Surface electron-diffraction patterns of β-FeSi$_2$ films epitaxially grown on silicon

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Semiconducting β-FeSi$_2$ is drawing much current research interest because of hoped-for silicon-based optoelectronics applications. The study of heteroepitaxial film growth on silicon depends heavily upon several transmission and reflection electron-diffraction techniques. Because of the complicated crystal structure of this material, the possibility of competing heteroepitaxial relationships, the propensity for formation of epitaxial variants by rotation twinning, and the uncertainty in the crystalline surface nets, the analysis of experimental diffraction patterns is complicated. A theoretical reference for a number of fundamental electron-diffraction patterns is provided and they are illustrated with a broad range of experimentally obtained patterns from the surfaces of epitaxial films. *In situ* transmission reflection high-energy electron diffraction (RHEED) (transmission electron diffraction with conventional RHEED instrumentation), from rough but epitaxial films, is of great utility and quite feasible with epitaxial systems such as this one, which exhibit a tendency toward islanding. The possibilities for experimentally distinguishing, with this technique, the competing epitaxial relationships on Si(111) are clarified; it is found that the β-FeSi$_2$(110) matching face is certainly present in these samples and the (101) may be also. An experimental determination of the two-dimensional space groups of the (100), (110), and (101) faces is also presented—in the first and third cases the surface unit meshes are different from the simple projections of the bulk crystalline unit cell.

I. INTRODUCTION: SURFACE ELECTRON DIFFRACTION IN β-FeSi$_2$

There is increasing research interest in β-FeSi$_2$ as an optoelectronic material in the form of epitaxial films on silicon substrates.[1] Electron diffraction plays a crucial role in the microstructural characterization of the films. Because of the complex crystal structure, the occurrence of competing heteroepitaxial relationships, and the propensity for forming epitaxial variants within a single epitaxial relationship, the calculation of theoretical transmission electron-diffraction patterns sometimes requires considerable effort from those who may not be specialists in the field. The same is true for reflection diffraction patterns and, for surfaces of fundamental interest, the two-dimensional space groups have not previously been clarified.

β-FeSi$_2$, when grown as epitaxial films on silicon wafers, exhibits a strong tendency to form islands, rough but continuous films, or sometimes films containing pinholes (although smooth films are also obtainable under the right conditions).[1-4] It has been observed by many researchers that such epitaxial films, which do not present a smooth surface, can exhibit transmission diffraction patterns when examined with conventional RHEED (reflection high-energy electron diffraction) equipment. The grazing incidence RHEED beam is able to pass through surface asperities and generate a transmission diffraction pattern similar to one obtained more conventionally with cross-sectioned samples in the TEM (transmission electron microscope). While rough surfaces are generally not desirable in practical applications, the transmission RHEED phenomenon is most useful for *in situ* phase identification and for determination of the heteroepitaxial relationship within the high-vacuum MBE (molecular-beam epitaxy) growth chamber. Furthermore, a quantitative analysis of transmission RHEED patterns can provide a characterization of the evolution of surface morphology during growth.[5] One certain advantage of transmission RHEED over conventional TEM diffraction is the avoidance of laborious sample preparation. The other forms of surface electron diffraction whose results will be considered in this article, besides transmission RHEED, are conventional (reflection) RHEED and LEED (normal incidence, low-energy electron diffraction).

During the growths of many dozens of epitaxial β-FeSi$_2$ films, we have found that it is possible to grow both rough and smooth ones, whose surface morphology is manifested as RHEED patterns in the form of conventional streaks (smooth films) or spots (rough films). Our basic technique was reactive deposition epitaxy (RDE, the deposition of iron onto a silicon substrate held in the general temperature range of 500–700 °C); other growth proce-

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dures were also explored, including solid-phase reactive epitaxy (SRE, the deposition of iron onto a cold substrate followed by thermal reaction), solid-phase epitaxy (SPE, codeposition of iron and silicon onto a cold substrate followed by thermal reaction and/or regrowth), and simple annealing after reactive deposition epitaxy. (Molecular-beam epitaxy—MBE, the codeposition of iron and silicon in stoichiometric proportion—has not been pursued thoroughly by us at the time of writing.) All of the films whose results are discussed in this article were grown in ultrahigh-vacuum MBE growth chambers and on well-ordered and atomically clean silicon surfaces.

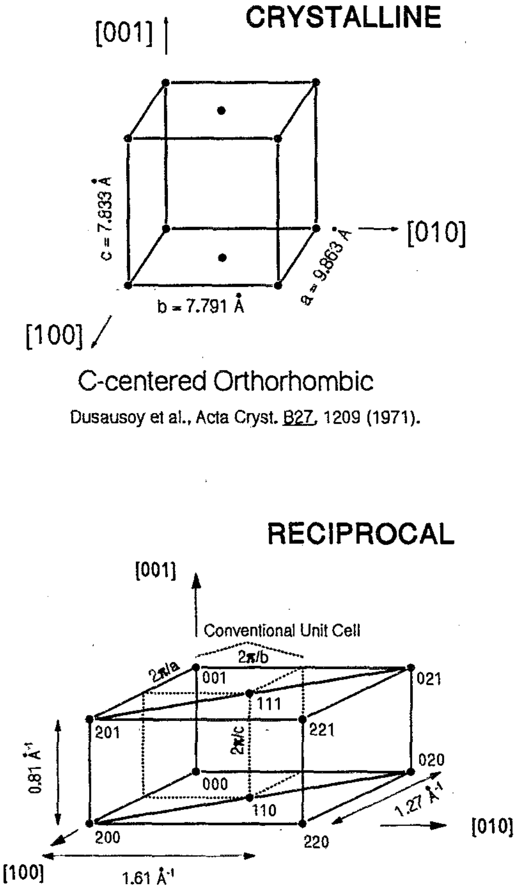
Our general observation is that roughness is dramatically increased whenever there is a need for massive up-diffusion of silicon from the substrate as with SRE and in contrast to SPE, for example. Roughness is also increased within the RDE growth mode as the growth temperature is increased, and can be rationalized as being permitted by increased surface mobility of the iron adatoms.

The purposes of this article are (i) to provide a registry of the relevant theoretical diffraction patterns as predicted from the reciprocal lattice, (ii) to illustrate them with examples of all of the above types of surface diffraction patterns, (iii) to clarify the possibilities for experimentally distinguishing the possible heteroepitaxial relationships, particularly with *in situ* transmission RHEED, and apply this knowledge to films grown on Si(111), and (iv) to present determinations of the space groups of the surfaces relevant to epitaxy on Si(001) and (111). Fundamental plan-view transmission diffraction patterns are presented in the Appendices.

II. PRELIMINARY CRYSTALLOGRAPHIC DATA

The most widely accepted source of information on the crystal structure of β-FeSi$_2$ is the article by Dusausoy *et al.*[6] The space group of β-FeSi$_2$ is Cmca (D_{2h}^{18}), no. 64 of the *International Tables for X-ray Crystallography.*[7] The unit cell of the end-centered crystalline lattice is shown in Fig. 1. Figure 1 also portrays the unit cell of the reciprocal lattice, which is indexed in the conventional way.

Although the slight difference between b and c is crucial for heteroepitaxial lattice matching, it is not so for the basic structure of the transmission diffraction patterns. Consequently, we have assumed $b \sim c$ in our calculation of the reciprocal lattice vectors; the b and c directions remain quite distinguishable in the transmission diffraction patterns because while the b axis is parallel to the centered face, the c axis is perpendicular to it. However, it will be seen that the b and c directions are not distinguishable in the surface reflection diffraction patterns, unless one's experimental apparatus provides much higher resolution than is customary. Thus, transmission patterns are sometimes necessary for distinguishing among the possible heteroepitaxial relationships.



Dusausoy et al., Acta Cryst. B27, 1209 (1971).

FIG. 1. The unit cells of the crystalline and reciprocal lattices of β-FeSi$_2$ are end-centered orthorhombic, with the extra lattice points centered on the c face by convention. The lengths of the reciprocal lattice vectors were calculated assuming $b \approx c = 7.8$ Å and $a \approx 9.9$ Å. The conventional crystalline unit cell on which the Miller indices are based is that of a simple orthorhombic lattice having the same parameters.

The space-group extinctions (beyond those which are customarily referred to as systematic absences and which are already absent from the reciprocal unit cell in Fig. 1) are portrayed in Fig. 2, which shows an extended portion of the reciprocal lattice. The extinctions exist only in two planes of the reciprocal lattice—the $l=0$ plane (where the centered points are extinguished) and the $k=0$ plane (where alternate rows of points are extinguished). We will derive the expected transmission diffraction patterns from Fig. 2.

On the other hand, while the bulk crystal structure is well known, there has never been an explicit determination

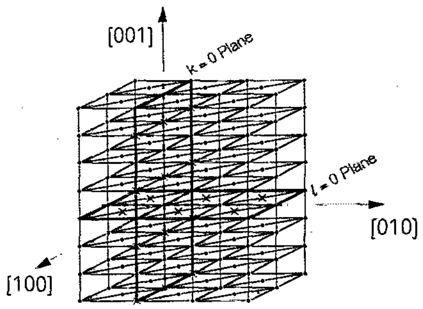


FIG. 2. An extended portion of the reciprocal lattice is shown, indicating points that are space-group extinguished.

or clarification of the structure of any fundamental surfaces of this material. The two-dimensional space groups are experimentally determined in this article from observed surface reflection-diffraction patterns.

III. PREVIOUSLY OBSERVED HETEROEPITAXIAL RELATIONSHIPS FOR GROWTH ON Si(001) AND (111)

The two heteroepitaxial relationships that have been observed for epitaxial films grown on the Si(001) face are[2,3]

type A: FeSi$_2$(100)/Si(001)

with FeSi$_2$[010]||Si⟨110⟩,

and

type B: FeSi$_2$(100)/Si(001)

with FeSi$_2$[010]||Si⟨100⟩.

The matching face parts of these two relationships are identical, but the azimuthal orientations differ by a rotation of 45° about the substrate surface normal. As illustrated in Fig. 3, there are two possible epitaxial variants for each type. (The epitaxial variants may also be called "rotation twins." They develop as "forced twins" during growth because of the symmetry difference between epilayer and substrate in the absence of any mechanism which would select one variant at the expense of the other.)

It is possible to grow films of predominantly one or the other epitaxial orientation, or films composed of domains of each type, but the type-A orientation has been found to pertain to the better quality epitaxial films which have been grown on Si(001) to date.[3] The two possible orientations are easily distinguished *in situ* by observing in the conventional RHEED pattern the 45° rotation of the surface reciprocal net about the substrate surface normal. In the following two sections of this article we will focus on the surface diffraction patterns which pertain only to the type-A orientation.

