Reflection high-energy electron diffraction patterns of $CrSi_2$ films on (111) silicon

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Highly oriented films of the semiconducting transition metal silicide, $CrSi_2$, were grown on (111) silicon substrates, with the matching crystallographic faces being $CrSi_2(001)/Si(111)$. Reflection high-energy electron diffraction (RHEED) yielded symmetric patterns of sharp streaks. The expected streak spacings for different incident RHEED beam directions were calculated from the reciprocal net of the $CrSi_2(001)$ face and shown to match the observed spacings. The predominant azimuthal orientation of the films was thus determined to be $CrSi_2\langle 210\rangle \| Si\langle 110\rangle$. This highly desirable heteroepitaxial relationship may be described with a common unit mesh of 51 Å^2 and a mismatch of -0.3%. RHEED also revealed the presence of limited film regions of a competing azimuthal orientation, $CrSi_2\langle 110\rangle \| Si\langle 110\rangle$. A new common unit mesh for this competing orientation is suggested; it possesses an area of 612 Å^2 and a mismatch of -1.2%.

I. INTRODUCTION

$CrSi_2$ is a narrow bandgap semiconductor with a forbidden energy gap near 0.3 eV.[1-3] The quest for epitaxial $CrSi_2$ films on silicon has attracted more attention than that of perhaps any other semiconducting silicide.[4-7] This effort was encouraged by a promising theoretical lattice match of the hexagonal $CrSi_2$ basal planes to the Si(111) face.[8] There is a possible common unit mesh of 51.1 Å^2 area with a mismatch of -0.3% for the so-called "type A" azimuthal orientation[9] (defined below).

It has proved difficult to obtain single crystal films because for the above matching face relationship, there is an alternative azimuthal orientation that competes effectively with type A. It is generally observed experimentally that the predominant matching face relationship to (111) silicon is constant over a fairly wide range of film growth temperatures, but that the films consist of regions of both azimuthal orientations. For the "type B" azimuthal orientation[9] (also defined below), a possible common unit mesh may be identified that has an area of only 17 Å^2. However, the mismatch is $+15.3\%$. This relatively poor mismatch value makes it seem unlikely that the type B orientation could in fact be a viable alternative. We will present below an alternative common unit mesh that may offer a better explanation for the occurrence of type B film domains.

Reflection high-energy electron diffraction (RHEED) is an effective tool for monitoring the azimuthal orientation of a film during growth. It is of particular value to the study of $CrSi_2$ epitaxy because of the technique's applicability to silicon molecular beam epitaxy (MBE) and because of the particular problems with control of azimuthal orientation of this silicide. Yet, to our knowledge, no RHEED pattern for this material has ever been published. The purpose of this paper is to report the high quality, streaked RHEED patterns that may be obtained from highly oriented $CrSi_2$ films, while providing an analysis of their geometrical structure, and determining with RHEED the azimuthal orientations of the films.

II. SAMPLE PREPARATION AND VERIFICATION OF THE MATCHING FACE RELATIONSHIP

We grew $CrSi_2$ thin films on (111) silicon wafers by *e*-gun evaporation of the metal onto hot substrates under ultrahigh vacuum. The silicon for silicide formation was supplied by the substrate.

To prepare the substrate surface, the wafer was etched for 30 s in buffered HF solution, and loaded immediately into the sample introduction chamber of the growth system. After its transfer into the growth chamber, the wafer was held at 400 °C for 15 min. During this step we observed the development of strong Kikuchi bands and the 7×7 reconstructed RHEED pattern of the silicon (111) surface. The substrate surface preparation was concluded with a "silicon beam clean," during which any remaining SiO_2 was etched by a low level silicon flux.[10] Our silicon beam clean consisted of an exposure of the surface to a silicon flux corresponding to a deposition rate of 0.2 Å/s for 250 s at 700 °C. This exposure of the wafer surface to the low level silicon flux results in an even sharper and brighter RHEED pattern than that obtained by heating alone. It was not possible to measure the amount of residual carbon or other impurities.

High purity chromium (99.95%) was deposited with an electron beam-heated evaporation source. During the growth, the preselected substrate temperature was maintained with a graphite heater, a feedback controller, and a tungsten-rhenium thermocouple near to or touching the back side of the rotating substrate. Although the system's base pressure is in the 10^{-11} Torr range, the pressure was typically in the 10^{-10} Torr range during growth.

