Atomic Structure of a (2×1) Reconstructed NiSi₂/Si(001) Interface

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Nickel disilicide/silicon (001) interfaces were investigated by aberration corrected scanning transmission electron microscopy (STEM). The atomic structure was derived directly from the high spatial resolution high angle annular dark field STEM images without recourse to image simulation. It comprises fivefold coordinated silicon and sevenfold coordinated nickel sites at the interface and shows a 2×1 reconstruction. The proposed structure has not been experimentally observed before but has been recently predicted theoretically by others to be energetically favored.

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Introduction.—The change in material properties at dimensions very much less than one micron drives comprehensive investigations to find new materials for low scale microelectronic applications. One particular effort is the review of all metallic silicides, with a view to both a replacement of $TiSi_2$ as an electrically conducting interconnect and concerning the growth of small scale epitaxial structures for new electronic devices [1].

The cubic NiSi₂/Si and CoSi₂/Si systems are of interest and often treated as relatives due to close crystallographic and electronic similarities, which both produce atomically flat epitaxial metal/semiconductor (001) junctions. The lattice mismatch $(a_{MeSi_2} - a_{Si})/a_{Si}$ is -0.4%for Me = Ni and -1.2% for Me = Co. The atomic structures of these interfaces have a substantial impact on the Schottky barrier heights and therefore have been studied extensively by conventional high-resolution transmission electron microscopy (HRTEM) [2–6]. Also important is an understanding of these interface structures to explain epitaxial growth modes [7].

Cobalt disilicide has received greater attention over the past decade because of its low electrical resistivity. However, nickel disilicide is an interesting borderline case in terms of growth since, of all the 3*d* metals forming desired silicides, Ni has the highest value of the product of diffusion coefficient and solid solubility in Si [8].

A 2 × 1 reconstruction has previously been observed at the CoSi₂/Si(001) interface [7,9,10]. However, the atomic structures proposed differ from our findings. For a short review of work on the structure of NiSi₂ and CoSi₂(001) interfaces with Si [4,7,9–11], see the work of Yu *et al.* [12]. Throughout this Letter, we use (and give in brackets) the notation introduced there. In their work, Yu *et al.* investigated different existing models for the NiSi₂/Si(001) and the CoSi₂/Si(001) interfaces theoretically by total energy calculations and compared them to two new models proposed by themselves. Their new models represent the same basic interface structure in an unrelaxed (sevenfold U model) and a relaxed (sevenfold R model) state. These models involve sevenfold coordinated metal and fourfold (sevenfold U) and fivefold (sevenfold R) coordinated silicon at the interface. The fivefold coordination of Si in the second one is due to the formation of Si dimers inducing a 2×1 reconstruction. For both NiSi₂/Si(001) and CoSi₂/Si(001), the calculations of Yu et al. showed the sevenfold R model to be the most stable configuration. Furthermore, these authors found that the experimental TEM data of Bulle-Lieuwma et al., interpreted originally in terms of the so-called Bulle-Lieuwma-de Jong-Vandenhoudt (BJV) model [10], also agree well with the newly suggested sevenfold R model. According to Yu et al., it would be not possible to unambiguously distinguish the sevenfold R model from the BJV model merely by means of TEM and HRTEM. To the best of our knowledge there is, as yet, no direct experimental evidence to substantiate the calculations of Yu *et al.* especially with regard to the NiSi₂/Si(001) interface. In the following, we present results which provide this evidence.

Experimental.—The investigated samples were prepared by molecular beam allotaxy (MBA), a method developed by Mantl and Bay [13] for the growth of buried thin films. In a first step, a characteristic distribution of NiSi₂ precipitates in an otherwise undisturbed Si matrix was grown by MBE [14]. In a second step, the samples were rapid-thermal-annealed at 800 °C for 30 s. Because of the high value of the product of diffusion coefficient and solid solubility of Ni in Si, the process window does not allow the growth of continuous NiSi₂ films. The cross section TEM samples were prepared by tripod polishing and low-angle ion milling at 3 kV in a Baltec RES010.

