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ATOMIC STRUCTURE AND PROPERTIES OF EPITAXIAL THIN-FILM SEMICONDUCTOR INTERFACES

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Abstract

Using high-resolution transmission electron microscopy we have studied atomic structure of interfaces between epitaxial thin films of metals, insulators or semiconductors on semiconductors. For epitaxial cobalt and nickel disilicide we find exceptionally uniform interfaces with a significant dependence of the Schottky barrier height on interface structure. For epitaxial alkaline-earth fluorides, the film growth and crystalline structure can be understood from the interface structure. We also report recent results on silicon based semiconductor superlattices.

In many cases the electronic properties of technologically important thin films on semiconductors are strongly influenced by atomic structure at their interfaces. Examples are Schottky barriers between metals and semiconductors or field-effect transistors involving transport at an insulator/semiconductor junction. Electron microscopy currently offers sufficient resolution (0.16 - 0.3 nm) to study the widest interatomic spacings in semiconductors and thus to gain valuable information concerning atomic structure at interfaces. However, when comparing this information with physical measurements e.g. electron transport, which commonly involve sampling macroscopic interface areas > 10^{14} atoms, interpretation is greatly facilitated by uniform interfaces. Most notable amongst these are epitaxial systems, which attain their uniformity through long-range order.

We have studied the interface structure of several epitaxial thin-film/semiconductor systems, grown by molecular-beam epitaxy (MBE). These include metals, insulators and semiconductors on Si and other semiconductors. Our studies provide examples of the three classical types of growth. That is commensurate (coherent), in which the overlayer maintains the same lattice parameter as the substrate, incommensurate, in which the interface is totally incoherent and discommensurate, in which commensurate regions are separated by misfit dislocations (discommensurations). Other details of the interface structure can be determined, such as flatness and sharpness and sometimes the local atomic configuration. The results can be related to the physical properties of these interfaces.

Experimental Details

Films were grown by a variety of vacuum evaporation techniques. Cobalt and nickel disilicides were fabricated in an ultra-high vacuum chamber with base pressure < 10^{-9} T by metal deposition on an in-situ cleaned Si surface followed by in-situ annealing. Uniform single-crystals have been grown on both (111) and (100) silicon substrates using annealing conditions described elsewhere[1].
Films of alkaline-earth fluorides were deposited in a similar vacuum chamber by effusion of the appropriate fluoride on substrates held at temperatures between 500-700 °C[2].

Ge_{x}Si_{1-x} films were grown on (100) Si substrates using molecular beam epitaxy in another UHV chamber[31]. The substrates were held at temperatures between 550-650 °C.

Samples were thinned for transmission electron microscopy with a combination of mechanical polishing and 4-6kV Ar⁺ erosion in cross-section geometry along (110) zone axes. In this manner, interfaces could be examined edge on for substrates in all the common orientations of semiconductor wafers and with instruments of resolution better than 3 Å. A JEOL 200CX top-entry electron microscope with spherical aberration coefficient Cₛ=1.2mm at 200kV accelerating voltage was used. It was operated in axial illumination close to the Scherzer defocus, where the instrument has point-to-point resolution 2.5 Å. Where necessary, image simulations were carried out to take account of multiple electron scattering, using the multislice algorithm developed by Cowley and Moodie[4].

Epitaxial Schottky Barriers

There has been a great technological drive for research on silicide/silicon contacts, both for schottky barrier and ohmic contacts to silicon devices[5]. This has arisen because of the metallic properties of the silicides and their comparative thermal and electrical stability. The best candidates for epitaxy are the cubic cobalt and nickel disilicides. These are formed as the final phase when reacting a thin film of the metal with a silicon substrate. Typically anneal temperatures of 700-900 °C and times of 30 minutes are required[6].

Several groups have studied the interface structure of these silicides with high-resolution microscopy[7][8][9]. From the point-of-view of the electronic properties of these epitaxial silicides, the investigation of “clean” growth has been a major breakthrough[11]. On (111) Si, these silicides are found to be a mixture of two orientations[7][10]. The two orientations are referred to as A and B: in the former the cubic silicide layer is aligned exactly with the substrate, in the latter it is rotated about (111) by 180° (a "hetero-twin"). Only through in-situ deposition and reaction on atomically-clean surfaces can this double-positioning be eliminated. With these methods, single crystals of CoSi₂ can be grown which invariably have the B orientation[6]. For NiSi₂, the situation is less straightforward, but even more intriguing. In this case it is possible through the use of UHV grown templates, to grow single-crystals of either A or B[11].

Figure 1 shows high-resolution images of each of these thin films in cross-section. Figure (1)a is from an A-type template and (1)b is from a B-type template. The exceptional uniformity and sharpness of these interfaces are clearly visible from these images. These are very similar to the interfaces found in the mixed A+B films studied by Cherns et. al.[8]. Using the two models proposed for these interfaces by Cherns, one can model the interface structure in figure 1. The principle of this modelling is the measurement of the relative shift of the lattices across an interface. This is a quantitatively accurate method of studying crystal-crystal interfaces in which the registration is uniform. It has been shown[11] that these measurements can be accurate to better than 0.3 Å under axial bright-field imaging conditions with an instrument of sufficient resolution. We have made such measurements of the NiSi₂ interfaces and find the shift to be consistent with the 7-fold model of Cherns, which is shown in figure 2 for both the A and B orientations. This is also consistent with the findings of Cherns et.al.[8], so that it appears that the interface structure is not associated with the considerable differences in growth and crystallography of the higher-quality UHV grown films.
Figure 1: HREM images from A (a) and B (b) type NiSi$_2$ templates on (111) Si.

