"Coreless defects" and the continuity of epitaxial $NiSi_2/Si(100)$ thin films

J. L. Batstone,[a] J. M. Gibson, R. T. Tung, and A. F. J. Levi
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 28 October 1987; accepted for publication 18 December 1987)

Epitaxial thin films of $NiSi_2$ on Si(100) have been grown by room-temperature deposition of Ni followed by a high-temperature reaction. Initial stages of epitaxy revealed by transmission electron microscopy show nucleation of crystallographically equivalent islands related by a translation vector $a/4\langle 111\rangle$ via the underlying silicon substrate. Coalescence of islands thus requires the generation of $a/4\langle 111\rangle$ dislocations, which is energetically unfavorable. We find that very thin films (~ 60 Å) do not coalesce, but choose to remain as islands leaving trenches of exposed substrate 15 ± 1.5 Å in width between them. We propose that the trench left between islands can be described as a *coreless defect* in the silicide.

The discovery that epitaxial $NiSi_2$ layers can be successfully grown on Si(111) substrates by Ni deposition and reaction[1] has led to renewed interest in the electrical[2–4] and structural[5] characteristics of such films. Of particular interest is the effect of $NiSi_2$ orientation on the magnitude of the Schottky barrier height (SBH). Despite initial controversy, it has been confirmed that for $NiSi_2(111)$, layers with the same orientation as the substrate (type A) have SBH = 0.65 eV (Si substrate *n* type), and for layers rotated 180° with respect to the substrate (type B), SBH = 0.79 eV (*n* type), with the SBH unaffected by the presence of misfit dislocations at the $NiSi_2/Si(111)$ interface.[2,4] In contrast, $NiSi_2(100)$ has a SBH = 0.48 eV (*n* type) which *does* appear to depend on the perfection of the layer.[6] As a result, a careful understanding of parameters controlling the epitaxy of $NiSi_2$ on Si(100) is required. Results from ultrathin films of $NiSi_2$ are presented. Transmission electron microscopy (TEM) has revealed initial stages of epitaxy which show island nucleation and growth followed by the introduction of dislocations. Because of the lower symmetry of $NiSi_2$ on Si(100), crystallographically equivalent islands related by a translation vector $a/4\langle 111\rangle$, less than a lattice vector of $NiSi_2$, occur.[7] In very thin films (~ 60 Å), coalescence of islands does not occur, leaving instead a *coreless dislocation* or *trench* in the silicide. The core energy is thus reduced at the expense of exposed island edge. We expect a critical thickness for continuity in such systems, which is not necessarily equal to the thickness at which misfit dislocation introduction will occur. The observation of island growth and hence discontinuous films has important ramifications in the fabrication of Schottky diodes from $NiSi_2/Si(100)$ layers.

Ultrahigh vacuum, molecular beam epitaxial (MBE) growth of $NiSi_2$ on Si(100) was performed[1] by room-temperature deposition of Ni followed by reaction at $\sim$450–550 °C to form single-crystal $NiSi_2$. Plan-view TEM samples of $NiSi_2$/Si were prepared by jet polishing in HF/HNO_3, and cross-sectional samples were prepared by mechanical polishing and Ar-ion milling. TEM was performed in a JEOL 4000EX.

Figure 1 shows a plan-view, bright-field image ($g = 200$) from a 58 Å *p*-type $NiSi_2/Si(100)$ film prepared by deposition of 16 Å of Ni and reaction at 495 °C. Two distinct defect types are immediately obvious, namely, the "dark bars" accurately parallel to [110] directions, 35 ± 1.5 Å in width, and the fine white lines 15 ± 1.5 Å in width. The identity of the dark bars is revealed in Fig. 2, which shows a ⟨011⟩ cross section through a dark bar, revealing small facets on the (111) planes whose dimensions agree well with the plan-view image. (111) facets have previously been shown to depend on the amount of Ni deposited at room temperature.[1] The (100) interface is known to be unstable with respect to the (111) interface,[8] possibly because of a lower density of dangling bonds in the interfacial plane. $NiSi_2/Si(111)$ interfaces show sevenfold coordination[9] of the metal atom at the interface, whereas $NiSi_2/Si(100)$ interfaces show sixfold coordination.[8,10] Thus the $NiSi_2/Si(111)$ interface is an energetically more stable configuration. The presence of faceting at the (100) interface results in films with low SBH's, with the diode ideality factor departing from unity.[6]

A domainlike structure can exist in $NiSi_2/Si(100)$ films, where the [011] and [01̄1] interfacial projected structures are related by a rigid shift displacement of $a/4\langle 111\rangle$. This is illustrated in Fig. 3. The boundary between domains is thus associated with interfacial dislocations of $a/4\langle 111\rangle$ type,[11] which have a misfit-relieving component in the interfacial plane. The white line contrast observed in Fig. 1 delineates between the different domains. This is clearly seen by observation of the dark bars that indicate facet directions. All facets within a given domain lie along the same [011]

