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HIGH RESOLUTION ELECTRON MICROSCOPY OF INTERFACES IN FUNCTIONAL MATERIALS

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Abstract: Our recent high resolution electron micrographic observation of various interfaces in functional materials such as semiconductor superlattice, superconducting perovskite ceramic, new engineering ceramics, fibre reinforced metal and ceramic-metal joining suggested that the traditional unified view of the interface structure in a number of directions taking into account the chemistry, polytype structures, thickness, bonding heterogeneity etc to make the structural theory useful for the future design of the interfaces in modern functional materials.

1. Introduction

Continuous improvements in the resolution of electron microscope and the resulting high quality high resolution observations of various interfaces not only advance our understanding of the details of the structure but also change our general views about them; The interface was shown to vary much more extensively than was hitherto considered, which in return expects a larger role for the high resolution electron microscopy in developing new functional materials. Many high resolution electron microscopes of 300-400 keV range newly established in industry supporting this view.

Modern functional materials are invariably in need of interfaces; Interfaces in strong shape memory alloys, semiconductor devices, engineering ceramics, nanocrystalline metals, fibre reinforced metals, ceramic-metal joint and above all the grain boundary of perovskite superconducting ceramics are thought important to the performance of the material.

In this report, we present some of our recent results of the above interfaces: They are hetero-interfaces in semiconductor superlattice GaAs/AlAs, engineering ceramic SiC polytype interfaces, superconducting perovskite ceramic Ba2YCu3O7-x, ceramic metal joined interfaces Al2O3/Nb, Si3N4/Ni-P-Ti and Si3N4/Cu-Ag-Ti, and fibre reinforced metal interface, C/Al.

They may be classified as a compositional interface where only chemical composition changes, a hetero-phase interface where only polytype structures change, a thick grain boundary not characterized by the orientational change alone, hetero-bond interfaces in joined ceramic/metal and carbon reinforced metal composite. Basic problems of these interfaces in characterizing the materials are discussed.

2. Compositional Interface

Chemical composition is the simplest variable to consider if crystalline parameters are not affected. A large freedom to design the interface atomic structure invites us to extend the structure theory to include this chemical aspects. Consequently this case is considered first. The GaAs/AlAs superlattice hetero-interface is a special case where the lattice spacing mismatch is nearly zero. It is
essentially a single crystal with chemistry change and allows us to concentrate our attention purely on the problem of element distribution across the interface. Sharpening of the compositional change across the interface and its detection are the basic problems. The latter imposes a tough problem to the electron microscopy especially in GaAs/Al$_{0.3}$Ga$_{0.7}$As superlattice, because of the smallness of the chemical change at the interface. An effort may be seen in Photo 1 and 2 where (110) and (010) cross sections are compared. The image difference is larger with a photograph taken along [010] because of the differences in the scattering power for (200) diffractions as shown in Table 1. The scattering power is nearly the same for Ga and As so that (200) GaAs is distinctly weak, compared with (200) AlAs as shown in figure 1. At a proper thickness of about 15nm the difference is very pronounced with the present electron microscope as shown in figure 2, where (200) images are calculated by multislice method for GaAs and AlAs 5, 10 and 15nm in thickness. The details are reported elsewhere(4).

<table>
<thead>
<tr>
<th>(HKL)</th>
<th>$I_{GaAs}$</th>
<th>$I_{AlAs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>110</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
</tr>
<tr>
<td>111</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
</tr>
<tr>
<td>211</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>16(f$<em>{Ga}$-f$</em>{As}$)$^2$ ~0</td>
<td>16(f$<em>{Ga}$-f$</em>{As}$)$^2$ ~0</td>
</tr>
<tr>
<td>400</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
<td>16(f$<em>{Ga}$+f$</em>{As}$)$^2$</td>
</tr>
</tbody>
</table>

Table 1. Crystal structure factors.

Figure 1. Changes of diffraction amplitudes with specimen thickness.
3. Translational Interface

The second simplest interface would be a stacking fault type structure where the chemistry, the crystal structure and the orientation are preserved across the interface. Only the lattice sites are translated with respect to each other and often the chemistry of the atomic layer differing from that of the bulk. An example is an UFO like structure recently observed by Hagege, whose details are reported in this proceedings \(^{(6)}\). Present high resolution electron microscopy can't identify the chemistry of the atomic layer yet. As for the lattice translation, weak-beam φ-fringe imaging \(^{(11)}\) is found more useful. Because the common beam diffraction condition is readily achieved and more precise values of the translation may be measured by this method.

4. Dislocation Network Interface

A small misorientation or a small changes in the lattice parameters are accomodated invariably by network of lattice dislocations. A gradual change in composition makes the network spread over the layer but allows the crystal to preserve the epitaxy. For an example in GaP diode doped by As, a confinement of such a network out from the luminescent layer is required. Such a structure is conventional to the interface theory but is an important technique of the structure design and a favoured subject of tomographic electron microscopy \(^{(13)}\).

