AN INTERFACIAL PHASE TRANSFORMATION IN $CoSi_2/Si(111)$

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ABSTRACT

A new type of phase transformation at the interface is described in $CoSi_2/Si(111)$ B (i.e. twinned) epilayers. Thin (25Å) $CoSi_2$ films are codeposited at room temperature on Si (111) with a Si-rich surface layer, and subsequently annealed. Plan-view transmission electron microscopy (TEM) shows that these films have low symmetry, the interface being characterised by a shift "R" between (220) planes in $CoSi_2$ and Si. X-ray diffraction from "R" films differs from otherwise identical films either grown without Si-rich surface layer, or not annealed, which have the conventional cubic structure ("C"); R-$CoSi_2$ cannot be indexed on a single reciprocal lattice. Cross-section high-resolution TEM suggests the presence of a separate (non-cubic) layer ≈9Å thick at the interface in these films. Annealing of R-$CoSi_2$ *in-situ* in the TEM shows a *reversible* transformation R⇔C occuring at temperatures varying from 180°C to 150K, depending on layer stoichiometry. R⇔C is thus a quasi-equilibrium, diffusionless transformation. We propose that R-$CoSi_2$ lowers interfacial free energy for certain stoichiometries, but that bulk constraints stop the entire layer from transforming.

$CoSi_2$ and $NiSi_2$ are the archetypal metal-semiconductor contacts, growing epitaxially on Si with low lattice mismatch to form a controllable Schottky barrier (see [1] for a recent review). Considerable effort has been devoted to the structural characterisation of $CoSi_2/Si(111)$ interfaces in the twinned, or B orientation, with the interface structure being the subject of some debate. High Resolution Electron Microscopy (HREM) [2], and X-ray Standing Wave (XSW) [3,4] studies determined rigid shifts consistent with either the 5-fold or (with the same rigid shift) the 8-fold coordinated interface: the 8-fold is more probable from energetics calculations [5,6], is consistent with recent Surface Extended X-ray Absorption Fine Structure (SEXAFS) data [7], and matches the form of HREM images [8]. The system thus seemed to be structurally well-understood. Here we show that $CoSi_2/Si(111)$ continues to provide surprises: under certain circumstances the epilayer can undergo a remarkable phase transformation in which a massive structural rearrangement appears, reversibly, at the interface.

We have used Transmission Electron Microscopy (TEM) of plan-view specimens to characterise thin B-$CoSi_2/Si(111)$ films grown under a wide variety of conditions [1]. Films grown by UHV codeposition at room temperature and subsequently annealed *in situ* at temperatures >300°C can show a characteristic "domain" contrast, as shown in Fig. 1. Layers in which this domain contrast is visible shall be referred to here as "R-$CoSi_2$". Films which are Co-rich, (or unannealed, or grown above 300°C), do not show domain contrast, and we shall refer to these conventionally structured films as "vanilla" or C-$CoSi_2$.

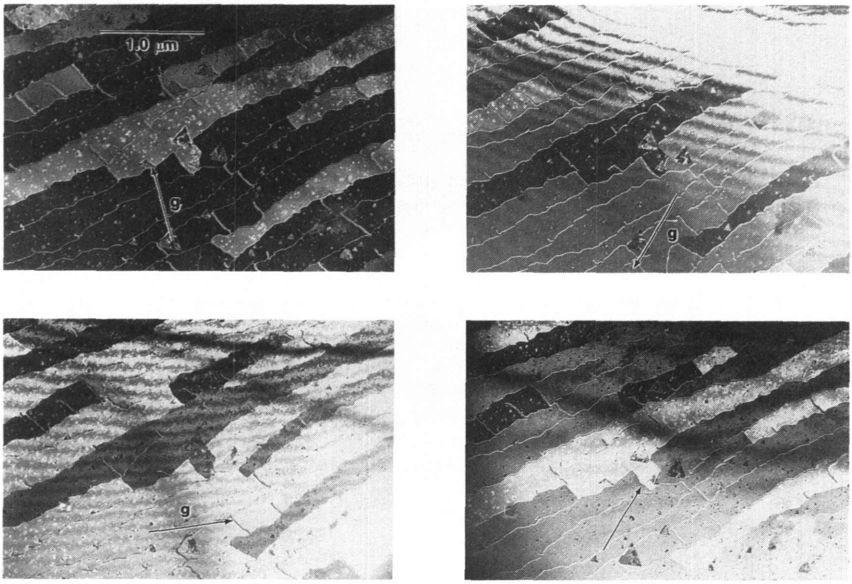

Fig. 1: Dark-field images in 3 symmetry-related <220>s at the [111] zone axis, with a -g image showing inversion

