Film/Substrate Registry as Measured by Anomalous X-Ray Scattering at a Reacted, Epitaxial Cu/Si(111) Interface

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We used anomalous x-ray-diffraction methods to measure the contribution of an epitaxial copper overlayer on silicon to the crystal truncation rods (CTR's). The intensities of the CTR's are analyzed to determine interface structure; the epitaxy of a large-misfit system, Cu on Si(111), can be described in relationship to this structure. Anomalous scattering observed at the Cu *K* edge along a Si CTR demonstrates copper atoms to be in registry with the Si(111) surface. The copper-atom registry at the interface can be modeled based on the known bulk η-Cu_3Si structure and observed epitaxy.

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The observed epitaxy of Cu on Si(111) seems anomalous in the context of the established principles of lattice matching [1]. The misfit of 15% between epitaxial copper and the Si(111) surface is outside the range of misfits commonly observed [(0–7)%]. We believe, however, that Cu on Si(111) is representative of a large class of heteroepitaxial systems for which epitaxy is controlled by the formation of an interfacial compound with a thickness of more than one monolayer. Often, epitaxy is hindered because the compound is not matched to the substrate leading to a disordered microstructure and polycrystalline growth. For lattice-matched, nonreactive systems, the interface structure that forms and the resulting epitaxy are often intuitively accessible by simply superposing the two lattices. Although similar mechanisms are at times applicable to reactive, semicoherent films, the situation typically is more complicated, and the structure of the interface must be measured to understand the epitaxy.

Studies of interface structures of reactive systems to determine their role in epitaxy are especially timely in light of recent efforts to grow thin-film superconductors [2] and other oxides such as $BaTiO_3$ [3] on a practical but reactive substrate such as silicon. In this Letter, we describe anomalous x-ray-scattering measurements of the contribution of the registered component of a reacted, incommensurate overlayer to the substrate crystal truncation rods (CTR's). We use the resulting structure determination to explain the observed epitaxy and to push the current understanding of interface structures beyond lattice-matched systems to those that are reactive and semicoherent.

For lattice-matched systems such as NiS_2 [4] and Ag [5] on Si(111), the observed epitaxy allows site coincidence to extend over large areas of the surface thereby lowering the interfacial free energy. For the reactive system $NiSi_2$ on Si(111), the lattice parameter matches to within 1% and the silicon is fourfold coordinated in both structures so that the bonding of the silicon across the interface is maintained. Both of these structural attributes lead to the growth of high-quality films. However, for the weakly interacting system Ag on Si(111), maximum site coincidence can occur for integer multiples of the simple geometric relationships between the structures. If copper were to grow on Si(111) with the same epitaxy as Ag on Si(111), a similar geometric matching would occur: Three Cu(110) planar spacings match two Si(110) planar spacings to within 0.1%. This epitaxy is *not* observed; rather the Cu$[1\bar{1}0]$ aligns with the Si$[2\bar{1}\bar{1}]$, producing a 15% lattice mismatch. Although this epitaxy cannot be understood in terms of lattice-matching arguments, consideration of the reaction between copper and silicon provides the answer: A silicide forms and lowers the interfacial free energy to accommodate the Cu-Si mismatch and rotation.

The formation of Cu_3Si at the Cu/Si interface is consistent with results obtained from surface-sensitive techniques [6]. Both the measured stoichiometry [6] and diffraction [7] indicate a reaction to a compound similar to the high-temperature form of copper silicide, η-Cu_3Si [8], for a copper coverage below 6 monolayers (ML, 1 ML$=7.83\times10^{14}$ atoms/cm^2). Based on a rhombohedral unit cell of η-Cu_3Si, the epitaxy is given by η-$Cu_3Si(111)\|Si(111)$ and η-$Cu_3Si[1\bar{1}0]\|Si[1\bar{1}0]$. Reflection high-energy electron-diffraction (RHEED) observations indicate that, for a coverage between 0 and 6 ML, the η-Cu_3Si nucleates as semicoherent islands having an average diameter of 2.3 nm. The lattice parameter is approximately that of the bulk silicide and results in a 7% misfit to the silicon substrate. After the islands coalesce at 6-ML copper coverage, fcc copper grows epitaxially [7]. While this picture of the Cu/Si(111) system is incomplete, these observations will be used in conjunction with CTR measurements to develop a specific structural model and illustrate how the interface can accommodate the dissimilar structures of copper and silicon.