The naturally preferred matching face relationship was determined with data such as that shown in Fig. 1. This is a copper *k*-alpha Bragg–Brentano x-ray diffraction pattern from a sample grown by depositing 1000 Å of chromium at 400 °C. Only one $CrSi_2$ film peak is seen, the (003) reflection at 42.6°. [In past work we have observed several other diffraction peaks within the angular range of Fig. 1, the (101),

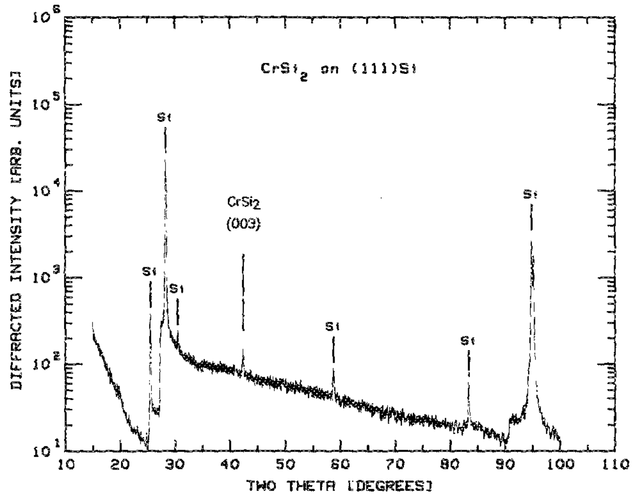

FIG. 1. A Bragg–Brentano x-ray diffraction pattern for a $CrSi_2$ film grown by depositing 1000 Å of chromium onto a (111) silicon wafer at 400 °C.

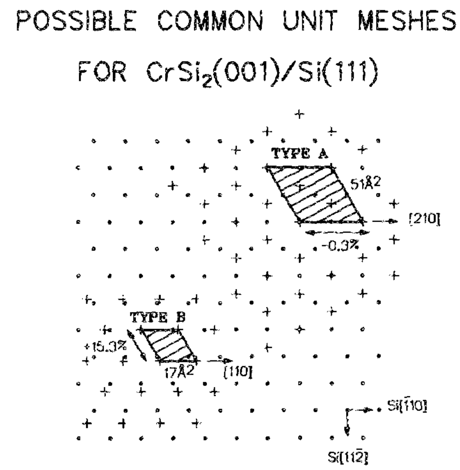

FIG. 2. Possible common unit meshes of the type A and B azimuthal orientations for $CrSi_2(001)/Si(111)$; ● silicon net points; + $CrSi_2$ net points. It is the relative orientations that are suggested; the relative positions are merely assumed.

(111), (200), and (112) peaks, from films which were obviously polycrystalline.[3]] In addition, there are strong substrate reflections as identified in Fig. 1.

Since the technique samples crystalline planes which are parallel to the macroscopic surface of the silicon wafer, a preference for the following matching face relationship is demonstrated:

$CrSi_2(001)/Si(111)$.

In a survey of growth temperature effects, we observed that the $CrSi_2(003)$ peak was dominant for temperatures of 800 °C and below. Although the 400 and 500 °C growths gave clean x-ray patterns, temperatures of 600 °C and above resulted in a loss of purity of the matching face relationship, with the $CrSi_2(111)$ reflection, and some others, appearing.

III. ANALYSIS OF HETEROEPITAXIAL RELATIONSHIPS

The complete specification of the heteroepitaxial relationship for the type A azimuthal orientation[9] is

$CrSi_2(001)/Si(111)$ with $CrSi_2\langle 210\rangle \| Si\langle 110\rangle$.

The type B azimuthal orientation[9] differs by a rotation of the film of 30° about the direction normal to the substrate's surface, to the following alignment:[11]

$CrSi_2\langle 110\rangle \| Si\langle 110\rangle$.

In Fig. 2, against the background of the crystalline net of the (111) silicon face, we show the crystalline net of the $CrSi_2(001)$ face in each of the two abovementioned azimuthal orientations, with the two suggested common unit meshes and the lattice matching information. It is customary to calculate the maximum mismatch in either length or angle using the substrate dimension as the reference, and the common unit mesh area using the silicide dimensions.[12] If the film must be in compression in order to be coherent, the mismatch is taken as positive.

For the type A orientation, the common unit mesh is the size of three primitive silicide unit meshes or essentially four silicon unit meshes; for the type B orientation, the silicide's own primitive unit mesh is the common unit mesh. We should emphasize that we have described the relative *orientations* of the silicide and silicon crystalline lattices; their relative *positions* are unknown.