A dedicated scanning transmission electron microscopy (STEM) VG HB501 equipped with the recently developed Nion spherical aberration corrector [15] was used to image the samples. The instrument was operated at 100 kV. The images were obtained from the high angle



FIG. 1. HAADF overview in cross section, zone axis [110].

annular dark field (HAADF) signal using an angular range of acceptance of 70 to 210 mrad. Unless stated otherwise, the images have not been manipulated besides gamma and contrast correction and geometric correction of the distortion caused by the nonorthogonal scanning coils. As shown by Pennycook and Jesson [16], in suitable imaging conditions, the HAADF signal depends on orientation and increases monotonically with Z and with the specimen thickness. In our case, we may neglect thickness and orientation variations within the field of the scans. Consequently, the image contrast is related to variations of Z, which allows atomic columns of different elemental composition to be distinguished. This is completely different from the common HRTEM situation where the dynamical solution of the electron scattering problem causes contrast reversals which make the identification of atoms with sites ambiguous.

Results.—The NiSi₂ is present as a layer of largely contiguous crystals as proved by plain view TEM dark field imaging (data not presented here). The orientation relation between the Si matrix (diamond structure) and NiSi₂ layer (CaF₂ structure) is (001)Si || (001)NiSi₂ and [110]Si || [110]NiSi₂. The predominant interface orientations of the NiSi₂ are (001) interfaces especially at the bottom (towards the substrate) and {111} interfaces (see Fig. 1). All images used in this work were obtained from the lower (001) interfaces.

In all those areas of the samples which were suitable for atomic resolution imaging, one of two different variants of image contrast at the interface was found (denoted variant 1 and variant 2 in the following, see Figs. 2 and 3). Variant 2 shows a twofold reconstruction along the interface. The structure model causing this contrast (Fig. 4) was deduced as follows.

The NiSi₂ crystal lattice projection is identical in all $\langle 110 \rangle$ directions. Therefore, in order to determine the



FIG. 3. High resolution HAADF image of the interface with apparent twofold reconstruction (variant 2). The position of the outermost layer of Ni atoms in the silicide is marked by a thin black line.

distances of atomic sites perpendicular to the interface, the position of the outermost layer of Ni atoms (indicated in Figs. 2 and 3; compare also Fig. 4) may be taken as a reference. The dumbbell positions in the silicon in variant 1 are shifted by $\frac{1}{4}$ **c** (**c** is the lattice vector in the [001] direction) with respect to that outermost Ni layer when compared to the dumbbell positions in variant 2 (see also Fig. 5). This indicates that variant 1 and variant 2 are possibly orthogonal projections of one and the same structure which must then be of a 2×1 type [17]. The Ni planes were used as a geometrical reference thus far because they can easily be identified in the HAADF images. However, the silicide is grown in a single crystalline Si matrix. Referring to the Si matrix, and regarding the given interface model, there are four different offsets for the silicide, connected by the four 4_1 screw operations of the silicon lattice (space group Fd3m): $(0,0,0), (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), [\frac{1}{2}, 0, \frac{1}{2}, (\frac{1}{4}, -\frac{1}{4}, \frac{3}{4})].$ Given the symmetry of the silicide lattice (Fm3m), this results in two crystallographically nonidentical growth positions of the silicide, (0,0,0) and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Two silicide domains grown in such different positions exhibit Ni planes shifted by $\frac{2n+1}{4}$ c against each other and interface domains differing by the orientation of reconstruction (e.g., either 2×1 or 1×2 , related to either variant 1 or variant 2 in the same sample orientation). This means that silicide domains showing different orientations of the reconstruction cannot be



FIG. 2. High resolution HAADF image of the interface (variant 1). The position of the outermost layer of Ni atoms in the silicide is marked by a thin black line.



FIG. 4 (color online). Averaged images of the interface structure and overlaid ball-and-stick display of the deduced model in $[\bar{1}10]$ (left) and [110] projection. The denotation of atomic planes corresponds with that used in Table I. The fcc unit cells are indicated.



