

Frustrated dimers at the $\text{CoSi}_2/\text{Si}(001)$ interface

M. Copel and J. Falta

IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 14 April 1993)

The interface between epitaxial CoSi_2 and $\text{Si}(001)$ has been investigated with medium-energy ion scattering. Ions are sharply dechanneled at the interface, due to an interfacial layer of reconstructed silicon. Both the intensity and angular distribution of the interface peak closely match simulations for a dimer reconstruction. The results are incompatible with models of the interface that do not include substantial displacement of silicon atoms, such as a pure composition modulation. The bond length of $2.6 \pm 0.1 \text{ \AA}$ is significantly longer than found at the $\text{Si}(001)$ surface, due to the repulsive interactions with coplanar, nondimerized Si atoms.

Understanding the structure and formation of solid-solid interfaces has been a long-standing challenge in materials research. Silicide/silicon interfaces have been the subject of particular scrutiny due both to the technological importance and the theoretical difficulties presented by the bonding of electronically dissimilar materials. Only recently have (001) interfaces been addressed, since they pose a more difficult preparation problem, even though the (001) face is universally preferred for applications.

The $\text{CoSi}_2/\text{Si}(001)$ interfaces reconstructs to a (1×2) periodicity, observed by transmission-electron-microscopy (TEM) studies of samples prepared by molecular-beam epitaxy (MBE).¹ The driving force for the reconstruction is provided by the dangling interface bonds on the CoSi_2 layer, which are not fully terminated by the substrate. Loretto, Gibson, and Yalisove¹ proposed a layer of silicon dimers bound into the silicide, which would reduce the density of dangling bonds from 2 to 1 monolayer (ML) ($1 \text{ ML} = 6.78 \times 10^{14}/\text{cm}^2$), similar to the formation of dimers on the $\text{Si}(001)$ surface. Subsequent studies of mesotaxial CoSi_2 layers formed by ion implantation into $\text{Si}(001)$ suggested a different structure, with $\frac{1}{2}$ ML of Si occupying sites on the CoSi_2 lattice.² The $\text{NiSi}_2/\text{Si}(001)$ also reconstructs, albeit with poorer interface ordering.³

We have investigated the structure of epitaxial $\text{CoSi}_2/\text{Si}(001)$ using medium-energy ion scattering (MEIS). For films as thin as 5-ML CoSi_2 , an interface peak appears in the Si signal. Since CoSi_2 has a CaF_2 structure, the overlayer shadows all atoms that are confined to the substrate lattice. (This is assuming that the interface bonds are confined to physically reasonable lengths, with distortions less than $\pm 0.2 \text{ \AA}$.) The existence of an interface peak for a pseudomorphic film implies that a layer of silicon is bound in a site that is an extension of neither the substrate nor the overlayer lattice. This is distinctly different from epitaxy on the (111) surface, where the CoSi_2 can be grown in a twinned orientation (B type), causing an interface peak without an interface reconstruction.^{4,5} Both the amplitude and the angular distribution of the interface peak that we have ob-

served for the $\text{CoSi}_2/\text{Si}(001)$ interface are compatible with a layer of dimerized silicon bound to the CoSi_2 . Furthermore, the structure of the dimer layer has been determined, and an anomalously long dimer bond length of $2.6 \pm 0.1 \text{ \AA}$ is found. Dimer formation at this interface is frustrated by the presence of 1 ML of coplanar Si, which occupies sites that are fourfold coordinated. The repulsive interactions between the Si dimers and the fourfold Si stretch the dimer bond length, relative to the value found by theoretical studies of dimerization of $\text{Si}(001)$.⁶⁻⁸

$\text{Si}(001)$ substrates were prepared by a standard recipe consisting of a light sputter followed by a 40-s flash to 1040°C in ultrahigh vacuum. After cooling, a Co template was prepared by depositing 2-ML Co, followed by 2-ML Si.^{9,10} The template was annealed to 470°C for 10 s, then alternating layers of Co and Si in a 1:2 stoichiometry were deposited at room temperature, to a thickness of 13-ML CoSi_2 . The sample was then annealed at 470°C until a clear $(\sqrt{2} \times \sqrt{2})R45^\circ$ low energy electron-diffraction pattern was observed, typically within 60 s.¹¹ The diffraction pattern observed with TEM in plan view showed a distinct pattern of $(\frac{1}{2}, \frac{1}{2}, 0)$ spots, indicative of an interface reconstruction.¹