There are generally three levels of domain contrast in weak-beam $\langle 2\bar{2}0\rangle$ dark-field images. A given domain cycles round the 3 contrast levels in images using the three $\langle 2\bar{2}0\rangle$s related by the 3-fold symmetry axis at [111]. This suggests a set of displacements **R** running along $[\bar{2}11]$ $[1\bar{2}1]$ and $[11\bar{2}]$, which, imaged in **g** = $[2\bar{2}0]$ will give 3 distinct values of **g.R**. The g-vector which produces neutral contrast in a given domain presumably has **g.R**=0 (i.e. g perpendicular to the displacement field) Weak beam images in $\langle\bar{4}22\rangle$ reflections show the domains, but with only 2 levels of contrast, suggesting that **g.R** takes only 2 values for this **g**. The observation of 3 levels of contrast in $\langle 2\bar{2}0\rangle$ but only 2 in $\langle\bar{4}22\rangle$ images confirms that the contrast must arise from a displacement field lying along the $\langle\bar{2}11\rangle$s. Reversing either the imaging g-vector or the sign of $\mathbf{s_g}$ (the deviation from the perfect Bragg position), is observed to invert the contrast of $\langle 2\bar{2}0\rangle$ images. The domains are closely linked to the interface morphology, and in particular the boundaries between domains almost invariably occur at $1/6<\bar{2}11>$ interfacial dislocations, which mark the position of steps at the interface [10].

This domain structure is open to a variety of interpretations. At the simplest level, the domain contrast is an indication of lowered symmetry in the bicrystal: the 3 <220> reflections are no longer equivalent for a given domain. The two most straightforward ways to modify the bicrystal symmetry are either by modifying the epilayer structure, or by adding a rigid shift at the interface. Thus the silicide could be distorted, e.g. by shearing the lattice along a particular $<\bar{2}11>$ in a given domain (so that the epilayer becomes monoclinic). Alternatively, a cubic epilayer whose interface has one of three displacements parallel to a $<\bar{2}11>$ would also lower bicrystal symmetry. These two classes of structural changes can be distinguished by imaging in an inclined $<11\bar{1}>_B$ reflection: rigid shift contrast at the interface arises from interference between diffraction from the upper and lower crystals, and thus domains should not appear in reflections from the silicide alone unless structural distortions dominate. Fig. 2 shows a typical pair of $<11\bar{1}>_B$ images (at high and low tilt from the [111]), and the contrast suggests that the domains do not arise from rigid shifts. (Contrast is similarly seen in other inclined silicide reflections.)

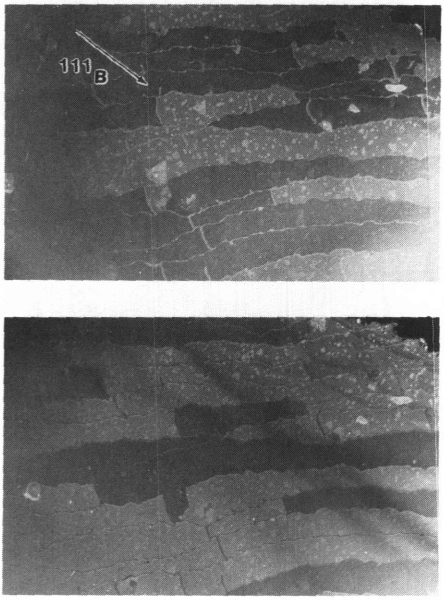

Fig. 2 Dark-field images in a <111>B reflection: since contrast comes from the epilayer alone, this at first sight suggests that "R" is not an interface phenomenon

