

The Role of Electron Microscopy in Materials Science*

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Abstract

The properties of the materials in a component or a device depend on structure and composition often on a scale of 10^{-10} to 10^{-6} m. Electron microscopy and microanalytical techniques provide a powerful means for determining the structure and composition on the appropriate scale, lead to an understanding of basic mechanisms, and by correlation or *in situ* experiments to explanations of bulk properties. Examples are given of the application of a variety of powerful electron optical techniques to a number of materials problems.

1. Introduction

Technological developments often depend on the availability of materials with new or improved properties, coupled with economic processes of production and methods of fabrication of components or devices. Examples are the technique of zone refining of crystals, which was an important step in developing materials of sufficient purity for semiconductor devices, and the development of high temperature superalloys for jet engines. The scientific and technological objectives relevant to the materials scientist may be summarized as follows:

- (1) Improve or develop new material, process of production, or fabrication of component or device for a particular application.
- (2) Establish composition/structure/property relationships involving (a) a correlation and (b) an understanding of the correlation.
- (3) Use information from (2) to help to achieve (1).

Electron microscopy and microanalytical techniques contribute to (2). The properties of materials depend on composition and structure often on a scale of 10^{-10} – 10^{-6} m, which is the range covered by electron microscopy. The scientific objectives are to determine (i) the structure and composition on the appropriate scale, (ii) the properties on a submicroscopic scale and (iii) the correlation between bulk properties and (i) and (ii). Electron optical techniques provide a powerful means of achieving (i) and to some extent (ii). The realization of objective (iii) is often not trivial, but information on (ii) can provide a very useful step. There are now many different electron optical techniques available, many of them highly sophisticated and requiring expensive equipment. It is an area of research where university–industry collaboration can be very effective.

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In this review a number of examples will be given which illustrate the way in which electron microscopy can contribute to the solution of both the scientific and technological problems posed by the structure/composition/property relationships.

2. Semiconductor Materials and Devices

Dislocations introduced during fabrication act as traps for charge carriers and thereby affect the performance of devices. Electron microscopy can be used as an essential step in the solution of a technological problem, and also to provide a deeper understanding of the electronic properties of dislocations.

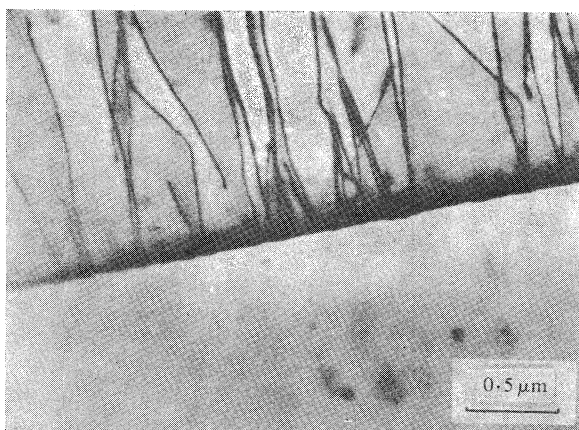


Fig. 1. Dislocations at the (100) interface between $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ and an InP substrate. [Al-Jassim *et al.* (1981).]

GaInAs Infrared Detectors

Some devices of this type are made by depositing layers of GaInAs from the vapour onto (100) InP substrates. A suitable composition is $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$, so that the lattices of the two structures are matched. The GaInAs bandgap then corresponds to a wavelength of $1.65\ \mu\text{m}$, which is appropriate for a particular type of infrared detector. The presence of a high density of dislocation recombination centres leads to a deterioration in efficiency. Fig. 1 shows an electron micrograph taken in a high voltage electron microscope of the cross section of a device including the interface (Al-Jassim *et al.* 1981). A high density of dislocation pairs ($10^8\ \text{cm}^{-2}$) is clearly generated at the interface and threads the layer to the surface. The performance of such a device is poor. By careful attention to the preparation of the substrate surface and to the evaporation procedures the dislocation density can be reduced to $10^5\ \text{cm}^{-2}$, resulting in satisfactory devices.

