Evidence for a Dimer Reconstruction at a Metal-Silicon Interface

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We show that the stable structure of a $CoSi_2$/Si(001) interface involves a 2×1 periodic array of Si dimers with bond length 0.23 ± 0.02 nm. We use a novel combination of quantitative transmission-electron diffraction, transmission-electron-microscope (TEM) imaging, and high-resolution TEM to solve the structure, and we have imaged separate 2×1 and 1×2 domains, ~100 nm in size, over many μm^2 of the interface.

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It is well known that the Si(001) surface consists of dimerized pairs of atoms with 2×1 symmetry.[1] Buried interface reconstructions have only recently been observed[2-8] and have conceptual similarity to surface reconstructions. Initially, preserved surface reconstructions were seen,[9] rather than intrinsic interface reconstructions. Here we provide convincing evidence for a well-ordered intrinsic dimer reconstruction at a buried silicon/metal-silicide interface, $CoSi_2$(001)/Si(001) 2×1, which bears a similarity to the clean Si surface, but is characteristic of the interface. The existence of periodically strained bonds at this Schottky barrier is important in understanding the electrical properties. In order to determine the structure of a reconstructed interphase boundary, which has not been achieved before, we have used a novel combination of techniques based on high-energy (~100 keV) transmission-electron scattering.

High-energy electron scattering is particularly suited to the study of interfaces since it is detectable, yet weak enough to be treated kinematically for a monolayer interface (provided the electron beam is not near grazing incidence). We have used transmission-electron microscopy (TEM) because a variety of experiments which yield complementary structural information is possible. In this study we have made measurements using two sample geometries: with the normal to the interface parallel to the electron beam (plan view), which allows for quantitative transmission-electron diffraction (TED) and diffraction contrast imaging, and with the normal to the interface perpendicular to the electron beam (cross section), which allows for high-resolution (HRTEM) imaging. (In the cross-sectional geometry the electron beam is at grazing incidence to the interface so the scattering must be treated dynamically.) Such observations are greatly facilitated if large, flat interfaces with well-defined orientations are available. In this respect, $CoSi_2$/Si(001) is ideal, since thin, single-orientation, epitaxial films have recently been grown.[10]

Molecular-beam-epitaxy (MBE) $CoSi_2$(001)/Si(001) layers, 2–10 nm thick, were formed by depositing a few monolayers of either pure cobalt or cobalt and silicon at room temperature and then annealing to ~500 °C. Such $CoSi_2$ "templates" can be thickened by code position at ~500 °C. The details of the technique are given elsewhere.[10] TEM specimens were prepared in cross section, [110] orientation, by mechanical thinning followed by 3-keV argon-ion milling, and in plan view, [001] orientation, by chemical etching with $3HF:5HNO_3:3CH_3COOH$. TEM was performed using a JEOL 4000 EX microscope operated at 100 keV for diffraction and imaging and at 200 keV for HRTEM imaging, where the point-to-point resolution is approximately 0.23 nm. Diffraction patterns were recorded by

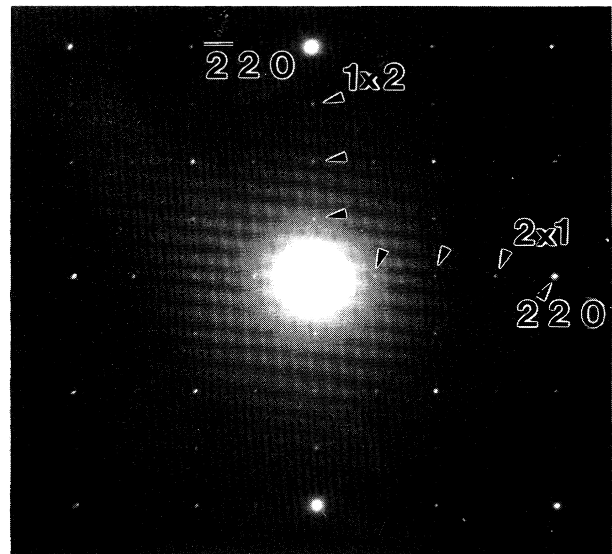

FIG. 1. A transmission-electron diffraction pattern taken at 100 keV from an ~2-nm layer of $CoSi_2$ on Si(001). The beam direction and foil normal are both close to [001]. The bulk silicon reflections, [220] and [$\bar{2}$20], are marked. Reflections in intermediate directions are due to the buried $CoSi_2$/Si(001) interface. [110] and [$\bar{1}$10] maxima originate from termination (these would be indexed as [1,0] and [0,1] in LEED), [$\frac{1}{2}$, $\frac{1}{2}$,0] and [$\frac{3}{2}$, $\frac{3}{2}$,0] come from 2×1 reconstruction, and [$\overline{\frac{1}{2}}$, $\frac{1}{2}$,0] and [$\overline{\frac{3}{2}}$, $\frac{3}{2}$,0] come from 1×2 reconstruction (these are all arrowed).