For growth on Si(111), the observed heteroepitaxial relationships are[8,9]

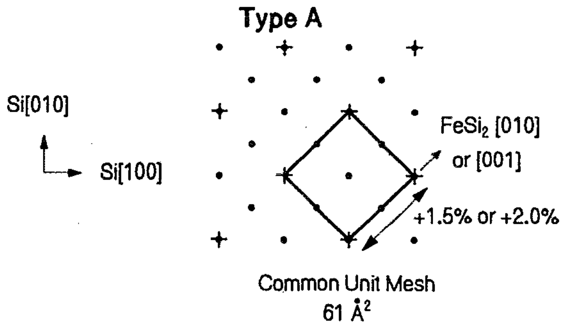
FeSi$_2$(110)/Si(111) with FeSi$_2$[001]||Si⟨011⟩,

and

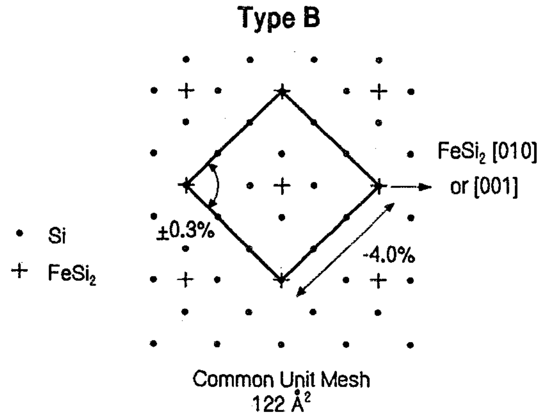
FeSi$_2$(101)/Si(111) with FeSi$_2$[010]||Si⟨011⟩.

(These two possibilities have not been given "type" designations.) Figure 4 shows the three possible epitaxial variants for each of these two heteroepitaxial relationships. In all the work of which we are currently aware, all the possible epitaxial variants of a given heteroepitaxial relationship [for growth on both (001) and (111) substrates] occur, resulting in composite diffraction patterns. This seems to be true even when a deliberate attempt is made (at least with SRE or RDE techniques), in using slightly misoriented substrates, to select a single variant.

In the past, these two orientations have been reported to coexist within the same films.[8] Researchers have not previously found easy and certain means to determine which of the two possibilities exist in a given film, nor a clear indication of which would be preferred for practical considerations. Although there is at present no well-established means to select only one or the other heteroepitaxial relationship through growth procedures, the (101) matching face has in certain circumstances been found to be dominant in SRE-grown films and the (110) with RDE.[10]



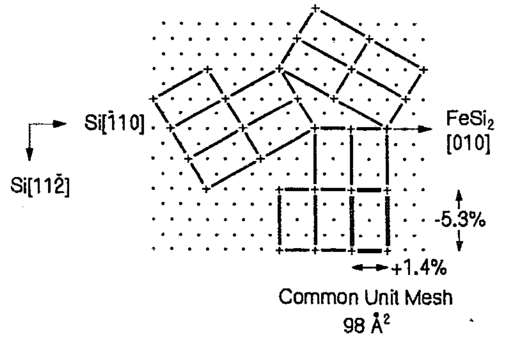
FeSi$_2$(100)/Si(001) with FeSi$_2$[010]||Si<110>



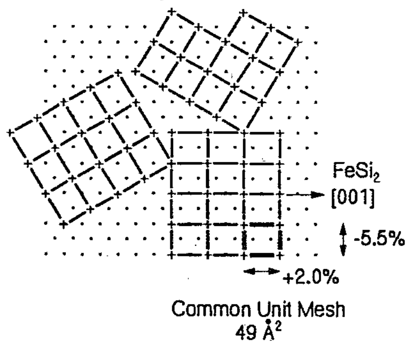
FeSi$_2$(100)/Si(001) with FeSi$_2$[010]||Si<100>

FIG. 3. Lattice matching of β-FeSi$_2$ to the Si(001) face has been observed experimentally to occur under two different heteroepitaxial relationships. They have the same matching faces, but different azimuthal orientations with respect to the silicon lattice. In addition, for each type, there are two distinct but crystallographically equivalent epitaxial variants.

For epitaxy on Si(111), there is a second type of twinning that could occur. In addition to the possible azimuthal rotations of 120° among crystallographically equivalent directions of the substrate surface, there could be a rotation of 180° such that the β-FeSi$_2$[001] direction [assuming the (110) matching face] is along either Si[$01\bar{1}$] or Si[$0\bar{1}1$]. Although these antiparallel directions are not crystallographically equivalent on the Si(111) face, they are similar enough that this type of twinning has been observed many times in the case of epitaxial NiSi$_2$(111)/Si(111).[11] [When the cubic NiSi$_2$[110] direction is parallel to Si[110], this is type A; when it is parallel to Si[$1\bar{1}0$], that is type B; these are unrelated to the type designations A and B which



FeSi$_2$(101)/Si(111) with FeSi$_2$[010]||Si<110>



FeSi$_2$(110)/Si(111) with FeSi$_2$[001]||Si<110>

FIG. 4. Lattice matching of β-FeSi$_2$ to the Si(111) face has been observed experimentally to occur, as for Si(001), under two different heteroepitaxial relationships; however, they correspond to two different matching faces. For each relationship, there are three distinct but crystallographically equivalent epitaxial variants.

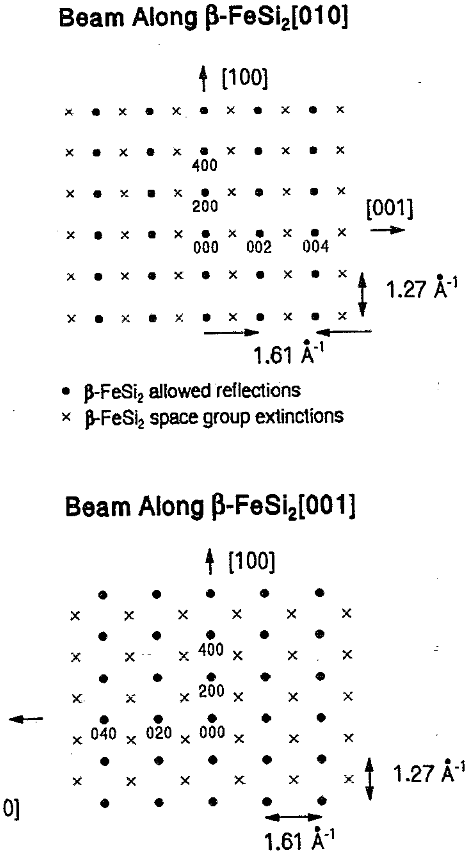


FIG. 5. Two individual β-FeSi$_2$ diffraction patterns as derived from Fig. 2, with the corresponding dimensions from the reciprocal lattice indicated. They belong to each of the two possible epitaxial variants; space-group extinctions make them indistinguishable. They should be seen together for a twinned type-A film on Si(001) with the incident beam along a Si⟨110⟩ direction.

pertain to films grown on Si(001).] This behavior may be extrapolated to the case of β-FeSi$_2$ because its crystal structure is a distortion of the cubic fluorite structure and one may establish a correspondence between the two lattices.

This 180° twinning was not manifested in any of the electron-diffraction patterns we have investigated to date, although it could have been if such twinning did indeed occur. In the one study of this phenomenon of which we are aware, the β-FeSi$_2$ film was found by x-ray diffraction to be in the pure type-B orientation and no regions corresponding to type A were found.[12] It is shown below that electron-diffraction patterns can reveal whether both types are present together in a sample but cannot positively identify either type if present as an untwinned film. It is our opinion that the options for preparing β-FeSi$_2$ films are so varied that it may be possible in the future to observe this type of twinning.

These epitaxial relationships are characterized by a few highly symmetrical electron-diffraction patterns which are seen with the incident beam along certain fundamental directions of the silicon substrates. Twinning results in the observation of composite diffraction patterns. Next, we present these theoretically predicted patterns, illustrate *them* with various experimental views, and try to clarify the possibilities for distinguishing the heteroepitaxial relationships which were mentioned above.

IV. SURFACE TRANSMISSION DIFFRACTION PATTERNS FOR TYPE-A EPITAXIAL FILMS GROWN ON Si(001)

Figure 5 presents two fundamental transmission diffraction patterns for β-FeSi$_2$ which were derived from Fig. 2. They pertain to an incident beam direction along a Si⟨110⟩ direction for the type-A azimuthal orientation, and each belongs to one of the two epitaxial variants. The two variants cannot be distinguished in this instance because space-group extinctions render these two patterns experimentally identical.

Figure 6 gives two possible experimental views of these patterns, via transmission RHEED or conventional TEM cross-sectional diffraction as calculated using standard procedures.[13] In the former, the silicon streak positions are indicated for reference; in the latter, the positions of the Si⟨110⟩ bulk diffraction spots are shown.

We present in Fig. 7 two experimental transmission RHEED patterns for type-A films, with the incident beam

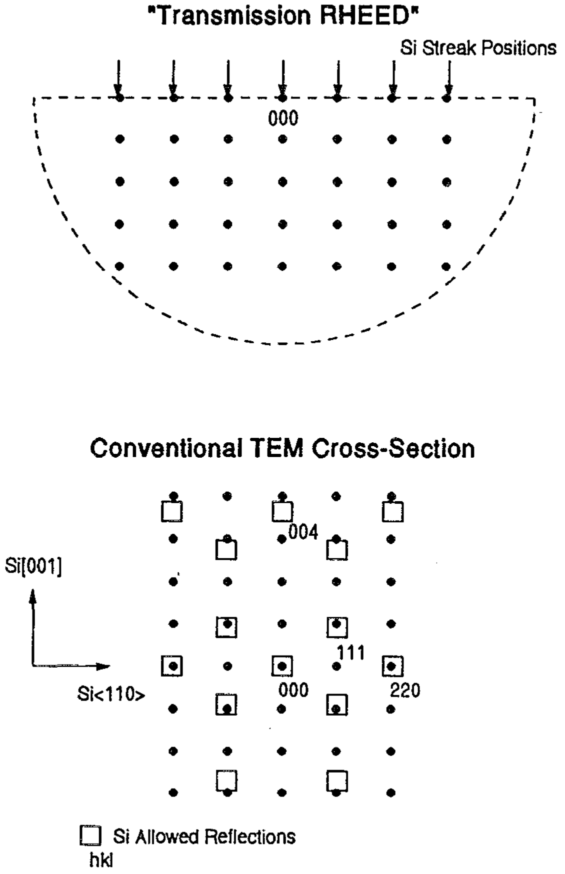


FIG. 6. The diffraction pattern of a twinned type-A β-FeSi$_2$ film grown on Si(001), with incident beam along Si$\langle 110\rangle$, may be viewed either with transmission RHEED from a rough film, or with conventional cross-sectional electron diffraction in the transmission electron microscope. The theoretical positions of the Si RHEED streaks and bulk diffraction spots are indicated for reference.