Samples were analyzed *in situ* with MEIS. Detailed descriptions of the technique and experimental apparatus have been previously published,¹² so only a brief explanation will be included. The sample was aligned with the $[11\bar{1}]$ axis parallel to an incident beam of 200-keV He^+ . In this aligned geometry, the topmost atoms of the CoSi_2 shadow the underlying crystal. Below the surface, only those atoms in sites deviating from the bulk crystal structure are visible to the beam. This can be due either to poor crystal structure, subsurface (interface) reconstruction, or thermal vibrations. For the Co portion of the energy spectrum (not shown), the channeling yield was 2% of the yield in a random geometry, indicating crystal quality comparable to the substrate.

Results for the Si portion of the spectrum reveal significant structure at the interface. In Fig. 1, a series of spectra are shown for slightly varying ion-beam orientations, where α is the angle between the beam and the surface. The top frames show an intensity plot of yield as a

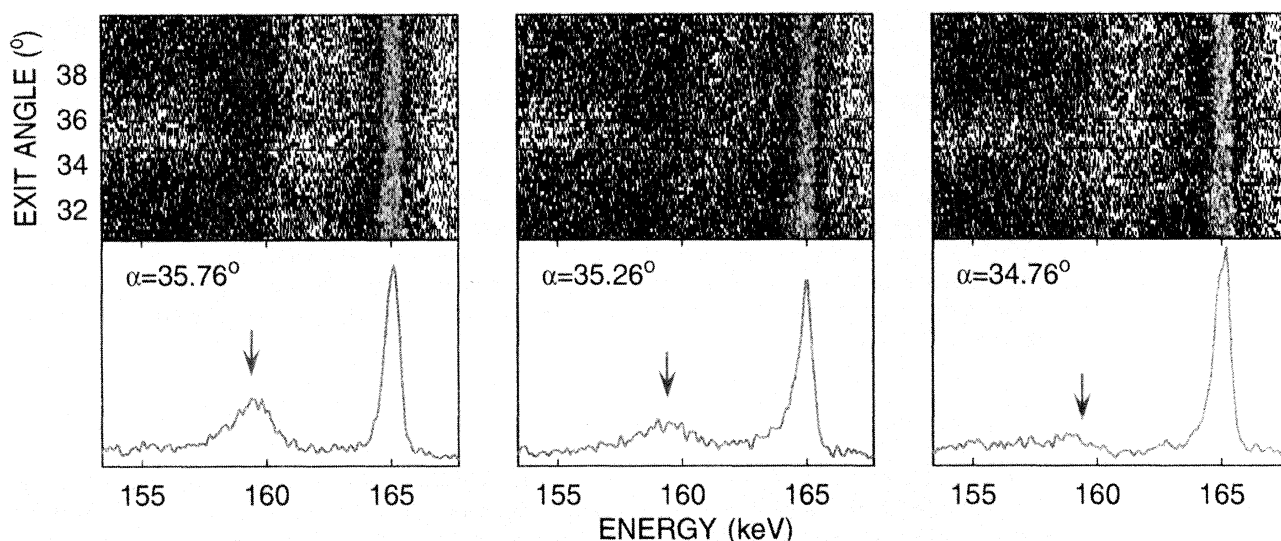


FIG. 1. Ion-scattering spectra for epitaxial $\text{CoSi}_2/\text{Si}(001)$. The top frames show intensity plots of energy as a function of scattering angle, after correction for the angular variation in scattering kinematics. The yield in the angular region between the dashed lines is displayed in the bottom frames. A peak appears at 159.6 keV due to backscattering from interface silicon, indicated by an arrow. The data are shown for several angles of incidence.

function of exit angle and energy. The bottom frames show a cut through the intensity plot, showing yield vs backscattered ion energy. Two prominent features can be seen in the spectra: a surface peak at 165.1 keV, and an interface peak at 159.6 keV. The interface peak varies in amplitude as the direction of the incident beam is changed. The largest interface peak is observed with $\alpha=35.76^\circ$. The peak decreases when aligned with $[11\bar{1}]$, corresponding to $\alpha=35.26^\circ$, and further decreases at $\alpha=34.76^\circ$. From a qualitative analysis, we can learn that a significant displacement of Si occurs and that the ion beam can be focused on the reconstructed atoms.