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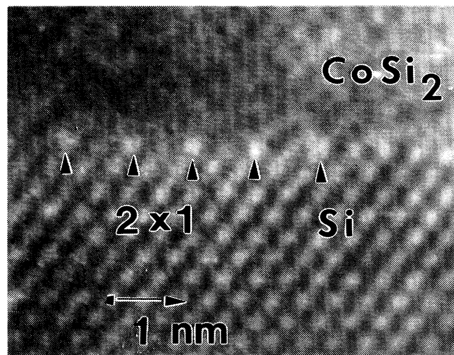
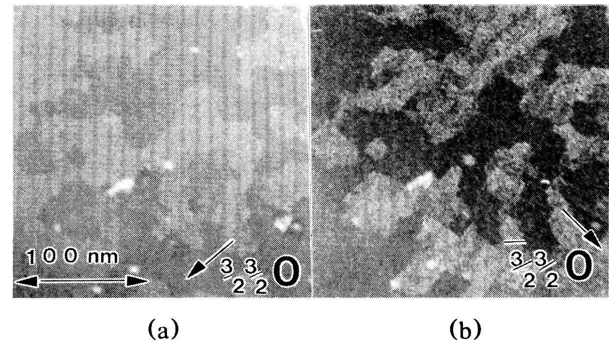


FIG. 2. A high-resolution TEM image taken along [110] showing doubling of the periodicity of the interface along the [$\bar{1}$10] direction. This is consistent with a $2\times n$ reconstruction.



(a) (b)

FIG. 3. Dark-field images taken from the diffraction pattern shown in Fig. 1. (a) Taken using the [$\frac{3}{2}$, $\frac{3}{2}$,0] reflection; areas where the dimer chains run along [110] (2×1 reconstruction) show above background contrast. (b) Taken using the [$\bar{\frac{3}{2}}$, $\frac{3}{2}$,0] reflection; areas where the dimer chains run along [1$\bar{1}$0] (1×2 reconstruction) show above background contrast. The images in (a) and (b) are complementary: The regions which are bright in (a) are dark in (b) and the regions which are dark in (a) are bright in (b). This indicates that the whole of the interface in the field of view is reconstructed as either 2×1 or 1×2.

direct exposure of the electron beam to a photographic plate using the linear-response region of the photographic emulsion. Negatives were digitized using a linear photodiode array connected to an AT&T personal computer. Background subtraction was carried out for the peak intensity measurements.

The reconstruction is seen most easily in plan-view transmission-electron diffraction patterns. Figure 1 shows a TED pattern taken at 100 keV from an ~2-nm-thick layer of $CoSi_2$(001) on Si(001). The sample has been tilted a few degrees away from the [001] zone axis to suppress dynamical scattering. In this orientation, bulk Si generates diffraction maxima at ⟨220⟩, ⟨400⟩, etc., and bulk $CoSi_2$, maxima at ⟨200⟩, ⟨220⟩, ⟨400⟩, etc. These are all seen in Fig. 1. Other diffraction maxima are visible at ⟨110⟩ (indexed as ⟨1,0⟩ in low-energy electron diffraction), which is the smallest Fourier component of the (001) surface. The scattering into these termination maxima is related to the roughness of surfaces and interfaces in the sample.[11] Reflections in fractional positions originate from the superpostion of a 2×1 and a 1×2 reconstruction (not a 2×2 since there are no ⟨001⟩ reflections). Since exposure to the air removes the Si(001) 2×1 reconstruction and the reconstruction at the surface of $CoSi_2$(001) we infer that the Si/$CoSi_2$(001) interface is responsible. This is confirmed in cross-sectional HRTEM images. Features such as that shown in Fig. 2, which has the appearance of a $2\times n$ interface reconstruction in ⟨110⟩ projection, are seen in thick regions.