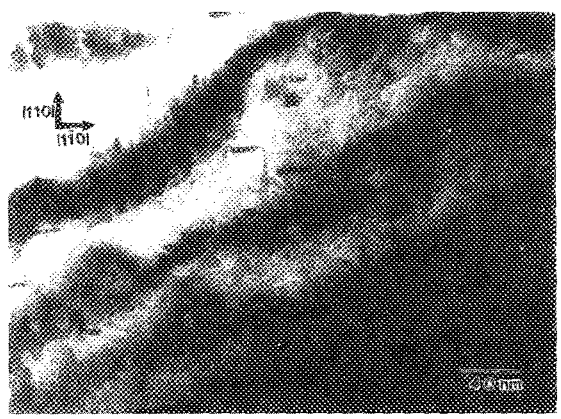

FIG. 1. Plan-view, bright-field image ($g = 200$) of a 58 Å film of $NiSi_2$ on *p*-type Si(100).

[a] Present address: Department of Materials Science and Engineering, The University, P.O. Box 147, Liverpool, L69 3BX, U.K.

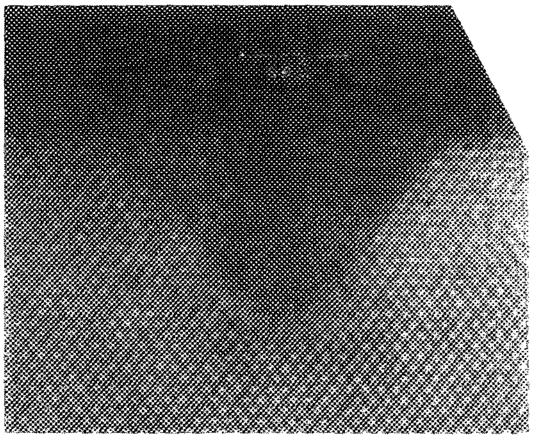

FIG. 2. ⟨011⟩ cross section showing a small facet on the (111) planes. The presence of facets results in poor diode behavior characterized by a reduction in Schottky barrier energy for both *n*- and *p*-type silicon, and an ideality factor significantly greater than unity.

direction and are not associated with dislocations. Introduction of a facet in the orthogonal direction requires the generation of a $a/4\langle 111\rangle$ dislocation and is thus equivalent to formation of a different domain. This can be confirmed by noting that in regions where two facets appear to meet, they are separated by a white dividing line. All white lines are closed loops and as such can be intepreted as defining the edges of discrete $NiSi_2$ islands, i.e., the film is discontinuous with islands separated by regular trenches. The white lines show zero contrast in the operating 020 reflection (which is forbidden in Si) because of the underlying exposed silicon surface. The lines do not lie accurately along either [011] or [100] and thus cannot be observed in a cross-sectional view. The dynamic evolution of island morphologies can be studied by using *in situ* TEM during crystal growth.[12] Preliminary *in situ* studies of $NiSi_2$ growth on Si(100) show that, initially, islands contain just one facet. Growth proceeds laterally, allowing islands of the same orientation to join up, resulting in several facets per island in agreement with our *ex situ* observations in Fig. 1. Lateral growth of islands occurs until an equilibrium island separation of 15 ± 1.5 Å is reached. The $NiSi_2$ film chooses to remain as discrete islands rather than coalescing to form a uniform thin film. The islanding behavior can be explained by considering the symmetry of the $NiSi_2$ and Si crystals, and the energetics of dislocation introduction. In continuous films of $NiSi_2$/Si(100), a lattice displacement vector of $a/4\langle 111\rangle$ separates crystallographically equivalent regions of interface. In the early stages of growth, nucleation of both the orthogonal interface structures is equally likely to occur. Thus coalescence of islands requires the generation of $a/4\langle 111\rangle$ dislocations. This would be true even for perfectly lattice-matched systems. Thus, for the case of a thin film with lower symmetry than the substrate, differences in symmetry lead to dislocations.[7] Even without coalescence, the individual islands are related by a lattice displacement vector via the underlying silicon substrate. If the film were continuous, the boundary region between islands would contain $a/4\langle 111\rangle$ dislocations, without the need for any additional lattice displacements or rearrangements. Consequently, we propose that the white lines in Fig. 1 due to trenches in the silicide, i.e., an absence of material, can be regarded as *coreless dislocations*. To our knowledge this unusual phenomenon is the first observation of a *coreless defect*. We suggest that the occurrence of coreless defects will be common among thin-film/substrate systems of different symmetries, for example, growth of silicon on sapphire.[7] Coreless defects are not restricted to simple line defects, but could also include planar defects that exhibit lower symmetry than the crystal in which they are based. Growth of GaAs/Si or GaAs/Ge results in symmetry-related defects, such as antisite domain boundaries separating energetically degenerate interfacial regions. In the case of a discontinuous film with an equilibrium island separation, coreless domain boundaries might exist. Recent studies of GaAs growth on misoriented Si(100) have shown that biatomic height steps can occur[13] such that nucleation of one orientation is favored, thus reducing the number of antiphase domain boundaries. It is interesting to speculate on the effect of wafer miscut on growth of $NiSi_2$/Si(100). Preferential nucleation of one island orientation could allow the growth of continuous films even at very low coverages by removing the symmetry constraint on coalescence.