For the limited number of film/substrate systems where compound formation is not important, such as lead on Ge(111), surface structures have been determined and used to explain the epitaxy [9]. However, a practical consequence of a reactive process is to bury the interface making it inaccessible to surface-sensitive structural probes. Moreover, the reaction process between copper and silicon is aggravated by sample preparation techniques and beam heating in an electron microscope [7]. X-ray diffraction was used as the only nondestructive technique able to probe the structure of the buried

Cu/Si(111) interface.

The sample investigated was a 100-nm-thick copper film deposited by molecular-beam epitaxy on a Si(111) surface heated to 100 °C. A copper flux equivalent to 0.02 nm/sec in a vacuum of 1×10^{-9} Torr was deposited on a 7.6-cm-diam Si(111) wafer that was cleaned using standard cleaning procedures to produce a sharp 7×7 Si(111) pattern just before growth. The sample was then mounted on a four-circle goniometer for x-ray-diffraction measurements at the X-14 beam line at the National Synchrotron Light Source (NSLS) [10]. Peak intensities along the Si CTR's were measured in the same way as described by Taylor *et al.* [11], and can be modeled based on weak, kinematic scattering from the interface.

From the treatment in Ref. [12], the structure factor $F(\mathbf{q})$ at scattering vector $\mathbf{q}$ of a Si CTR for an overlayer on a Si(111) surface can be written in the kinematical approximation:

$$F(\mathbf{q})=F_{\mathrm{Si}}(\mathbf{q})+\left([f_{\mathrm{Cu}}+f'_{\mathrm{Cu}}(E)+if''_{\mathrm{Cu}}(E)]\sum_j^{\mathrm{Cu}}\exp(-q_{xy}^2\langle u_{xy}^2\rangle_j)\exp(i\mathbf{q}\cdot\mathbf{r}_j)\right)+\left(f_{\mathrm{Si}}\sum_j^{\mathrm{Si}}\exp(-q_{xy}^2\langle u_{xy}^2\rangle_j)\exp(i\mathbf{q}\cdot\mathbf{s}_j)\right). \quad (1)$$

This structure factor is separated into three terms: The first, $F_{\mathrm{Si}}(\mathbf{q})$, describes the truncation of the silicon lattice [12]; the second and third terms in large parentheses describe the contribution of the overlayer to the scattering. The overlayer terms include contributions from possible modifications of the silicon surface and contributions from a copper silicide film. To model interface disorder expected for films with large misfit, a static Debye-Waller factor $q_{xy}^2\langle u_{xy}^2\rangle_j$ was added to the structure factor for the overlayer, where the $\langle u_{xy}^2\rangle_j$ are the mean-square displacements of the overlayer atoms from their sites and q_{xy} is the in-plane scattering vector. The q-dependent x-ray atomic scattering amplitudes for copper and silicon are f_{Cu} and f_{Si}. The energy-dependent, anomalous dispersion corrections are $f'_{\mathrm{Cu}}(E)$ and $f''_{\mathrm{Cu}}(E)$; these corrections were experimentally determined using the method outlined in Ref. [13]. The sum is taken over all copper sites $\mathbf{r}_j$ and silicon sites $\mathbf{s}_j$, within the silicon surface unit cell. The square of the amplitude of the structure factor of Eq. (1) is then the intensity of a Si CTR.

We have measured the Si CTR intensity for Cu on Si(111) for the smallest, nonzero, in-plane scattering vector, and a strong departure from any simple truncation of the Si(111) surface is apparent. We illustrate this in Fig. 1 by comparing the measured CTR intensity with a structure-factor calculation for a silicon surface truncated by a bilayer of silicon atoms in the bulk positions. While the low q_{xy} data in Fig. 1 clearly indicate this deviation from a bilayer truncation, similar data for larger in-plane scattering vectors do not. The inconsistency in the q_{xy} dependence arises either from a disordered silicon surface [14] or from copper atoms modifying the basic structure/diffraction characteristics of the silicon/silicide interface.