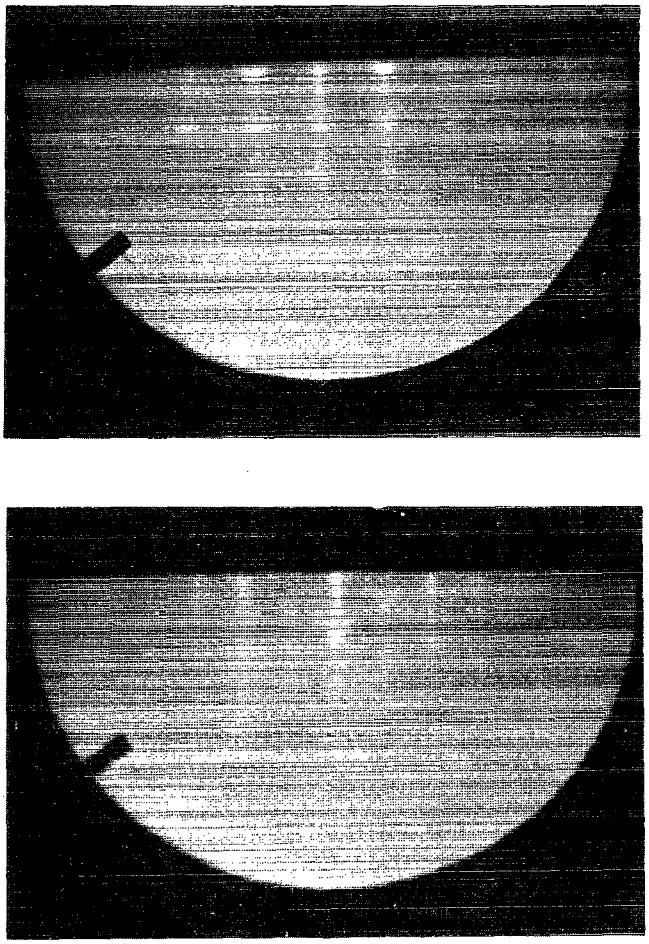


FIG. 7. Transmission RHEED patterns for an epitaxial type-A β-FeSi$_2$ film grown on Si(001). The incident beam is (a) along a Si$\langle 110\rangle$ direction and (b) along a Si$\langle 100\rangle$ direction.

along Si$\langle 110\rangle$ and $\langle 100\rangle$ directions, respectively. These patterns actually have a mixed spot-streak character. The spot features are due to the transmission diffraction process with a rough surface, as just described; the streak features are due to surface reflection diffraction from regions of the epitaxial film which are sufficiently smooth and large.

For the case of the incident beam along a Si$\langle 110\rangle$ direction, the experimental pattern is an excellent representation of the predicted RHEED pattern as presented in Fig. 6(a). From our prior observations of silicon RHEED patterns, the vertical columns of spots are at the correct lateral spacing as predicted. Because of the use of a nonzero angle of incidence, the specular spot is in the horizontal row which is second from the top.

In Fig. 8(a) we show a conventional TEM cross-sectional diffraction pattern with the incident beam along Si$\langle 110\rangle$. It is an excellent example of the theoretically predicted pattern in Fig. 6(b). The reader may notice the forbidden Si 200 spots which occur by double diffraction.

Figure 9 presents a third fundamental β-FeSi$_2$ transmission diffraction pattern which was derived from Fig. 2. It pertains to an incident beam along a Si$\langle 100\rangle$ direction for the type-A azimuthal orientation. The patterns are identical for each of the two possible epitaxial variants. The relevant beam directions are, for example, along FeSi$_2$[011] and [01$\bar{1}$]. Possible experimental views of this pattern are depicted schematically in Fig. 10, again with appropriate silicon substrate diffraction features for reference.

This pattern for an incident beam along Si$\langle 100\rangle$ is very nicely revealed in the transmission RHEED pattern of Fig. 7(b). This RHEED pattern is also of mixed spot-streak character, but the centered rectangular array of spots is very distinct. It should be clear that the heteroepitaxial relationship may be unambiguously determined from transmission RHEED patterns such as those of Fig. 7.

The TEM cross-sectional diffraction pattern for incident beam along Si$\langle 100\rangle$ is also shown in Fig. 8(b). There is excellent agreement between it and the predicted pattern of Fig. 10(b).

The experimental diffraction patterns of these twinned epitaxial films grown on Si(001) are as predicted from the reciprocal lattice; furthermore, we make the point with Figs. 7 and 8 that the experimental techniques of transmission RHEED and conventional TEM cross-sectional diffraction give equivalent results. In the case of surface reflection diffraction, however, the crystalline nets of the β-FeSi$_2$ surfaces are not known, and in fact will be deter-

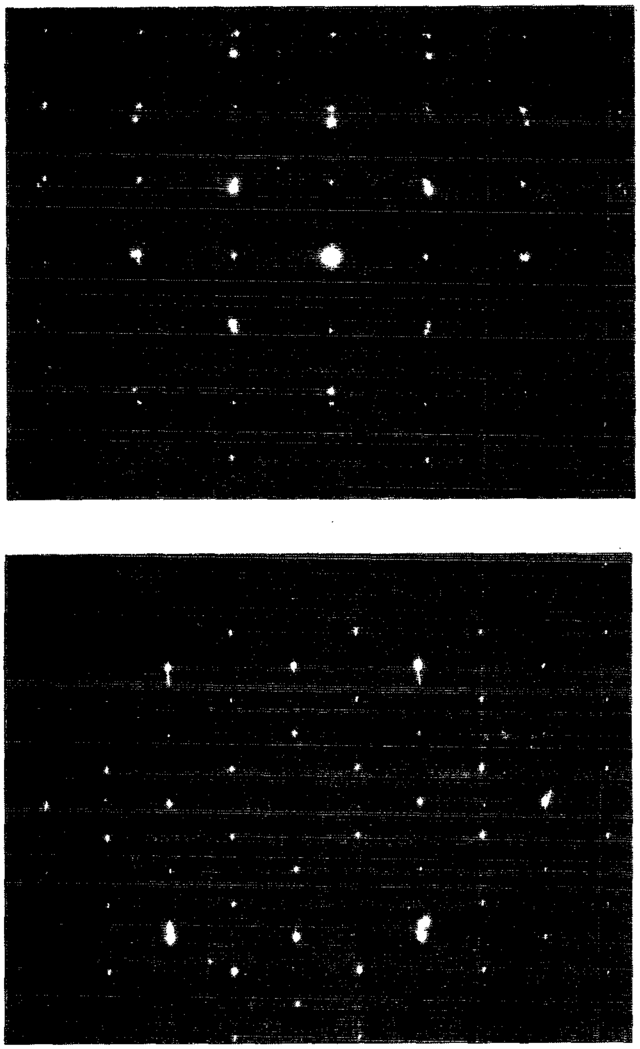


FIG. 8. TEM cross-sectional diffraction patterns as seen (a) along Si⟨110⟩ and (b) along Si⟨100⟩ for a twinned type-A β-FeSi$_2$ film grown on Si(001). In (a) the forbidden Si 002 reflection is seen.

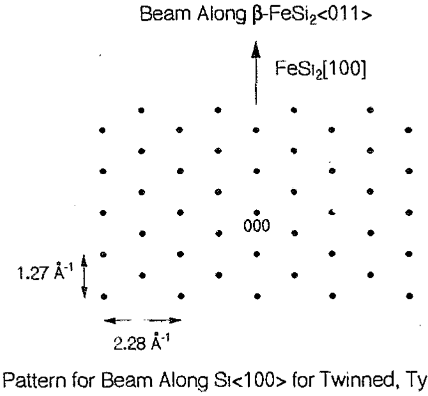


FIG. 9. The (composite) diffraction pattern seen with incident beam along a Si⟨100⟩ direction for a type-A film on Si(001) is made of two identical patterns from the two possible epitaxial variants. The incident beam is along β-FeSi$_2$⟨011⟩, such as [011] and [0$\bar{1}$1].

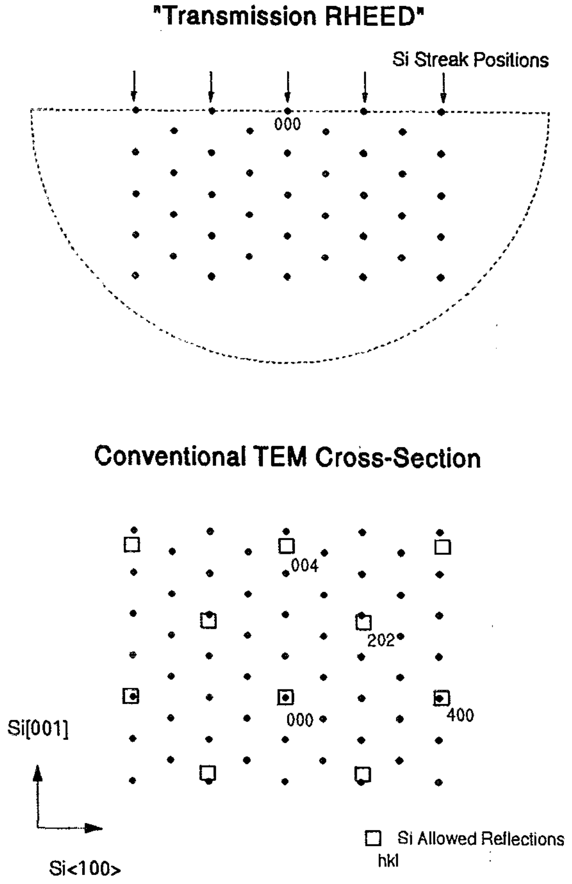


FIG. 10. The (composite) diffraction pattern of a twinned type-A β-FeSi$_2$ film grown on Si(001), with incident beam along Si⟨100⟩, is predicted for transmission RHEED and for conventional cross-sectional TEM. The positions of the Si RHEED streaks and bulk diffraction spots are indicated for reference.

mined from the geometrical structure of the reflection diffraction patterns.

V. SURFACE REFLECTION DIFFRACTION PATTERNS FOR EPITAXIAL TYPE-A FILMS GROWN ON Si(001)

It is often observed that the crystalline nets of clean semiconductor surfaces are different from the bulk lattice planes which are parallel to those surfaces. Consequently, while we know that the surface nets of epitaxial β-FeSi$_2$ films must be commensurate with the corresponding lattice planes, they may be altered through reconstruction. We begin this discussion, therefore, with a presentation and interpretation of the experimental diffraction patterns.