IV. EXPERIMENTAL RHEED PATTERNS AND DETERMINATION OF AZIMUTHAL ORIENTATION

We will present RHEED patterns which were obtained from a film grown by depositing 300 Å of chromium at 600 °C, and given a post-growth anneal at 900 °C. The 900 °C post-growth anneal did not alter the epitaxial relationship of the as-grown film, but brought forth the highest quality RHEED patterns, in terms of streak sharpness and brightness.

We show in Fig. 3 two RHEED patterns which were observed with the incident beam (a) along a $Si\langle 112\rangle$ direction and (b) along a $Si\langle 110\rangle$ direction. The lateral streak spacings on the RHEED screen were 10 and 17 mm, respectively. Each pattern was repetitive with an azimuthal rotation of the sample by any multiple of 60°. The silicon directions are known from the position of the flat on the wafer. The $CrSi_2$ crystallographic directions which correspond to the two beam directions of Fig. 3 are determined below.

These streaks are bright and sharp, and of a similar quality to those obtained from a clean Si(111) surface. The RHEED pattern suggests to us that the $CrSi_2$ surface is well-ordered on a scale at least as large as the coherence length of the electron beam (~ 100 Å) and sufficiently smooth that there is no transmission electron diffraction pattern seen, as is often the case with rough (but still epitaxial) films.

It is possible to use this streak pattern to determine the azimuthal orientation of the film. The RHEED streak spacing that is expected for various incident beam directions may be calculated from the reciprocal net of the $CrSi_2(001)$ face. For certain principal directions there will be zones of reciprocal lattice rods with a particular intrarow rod spacing a^*. These zones will create streaks on the RHEED screen hav-

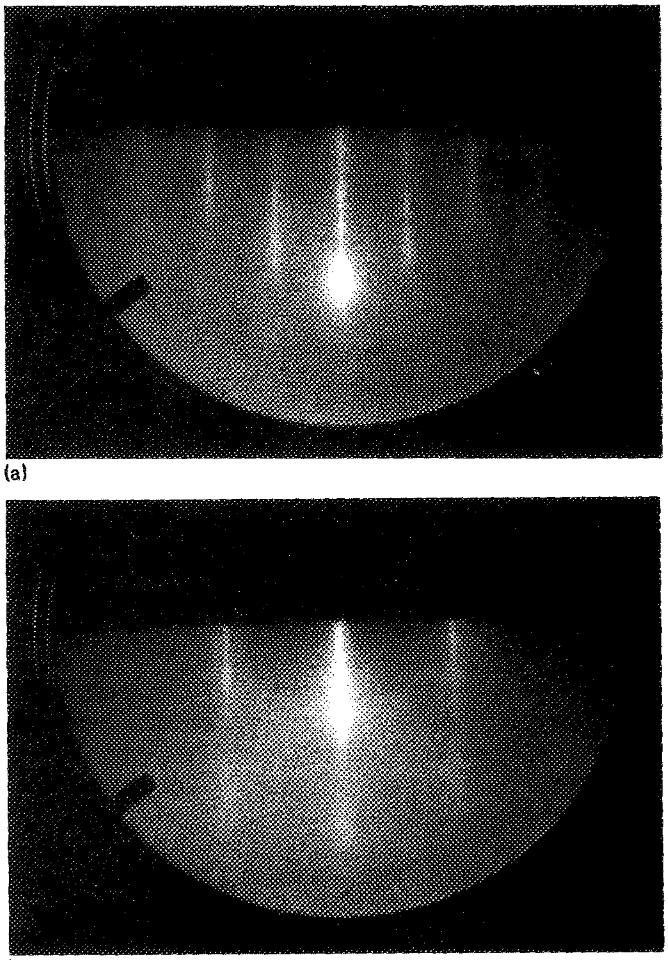
(a)
(b)

FIG. 3. $CrSi_2$ RHEED patterns with the incident beam along the substrate directions (a) Si⟨112⟩ and (b) Si⟨110⟩. The film was prepared by depositing 300 Å of chromium at 600 °C. The RHEED pattens were obtained after a post-deposition anneal at 900 °C.

ing a spacing (W) given by

$$W = \lambda L a^*/2\pi, \tag{1}$$

where λ is the deBroglie wavelength of the incident electrons and L is the distance from the point of incidence on the sample surface to the RHEED screen.[13]

The crystalline surface net of the $CrSi_2(001)$ face, from which we will derive the reciprocal net and the expected RHEED streak spacings, is shown in Fig. 4. Some principal crystallographic directions, and the area of the crystalline unit mesh, are indicated. Common choices for the basis vectors of the crystalline net and other relevant quantities are given in Table I. The Cartesian unit vectors, with which the basis vectors are expressed, are also shown in Fig. 4.