The area of the Si interface peak as a function of scattering angle and beam angle can be extracted and normalized to units of Si monolayers (Fig. 2). The angular dependence of the yield is similar to that observed by varying the incident angle: there is an asymmetry in the blocking dip, with larger yields observed at exit angles greater than 35.26° , which is the $[11\bar{1}]$ blocking direction. The smooth curve in Fig. 2 is a Monte Carlo simulation based on a dimer reconstruction of the interface, with the silicon dimers bonded to the Co atoms closest to the interface. The curve was generated using the best fit for the dimer model, which is described below. Alternatively, an interface composed of a composition modulation of the topmost Si layer was proposed by Bulle-Lieuwma, de Jong, and Vandenhoudt.² In this model, only modest displacements of interface atoms are predicted, due to relaxation. For physically reasonable values of the interplanar spacing, the interface remains shadowed by the overlying CoSi_2 , thus giving no interface peak at all, which is inconsistent with our data.

Optimization of the dimer model involved Monte Carlo simulations for a variety of dimer bond lengths and interplanar spacings. For symmetric-dimer models, the simulations were averaged over two domains rotated by

90° . Asymmetric-dimer models were averaged over four orientations. A tetragonal distortion of the epilayer of -1.5% was used, in agreement with the measured CoSi_2 bond angles. The goodness of fit as a function of these parameters is displayed in Fig. 3. The data can be accurately modeled by a dimer bond length of $2.55 \pm 0.1 \text{ \AA}$, with the dimer plane located $1.05 \pm 0.25 \text{ \AA}$ below the Co plane. The positions of the Co atoms were kept fixed, since the experiment is insensitive to Co displacements of the amplitude that would accompany the dimer reconstruction. The resulting Si-Co distance is 2.28 \AA . The fit

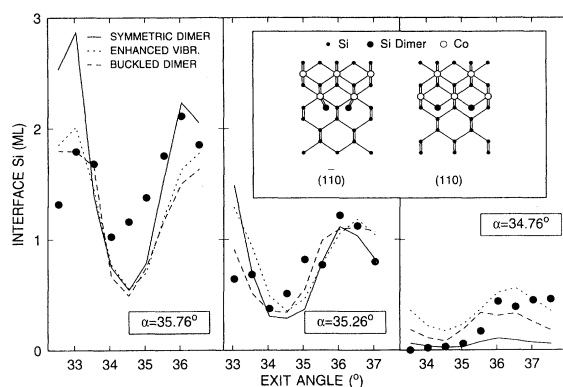


FIG. 2. The silicon interface peak area as a function of exit angle. The amplitude is strongly dependent on both incidence and exit angle. Simulations are shown for a symmetric-dimer model with bulk thermal vibration amplitude, buckled dimers, and a symmetric-dimer model with enhanced vibrations. Simulations for interface models based on composition modulation give infinitesimal yields. A ball-and-stick model of the interface, viewed both parallel and perpendicular to the dimers, is included.

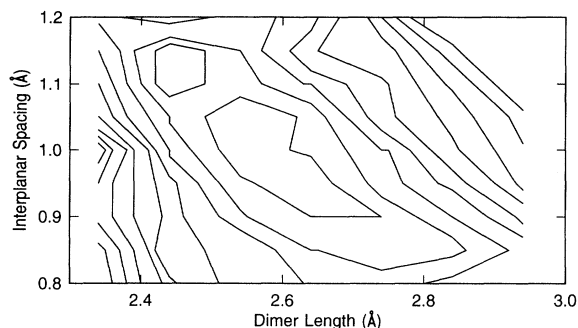


FIG. 3. The contour plot of goodness-of-fit as a function of dimer bond length and Co-Si interplanar spacing. No scaling of simulated yields is included in the optimization, and all other structural parameters are kept fixed.

could also be improved by altering two other parameters. The thermal vibration amplitude of the dimers can be enhanced from bulklike values, 0.075 to 0.175 Å (dotted line in Fig. 2). This could be caused by either a dynamic buckling of the dimer layer or by some disorder at the interface. It is unlikely that significant disorder exists at the interface, since the simulated yields have the same magnitude as the data, and no scaling has been used to improve the fit. In comparison, studies of $\text{CoSi}_2/\text{Si}(111)$ found that disorder resulted in interface peak intensity a factor of 2 lower than simulated yields.⁵ Alternatively, a static buckling of the dimer layer can be introduced which improves the fit (dashed line in Fig. 2). The optimum value for the dimer buckling was 0.5 Å, with the dimer atoms located 0.8 and 1.3 Å below the Co, and a dimer spacing of 2.6 Å. In this model, the Co-Si interatomic spacings are 2.23 and 2.45 Å, assuming no relaxation of Co.