Excellent examples of RHEED streak patterns are shown in Fig. 11 for type-A β-FeSi$_2$(100)/Si(001) with the incident beam (a) along Si⟨110⟩ and (b) along Si⟨100⟩. Their geometry is clarified in Fig. 12, which is a schematic representation of these experimental RHEED patterns with the silicon streak positions added (where they are seen with the same apparatus under identical conditions) for reference.

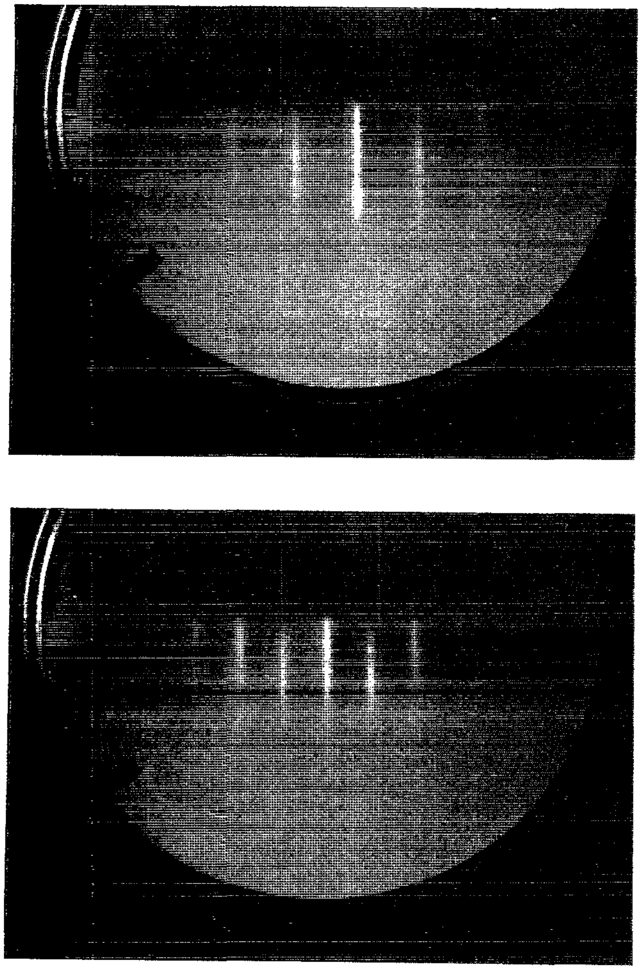


FIG. 11. Conventional RHEED streak patterns for an epitaxial type-A β-$FeSi_2$ film grown on Si(001). The incident beam is (a) along a Si⟨110⟩ direction and (b) along a Si⟨100⟩ direction.

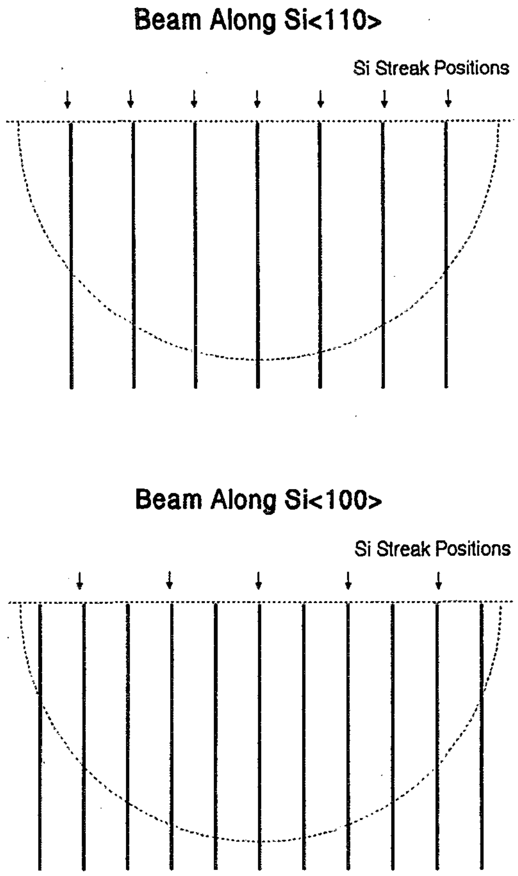


FIG. 12. The silicon streak positions were added to this schematic portrayal of the RHEED streak patterns of type-A β-$FeSi_2$(100)/Si(001) to show that they are 1×2 patterns, as referenced to silicon. Twinning is not a factor, since both epitaxial variants have the same RHEED pattern.

From these RHEED patterns the reciprocal net of the β-$FeSi_2$(100) surface was obtained and is presented in Fig. 13. It has the appearance of a centered square net of sides ~ 1.6 Å^{-1} to within the accuracy of RHEED (and, ignoring the small difference between the b and c lattice parameters, we will speak of it as centered square). These are $c(2\times2)$ β-$FeSi_2$ patterns as referenced to those of the primitive unreconstructed silicon (001) surface mesh, or $c(1\times1)$ as referenced to the β-$FeSi_2$(100) lattice planes. This experimentally determined reciprocal net is, in fact, a composite from the two epitaxial variants, whose nets must themselves be the same as this centered square net.

From this experimentally determined reciprocal net the crystalline net of the $FeSi_2$(100) face was derived and is also shown in Fig. 13. It is a centered square net with sides ~ 7.8 Å. This crystalline surface net is not simply the projection of the bulk lattice, which would yield a simple square net of the above dimension (again ignoring the difference between b and c), but the two are commensurate.

Using the conventional 7.8×7.8 Å^2 unit mesh, Miller indices were placed on the reciprocal net of Fig. 13. It is seen that the condition limiting possible reflections is

$$h+k=2n.$$

This is the only known condition limiting possible reflections; the two-dimensional plane group of the exposed β-$FeSi_2$(100) face is therefore *cm* (no. 5).[7]

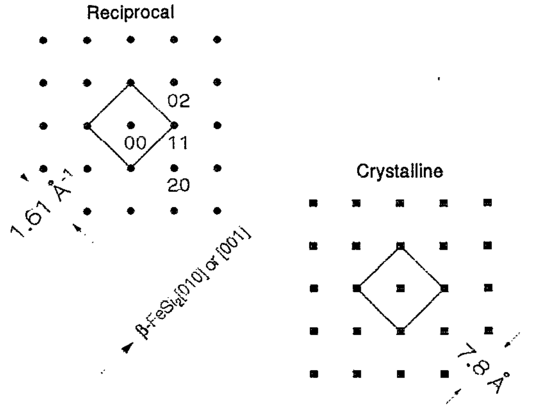


FIG. 13. The reciprocal net of the β-$FeSi_2$(100) surface, as derived from Fig. 12, is a centered square net with sides of ~ 1.61 Å^{-1}. The corresponding crystalline surface net is likewise a centered square net, with sides of ~ 7.8 Å.

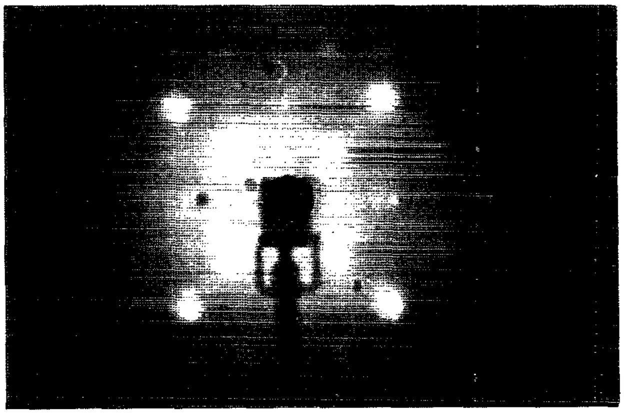


FIG. 14. LEED pattern for an epitaxial type-A β-FeSi$_2$ film grown on Si(001). The primary beam energy was 65 eV (Ref. 15).

What could be the origin of this centered surface net? If one considers the four bulk sublattices of the β-FeSi$_2$ crystal structure as identified by Dusausoy *et al.*, there is one of them that could terminate the surface under consideration with a centered rectangular unit mesh: $\mathrm{Fe_I}$.[6] All of the others could provide only a simple unit mesh. We might conclude that the exposed (100) surface is terminated by iron atoms occupying the positions of the bulk $\mathrm{Fe_I}$ sublattice; to the contrary, however, recent reports of scanning tunneling microscopy studies suggest a Si-terminated surface.[14]

We would like now to discuss the interesting experimental disagreement between RHEED and LEED (low-energy electron diffraction). A LEED pattern for a representative film is shown in Fig. 14.[15] This experimental pattern is interpreted in Fig. 15, which is a schematic representation of the LEED pattern together with the LEED spots of the unreconstructed Si(001) face placed on it for reference. This simple square pattern (again ignoring the small difference between b and c) is 2×2 as referenced to unreconstructed silicon. From this LEED pattern one may derive a simple square (100) surface net with sides of 7.8 Å, which is simply the projection of the bulk lattice.

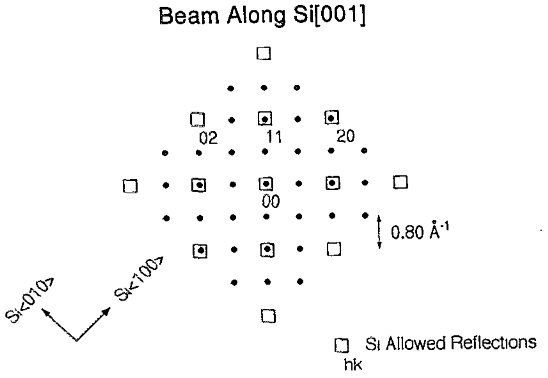


FIG. 15. The silicon spot positions were added to this schematic portrayal of the experimental LEED pattern of type-A β-FeSi$_2$(100)/Si(001) to show that the apparent reciprocal net of this surface is a simple square 2×2 pattern, in contrast to the RHEED results.