The basis vectors of the reciprocal net ($\mathbf{a}_i^*$) are derived from those of the real crystalline net ($\mathbf{a}_i$) according to

$$\mathbf{a}_1^* = 2\pi \mathbf{a}_2 \times \mathbf{n}/A \tag{2}$$

and

$$\mathbf{a}_2^* = 2\pi \mathbf{n} \times \mathbf{a}_1/A \tag{3}$$

with

$$A = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{n}. \tag{4}$$

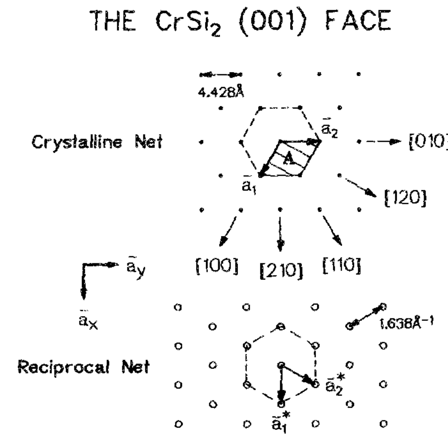

FIG. 4. The crystalline net and the reciprocal net of the $CrSi_2(001)$ surface. The Cartesian unit vectors, which were used to express the basis vectors, are shown.

$\mathbf{n}$ is a unit vector normal to the surface and A is the area of the crystalline unit mesh.[14] $\mathbf{n}$, A, and the resulting reciprocal net basis vectors are also given in Table I. Both the crystalline net and the reciprocal net of the $CrSi_2(001)$ face are close-packed hexagonal arrays. However, their orientations differ by a rotation of 30°, as drawn in Figure 4.

One may see in Figure 4 that for an incident RHEED beam directed along $CrSi_2$⟨110⟩ (or ⟨100⟩), the intrarow rod spacing of the Zeroth Zone would be 1.638 $Å^{-1}$. Along $CrSi_2$⟨210⟩, it is $\sqrt{3}$ times this value, or 2.837 $Å^{-1}$. Our RHEED screen distance is roughly 3.1×10^{-1} m and the electron wavelength corresponding to our acceleration voltage of 10 kV is 0.122 Å.[13] The expected RHEED streak spacings, according to Eq. (1), are 10 and 17 mm, respectively, for the two rod spacings.

Since the experimental and theoretical streak spacing values agree, it remains merely to determine the azimuthal orientation. A match is obtained with $CrSi_2$⟨110⟩ parallel to Si⟨112⟩ and with $CrSi_2$⟨210⟩ parallel to Si⟨110⟩. Thus, a type A azimuthal orientation of the film is found. For the type B orientation, the streak spacings would simply be interchanged for the two incident beam directions as referenced to silicon. That is, for type B one would observe a 10 mm spacing with the incident beam along Si⟨110⟩ and a 17 mm spacing along Si⟨112⟩. If both azimuthal orientations were present in the film, one would observe a RHEED patten which is a composite.

Indeed, a close examination of Fig. 3(b) shows a rather weak "extra" streak just to the left of the strong left-hand streak and possibly one next to the strong right-hand streak,

TABLE I. Structural parameters for the $CrSi_2(001)$ face.

Unit vector normal to the surface	$\mathbf{n} = (0,0,1)$
Area of primitive unit mesh	$A = 16.98$ $Å^2$
Basis vectors of crystalline net	$\mathbf{a}_1 = 4.428(\sqrt{3}/2, -1/2, 0)$ Å
	$\mathbf{a}_2 = 4.428(0,1,0)$
Basis vectors of reciprocal net	$\mathbf{a}_1^* = 1.638(1,0,0)$ $Å^{-1}$
	$\mathbf{a}_2^* = 1.638(1/2, \sqrt{3}/2, 0)$

which we ignored in the preceeding discussions. Our interpretation is that this is in fact a composite RHEED pattern. These extra streaks are at the positions of two of the strong streaks of Fig. 3(a). Thus, it appears that the film is essentially of the type A orientation, but enough type B is present to generate the two extra streaks seen in Fig. 3(b). We can report that with a growth temperature of typically 400 °C, the RHEED pattern is most definitely a composite, consisting of strong representations of both patterns of Fig. 3, and is identical for both incident beam directions under discussion.