5. Polytype Interface

Traditional coincidence-site lattice analysis faces a new frontier in understanding polytype interfaces, where the unit Bravais lattice is often too large to be physically meaningful. A more flexible account of the structures is in terms of a composite of twin and other low order coincidence systems such as \(\Sigma 5\) and \(\Sigma 9\). For an example a polytype boundary of α-SiC is shown. Photo 3 and 4 are observed in high purity SiC vapor redeposited at 2800K. Single crystals plates a few mm in diameter and 100-200μm in thickness form along with occasional bicrystals. The bicrystals are sliced parpendicular to the interface and parallel to a principal axis of the crystal, lapped by diamond paste and finally ion-thinned by Ar\(^+\) at 5 KeV to observe in a high resolution electron microscope.

The interface in Photo 3 is periodically ordered but neighboring crystals are polytypes (the left hand side is 6H and the right hand side is 15R). The unit lattice is consequently large as is shown in black circles in figure 3. The coincidence lattice, therefore, is very large and are marked by two double circles. The power of the

Figure 2. Calculated (010) images.
analysis of coincidence site lattice theory to describe the orientation of periodically ordered interfaces is still evident but the spacing is too large to be physically meaningful and an occasional changes in the stacking periodicity in both 6H and 15R structures is not easy. Examples of the faults may be observable at A and B areas of the photo 3. Combination of 13 and 19 structures explains this polytype interface in a more simple way. The interface may be accounted as an alternative layer of roof-like thin layer of single crystals separated by a pair of thin bicrystals in twin relationship to the former roof-like single crystals with one unit structure of 19 along the interface as is indicated by a double line in figure 3. Changes in the interface structures caused by the occasional failure of the stacking periodicity in 6H and 15R crystals are simply accommodated by the top corner of the roof-like single crystals. Here is an area to modify the conventional coincidence-site lattice theory. These 19 structure is surrounded by coherent 13 and bulk crystals. The imposed restriction allows us to assume the atomic configuration. It is an ideal system for image matching experiments.

6. "Thick" Interface

In history, grain boundaries in sintered ceramics are believed to contain an amorphous layer but not those in metals. Recent high resolution observations showed many exceptions although there is such a general tendency. For example, no such layer was noted in SiC boundaries as was just described. In contrast, an amorphous or nanocrystalline layer was found in the grain boundary of new FeNdB magnet alloy. The thick layer is considered as the source of its remarkable performance. The migration of a magnetic domain across the thick interfaces is prohibited because no structure with a strain field to assist nucleation of a domain on the other side of the boundary is available with the structure. Indeed a failure in the heat treatment of the alloy showed fine precipitates in the matrix next to the boundary layer and the magnet was found no more strong. The deterioration is attributed naturally to the strain field of the fine precipitates that could cooperate with the magnetostriction and thus facilitate the nucleation of a domain on the other side of the boundary. Recently perovskite superconducting ceramics are found to have such a layer. Figure 5(a) shows an example of such a boundary in sintered Ba2YCu3O9−δ fired at 1200K for 100Ks and air cooled. The diffraction pattern (b) taken with the aperture placed across the boundary showed a square pattern for the crystal above and lines of spots for the crystal below. Apparently the crystal above is nearly parallel to (001), while the crystal below is nearly
perpendicular to the C axis. It is a typical large angle grain boundary. An amorphous layer of about 1.5nm may be seen in figure 5(a). The halo in the diffraction pattern (b) comes from this "thick" boundary layer. Such a layer has been considered by Chu et al[15] as the region with very high Tc. Kishio et al[16], on the other hand, considered that the layer is not superconducting but rather contribute as nonconducting Josephson barrier where the tunneling current is likely to be affected by the thickness. Other possibility of the region is the flux pinning effect that should contribute to the more important property Jc of the material. All these arguments are just speculations at present, but the characterization of the role of the "thick" boundary is undoubtedly an important subject of the interface engineering.

7. Ceramic-Metal Joined Interface

One of the basic problems of the ceramic-metal joining is the achievement of pure atomic interface free from reaction product layer. Differences in the thermal expansion coefficients are generally unavoidable so that the simple interface structure absorbing the strain by the deformation of metal is sought for. A reactive product layer is usually brittle, prepares a stress concentration to ceramic and deteriorates the mechanical property of the joined body. The observation of pure ceramic-metal interface by Ruhle et al[9] was well appreciated from this point of view. Experiments in Japan[17,18], however, showed oxides are present at the Al2O3-Nb joined interface.

8. Fibre Reinforced Metal Interface

As another example of interface design, the interface structure of carbon fibre/aluminium matrix is examined. The composite strength was found deteriorated drastically upon precipitation of Al4C3 on the surface of carbon fibre. An epitaxial growth of the aluminium carbide on the carbon fibre is noted. A selective attack of the fibre surface along the curving basal plane of the partially graphitized fibre is also shown. A mechanism proposed for the strength decrease is interfacial crack between the carbon fibre and the carbide lamellae by the thermal stress. The small crack is indeed observed which may serve as the site of stress concentration on the fibre surface. The thermal stress is relieved well along the Al/carbon interface due to easy movement of dislocations in aluminium. Indeed, high resolution micrographs detected dislocations in Al near the interface.

9. Conclusion

The present high resolution electron microscopic observations show that the technique has become applicable to wide range of interfaces.
and opened new frontiers of the interface study. The interface researches should expand to the design of new functional interfaces in modern materials.

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