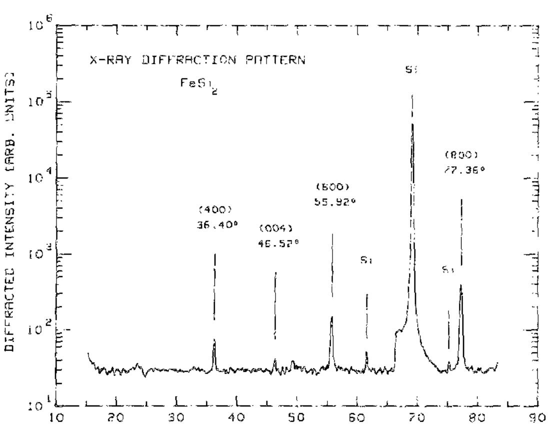


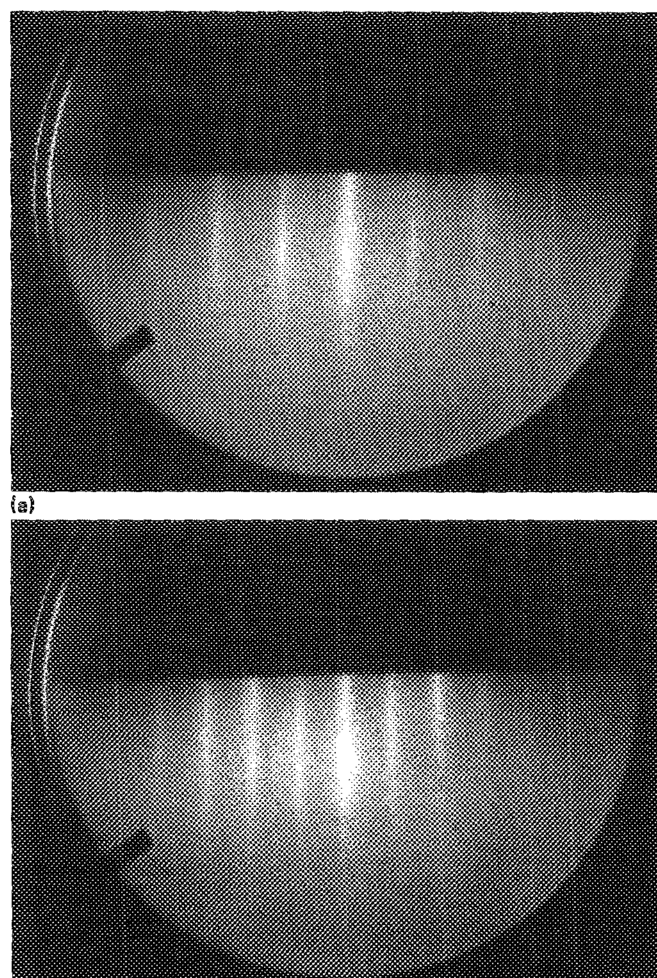
FIG. 2. Bragg–Brentano x-ray diffraction pattern for a ~5000-Å-thick beta-$FeSi_2$ film grown by MBE at 450 °C.

silicon substrate—the copper k-alpha (400) reflection at 69.1° and the k-beta (400) reflection at 61.7°. Finally, there is an additional film reflection at ~46.3°. We attribute this peak to a beta-$FeSi_2$ (004) or (040) reflection. Noting the logarithmic scale of the pattern, one should recognize that this peak is relatively very weak.

There are no other reasonable matches for beta-$FeSi_2$ reflections to the (h00)-labeled peaks in Fig. 2. In addition, there are no reasonable matches for alpha-$FeSi_2$, a high-temperature tetragonal phase which possesses a metallic band structure.[10] Thus, Fig. 2 suggests a very strong tendency toward the matching face relationship of Fig. 1.

Our identification of the phase formed as beta-$FeSi_2$ is supported by verification of the film compositions with Rutherford backscattering spectrometry. Measurements on a number of films grown at 500 and 550 °C indicated an Fe/Si ratio that agrees with the stoichiometric composition to within experimental error (±10%).

Observations of RHEED patterns during and after growth suggested that the films are well aligned with the substrate in azimuthal orientation as well as in matching face, and that they are smooth on a scale at least as large as the coherence length of the incident electron beam (~100 Å).[11] We show, in Fig. 3, two representative RHEED patterns for films grown by depositing 100 Å of iron at 500 °C



(a)

(b)

FIG. 3. RHEED patterns for $FeSi_2$ grown by deposition of 100 Å of iron at 450 °C with the incident electron beam along (a) Si(110) and (b) Si(100).