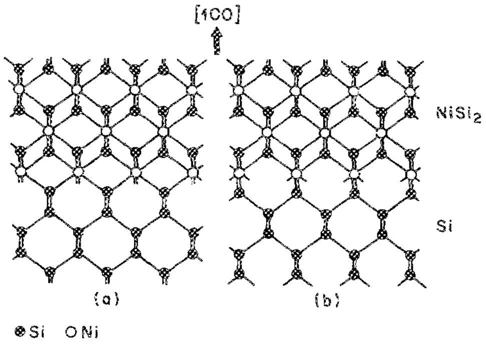

FIG. 3. $NiSi_2$/Si(100) interface as viewed in the (a) [011] and (b) [0$\bar{1}$1] projections. A rigid shift displacement of $a/4\langle 111\rangle$ is required to join the two sections of interface.

The film thickness at which the coalescence of two energetically equivalent domains will occur is determined by a balance between the relative surface free energies of the $NiSi_2$ and exposed Si and the dislocation strain energy. The expenditure in energy required for dislocation generation at the $NiSi_2$/Si(100) interface and the subsequent associated dislocation strain energy presumably is unfavorable compared with the gain in $NiSi_2$ surface free energy from island formation. Predictions of the critical thickness for coalescence are performed by equating the energy of a discontinuous film with no dislocation with the energy of a continuous film containing a $a/4\langle 111\rangle$ dislocation. For a discontinuous film displaying islandlike growth, the film energy can be written as

$$E_I = 2t\sigma_{dv} \cos\theta + x\sigma_{sv}, \quad (1)$$

where t is the film thickness, x the trench width, and θ the thin-film/substrate contact angle, σ_{dv} is the $NiSi_2$ surface free energy, and σ_{sv} is the silicon surface free energy. For island growth,[14]

$$\sigma_{sv} = \sigma_{sd} + \sigma_{dv} \cos\theta,$$

where σ_{sd} is the interfacial energy. Let us assume that

$\cos\theta = 1$ for a layer by layer growth mode. This suggests that $\sigma_{sd} < \sigma_{sv}$ for epitaxy to occur. This is not, in fact, inconsistent with our observations of discrete islands. Discontinuous films occur as a result of symmetry considerations; thus continuous two-dimensional growth is frustrated. Nevertheless, each individual island can have a zero contact angle. Thus (1) becomes

$$E_1 = 2t\sigma_{dv} + x(\sigma_{sd} + \sigma_{dv}). \quad (2)$$

For the continuous film containing a dislocation, the film energy E_2 may be written as

$$E_2 = E_0 + x(\sigma_{dv} + \sigma_{sd}), \quad (3)$$

where E_0 is the dislocation core energy. Equating E_1 and E_2 enables the critical thickness t_c for film coalescence to be expressed as

$$t_c = \tfrac{1}{2}(E_0/\sigma_{dv}). \quad (4)$$

The thickness t_c at which island coalescence is forced to occur resulting in symmetry-related defects can be different from the thickness at which introduction of misfit dislocations reduces the strain energy of the film. The critical thickness for dislocation introduction during growth of $NiSi_2$/Si(100) is therefore dependent on two factors. In general, the transition from strained layer growth to dislocated growth of thin epitaxial films depends on both the film thickness and island lateral dimensions. In a continuous $NiSi_2$/Si film, the average spacing of dislocations required to relieve the 0.4% misfit is 873 Å for $a/2\langle 011\rangle$ dislocations. This dislocation type is commonly observed in thick $NiSi_2$ films. The average lateral island dimension shown in Fig. 1 is <400 Å; thus the required generation of dislocations between different domains on coalescence to accommodate a rigid shift displacement of $1/4\langle 111\rangle$ would actually reverse the sense of strain in the thin films. As a result, for film thicknesses below the critical thickness for dislocation introduction, dislocation-free island growth will be energetically favorable.