The discrimination between these two possibilities is the critical issue. A subtle, but extremely powerful, aspect of the use of CTR characterization makes this discrimination straightforward. The copper site occupancy and registry with the silicon lattice can be determined by measuring the anomalous x-ray-scattering intensity of the CTR as the incident x-ray energy is scanned across the Cu K absorption edge. The change in energy results in significant changes in f'_{Cu} and f''_{Cu} (≈ 6 e.u. or $>20\%$ of f_{Cu}) while the x-ray-scattering factor for silicon, f_{Si}, remains essentially unchanged. Indeed, the intensity of the CTR associated with the silicon surface at the position marked with a cross in Fig. 1 was observed to vary as the copper scattering factor was changed, as shown in Fig. 2. Because the atomic scattering factor of copper alone was changed as the incident energy was scanned through the Cu K edge, the change in the observed CTR scattering of Fig. 1 uniquely provides direct evidence that copper is in registry with the silicon surface. Similar changes were observed all along the silicon $(\frac{2}{3},\frac{2}{3},\overline{\frac{4}{3}})$ rod. The lack of anomalous scattering at CTR's with larger in-plane scattering vectors shows that the registry is not perfect and is strongly affected by disorder in the overlayer.

Based on the observed anomalous scattering, we were able to determine that the CTR intensity variations result from portions of the silicide in registry with the silicon substrate. However, the scattering from the registered silicide along many of the Si CTR's is weak due to disorder, and an unambiguous structural determination cannot be made. Therefore, with this limitation in mind, we considered models of the overlayer only for the high-symmetry sites of plane group $p3m1$. These correspond

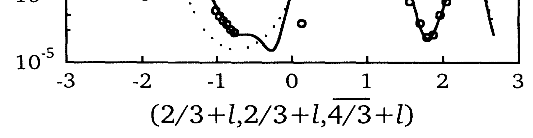

FIG. 1. Intensity along the $\mathrm{Si}(\frac{2}{3},\frac{2}{3},\overline{\frac{4}{3}})$ CTR. The open circles are data, the dotted line is the intensity expected from a bilayer truncation without overlayer, and the solid line is calculated from the model of Fig. 3. The cross indicates the point in reciprocal space where the data of Fig. 2 were taken.

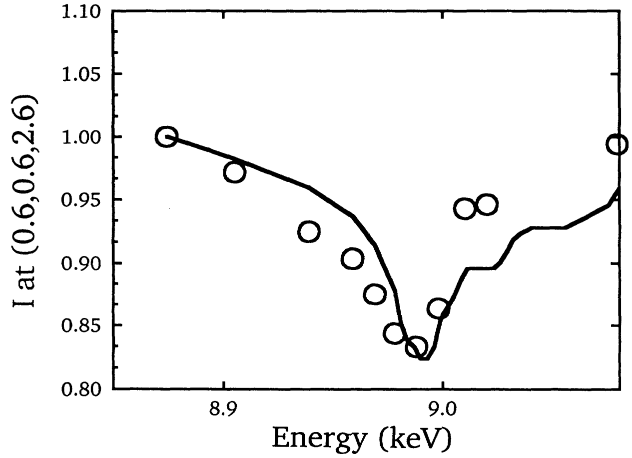

FIG. 2. Intensity I at the (0.6,0.6,2.6) point in reciprocal space vs incident x-ray energy. The open circles are observations and the solid line is the energy dependence of the intensity based on the model of Fig. 3.

to the silicon surface sites at the top site, the fourfold-coordinated hollow site ($T4$), and the threefold-coordinated hollow site ($H3$). This model then includes general characteristics that can describe a single close-packed copper layer, a single layer truncation of silicon, copper interstitials at hollow sites of the bilayer truncation, or η-Cu_3Si on bilayer truncated silicon. Our fitting procedure optimized the height and scattering amplitude of a single scattering center at each site relative to the silicon surface. The parameters that provided the best fit to the data of Fig. 1 (see Table I) define a structure similar to an η-Cu_3Si unit cell on an unrelaxed Si(111) bilayer.