It is instructive to compare the $\text{CoSi}_2/\text{Si}(001)$ interface with results for the $\text{Si}(001)$ surface. Self-consistent pseudopotential calculations were used in Ref. 6 to derive a dimer bond length of 2.35 Å, with a buckling of 0.48 Å. The dimers were located 1.39 and 0.92 Å above the nearest Si plane. Other theoretical studies give similar results.^{7,8} Experimental studies yield conflicting results, with bond lengths varying from 2.4 (Ref. 13) to 2.54 Å (Ref. 14). Unlike the $\text{Si}(001)$ surface, there is an important constraint on movement of dimer atoms at the $\text{CoSi}_2/\text{Si}(001)$ interface in the form of coplanar Si atoms that do not dimerize. With the dimer bond length of 2.6 Å, the interatomic spacing between the dimerized and

nondimerized Si is only 2.32 Å, which is abnormally small for nonbonding Si. It is likely that a repulsive interaction limits the dimerization, as observed by experiment.

The influence of growth conditions on interface structure is an issue that deserves some discussion, especially in light of the different conclusions found in studies of MBE and mesotaxial samples. Samples were also prepared by solid-phase epitaxy (SPE) of $\text{Si}/\text{Co}/\text{Si}(001)$ sandwiches. The thickness of these samples was limited by a tendency toward island formation; however, for films ≈ 5 ML thick, an interface peak was observed. The interface peak exhibited the same qualitative behavior as before: the peak was larger for incident angles further from the surface, and exhibited a similar angular distribution. Unfortunately, difficulties in deconvolving the interface peak from the surface peak precluded a detailed quantitative analysis. Nonetheless, we conclude that the interface structure is not strongly dependent on sample preparation.

A second complication may arise from the effects of strain relief. A pseudomorphic $\text{CoSi}_2/\text{Si}(001)$ film undergoes a tensile strain of 1.2%. The thin samples grown by $\text{Si}/\text{Co}/\text{Si}(001)$ SPE were fully strained. The thicker samples prepared by the template technique showed some sign of strain relief, in the form of a broadening of the $[11\bar{1}]$ channel. This could have two effects on our conclusions. First, it could alter the focusing of ion trajectories, which would change the dimer bond length from 2.6 to 2.7 Å. Second, the introduction of strain relief defects could increase the interface disorder. But regardless of the degree of strain relief, the data support a dimer reconstruction at the interface.

We have examined the interface of epitaxial CoSi_2 with MEIS, and found that significant quantities of Si are displaced at the interface. Not only are the data compatible with a dimer reconstruction, they are clearly incompatible with a reconstruction based only on composition modulation. Extensive modeling of the interface has been used to show that the dimers have a bond length of 2.6 ± 0.1 Å, distinctly larger than the values of 2.35 Å calculated for the $\text{Si}(001)$ surface.⁶ The longer bond length can be explained on the basis of the local geometry, which confines the movement of the dimer atoms.

We wish to thank F. K. LeGoues for providing TEM analysis, R. M. Tromp for helpful discussions, and S. Gillespie for guidance.

¹D. Loretto, J. M. Gibson, and S. M. Yalisove, *Phys. Rev. Lett.* **63**, 298 (1989).

²C. W. T. Bulle-Lieuwma, A. F. de Jong, and D. E. W. Vandenhoudt, *Philos Mag. A* **64**, 255 (1991).

³R. T. Tung, A. F. J. Levi, J. P. Sullivan, and F. Schrey, *Phys. Rev. Lett.* **66**, 72 (1991).

⁴E. J. van Loenen, J. W. M. Frenken, J. F. van der Veen, and S. Valeri, *Phys. Rev. Lett.* **54**, 827 (1985).

⁵A. E. M. J. Fischer, T. Gustafsson, and J. F. van der Veen,

Phys. Rev. B **37**, 6305 (1988).

⁶J. Ihm, M. L. Cohen, and D. J. Chadi, *Phys. Rev. B* **21**, 4592 (1980).