This example is typical of the way electron microscopy can be used to improve device performance by changing fabrication methods. In many cases the manufacturers arrive at the solution by intelligent empiricism guided by previous experience: electron microscopy then provides 'underpinning' and the background information useful for development of subsequent devices; in some cases the electron microscope observations suggest the particular cause of the dislocation structure and a possible cure.

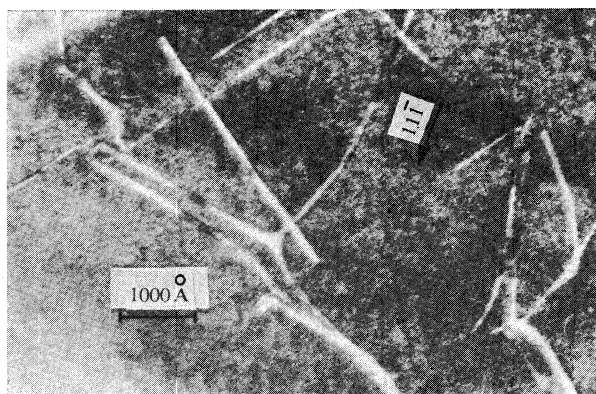


Fig. 2. Micrograph of an extended dislocation node in diamond. [P. Pirouz, unpublished.]

Structure and Electronic Properties of Dislocations

Although the electronic effects of dislocations are well known to the device manufacturer, our understanding of the basic electronic properties of dislocations is rather limited. Shockley (1953) was the first to suggest that the core of a 60° dislocation in the diamond cubic lattice consisted of a row of dangling bonds and Read (1954) derived the properties of the one dimensional band corresponding to this model. However, in the diamond cubic structure glide dislocations with the Burgers vector $\frac{1}{2}[110]$ could glide either between the widely or narrowly spaced planes of atoms constituting the (111) planes. Shockley's 60° dislocation is assumed to lie between the wide planes of atoms ('shuffle' dislocation): on the other hand, if the dislocation lies between the narrow planes (glide dislocation), it can dissociate into partial dislocations separated by a stacking fault ribbon, reducing the strain energy; in addition the direction of the dangling bonds is such that reconstruction across the core is possible (Hirsch 1979, 1980; Jones 1979, 1981; Marklund 1979, 1980), leading to a further reduction in energy. Ray and Cockayne (1971) were the first to show, using the weak beam technique (Cockayne *et al.* 1969), that dislocations in Si are dissociated into two partial dislocations, and since then much evidence has been obtained showing that dislocations introduced by glide in elemental semiconductors and III-V and II-VI compounds are generally dissociated. Fig. 2 shows a micrograph (taken recently by P. Pirouz) of a dissociated node in diamond, providing the first evidence that in diamond also the dislocations are dissociated.

Hornstra (1958), however, suggested an alternative configuration for a 30° partial. Fig. 3a shows a projection of the atomic rows along [110] for a 30° glide partial; one of Hornstra's configurations can be derived from this by removing the row of black atoms (in centre of figure). Recently, attempts have been made to distinguish between these two possibilities by high resolution electron microscopy (Spence and Olsen 1981; Bourret *et al.* 1981; Anstis *et al.* 1981). Fig. 3b shows an experimental image (*above*) compared with calculated images (*below*) for the Hornstra 'shuffle' (s) and glide (g) configurations, showing a good match with the glide configuration. The thickness of the specimen was determined from the relative intensities of the forbidden 002 and other reflexions, and the defocus determined from diffractograms

from the amorphous surface layer. Pairs of atoms are black on the image. In all cases in which the models could be distinguished unambiguously, the 30° partial has been found to be of the glide type.