Although the emphasis of this paper is on the interpretation of the RHEED patterns, we would like to comment briefly on the epitaxial quality of the films. Transmission electron microscopy has not confirmed the existence of large-area single-crystal films, for any growth temperature we tried. In addition, MeV He ion backscattering measurements confirmed the stoichiometry of the films but no channeling effect was observed. Thus, it seems that strong, sharp, and virtually pure (i.e., not composite) RHEED streak patterns are obtainable from films that are not necessarily of a large-area single-crystal structure.

V. RATIONALE FOR THE TYPE B AZIMUTHAL ORIENTATION

We (and others[6,9]) have characterized the lattice matching of the type B azimuthal orientation with a common unit mesh of 17 Å^2 area and a mismatch of + 15.3%. This mesh area is quite small (and therefore quite good) but the magnitude of the mismatch is so large that one might not expect any natural preference for this orientation. In addition, Markov and Milchev state, in a presentation of their theory of heteroepitaxial interfaces, that "if several epitaxial relationships are possible for a given overgrowth material on one and the same substrate plane, the relationship connected with negative misfit should be favored."[15] Yet the type B orientation has been observed by several investigators[6,9] and we have strong evidence for its existence in our RHEED patterns.

There is another possible lattice matching for this heteroepitaxial relationship which may be more convincing. We show in Fig. 5 the crystalline net of the $CrSi_2(001)$ face, and an alternative type B common unit mesh, against the crystalline net of the Si(111) face. This common unit mesh has an area of 612 Å^2 and a *negative* mismatch of only − 1.2%. This mismatch value should be considered promising but there is some doubt about the workability of such a large common unit mesh. One may gain a perspective by considering the unit mesh of the reconstructed Si{111}(7×7) surface. It is identical to that shown in Fig. 5. We reason that if a unit mesh of 612 Å^2 is workable for the most commonly observed reconstruction of the Si(111) surface, it should be suitable as well for the alignment of this heteroepitaxial system.

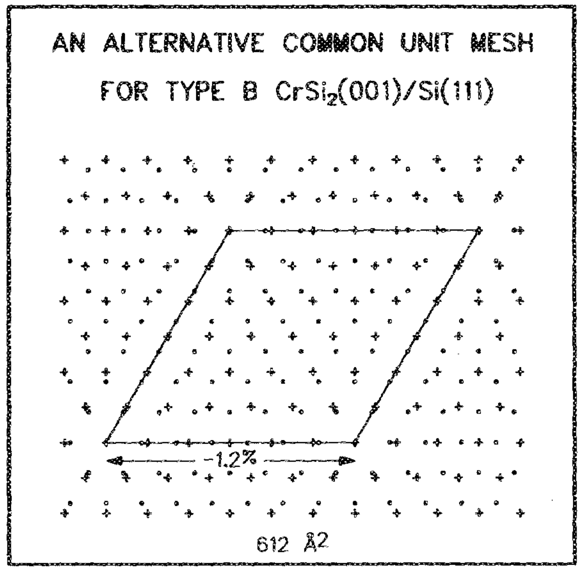

FIG. 5. An alternative common unit mesh for the type B azimuthal orientation; ● silicon net points; + $CrSi_2$ net points. The film net is actually drawn coherent with the substrate; as for Fig. 2, the relative positioning is merely assumed.

VI. SUMMARY AND CONCLUSIONS

$CrSi_2$ films grow on clean Si(111) surfaces with a strong preference for the matching face relationship of $CrSi_2(001)$/Si(111). With the right growth conditions, the films exhibit symmetrical RHEED patterns with very sharp and bright streaks. The streak spacings observed for various incident beam directions agree with those calculated for an unreconstructed $CrSi_2${001}(1×1) face. Thus, we have not observed with RHEED any reconstruction of this silicide surface.

RHEED patterns may be used to determine the azimuthal orientation of a film with respect to its substrate. For the samples discussed in this paper, the highly desirable type A azimuthal orientation, $CrSi_2\langle 210\rangle \| Si\langle 110\rangle$, predominated. RHEED also revealed the presence of film regions of the type B orientation.

The type A lattice matching is so excellent in theory that it seems surprising that any type B domains occur. The understanding of this phenomenon was strengthened with the observation that the unit mesh of the reconstructed Si{111}(7×7) surface is a possible common unit mesh pertaining to the type B heteroepitaxial relationship, and that for this definition of the type B common unit mesh there is a small negative mismatch.

The relative importance (to selection of the preferred heteroepitaxial relationship) of the two factors in the lattice matching tradeoff (the minimal unit mesh area and the precision of the match) is not well understood, nor are there absolute limits.[16] We wonder whether a 7×7 reconstruction of the substrate surface prior to film growth might contribute to the unexpected tendency to form type B domains.

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