⁷K. C. Pandey, in *Proceedings of the 17th International Conference on the Physics of Semiconductors*, edited by D. J. Chadi and W. A. Harrison (Springer, Berlin, 1984), p. 55.

⁸S. Tang, A. J. Freeman, and B. Dely, *Phys. Rev. B* **45**, 1776 (1992).

⁹R. T. Tung, J. M. Gibson, and J. M. Poate, *Phys. Rev. Lett.* **50**,

- 429 (1983).
- ¹⁰S. M. Yalisove, R. T. Tung, and D. Loretto, *J. Vac. Sci. Technol. A* **7**, 1472 (1989).
- ¹¹S. M. Yalisove and J. L. Batstone, in *Heteroepitaxy on Silicon: Fundamentals, Structures, and Devices*, edited by H. K. Choi, R. Hull, H. Ishiwara, and R. J. Nemanich, MRS Symposia Proceedings No. 116 (Materials Research Society, Pittsburgh, 1988), p. 439.
- ¹²J. F. van der Veen, *Surf. Sci. Rep.* **5**, 199 (1985).
- ¹³M. Aono, Y. Hou, C. Oshima, and Y. Ishizawa, *Phys. Rev. Lett.* **49**, 567 (1982).
- ¹⁴W. S. Yang, F. Jona, and P. M. Marcus, *Phys. Rev. B* **28**, 2049 (1983).

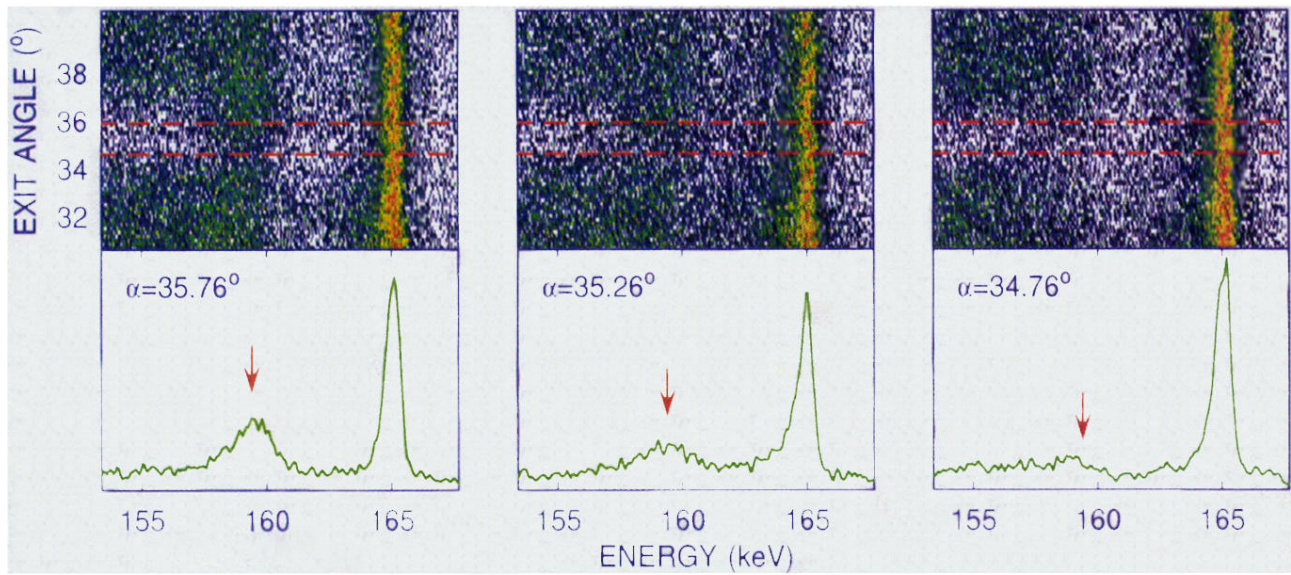


FIG. 1. Ion-scattering spectra for epitaxial $\text{CoSi}_2/\text{Si}(001)$. The top frames show intensity plots of energy as a function of scattering angle, after correction for the angular variation in scattering kinematics. The yield in the angular region between the dashed lines is displayed in the bottom frames. A peak appears at 159.6 keV due to backscattering from interface silicon, indicated by an arrow. The data are shown for several angles of incidence.