The bulk Cu_3Si structure is rhombohedral [8] consisting of an *ABC* stacking sequence of a hexagonal arrangement of atoms lying in planes labeled α, β, and B in Ref. [8] along the $\langle 111 \rangle$ direction, as illustrated in Fig. 3. The planes labeled α and β are occupied by copper only, while plane B is occupied by a mixture of silicon and copper. A cross section of the silicon/interface/η-Cu_3Si structure is shown in Fig. 3. The parameters in Table I are consistent with η-Cu_3Si that is modified at the interface such that the first silicide copper plane (labeled α in Fig. 3) is placed within the silicon bilayer at threefold hollow sites, $H3$. The position of the B plane in the Cu_3Si overlayer coincides approximately with the next silicon plane of the substrate (0.25 nm of Table I compares with 0.235 nm for bulk silicon). The fit is improved further if a second copper layer (labeled β in Fig. 3) is placed between the first copper layer and the silicon at fourfold-coordinated hollow sites, $T4$. These three layers, α, β, and B, are sufficient to model the data and define the η-Cu_3Si structure one unit cell high. Layers further from the interface lose coherence and do not contribute to the Si CTR as expected in a disordered, semicoherent overlayer [15].

TABLE I. Fit parameters based on the η-Cu_3Si structure.

Composition of layer	In-plane position	Height (nm)	$q_{xy}^2\langle u_{xy}^2\rangle$
Top of bilayer, Si	⋯	0.0	0.0
α layer, Cu	$H3$, hollow site	−0.011	1.92
β layer, Cu	$T4$, hollow site	0.19	2.14
B layer, $\frac{1}{3}$ Cu + $\frac{2}{3}$ Si	Top site	0.25	1.43

Independent of the details of our model, the anomalous scattering results clearly delineate several structural features of the interface. The observed anomalous scattering at the Cu K edge contributes to a Si CTR only if copper atoms are in registry with the silicon substrate. Part of the silicide overlayer that contains copper atoms strongly bonds to the silicon and acts as a nucleus for the semicoherent silicide. The disorder in the overlayer, that was also directly observed in the x-ray scattering, is a reflection of the silicide/silicon misfit that must be accommodated if epitaxy is to develop. If, as suggested by RHEED, η-Cu_3Si domains nucleate and coalesce, a disordered misfit dislocation network and small-angle grain boundaries will naturally result. Because the diameter of the domains defined by the grain boundaries and dislocation network is small (2.3 nm), variations in size and orientation of the domains can cause random in-plane displacements large enough to significantly reduce

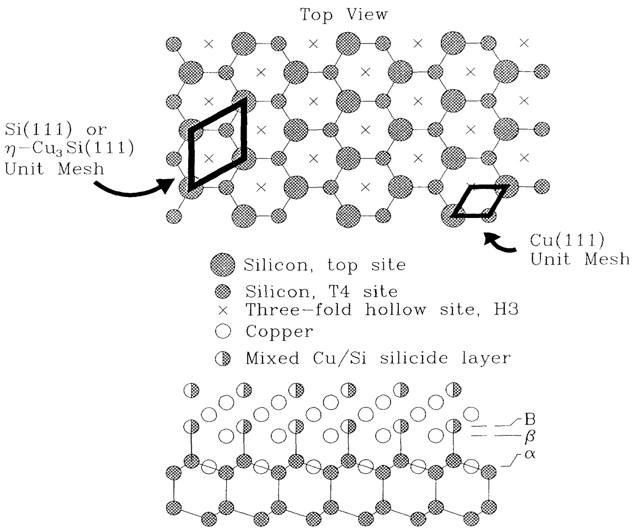

FIG. 3. Model of the copper silicide/silicon interface. Upper drawing is a top view showing the structure of the unreconstructed Si(111) bilayer truncated surface and its high symmetry sites. Lower drawing is a cross-sectional view of the silicide/silicon interface.

the scattering for higher-order CTR's. For a highly disordered network, the scattering from the overlayer interface is dominated by contributions from the registered atoms located at the center of the domains. We believe that the structure of the interface derived above represents this registered portion of the silicide. The epitaxy is then determined by the fit of the registered portion of the η-Cu$_3$Si overlayer onto the silicon. This fit allows the silicide and silicon to be connected by Si-Si bonds across the interface, and the α-Cu layer to be placed in $H3$ hollow sites. These structural elements of the registry allow the interfacial free energy to be lowered sufficiently to offset the misfit of the copper silicide on silicon and determine the epitaxy. This notion is consistent with recently reported calculations of the free energies of the $H3$ surface sites [16].