FIG. 5 (color online). High resolution HAADF image of $NiSi_2/Si$ interface regions showing the reconstructed (right part of image) as well as the unreconstructed view (left). The proposed model structures are overlaid. The two pairs of black and white lines indicate the distance between the silicon dumbbells and the first layer of Ni at the two respective interfaces (see text).

contiguous, or must be divided by stacking faults, or by interface edge dislocations [18-20], or strained at their domain boundary. The translation vectors between the origins of the two different growth positions are $\frac{a}{4}\langle 111\rangle$; thus, interface edge dislocations at those domain boundaries would have to have a Burgers vector of $\mathbf{b} = \frac{a}{4} \langle 111 \rangle$ as found in the cited publications for the $NiSi_2/Si(001)$ interface. The dislocations reported there were mostly dividing domains on flat parts of the interface. The misfit in the NiSi₂/Si system would lead to a mean distance of 48 nm between $\frac{a}{4}\langle 111 \rangle$ dislocations for complete relief of interface strain. In our experiments, we did not find such interface edge dislocations at plane interfaces. In all cases, the two domains were separated by {111} facets in the STEM image. The silicide layers were formed from individual coherent NiSi2 precipitates in a silicon matrix [14] with either one of the two growth positions. During annealing, the precipitates coalesce by diffusion of Ni. This growth process allows several mechanisms to accommodate the interface strain including stacking faults.



FIG. 6. Filtered high resolution HAADF image including the area shown in Fig. 5. Upper right: Magnitude of Fourier transform (FT) of the original image. Lower right: Magnitude of the FT of the image as shown. No corrections of scan distortions were applied; thus, the (001) and (220) lattice planes appear wavy and not orthogonal in the image. For details see text.

TABLE I. Distances between (001) atom planes estimated from images of variant 1. Labeling as in Fig. 4.

Plane distance	$d/{ m \AA}$	$\frac{d}{c}$
Ni2–Si1	4.0 ± 0.2	0.74
Ni1-Si2	2.7 ± 0.2	0.50
Si1–Si4	3.9 ± 0.2	0.72

Thus, the interface dislocation density in our case may be considerably below the value given above.

Images such as that in Fig. 5 simultaneously showing both variants support our findings. The different distances between the Ni planes and atomic planes in the silicon matrix are indicated there. Figure 6 shows an image with slightly lower magnification centered around the same area as Fig. 5 and is bandpass filtered to smooth the contrast and to remove some low spatial frequency background. In area A, overlapping Si and NiSi₂ are imaged. The contrast along the line indicated by arrow 1 could be due to a stacking fault between the two silicide regions with their different levels of Ni planes or caused by a silicon/silicide{111} interface overlapping with the silicide in the direction of the beam.

We used the information given by the atomic resolution HAADF images of both variants to find the atom positions. The fact that, in such images from more than two dozen locations of two independently grown samples, we did not see any variants other than the two mentioned, gives us reason to believe that this model is the predominant (001) interface structure in this system. The contrast of the dimerized Si atoms in images of variant 2 appears relatively blurred. This might be due to a static effect, the overlap of domains with the same orientation of the dimers but differing by a shift of the dimer rows of $\frac{1}{2}$ [110] (notation according to Fig. 4), or the existence of a soft acoustic phonon mode executed by the dimers as a whole, which seems possible since the bonding directions of the dimers imply a very low potential gradient in [110]. At present, we cannot distinguish between either of the two given explanations from our results.

Table I gives (001) plane distances at the interface which were estimated from the images. The values are multiples of $\frac{1}{4}c$ within the errors. For the lattice constant, we used the approximate value of c = 5.4 Å for both Si and NiSi₂, which is justifiable regarding the precision of the measurements. Consecutive atomic planes parallel to

TABLE II. Rigid shift values s_n of {111} planes across the interface. For illustration, see Fig. 7.

n	Orientation	Lattice plane	$s_n/d_{\{hkl\}}$
1	[110]	(111)	$\frac{5}{8}$ (equivalent to $-\frac{3}{8}$)
2	[110]	$\langle 1\bar{1}1 \rangle$	$\frac{3}{8}$



FIG. 7 (color online). Illustration of the rigid shift of {111} lattice planes (black arrows) at the proposed interface model.

(001) are thus approximately $\frac{1}{4}c$ apart. However, the errors are quite large due to the signal-to-noise ratio and also due to the finite stability of the scanning supplies in the STEM. A more exact estimation of those spacings, probably by HRTEM, could yield spatial deviations from the bulk crystal at the interface region.