Without resorting to detailed structural modeling we can use HRTEM images to obtain the relative shift between the Si and $CoSi_2$. Images recorded at Scherzer defocus, in regions where the Si and $CoSi_2$ are both thin enough to be before the first contrast reversal (i.e., conditions under which the image of both crystals can be simply interpreted as projections of their structure[12,13]), show the shift to be approximately $(a/8)$[001]. This is consistent with the simple, unreconstructed, sixfold model which was proposed for $NiSi_2$/Si(001).[13]

The separate 2×1 and 1×2 domains can be resolved in dark-field images taken from plan-view samples. Figure 3(a) was taken using the [$\frac{3}{2}$, $\frac{3}{2}$,0] reflection, which originates from 2×1 domains, and Fig. 3(b) was taken using the [$\bar{\frac{3}{2}}$, $\frac{3}{2}$,0] reflection, which originates from 1×2 domains. These micrographs are complementary: Regions which are bright in 3(a) are dark in 3(b) and regions which are dark in 3(a) are bright in 3(b), which demonstrates unambiguously that the entire interface is reconstructed as 2×1 and 1×2. If the same area is imaged using bulk-silicon reflections, line defects are visible at the domain boundaries. Conventional two-beam diffraction contrast indicates that the strain field around these defects is consistent with their having a Burgers vector of $\frac{1}{4}$⟨111⟩ (the analysis is not presented here).

Plan-view [(001) orientation] TED patterns not only give the clearest evidence for a reconstruction but they

TABLE I. Measured intensities of interface reflections. These values are from digitized diffraction patterns taken from two different areas of the same sample. Intensities, $\times 10^{-5}$, are all expressed as fractions of the main beam.

Reflection	Measured intensities	Calculated intensities Silicon dimers	Calculated intensities Compositional modulation
0 $\frac{1}{2}$ $\frac{1}{2}$	8.5 ± 0.4	8.9	5.9
0 $\frac{3}{2}$ $\frac{3}{2}$	6.2 ± 1.0	5.2	1.5
0 $\frac{5}{2}$ $\frac{5}{2}$	0.3 ± 0.1	0.4	0.4

can be quantified and modeled with kinematical theory. Intensities measured for several samples are approximately constant. We therefore conclude that the 2×1 reconstruction is always present at the interface. Table I shows intensities averaged over TED patterns from two regions of the same sample. The intensity of the each reflection is given as the average between the two symmetry-equivalent reflections, (h,k,l) and $(\bar{h},\bar{k},\bar{l})$ and the 2×1 and 1×2 contributions. There is an absolute scaling factor for these intensities, which is difficult to determine experimentally to better than within a factor of 2. However, the relative values are accurate to the errors quoted in Table I ($\sim10\%$ under favorable conditions).

We can use the relative intensity of the fractional-order maxima to determine whether the reconstruction is compositional or displacive. Simple kinematical calculations show that the ratio of the intensities $\langle 0,\frac{1}{2},\frac{1}{2}\rangle/\langle 0,\frac{3}{2},\frac{3}{2}\rangle$ will be ~2 for a purely displacive modulation (independent of the magnitude of a small displacement) and ~4 for a purely compositional modulation. Calculated values for a displacive modulation (silicon dimers) and a compositional modulation (removing alternate silicon atoms) are given in Table I. (We used a Debye-Waller factor of 4×10^{-2} nm^2, though the calculations are fairly insensitive to this parameter at small scattering angles.) Clearly, the primary structural component of the reconstruction involves atomic displacement in the plane of the interface rather than a difference in composition.

Our model for the reconstructed interface must therefore involve atomic displacements (to be consistent with the quantitative TED) and must generate a rigid shift of $\frac{1}{8}[001]$ between the Si and $CoSi_2$ (to be consistent with HRTEM). We propose the model shown in Fig. 4. This is essentially the sixfold model originally proposed for $NiSi_2$/Si(001) by Cherns, Hetherington, and Humphreys,[12] with an extra plane of silicon atoms at the interface. The silicon and cobalt preserve their fourfold and eightfold coordination except for the additional silicon atoms, which can form dimer chains, in analogy to the Si(001)$\sqrt{2}\times1$ surface, reducing the number of dangling bonds per atom from 2 to 1. The magnitude of the displacement, Δx, can be deduced by finding the best fit to the TED intensities. This gives a silicon dimer length of 0.23 ± 0.02 nm. The dimer bond length at the Si(001) 2×1 surface is within this range though the exact value is uncertain.[1]

We have used the silicon-dimer model to simulate HRTEM images using the multislice method.[14] Simulations show that the 2×1 reconstruction is not clearly visible until the first contrast reversal in the $CoSi_2$, at a thickness of ~10 nm. This is consistent with our observations.