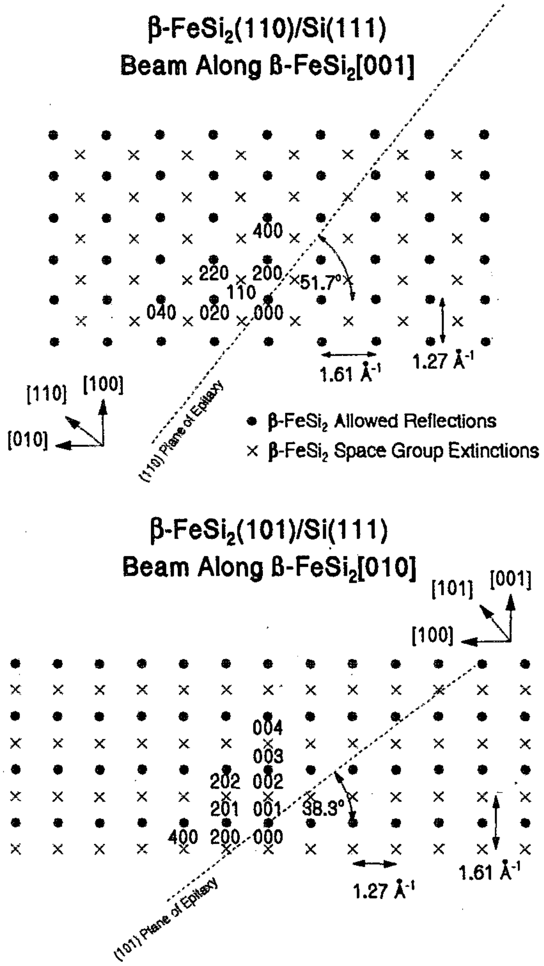


FIG. 16. These two diffraction patterns are derived from Fig. 2; they correspond to each of the two possible heteroepitaxial relationships for growth on Si(111). The incident beam is along Si⟨110⟩.

Why do LEED and RHEED suggest different surface structures? We can only speculate now that the difference is in the depth of penetration of the electron beam. RHEED is the shallower of the two, probing only the outermost monolayer and yielding a centered square net. LEED, on the other hand, probes deeper because some of the normally incident electrons pass between the atoms of the outer monolayer and are scattered from deeper atoms, yielding a simple rectangular net which is consistent with the bulk structure of this silicide.

VI. SURFACE TRANSMISSION DIFFRACTION PATTERNS FOR EPITAXIAL FILMS GROWN ON Si(111)

For epitaxial films grown on Si(111), the two fundamental azimuthal directions of reference are Si⟨110⟩ and ⟨112⟩. First, we portray in Fig. 16 the theoretical diffraction patterns, derived from Fig. 2, which should be seen with an incident electron beam along a Si⟨110⟩ direction. In this configuration, the incident beam is also along either FeSi$_2$[001] or [010], depending on which epitaxial relationship prevails. Space-group extinctions make the two theo-

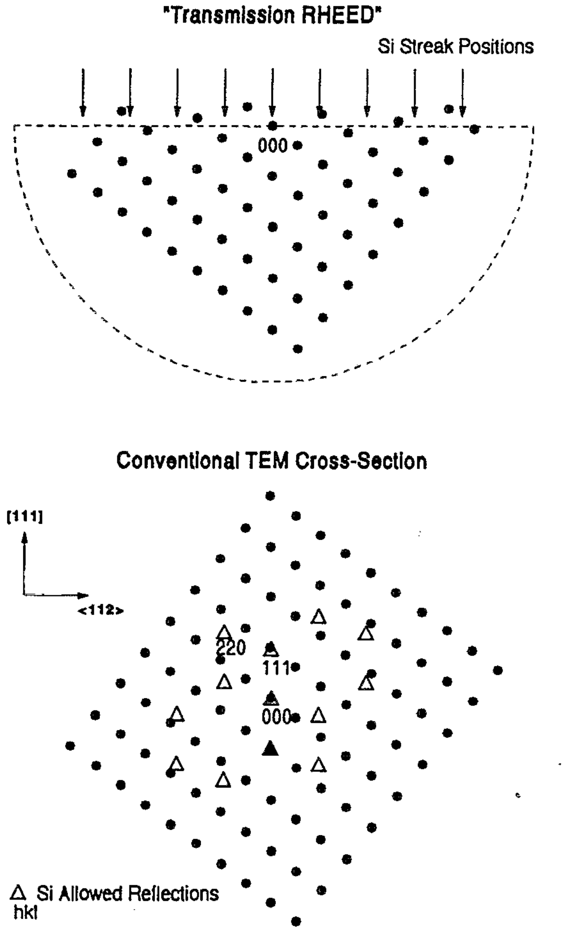


FIG. 17. The diffraction pattern of an epitaxial β-FeSi$_2$ film grown on Si(111), with incident beam along Si⟨110⟩, may be viewed either with transmission RHEED from a rough film, or with conventional TEM cross-sectional electron diffraction. Unfortunately, the two possible heteroepitaxial relationships cannot be distinguished because their patterns are identical. The positions of the Si RHEED streaks and bulk diffraction spots are indicated for reference.

retical patterns identical in form and thus the experimental pattern for this beam direction cannot resolve the two possible epitaxial relationships. However, observations do offer the possibility of revealing whether the "180 degree twinning" occurs in β-FeSi$_2$ grown on the Si(111) surface. This possibility is based on the fact that these two-dimensional patterns do not have a mirror line normal to the plane of epitaxy and passing through the origin of reciprocal space. If this type of twinning does occur, these simple patterns will not be seen; instead, composite patterns are predicted. The composite patterns will, by contrast, have such a mirror line. We must add that it is not possible by electron diffraction to identify which orientation is actually present in an untwinned film; this is because of the presence of a mirror line in the Si⟨110⟩ pattern.

In Fig. 17, we present possible experimental views of these patterns, by transmission RHEED and conventional TEM cross-sectional diffraction. The silicon (110) streaks and spots have been added for reference purposes, as is customary.

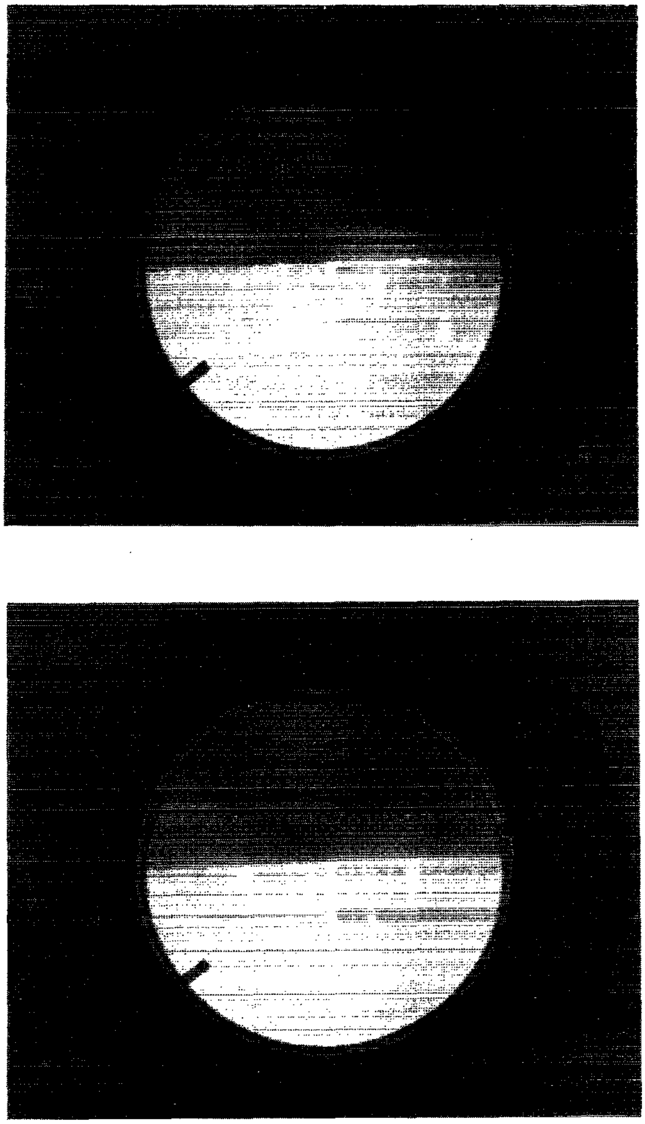


FIG. 18. Transmission RHEED patterns for an epitaxial β-FeSi$_2$ film grown on Si(111). The incident beam is (a) along a Si⟨110⟩ direction and (b) along a Si⟨112⟩ direction.

This basic pattern along Si⟨110⟩ was obtained by both experimental techniques; the results are presented in Figs. 18(a) and 19(a). Again, the transmission RHEED pattern has mixed spot and streak character, with the spot pattern corresponding well to the β-FeSi$_2$[010] or [001] patterns of Fig. 16. In the experimental cross-sectional TEM diffraction pattern the silicon spots are present as predicted in Fig. 17, together with the β-FeSi$_2$ spot pattern; the correspondence with the experimental pattern is complete. Clearly, because there is no mirror line, there is no 180° twinning observed.

The second basic diffraction pattern, for an incident beam along a Si⟨112⟩ direction, is given for each matching face in Fig. 20. It is a fact that there is no FeSi$_2$ reciprocal lattice vector which is parallel to Si⟨112⟩ for these heteroepitaxial relationships, although a nicely symmetric diffraction pattern may be seen. Thus, we designate the possible diffraction patterns as (i) "incident beam