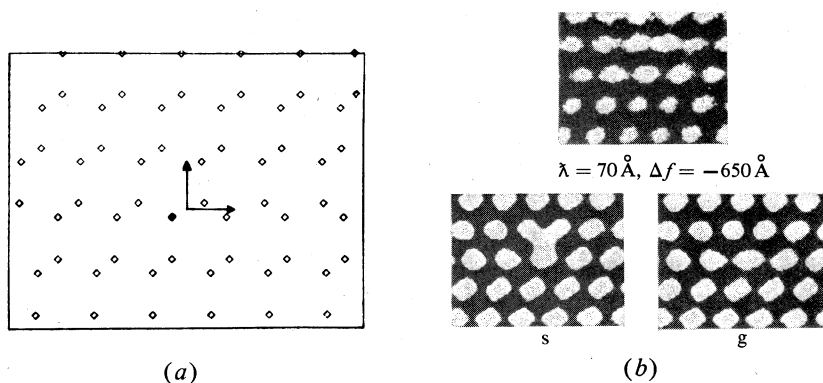


Fig. 3. (a) Projection of atomic rows along $[110]$ for a 30° glide partial; removal of the black row (at centre) generates a Hornstra (1958) 'shuffle' configuration.

(b) Experimental image (top) of 30° partial in Si taken in JEM 200CX, for a thickness of 70 \AA and defocus -650 \AA . Calculated images (below) for shuffle (s) and glide (g) configurations. [Anstis *et al.* (1981).]

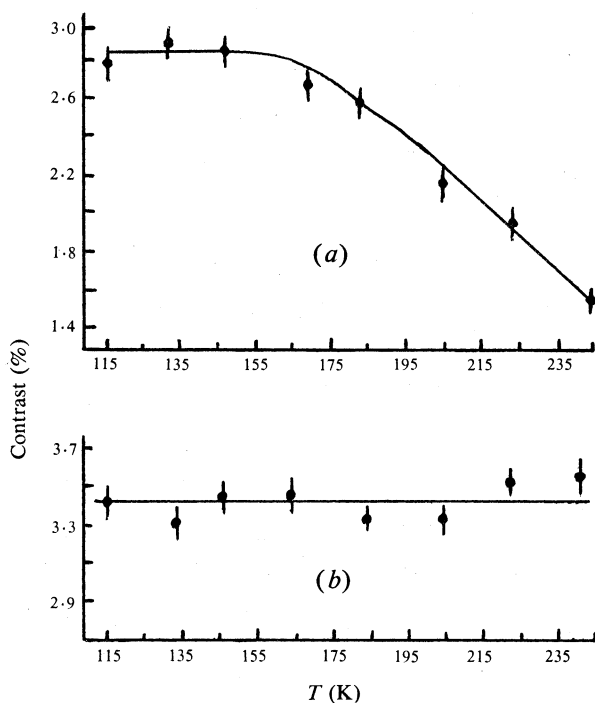


Fig. 4. Temperature dependence of EBIC contrast for (a) screw and (b) 60° dislocations in Si (without EPR centres). [Ourmazd *et al.* (1981b).]

Information on the electronic properties can be obtained using electron beam induced conductivity (EBIC) measurements. Ourmazd *et al.* (1981a) have reported different levels of contrast and a different dependence on beam chopping frequency for 60° and screw dislocations in Si, introduced by low temperature deformation (420°C), following predeformation at 850°C , which suggests different energy levels in the bandgap. Under these conditions of deformation no electron paramagnetic resonance (EPR) centres are observed. If the predeformation occurs at 700°C , EPR centres, at least some of which are associated with point defects, are present and the EBIC contrasts for 60° and screw dislocations are identical, presumably determined by the point defects associated with the dislocations. Fig. 4 shows the temperature dependence of the EBIC contrast for 60° and screw dislocations without EPR centres (Ourmazd *et al.* 1981b). Measurements of this type as a function of doping should give the energy levels associated with individual dislocations.

Impurities of course play a very important part in determining the electronic properties of dislocations. Bourret *et al.* (1981) have obtained structural evidence for small particles of a certain oxide phase at dislocations in Si.