We noted earlier that the line defects which lie between domains have a Burgers vector of $\frac{1}{4}\langle111\rangle$. The

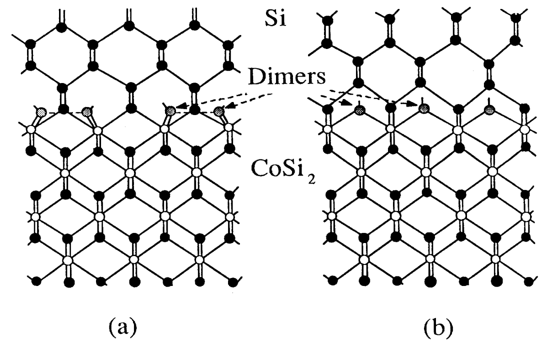


FIG. 4. A schematic of our model for the $CoSi_2(001)/Si(001)$ 2×1 interface viewed along two mutually perpendicular directions: (a) [110] and (b) $[\bar{1}10]$. An extra layer of silicon atoms (shaded), which dimerize to generate the reconstruction, is bonded to the cobalt atoms at the interface. Doubling occurs along $[\bar{1}10]$ but not along [110], corresponding to a 1×2 reconstruction.

appearance of such defects at the Si(001)/$CoSi_2$(001) interface as a result of monolayer steps has been predicted from symmetry considerations.[15] This is in agreement with our interface model insofar as a monolayer step would transform a 2×1 to a 1×2 domain [in analogy to the Si(001) surface].

In conclusion, we have shown that the stable structure of a $CoSi_2$/Si(001) interface is a 2×1 periodic array of silicon dimers, bond length 0.23 ± 0.02 nm, similar to the Si(001) 2×1 surface. We have used a novel combination of quantitative TED and imaging in plan view and HRTEM in cross section to achieve this result. We have successfully imaged separate 1×2 and 2×1 domains, ~100 nm in size, over many μm^2 of the interface. Every single-monolayer step at the interface is therefore visible as a domain boundary. The existence of a reconstruction would be expected to have a large impact on the electronic and other properties of this interface. We therefore feel that this system, a buried, periodic array of silicon dimers, is well suited for further experimental and theoretical investigations.

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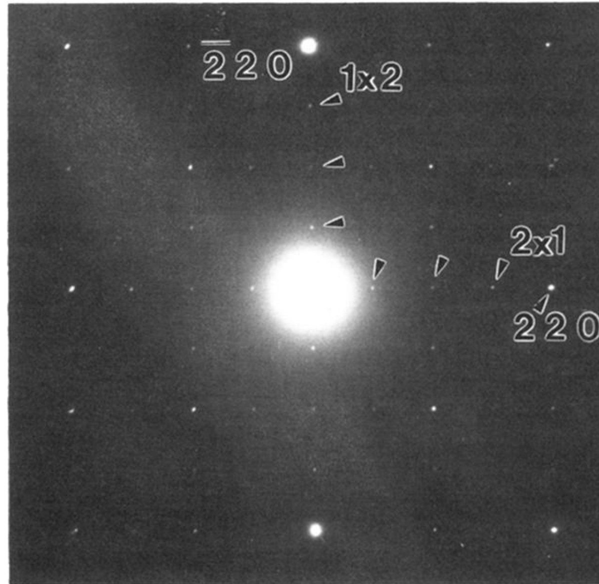

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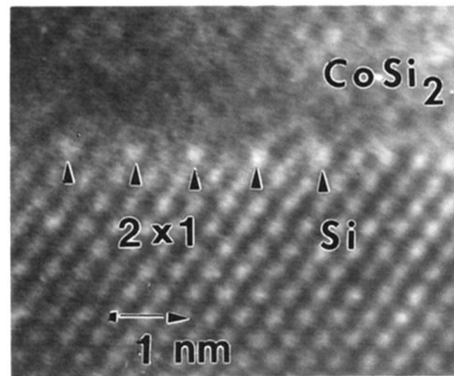

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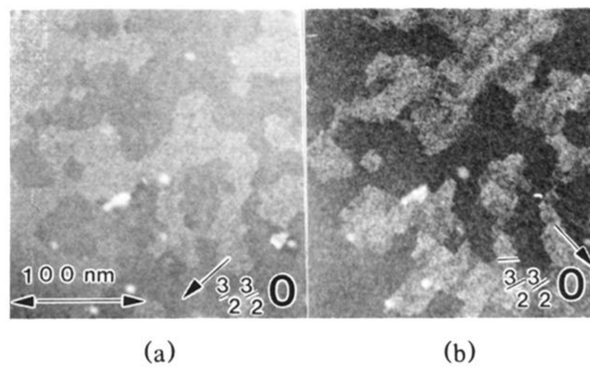

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