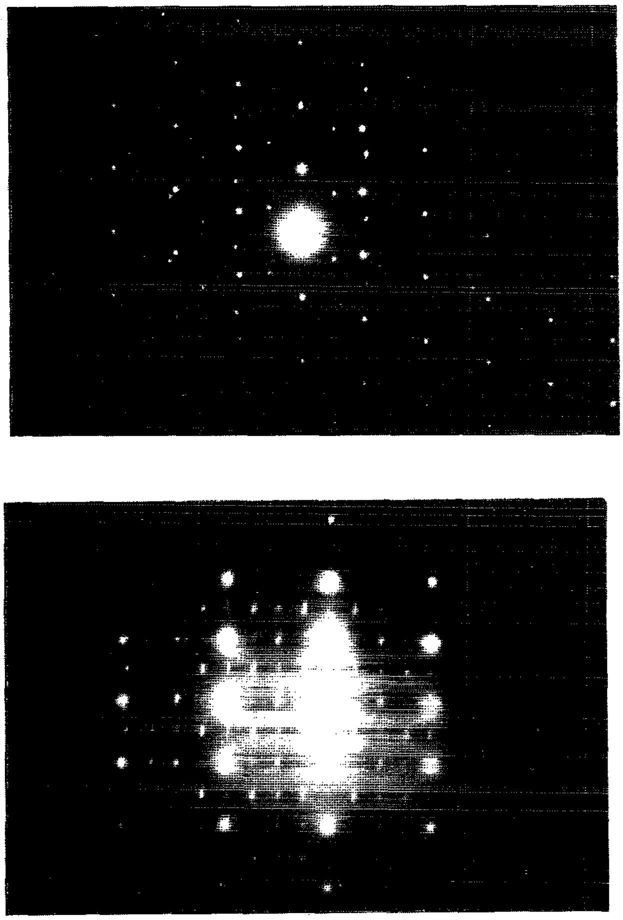
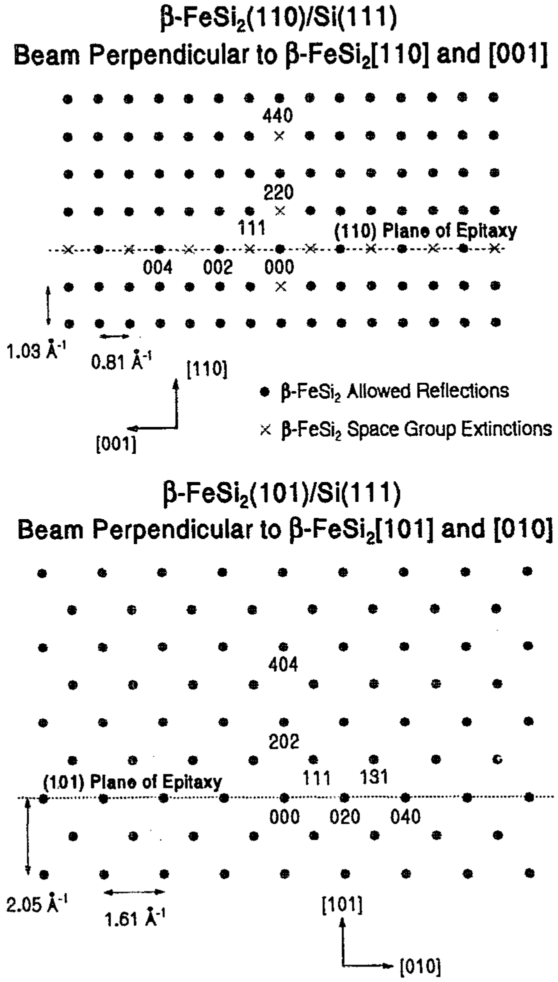


FIG. 19. TEM cross-sectional diffraction patterns for an epitaxial β-FeSi$_2$ film grown on Si(111). The incident beam is (a) along a Si⟨110⟩ direction and (b) along a Si⟨112⟩ direction.



β-FeSi$_2$(110)/Si(111)
Beam Perpendicular to β-FeSi$_2$[110] and [001]

β-FeSi$_2$(101)/Si(111)
Beam Perpendicular to β-FeSi$_2$[101] and [010]

FIG. 20. The diffraction patterns with incident beam along a Si⟨112⟩ direction for a twinned epitaxial film on Si(111) are the patterns presented above for both matching face possibilities. If both heteroepitaxial relationships occurred within a film, the composite pattern would be identical to the upper simple pattern in this figure. Indeed, the experimental pattern resembles that of the β-FeSi$_2$(110) matching face.

perpendicular to [110] and [001]" for the (110) plane of epitaxy, and (ii) "incident beam perpendicular to [101] and [010]" for the (101) plane of epitaxy.

Can we distinguish the two planes of epitaxy from these patterns? One should note that the spots of the lower pattern are a subset of the spots of the upper pattern. Thus, a composite pattern would have the same geometrical structure as the simple upper pattern in Fig. 20.

We provide in Fig. 21 the possible experimental views along Si⟨112⟩ of the pattern corresponding to the (110) matching face, with the silicon streaks and spots for reference. Because the experimental "transmission RHEED" pattern [Fig. 18(b)] and the TEM cross-sectional diffraction pattern [Fig. 19(b)] are well represented by Fig. 21, we conclude either that the (110) matching face prevails, or that both matching faces are present; certainly, the (101) matching face does not exist by itself. A careful look at the two experimental patterns does suggest that they are composites and not just that of the (110) face alone. It seems to us that there is a subset of relatively bright spots that duplicates the pattern of the (101) matching face.

VII. SURFACE REFLECTION DIFFRACTION PATTERNS FOR EPITAXIAL FILMS GROWN ON Si(111)

Experimental RHEED streak patterns for a representative epitaxial film are presented in Fig. 22 for the two principal azimuthal orientations of the Si(111) substrate. The streak patterns are interpreted in Fig. 23, which shows them schematically along with the Si streak positions. The RHEED patterns are 2×4, along Si[110] and [112] respectively, as referenced to those of the unreconstructed Si(111) surface. The apparent hexagonal symmetry of this composite reciprocal net is proof that the three domains of epitaxial variants exist in the sample.

The LEED results are, in contrast to the results for epitaxy on Si(001), in agreement with RHEED. A representative experimental pattern is shown in Fig. 24 and is also interpreted in the lower part of Fig. 23, where the positions of the Si LEED spots are shown for reference.[14]

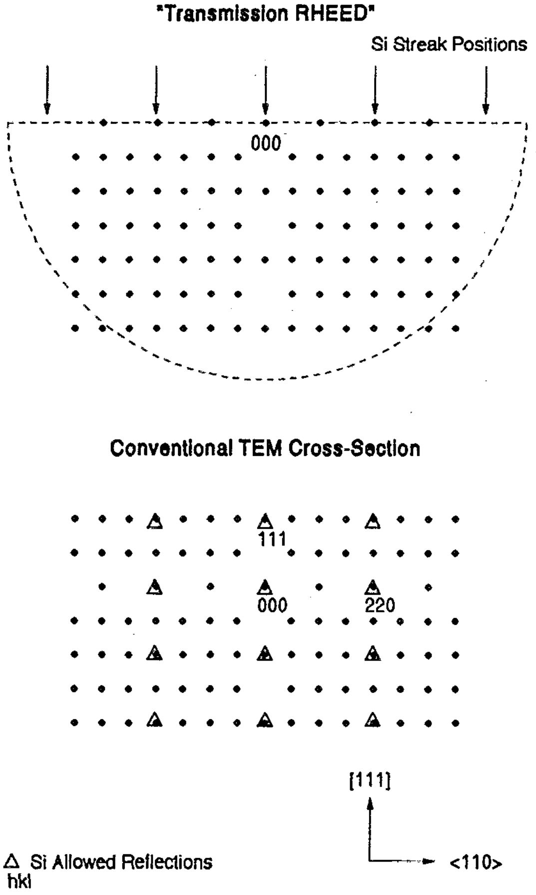


FIG. 21. We present in this figure the two possible views of the diffraction pattern seen along Si⟨112⟩, for the (110) matching face to Si(111). It is this view that confirms the existence of the (110) matching face. Again, the position of the Si RHEED streaks and bulk diffraction spots are indicated for reference.

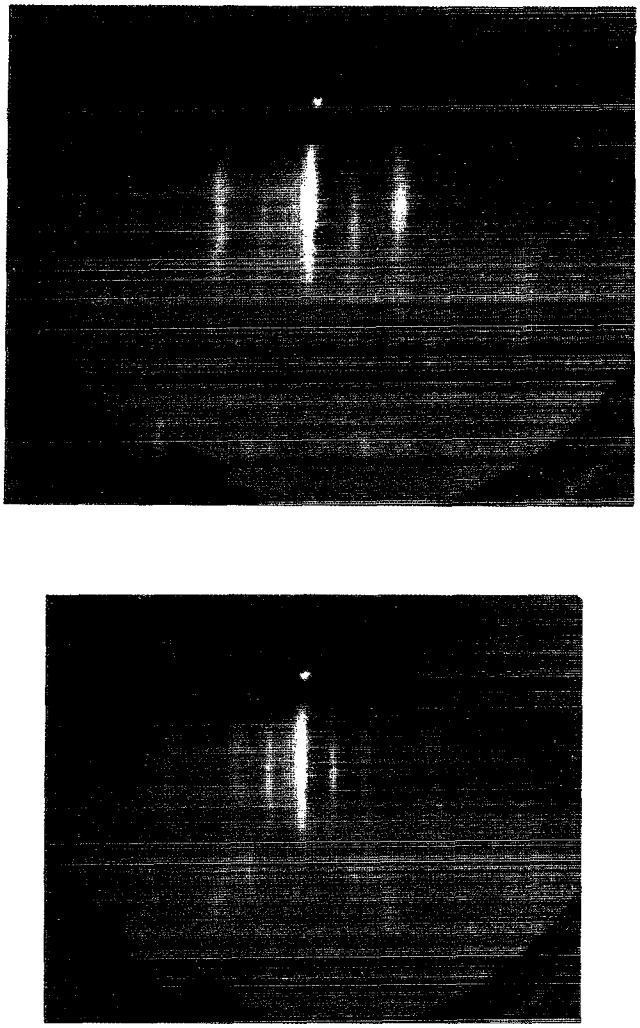


FIG. 22. Conventional RHEED streak patterns for an epitaxial type-A β-$FeSi_2$ film grown on Si(111). The incident beam is (a) along a Si⟨110⟩ direction and (b) along a Si⟨112⟩ direction.

It is seen that LEED also yields a 2×4 pattern experimentally.

It is not possible to derive directly the reciprocal net of the surface of these epitaxial films, because RHEED and LEED sample a composite net formed from those of the three epitaxial variants; however, it may be inferred by comparing the experimental results to that which is predicted for the projection of the bulk (110) lattice planes onto this surface. The crystalline net of the (110) lattice planes as derived from Fig. 1 is the rectangular net portrayed in the upper part of Fig. 25, and its reciprocal net is also rectangular as shown. The composite reciprocal net, which is due to the three epitaxial variants, is obtained by superposing the original net with additional nets rotated by 120° and 240° about the surface normal direction. This result is shown in the lower part of Fig. 25. Recognizing first the Star of David pattern in the center of the predicted composite reciprocal net, one concludes that the correspondence in form between the experimental and calculated patterns is exact. We also find that the dimensional scale with respect to the silicon surface spots and streaks is as predicted. We conclude that the actual surface of epitaxial β-$FeSi_2$ grown on Si(111) consists of three domains rotated by multiples of 120° whose crystalline nets are as portrayed in the upper part of Fig. 25.

We find in our own work and in the literature that LEED and RHEED experiments always produce diffraction patterns based on the form of the composite reciprocal net shown in Fig. 25, even when the (101) plane of epitaxy is known to be present. Could these patterns also be produced by a surface net based upon the projection of the bulk β-$FeSi_2$(101) lattice planes? They can, with the necessary plane group extinctions.