Intense streaks of two distinct spacings are seen, with the incident electron beam respectively along Si⟨110⟩ [Fig. 3(a)] and along Si⟨100⟩ [Fig. 3(b)]. The well-developed streaks are characteristic of a smooth surface of an epitaxial film.

The observed RHEED streak spacings are in agreement, to within the accuracy of the measurements, with the values predicted for the (100) $FeSi_2$ face with the incident electron beam along $FeSi_2$⟨010⟩ [Fig. 3(a)] and along $FeSi_2$⟨011⟩ [Fig. 3(b)].[9] Each pattern is repetitive with azimuthal rotations of the sample of any multiple of 90°. Thus, the expected azimuthal orientation as illustrated in Fig. 1, $FeSi_2$[010]||Si⟨110⟩, is confirmed by RHEED.

Structural characterization by transmission electron microscopy (TEM) also suggests that epitaxial films were obtained. We show, in Fig. 4, a transmission electron microscopy plan view and transmission electron diffraction pattern for a film grown by RDE by depositing 100 Å of iron at 500 °C. The contrast in the bright-field plan view is due to lateral variations in film thickness; however, no grain boundaries were seen for this or lower magnifications. TEM examinations of a number of samples confirmed a strong tendency toward island formation within this heteroepitaxial system. Somewhat thinner films grown at this temperature exhibited the spotty but highly oriented RHEED pattern characteristic of a discontinuous epitaxial film. While the surface morphology has not been optimized, the film is nevertheless of an apparently large-area single-crystal structure.

The electron diffraction pattern shown in Fig. 4 is representative of those obtained from all regions of the 3-in-diam sample. The strong, clear diffraction spots are a composite pattern due to both the film and the silicon substrate. This experimental pattern is consistent with a kinematically calculated composite pattern for film and substrate aligned as was portrayed in Fig. 1.[9] Thus, the predicted heteroepitaxial relationship is also confirmed by TEM analysis.

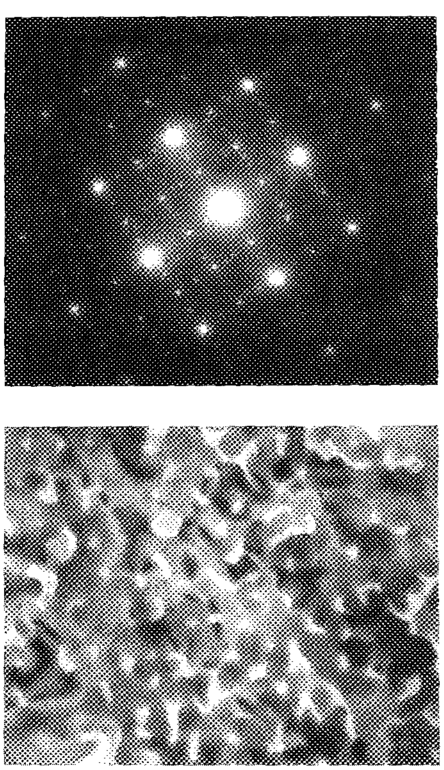


FIG. 4. Transmission electron microscopy plan view (100 000×) and electron diffraction pattern. An area 700×900 nm^2 is shown. The 100 keV incident electron beam was aligned with Si[001].

We would like to review two potential problems with the above characterization of epitaxy in this system. First, the expected rotation twins were not detected. We know of no aspect of the substrate preparation which would have favored kinetically one of the two distinct but equivalent azimuthal orientations. As a practical matter, the experimental observation of a twinned microstructure may be difficult because the b and c lattice parameters are very similar, differing by only 0.5%. Second, the (004)/(040) x-ray diffraction peak, which was observed with a relatively thick sample, may indicate a tendency toward a deterioration of the epitaxial relationship for relatively thick films. We did not detect regions of this texture in the thinner films with any of the techniques available to us.

In conclusion, $FeSi_2$ films were grown which possess a very high degree of epitaxial alignment with the silicon substrate, even though there is a strong tendency to islanding. The questions of the existence of rotation domains and of the possibility of pseudomorphic growth require additional research. We have indications that the film morphology may be improved by growth at lower tempeatures.[9] Nevertheless, these present results lend support to the belief that films suitable for optoelectronic device development may be obtained.

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