X-ray diffraction provides a more quantitative picture of the changes in the reciprocal lattice, although it will average over all the domains. Fig. 3 shows typical rod scans for R and C structures along the $20l$ and $\bar{1}0l$ rods (i.e. $2/3\langle\bar{4}22\rangle+l[111]$ and $-1/3\langle\bar{4}22\rangle+l[111]$ rods in reciprocal space, expressed in the hexagonal indices appropriate for the Si(111) surface [9]). The structural rearrangement is evident in the strong modification of the 201 rod, where the $\langle 31\bar{1}\rangle_B$ and $\langle 0\bar{4}0\rangle_B$ R-$CoSi_2$ peaks are shifted and split about the C positions. The $10l$ and $11l$ rods show similar splittings and shifts, though to a rather lesser degree. The explanation for the splittings seems likely to be related to the presence of three inequivalent domains, which are averaged in X-ray diffraction. Thus $10l$, $11l$, and $20l$ rods are consistent with a distortion of the epilayer in which the lattice is either sheared or rotated (although it is difficult to find a distortion which is exactly consistent with all three rods). The problem with this picture lies in the $\bar{1}0l$ rod, where the $\langle 1\bar{1}1\rangle_B$ and $\langle 022\rangle_B$ silicide reflections are left invariant. In order to move the positions of the $\langle 31\bar{1}\rangle$ and $\langle 0\bar{4}0\rangle$ without splitting any of the 3 $\langle 1\bar{1}1\rangle_B$ reflections (i.e. without moving the $\langle 1\bar{1}1\rangle_B$ in any of the 3 domains), the effective reciprocal lattice of R-$CoSi_2$ must be buckled, i.e. aperiodic. Thus X-ray diffraction appears only to be consistent with a picture in which the structural distortion of R-$CoSi_2$ is not uniform through the epilayer, but has a shape-transform that extends far from the silicide reciprocal lattice. Simultaneously, the strength of the modifications to the silicide diffraction pattern suggests that a single layer alone may not be sufficient (note that the C-$CoSi_2$ diffraction closely resembles the expected behaviour for the strained bulk).

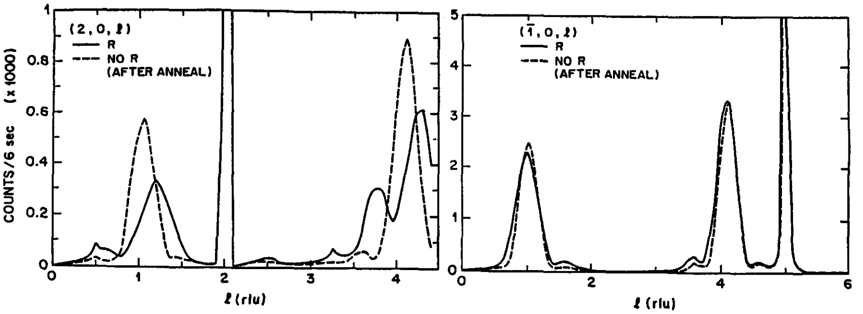

Fig. 3: X-Ray diffraction along the ($20l$ and $\bar{1}0l$ rods, showing large splittings in all reflections along certain rods, while others are unaffected: this implies that R-$CoSi_2$ lacks a reciprocal lattice, and suggests that R is an interface phenomenon.

HREM of this R-$CoSi_2$ suggests one possible solution to this apparent dilemma. Fig. 4 shows HREM images from R-$CoSi_2$ cross section samples prepared by 4kV ion milling at 25°C (a) and 2kV ion milling at 100K (b). While (a) shows all the features we would expect of C-$CoSi_2$, (b) appears to show a separate layer, more than one monolayer thick. While interpretation of HREM is difficult, the interface region in 4(b) appears to be drastically different from 4(a): while 4(a) matches simulated images for the C structure [8], no match can be found for 4(b): thus it currently seems possible (in view of HREM, and the apparent conflict between X-ray diffraction and plan-view TEM) that R-$CoSi_2$ has a broad interface region whose structure differs greatly from that of either silicide or Si: this interface region lowers the symmetry of the bicrystal, and thus gives rise to a domain structure.