We show in Fig. 26 a crystalline net for the (101) face which is based on the conventional unit mesh of the (101) lattice planes (12.6×7.8 Å^2), together with its calculated reciprocal net. Miller indices which are based on the conventional unit mesh have been added to the calculated reciprocal net. This reciprocal net will be experimentally identical to that of the (110) face with the imposition of the plane group extinctions as shown in the lower part of the figure. The condition limiting these possible (hk) reflections is

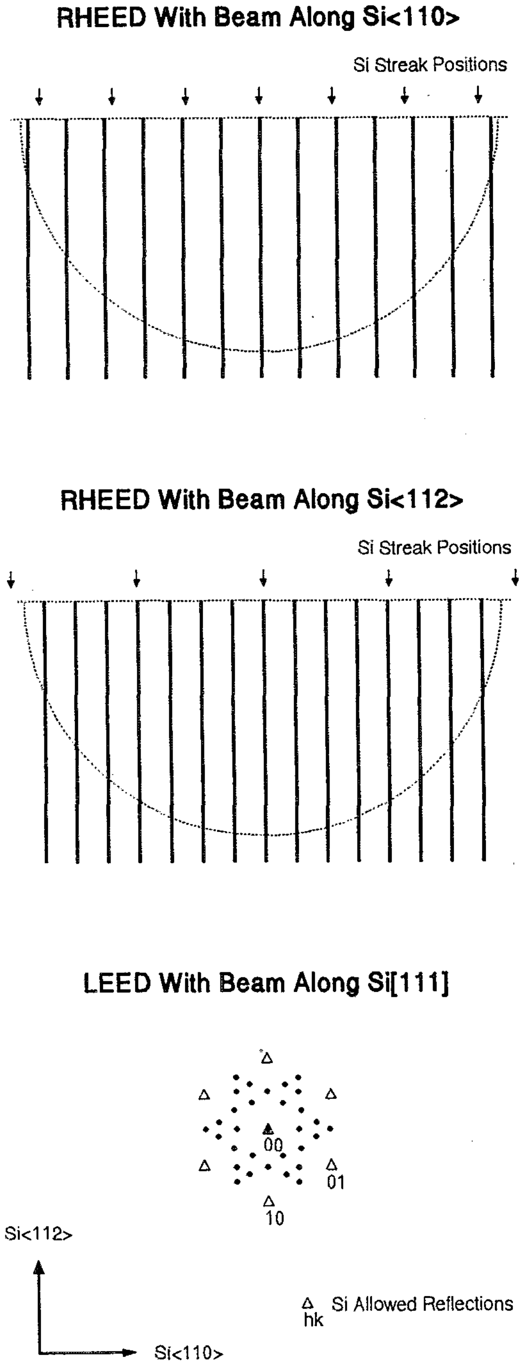


FIG. 23. The silicon streak positions added to the above schematic portrayal of the RHEED streak patterns of epitaxial β-FeSi$_2$/Si(111) show that they are 2×4 patterns as referenced to silicon. The LEED pattern is in agreement with this.

$$h=2n,$$

with the h direction along the longer side of the conventional unit mesh.

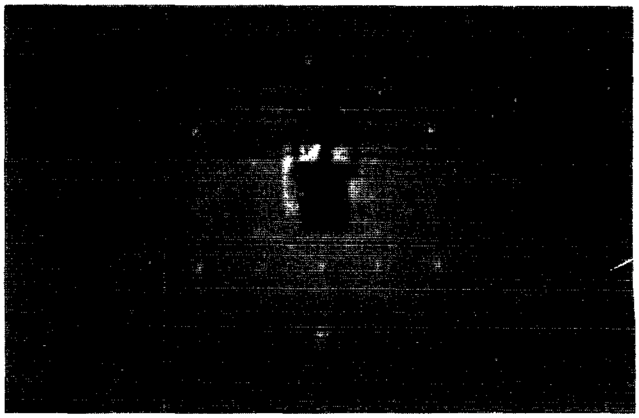


FIG. 24. LEED pattern for an epitaxial type-A β-FeSi$_2$ film grown on Si(111). The primary beam energy was 50 eV (Ref. 15).

There is only one (two-dimensional) plane group that is consistent with this experimental determination of the necessary plane group extinctions: *pmg* (no. 7), with a primitive rectangular unit mesh.[7] To realize the above extinctions, the basis of surface atoms must be located at the special positions of either $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$, or $(0,0)$ and $(\frac{1}{2},0)$. This special condition effectively converts the conventional unit mesh into one which is half as long, and

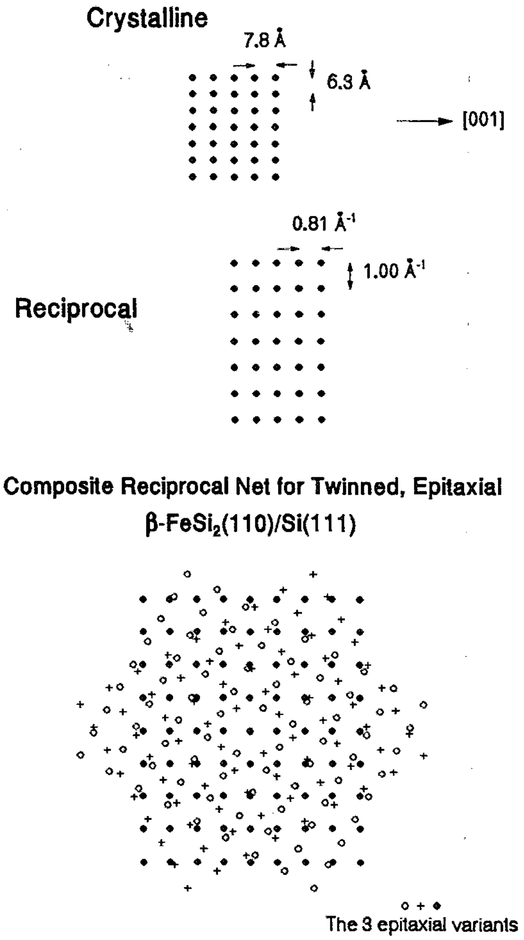


FIG. 25. The two-dimensional nets of the β-FeSi$_2$(110) surface are given. From the reciprocal net, the composite LEED pattern of a twinned epitaxial film grown on Si(111) is predicted.

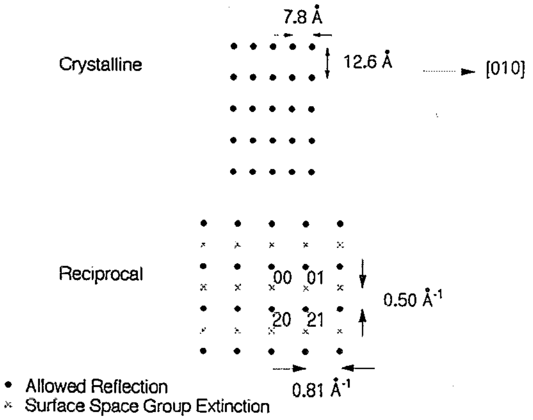


FIG. 26. The conventional unit mesh of the (101) surface of β-FeSi$_2$ is the projection of the bulk unit cell onto this surface. The experimentally required space-group extinctions of the reciprocal net derived from the conventional unit cell are indicated.

therefore identical to that of the (110) face. Indeed, these extinctions seem likely from an examination of the four possible iron and silicon bulk sublattices which might terminate this face.

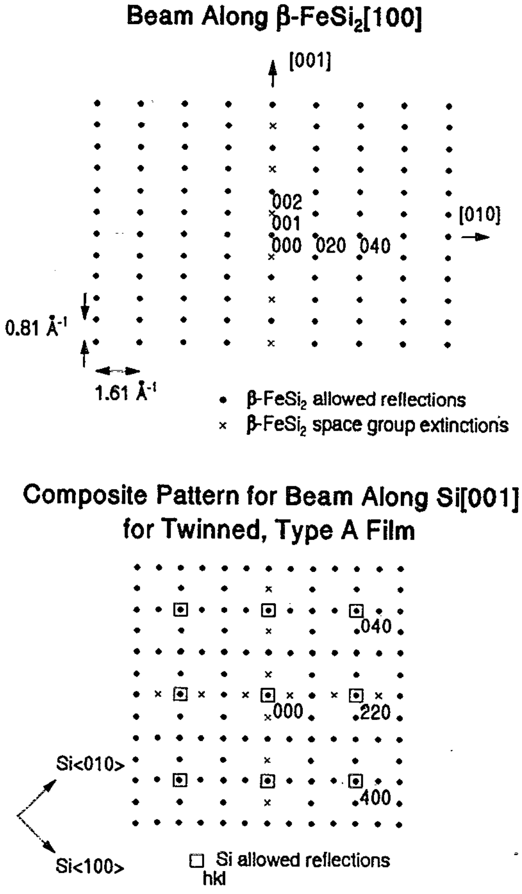


FIG. 27. An epitaxial β-FeSi$_2$ film grown on Si(001) in the type-A orientation normally contains equal numbers of rotation twins whose azimuthal orientations differ by a rotation of 90° about the surface normal. Consequently, the plan-view diffraction pattern is a composite as predicted here and demonstrated experimentally in Fig. 28.

By contrast, no plane group extinctions are needed in order to explain the experimental surface reflection diffraction patterns with the primitive net of the (110) face. We thus determine its plane group to be $p1$ (no. 1).[7]

VIII. SUMMARY AND CONCLUSIONS

There is a rich variety of surface electron diffraction patterns which play a role in the evaluation of the epitaxy of β-FeSi$_2$ on silicon. They include both transmission and reflection diffraction patterns. Because of the symmetry differences between the matching silicide faces and the silicon substrate, epitaxial films of a single heteroepitaxial relationship are typically composed of epitaxial variants distributed with equal probability. Consequently, the diffraction patterns are often composites formed from those of the individually twinned regions.

While the islanding tendency is not welcome from the standpoint of practical applications, at least it may be turned to one's advantage within the sphere of basic studies of the epitaxy of β-FeSi$_2$. *In situ* transmission RHEED affords a particularly convenient method for the determination of heteroepitaxial relationships and a confirmation of the occurrence of rotation twinning. There is a need for a complete understanding of the experimental factors influencing growth morphology, so that smooth or rough surfaces may be obtained as the needs demand. If and when the additional techniques are found to control the twinning tendency, it should be immediately apparent in the experimental surface diffraction patterns.