The amount of Ni deposited prior to reaction is likely to affect the growth mode of the film and hence the defect structure in the film. Growth of thick $NiSi_2$ films is known to proceed via the sequence[15] $Ni \rightarrow Ni_2Si \rightarrow NiSi \rightarrow NiSi_2$, whereas thin "template" growth avoids the formation of some intermediate phases.[1] Control of thin-film continuity is thus critically dependent on the deposited Ni thickness. The effect of increasing the amount of deposited Ni is clearly seen in Fig. 4. A bright-field ($g = 220$) image shows a 750-Å-thick reacted $NiSi_2$/Si(100) film (above the critical thickness for dislocations), which contains a regular network of interfacial dislocations. Both $a/2\langle 011\rangle$ and $a/4\langle 111\rangle$ dislocations are present to relieve the misfit strain. No faceting at the interface is observed.

In summary, the initial stages of nucleation and growth of ultrathin films of $NiSi_2$ on Si(100) have been investigated. $NiSi_2$ nucleates as islands on the Si surface in two crystallographically equivalent orientations. Small interfacial facets are observed within the islands. The thin films remain as

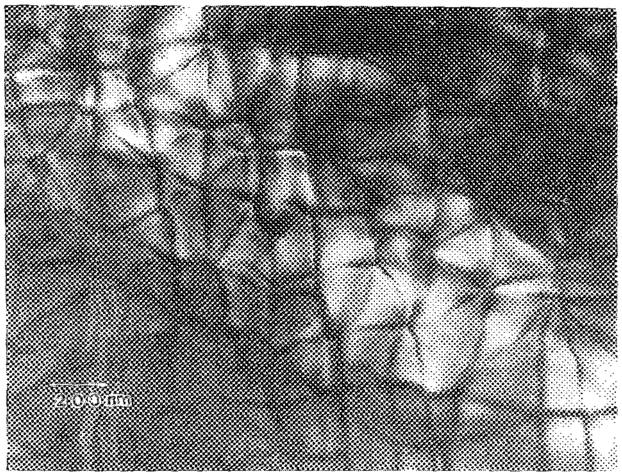

FIG. 4. Bright-field image of a 750-Å-thick film of $NiSi_2$/Si(100) revealing misfit dislocations.

islands, because coalescence of islands requires the generation of a $a/4\langle 111\rangle$ dislocation to accommodate the rigid shift displacement. For ~60 Å films, this is energetically unfavorable, and an equilibrium island separation of 15 ± 1.5 Å is observed. This appears as unusual white line contrast because of the underlying exposed silicon. We propose that the region between islands is appropriately described as a *coreless dislocation*. Such coreless defects are expected to occur at low coverages in epitaxial systems where the symmetry of the overlayer and substrate differs. The discontinuity of thin $NiSi_2$/Si(100) films and the presence of interfacial facets results in poor reproducibility of electrical characteristics.

We wish to acknowledge valuable discussions with D. Cherns and the expert technical assistance of M. L. McDonald.

[1]R. T. Tung, J. M. Gibson, and J. M. Poate, Phys. Rev. Lett. 50, 429 (1983).
[2]R. T. Tung, Phys. Rev. Lett. 52, 461 (1984).
[3]M. Liehr, P. E. Schmidt, F. K. LeGoues, and P. S. Ho, Phys. Rev. Lett. 54, 2139 (1985).
[4]R. J. Hauenstein, T. E. Shlesinger, T. C. McGill, B. D. Hunt, and L. J. Schowalter, Appl. Phys. Lett. 47, 853 (1985).
[5]E. J. van Loenen, J. W. M. Frenken, J. F. van der Veen, and S. Valeri, Phys. Rev. Lett. 54, 827 (1985).
[6]A. F. J. Levi, R. T. Tung, J. L. Batstone, J. M. Gibson, M. Anzlowar, and A. Chantre, Mater. Res. Soc. Symp. Proc. 77, 271 (1987).
[7]R. C. Pond, Mater. Res. Soc. Symp. Proc. 56, 3 (1986).
[8]D. Cherns, C. J. D. Hetherington, and C. J. Humphreys, Philos. Mag. A 49, 165 (1984).
[9]D. Cherns, G. R. Anstis, J. L. Hutchinson, and J. C. H. Spence, Philos. Mag. A 46, 849 (1982).
[10]J. L. Batstone, J. M. Gibson, R. T. Tung, A. F. J. Levi, and C. A. Outten, Mater. Res. Soc. Symp. Proc. 82, 335 (1987).
[11]D. Cherns and R. C. Pond, Mater. Res. Soc. Symp. Proc. 25, 423 (1984).
[12]J. M. Gibson, J. L. Batstone, and R. T. Tung, Appl. Phys. Lett. 51, 45 (1987).
[13]P. E. Wierenga, J. A. Kubby, and J. E. Griffith, Phys. Rev. Lett. 59, 2169 (1987).
[14]M. J. Stowell, in *Epitaxial Growth B*, edited by J. W. Matthews (Academic, New York, 1975), p. 437.
[15]H. Foll, P. S. Ho, and K. N. Tu, Philos. Mag. 45, 31 (1982).