During the TEM experiments described above, it was noted that electron irradiation of R films over prolonged periods leads to a phase transformation into the high-symmetry structure which we observe in unannealed films. The rate of this damage transformation increased rapidly with increasing voltage, occurring in a few seconds at 200kV. A similar transformation can be produced by He ion irradiation, the characteristic interface peak in RBS disappearing during observation after doses as low as 5×10^{14} cm^{-2}: TEM of irradiated material confirms that the loss of the interface peak coincides with loss of R.

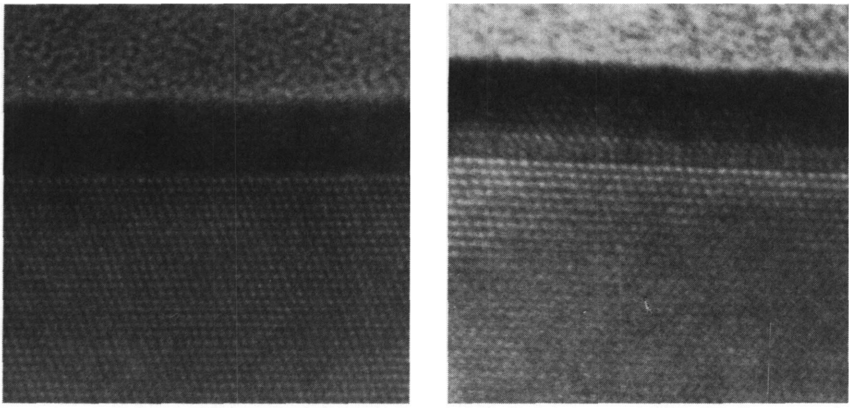

Fig. 4: HREM images of the silicide-Si interface for (a) C-$CoSi_2$ and (b) R-$CoSi_2$. Note that the {111} planes in (a) change direction abrubtly at the interface, while those in (b) appear vertical over a finite distance near the interface.

The transformation from R to C is irreversible when initiated by radiation damage effects. However, we have also observed a reversible transformation of the same kind occuring at ≈100-200°C on heating these films *in situ* in the electron microscope. Both the R⇒C (heating) and the C⇒R (cooling) phase transformations proceed slowly, but the transformation rate increasing rapidly with increasing overheating or undercooling. As for the irradiation-induced transformation, there is a marked tendency for nucleation of the C phase to occur at domain boundaries (i.e. at $1/6\langle\bar{2}11\rangle$ dislocations). There is evidence for strong pinning of the transformation front, as might be expected for a highly-strained transformation. Not all domains in a given region transform at the same time, and we have observed large local variations in the transformation temperature. Indeed, many films are mixed in character at room temperature: on heating, the fraction of C increases, and on cooling to liquid nitrogen temperatures the interface transforms fully into the R phase. In addition, a thickness-dependence of the transformation was observed in the thin TEM samples, with areas where the substrate was ≈1μm thick undergoing the transformation (in both directions) at temperatures on average ≈10-20°C higher than regions where the sample thickness was only 500Å. This effect seems to imply a strong link between the transformation temperature and the epilayer strain; the most obvious effect of sample thickness is strain relaxation in the thin films, with an appreciable fraction of the epilayer strain being taken up in the substrate for the thinnest regions of sample. Extrapolation of this thickness dependence suggests that the transformation is likely to occur at ≈220°C(±30°C) in bulk material. The transformation was reversible, with domains of a given type almost invariably reverting to the same type after heating into the unsheared form and subsequent quenching back into the sheared state. On a few occasions a domain was observed to switch type on thermal cycling. This tended to occur during the first cycle, and is again likely to be linked to a change in the strain field in the thin film, so that the domain structure which minimises strain in the TEM sample may be different from that produced following the anneal in the bulk.

In conclusion, we have observed an interfacial phase transformation in annealed $CoSi_2$/Si(111) epilayers. The low temperature phase has an interfacial layer several monolayers thick. At some strain- and composition-dependent temperature, the silicide transforms reversibly into the cubic phase with a high-symmetry interface structure which does not yield an interface peak in RBS. We deduce that the cubic interface is not the equilibrium structure for films at this stoichiometry at room temperature. The driving force for this phase transformation must arise principally from the interfacial energy.

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