Figure 2: Models of the interface structure for both A and B (111) NiSi$_2$ interfaces\[8\.]

Figure 2: Models of the interface structure for both A and B (111) NiSi$_2$ interfaces\[8\.].
The template method has also enabled the growth of uniform (100) films for the first time. Figure 3 shows an example of the interface from one such film. It was pointed out that this image appears to be consistent with a simple six-fold coordinated model of interface structure\textsuperscript{[9]}\textsuperscript{.} This is also in agreement with more recent work of Cherns et al.\textsuperscript{[12]} One odd feature of our images, however, is that the interface image is extended over more than a single (200) planes, which is apparently not in agreement with multislice image calculations\textsuperscript{[12]}\textsuperscript{.} This may be the result of a higher step density in our (100) substrates or films. Nevertheless a major advantage of the rigid-shift method of interface structure determination is its insensitivity to such detailed interface topography, in contrast to direct image simulation which also suffers from a comparative loss of accuracy.

Finally, figure 4 shows an image from a co-deposited sample of CoSi\textsubscript{2}. In contrast to the NiSi\textsubscript{2} interfaces these do not seem to well fit the 7-fold model but instead give better agreement with the 5-fold model of Cherns et al. Again this determination is based on rigid shift measurements. The figure also shows the core of a misfit dislocation with burger's vector \textfrac{a}{6} (112). It is believed that these misfit dislocations play a prominent role in the growth of the B phase for the silicides and other CaF\textsubscript{2} structure films\textsuperscript{[13]}.
One of the most exciting aspects of these experiments is the ability to grow for the first time single crystal Schottky barriers on silicon. This has various interesting applications but also has great physical importance because it permits the measurement of Schottky barrier height in extremely well characterized systems. The results of these measurements, made by Tung\textsuperscript{[14]} are summarized in table 1 for (111) NiSi\textsubscript{2}.

Table 1: Barrier height of NiSi\textsubscript{2} films on Si (111)\textsuperscript{[14]}

<table>
<thead>
<tr>
<th>ORIENTATION</th>
<th>BARRIER HEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.65 eV</td>
</tr>
<tr>
<td>B</td>
<td>0.79 eV</td>
</tr>
</tbody>
</table>

Clearly, the single-crystal nature of our films has brought out some intrinsic dependence of Schottky barrier height on atomic structure. Furthermore we can provide close approximations to the atomic structure for theoretical studies. It does not appear that our data fit conveniently within most current theories, which have evolved to explain the apparent insensitivity of Schottky barrier height to most parameters other than the type of metal involved\textsuperscript{[5]}. It seems likely that barrier heights may be sensitive to atomic structure in other systems, if only these regimes could be experimentally explored, and the results are thus of considerable significance to Schottky barrier formation.

Another unique feature of these silicide films has been investigated by Hensel et al.\textsuperscript{[15]}. These authors have found that films, grown in the same system as those studied here, exhibit exceptionally high electrical conductivity. Unlike most films of thickness \( \approx 100\text{Å} \) these films do not show a significant increase in their resistivity in thin film form. This unique behaviour which occurs under circumstances when the film thickness is less than the mean-free path (of order 400Å at room temperature), implies that the scattering of electrons off the boundaries is primarily specular. Apart from this testimony to the uniformity of the interfaces and surfaces of these films, this result has exciting physical and technological implications.

**Epitaxial Insulators on Semiconductors**

The success found in epitaxial growth of the near-noble silicides on silicon, which have the CaF\textsubscript{2} structure, led to interest in the growth of the insulating alkaline-earth fluorides on semiconductors\textsuperscript{[161,2]}. Considerable success has recently been obtained using clean conditions for such growth\textsuperscript{[17]} including the fabrication of a field-effect transistor. One very intriguing observation of growth on (111) semiconductors is that, provided the misfit is moderate (between 0.5 and 5%), the films are single-crystals of the B orientation. This suggests that misfit favours the growth of the 180\(^\circ\)-rotated B orientation. An anomalous result is that some large mismatch systems, such as the 10% mismatch BaF\textsubscript{2} on (111) Ge, comprise a mixture of A and B (approximately 50% each).