For growth on Si(001), the films assume a fixed matching face but two distinct azimuthal orientations oc-

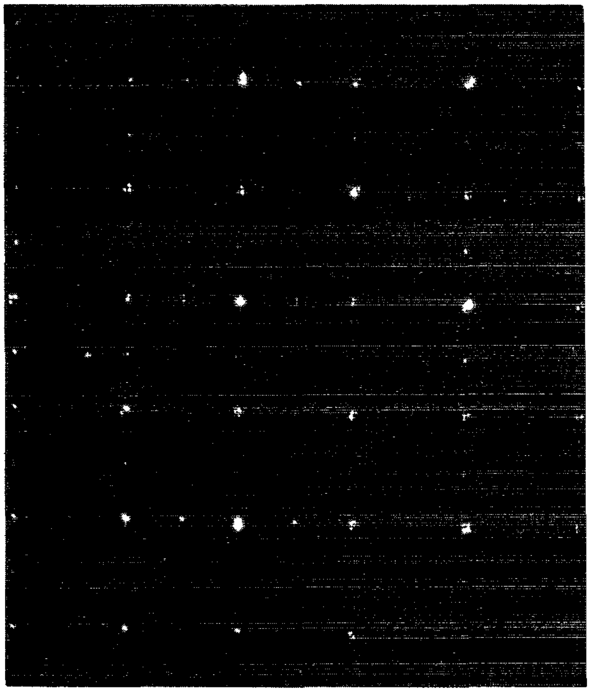


FIG. 28. TEM plan-view diffraction pattern for an epitaxial β-FeSi$_2$ film grown on Si(001).

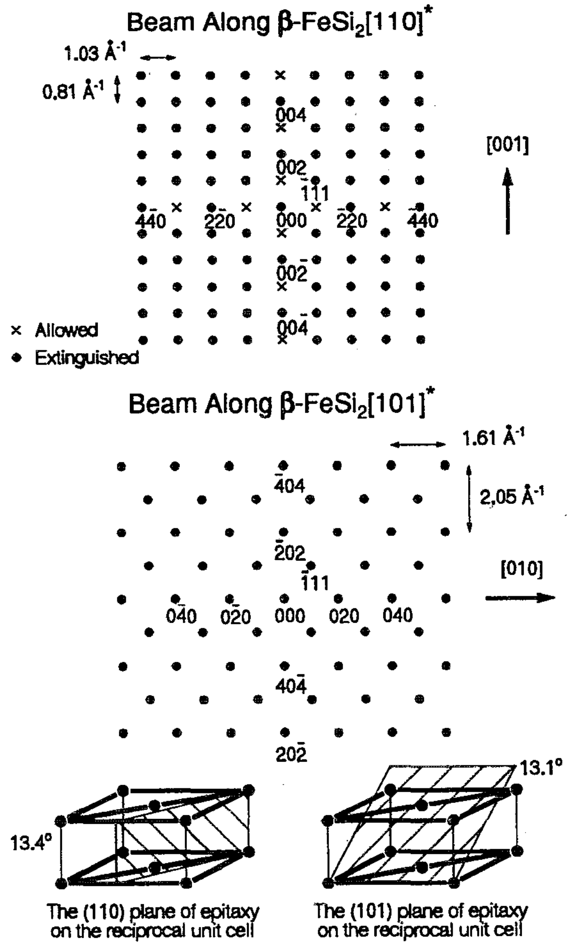


FIG. 29. The predicted plan-view diffraction patterns of twinned epitaxial films on Si(111) are based on the above views of reciprocal lattice planes. The planes of epitaxy are actually tilted away from these reciprocal lattice planes by 13.4° and 13.1° respectively, as shown in the lower part of this figure. Nevertheless, our explanation of the experimental pattern utilizes these views of the reciprocal lattice planes.

cur. They are easily distinguished with surface electron diffraction. The more desirable type-A azimuthal orientation was studied and for it rotation twinning was observed.

For growth on Si(111), two different matching faces (and their corresponding azimuthal orientations) have been observed. At the present time it is known that the (110) matching face was definitely present in all of these samples which were available to us for characterization, and that the (101) face was probably present also. Regarding the possibilities for twinning, the three 120°-rotated domains were always present but the 180° twinning phenomenon was not observed in any of the samples of the present study.

In contrast to the bulk crystal structure, the two-dimensional space groups of the crystalline surfaces of epitaxial films have not been known previously. Two of the three surface nets which we have observed are different from the basic projections of bulk crystalline lattice planes. For epitaxy on Si(001), it appears that the (100) surface net is a centered, rather than simple, square net (ignoring the small difference between *b* and *c*). We have also noted

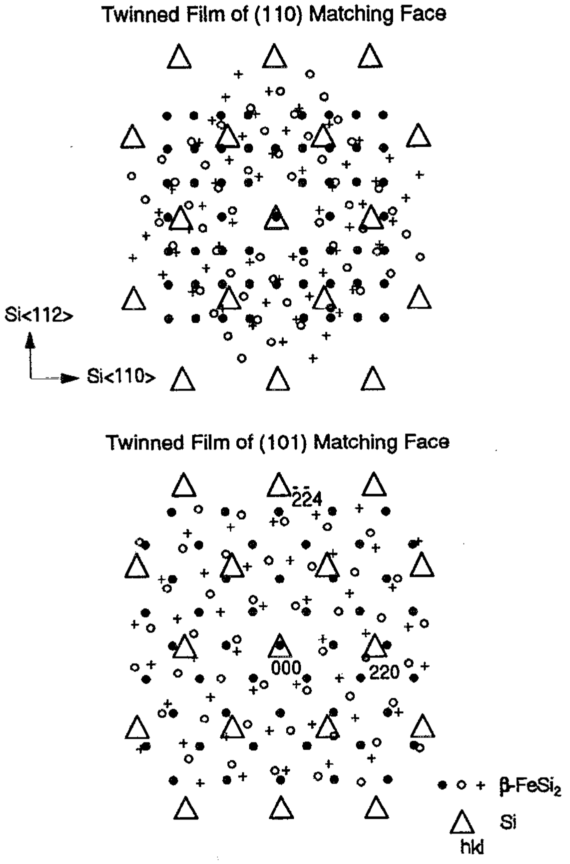


FIG. 30. The predicted plan-view diffraction patterns for twinned epitaxial films grown on Si(111) are shown for both matching face possibilities. It would appear that the two cases are experimentally distinguishable.

the interesting result that this surface's structure as indicated by RHEED is different from that indicated by LEED. Our hypothesis is that RHEED samples a film volume more nearly restricted to the first surface layer than does LEED.

As to the surface nets of epitaxial films grown on Si(111), on the other hand, RHEED and LEED are in complete agreement. The projection of the (110) bulk lattice plane provides a reciprocal net that, suitably twinned, corresponds to the 2×4 experimental RHEED and LEED patterns. In order for the bulk (101) lattice planes to provide an interpretation of the experimental results, there must be surface space group extinctions in its reciprocal net.

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APPENDIX A: PLAN-VIEW DIFFRACTION PATTERNS FOR TYPE-A β-FeSi$_2$(100)/Si(001)

The transmission electron-diffraction patterns in plan view are basic to the characterization of heteroepitaxial relationship. However, because they are not surface diffraction patterns, they are auxiliary to the theme of this article and were therefore placed in these Appendices.

We present in the upper part of Fig. 27 the transmission diffraction pattern with incident beam along β-FeSi$_2$[001], as derived from Fig. 2. Due to the rotation twinning, a composite pattern based on this one is expected for an epitaxial film grown on Si(001). In the lower part of Fig. 27, we present the predicted composite pattern for the type-A orientation, with the silicon diffraction spots for incident beam along Si[001] added for reference.

A representative experimental pattern obtained with plan-view TEM is shown in Fig. 28. The theoretical pattern of the twinned film may be very clearly seen in the photograph. Among the subset of spots which are part of the predicted composite pattern, the relatively bright ones come from domains of both azimuthal orientations, while the relatively dim ones are due to only one or the other type of twin. In addition, some space-group-extinguished spots for β-FeSi$_2$ are also seen via double diffraction.

APPENDIX B: PLAN-VIEW DIFFRACTION PATTERNS FOR β-FeSi$_2$(110) or (101)/Si(111)

The possible planes of epitaxy for β-FeSi$_2$ grown on Si(111) are not parallel to any low-index family of reciprocal lattice planes. Only the line of reciprocal lattice points on the [001] or [010] axes may precisely intersect the very large Ewald sphere typical of high-energy electron diffraction. Consequently, the theoretically expected plan-view diffraction patterns (based on a kinematic analysis and the Ewald sphere construction) are linear, rather than two-dimensional, arrays of diffraction spots.

However, because of experimental nonidealities we have found it necessary to relax the strict geometrical condition of the Ewald sphere construction in order to explain the experimental pattern. We construct the predicted plan-view diffraction patterns from the [110]* and [101]* reciprocal lattice planes as portrayed in Fig. 29.

Possible experimental views for twinned films of both matching faces are shown in Fig. 30, along with the Si(111) diffraction pattern. Close examination reveals that the two composite β-FeSi$_2$ patterns are nearly identical but probably experimentally distinguishable. An experimental TEM plan-view diffraction pattern is presented in Fig. 31. The strong silicon spots are seen and there are some additional ones attributable only to β-FeSi$_2$. In comparison with either possible pattern in Fig. 30, many predicted β-FeSi$_2$ spots are absent.

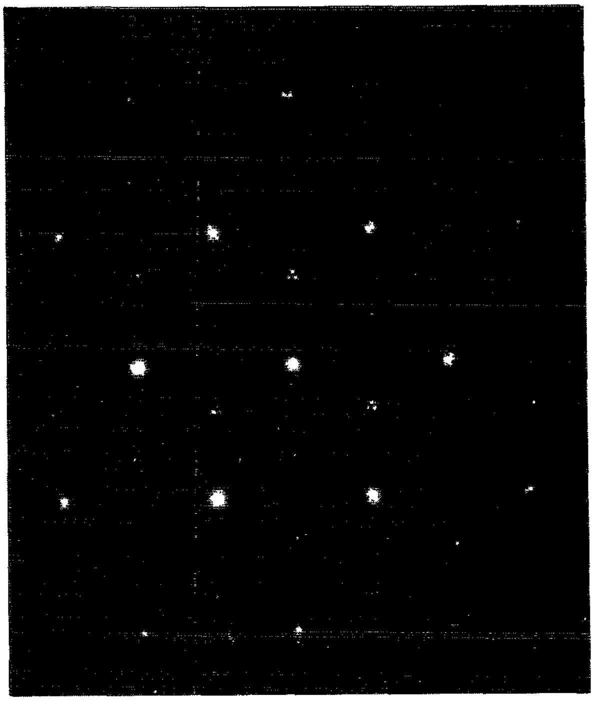

FIG. 31. TEM plan-view diffraction pattern for an epitaxial β-FeSi$_2$ film grown on Si(111).

The β-FeSi$_2$ reflections are clearly triplets of small spots. This demonstrates the presence of the three epitaxial variants. The positions and sizes of these triplets of spots are more consistent with the (110) plane of epitaxy than with the (101).

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