TEM and HRTEM investigations of epitaxial interfaces are interpreted in many cases by the measurement of the geometric phase shift between the spatial frequencies of the Si and the silicide lattices across the interface, the so-called rigid shift analysis [4,10]. For comparison, the rigid shift values for {111} planes in our model are given in Table II. Figure 7 illustrates the geometrical situation. The {111} planes in the silicon are assumed to pass through the center of the dumbbells as this has been usual in previous TEM based analysis.

The interface structure (Fig. 4) derived straightforwardly from our HAADF signal represents the sevenfold R model advocated by Yu *et al.* [12].

Conclusion.-We investigated the structure of the $NiSi_2/Si(001)$ interface at buried layers. The structure exhibits an (001) layer of dimerized Si atoms. The reconstruction occurred in two orthogonal directions, for which the Ni layers in the silicide are shifted by $\frac{1}{4}c$, respectively. This implies the occurrence of stacking faults or other defects or strain in epitaxial NiSi₂ films in Si if both directions of reconstruction coexist. With respect to the $NiSi_2/Si(001)$ interface, our results give experimental evidence for the theoretical results of Yu et al. [12], who proposed their sevenfold R model to represent the energetically favored interface structure for both the $CoSi_2/Si(001)$ and the $NiSi_2/Si(001)$ interfaces. The results shown here, in addition to finally solving a well investigated but unresolved structure, also provide a good example of the suitability of highresolution HAADF-STEM in exploring partly nonperiodic structures such as these interfaces.

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- P.R. Besser *et al.*, Mater. Res. Soc. Symp. Proc. 766, E10.1.1 (2003).
- [2] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B 37, 10623 (1988).
- [3] R.T. Tung et al., Phys. Rev. Lett. 66, 72 (1991).
- [4] P. Werner, W. Jäger, and A. Schüppen, J. Appl. Phys. 74, 3846 (1993).
- [5] Y. Khang et al., J. Vac. Sci. Technol. B 12, 2094 (1994).
- [6] A. Kikuchi, Jpn. J. Appl. Phys. 37, 653 (1998).
- [7] V. Buschmann et al., Philos. Mag. Lett. 77, 147 (1998).
- [8] S. Mantl, J. Phys. D 31, 1 (1998).
- [9] D. Loretto, J. M. Gibson, and S. M. Yalisove, Phys. Rev. Lett. 63, 298 (1989).
- [10] C.W.T. Bulle-Lieuwma, A.F. de Jong, and D.E.W. Vandenhoudt, Philos. Mag. A 64, 255 (1991).
- [11] D. Cherns, C. J. D. Hetherington, and C. J. Humphreys, Philos. Mag. A 49, 165 (1984).
- [12] B. D. Yu et al., in Advanced Interconnects and Contacts, edited by D. C. Edelstein, T. Kikkawa, M. C. Ozturk, K.-N. Tu, and E. J. Weitzman (Materials Research Society, Warrendale, PA, 1999); J. Vac. Sci. Technol. B 19, 1180 (2001).
- [13] S. Mantl and H. L. Bay, Appl. Phys. Lett. 62, 267 (1992).
- [14] S. Teichert et al., Thin Solid Films 336, 222 (1998).
- [15] O. L. Krivanek, N. Delby, and A. R. Lupini, Ultramicroscopy 78, 1 (1999).
- [16] S. J. Pennycook and D. E. Jesson, Phys. Rev. Lett. 64, 938 (1990).
- [17] Actually, we deal with a $2\sqrt{2} \times \sqrt{2}$ -*R*45° reconstruction, but it has been common in earlier publications on these interfaces to use the [110] and $[1\overline{1}0]$ lattice vectors as the base for the description of the reconstruction.
- [18] D. Cherns and R. C. Pond, Mater. Res. Soc. Symp. Proc. 25, 423 (1984).
- [19] R.C. Pond and D. Cherns, Surf. Sci. 152/153, 1197 (1985).
- [20] W.-J Chen and F.-R. Chen, Philos. Mag. A 68, 605 (1993).