This result can be reconciled with high-resolution electron microscopy of the interfaces in cross-section. Figure 5 shows both the 5% BaF\textsubscript{2} (100) InP interface (a) and the 10% mismatch BaF\textsubscript{2} (111) Ge interface (b). The first interface is seen to be dicommensurate, i.e. contains commensurate (coherent) regions separated by misfit dislocations.
(discommensurations). This corresponds to the case of B epitaxy on (111). On the other hand the 2nd interface appears to be totally incommensurate (incoherent). Thus it appear that the dominance of the B phase is associated with locally coherent interfaces. On the other hand, the incoherent interface is associated with A+B. It certainly is odd that epitaxy can occur with an incoherent interface. This suggests that the epitaxial relationship is not determined by interlayer bonding. A simple explanation is "grapho-epitaxy": that is the alignment of islands of the overlayer with steps on the substrate. This is particularly clear for (111) epitaxy since we can see that islands in plan-view have triangular shapes with (110) sides\footnote{\textsuperscript{1}}. Since the substrate would be expected to exhibit a "hexagonal" pattern of (110) steps, associated with the trace of (111) slip planes, this would lead to the pinning of both A and B orientations at steps and corners. This is also consistent with the observation of (111) texture in (100) epitaxy with high misfit and even on amorphous substrates.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Interfaces between epitaxial alkaline earth fluorides and semiconductors. a) BaF\textsubscript{2} on (100) InP and b) BaF\textsubscript{2} on (111) Ge.}
\end{figure}

It remains to explain the dominance of the B orientation when the misfit is reasonable but non-zero. This is also in agreement with the silicide epitaxy, where the higher mismatch CoSi\textsubscript{2} (-1.2\%) on Si grows more readily as a single crystal, and with the B orientation, than the lower mismatch NiSi\textsubscript{2} (-0.5\%). A simple explanation lies in the type of misfit dislocations found beneath B islands. These have burger's vectors $b=a/6 \ (112)$ in contrast to the $a/2\ (110)$ type found beneath A islands. The energy of dislocations is dependent on $b^2$ and so the introduction of such dislocations should be more favourable. Thus the dominance of B could occur because of its relative ease of misfit relief during growth, a unique observation to our knowledge. It is indeed unusual that increased misfit can lead to better quality epitaxy.

**Semiconductor on Semiconductor**

There are several attractive attributes to a Si/Ge\textsubscript{x}Si\textsubscript{1-x} alloy superlattice. Potentially higher mobilities and modulation doping are amongst these. We have studied the interface structure of such a superlattice in cross-section, as shown in figure 6. In this case the practical aspects
of HREM imaging are somewhat different since the structure and orientation of the material on either side of the interface are identical. The only difference which enables imaging is the difference in structure factor across the interface. We have studied the visibility of such interfaces in some detail. The visibility is a function of the resolution required, since noise limits the visibility of the weakest interfaces, and can be improved by optimal choice of defocus and thickness. We estimate that interfaces with Ge concentrations as low as 5% can be detected with 1-2 atomic layer accuracy. As a result we can conclude that the interfaces shown in Figure 6, in a 40% concentration superlattice, exhibit no detectable interdiffusion on the atomic scale. The interfaces are locally sharp but a 1-3 layers roughness could be attributed to the random arrival of Ge atoms.

Conclusions

We have demonstrated that high-resolution electron microscopy can reveal very useful information about interfaces between epitaxial thin films and semiconductors. These interfaces are very attractive because their uniformity allows excellent correlation between atomic structure and macroscopic physical properties. In this manner we can better understand Schottky barrier formation, growth of thin films and electronic properties in superlattices.

The authors wish to acknowledge the assistance of M.L. McDonald and discussions with J.M. Poate and J.C. Bean.

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5. see, for example "Silicides for VLSI Applications", S.P. Murarka, Academic Press (New York), 1983


11. J.M. Gibson, to appear in Ultramicroscopy


**DISCUSSION**

**D.R. Clarke:** Could you describe the crystallography of the interfaces you considered in terms of the CSL and '0' lattice terminologies?

**J.M. Gibson:** Yes, but the orientations considered here are simply the $\Sigma 1$ and $\Sigma 3$, ignoring lattice mismatch, so that these concepts are not very fruitful. However, in considering misfit dislocations and other possible defects, the '0' lattice concept and a full consideration of crystal symmetry such as described by Pond in this volume has been very useful.
K.L. Merkle: The specular reflection in CoSi$_2$ is a very interesting observation. Do the films actually exhibit bulk resistivity? What is the smallest thickness at which the effect is observed?

J.M. Gibson: There is a slight increase in resistivity but it is not yet clear that this cannot be explained simply by lack of continuity in films $< 100$ Å thick. More details are given in reference 15. Films below 100 Å ($< \lambda/4$) thick still show significant amounts of specular scattering.

D. Ast: Have you measured the Schottky barrier on p type material? If yes, are they "inverse" in the sense that they add up to the band gap?

J.M. Gibson: Yes, the Schottky barrier heights on n and p type end up to the band gap for (111) NiSi$_2$ films. The values are also closely identical if measured with the I-V and C-V technique (see ref 14).

M. Rühle: On your HREM micrographs only one set of misfit dislocations at the interface could be observed. Is it possible that there exist other misfit dislocations (due to lattice mismatch) which you may miss in the HREM studies?

J.M. Gibson: Three $1/6 \langle 112 \rangle$ sets are indeed present and can easily be seen in plan-view weak-beam TEM. A cross-section sample can be tilted $-30^\circ$ to observe this dislocation network so that one can avoid effects from inclined dislocations.