We have considered the complex surface and interface microstructure for this reactive system, Cu on Si(111), broken it into its component parts, and offer a comprehensive analysis of the observed epitaxy. The measurements of the Si CTR presented here characterize the interface buried by the Cu/Si reaction. After this reaction is complete, the surface of the η-Cu$_3$Si layer provides sites with the proper symmetry to determine the observed epitaxy of fcc copper on Si(111). This epitaxy involves a 30° rotation on the Cu(111) unit mesh relative to the silicon or silicide (111) unit mesh; see top view of Fig. 3. This rotation is accomplished by a straightforward filling of the remaining sites of the terminating copper layer of the silicide, α or β, to form a close-packed (111) plane of fcc copper; RHEED oscillations have been used to observe the dynamics of this site filling and transition to the overgrowing epitaxial copper [7]. Similar arguments may well explain the rotational and strain-relief aspects of the epitaxy that has been observed in other reactive systems such as transition metals on sapphire and the rare earths on rare-earth fluorides; see Ref. [17] for a recent review.

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[1] A. Zur and T. C. McGill, J. Appl. Phys. **55**, 378 (1984).

[2] Li Luo, R. E. Muenchausen, C. J. Maggiore, J. R. Jimenez, and L. J. Schowalter, Appl. Phys. Lett. **58**, 419 (1991).

[3] R. A. McKee, F. J. Walker, J. R. Conner, E. D. Specht, and D. E. Zelmon, Appl. Phys. Lett. **59**, 782 (1991); R. A. McKee, F. J. Walker, and J. R. Conner, in "Heteroepitaxy of Dissimilar Materials," edited by J. P. Harbison, R. F. C. Farrow, A. Zangwill, and P. S. Peercy, MRS Symposia Proceedings (Materials Research Society, Pittsburgh, PA, to be published).

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

[5] F. K. LeGoues, M. Liehr, and M. Reiner, Mater. Res. Soc. Symp. Proc. **94**, 121 (1987).

[6] A. Taleb-Ibrahimi, V. Mercier, C. A. Sebenne, D. Bolmont, and P. Chen, Surf. Sci. **152/153**, 1228 (1985).

[7] F. J. Walker, J. R. Conner, and R. A. McKee, in *Thin Film Structures and Phase Stability,* MRS Symposia Proceedings No. 187, edited by B. M. Clemens and W. L. Johnson (Materials Research Society, Pittsburgh, PA, 1990), p. 249; F. J. Walker and R. A. McKee (unpublished).

[8] Jan Ketil Solberg, Acta Cryst. Sect. A **34**, 684 (1978).

[9] H. Huang, C. M. Wei, H. Li, B. P. Tonner, and S. Y. Tong, Phys. Rev. Lett. **62**, 559 (1989).

[10] A. Habenschuss, G. E. Ice, C. J. Sparks, and R. Neiser, Nucl. Instrum. Methods Phys. Res., Sect. A **266**, 215 (1988).

[11] M. S. Taylor, I. Majid, P. D. Bristowe, and R. W. Balluffi, Phys. Rev. B **40**, 2772 (1989).

[12] I. K. Robinson, R. T. Tung, and R. Feidenhans'l, Phys. Rev. B **38**, 3632 (1988).

[13] J. J. Hoyt, D. DeFontaine, and W. K. Warburton, J. Appl. Cryst. **17**, 344 (1984).

[14] I. K. Robinson, W. K. Waskiewicz, R. T. Tung, and J. Bohr, Phys. Rev. Lett. **57**, 2714 (1986).

[15] E. D. Specht, G. E. Ice, C. J. Peters, C. J. Sparks, N. Lucas, X.-M. Zhu, R. Moret, and H. Morkoc, Phys. Rev. B **43**, 12425 (1991).

[16] E. Wimmer, A. J. Freeman, C.-L. Fu, P.-L. Cao, S.-H. Chou, and B. Delley, in *Supercomputer Research in Chemistry and Chemical Engineering,* edited by Klavs F. Jensen and Donald G. Truhlar, ACS Symposium Series Vol. 353 (American Chemical Society, Washington, DC, 1987), p. 49.

[17] R. F. C. Farrow, J. Cryst. Growth **104**, 556 (1990).