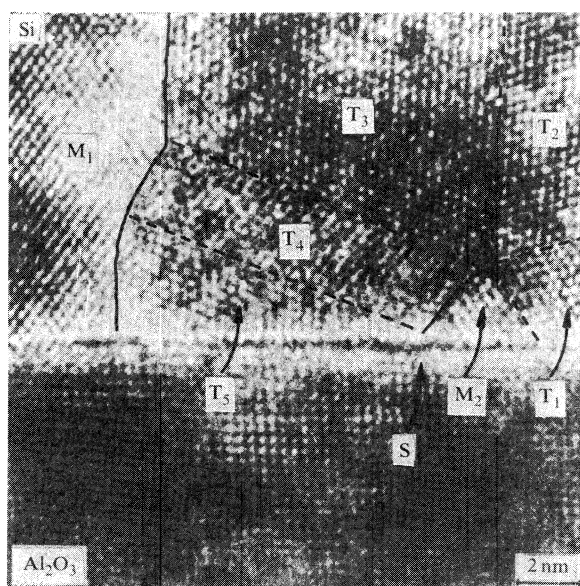


Fig. 5. Twinning in Si at the interface between Si and sapphire. [Abrahams *et al.* (1981).]

Silicon-Sapphire Epitaxial Layer Structures

Because of the electrically insulating properties of sapphire ($\alpha\text{-Al}_2\text{O}_3$), devices made by depositing Si layers have useful properties (e.g. faster switching). However, the different crystal structures result in significant lattice mismatch at the interface. High resolution electron microscopy has revealed that the mismatch appears to be accommodated by multiple twinning in the vapour deposited Si (Abrahams *et al.* 1981; Hutchison *et al.* 1981). Fig. 5 shows a lattice image of a Si- Al_2O_3 interface, showing the differently twinned region in the Si. It is not yet clear at which stage in the growth the process twinning occurs, nor the conditions under which such twins might be eliminated.

3. Solid State Electrolytes

Sodium β'' alumina ($\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$) is a superionic conductor used as the electrolyte in the sodium-sulfur cell. The structure, shown in Fig. 6, consists of alternate stacking of spinel-type blocks and 'conduction planes' of composition Na_2O . The spinel-type blocks are joined by Al-O-Al bridges across the conduction planes, and the Na^+ ions are able to move readily in the conduction planes. One of the factors limiting the lifetime of a sodium-sulfur cell is the failure of the β'' alumina in service.

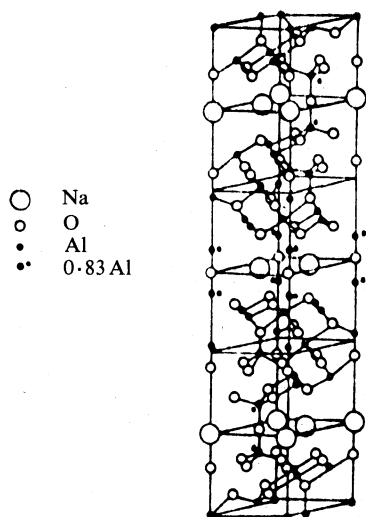


Fig. 6. Structure of sodium β'' alumina. The c axis is vertical and the conduction planes contain Na and O.

Electron microscope observations have been carried out in an attempt to elucidate the microstructural changes responsible for the failure. The crystal is highly radiation sensitive; Fig. 7 shows a sequence of high resolution images (electron beam along $(11\bar{2}0)$) taken of the same area at 15 s intervals at 200 kV (Hull *et al.* 1981; Matsui and Horiuchi 1981). The rows of brightest spots define the conduction planes, some of which are observed to disappear with time. Fig. 8 shows dislocation half loops expanding in an area where the conduction planes are inclined to the beam. Other experiments have clearly shown that the half loops form the perimeter of the removed conduction planes. These observations leave little doubt that the conduction planes are removed by the formation of oxygen ion vacancies, their aggregation into discs on the conduction planes and their subsequent collapse and shear forming a faulted vacancy-type dislocation loop. Preferential nucleation occurs at the surface. By measuring the displacement of the planes on either side of a collapsed conduction plane, in two different orientations, the displacement vector across the fault has been determined to be $\frac{1}{36}[5\bar{5}0\bar{2}]$, which is equivalent to two corner sharing oxygen tetrahedra sliding over one another to become edge sharing (Hull *et al.* 1981). Missing conduction planes occur in battery material (before electron irradiation), particularly after use, but it is not clear whether a mechanism similar to that observed by the electron microscope occurs during operation, nor whether such a mechanism is responsible for the eventual failure.

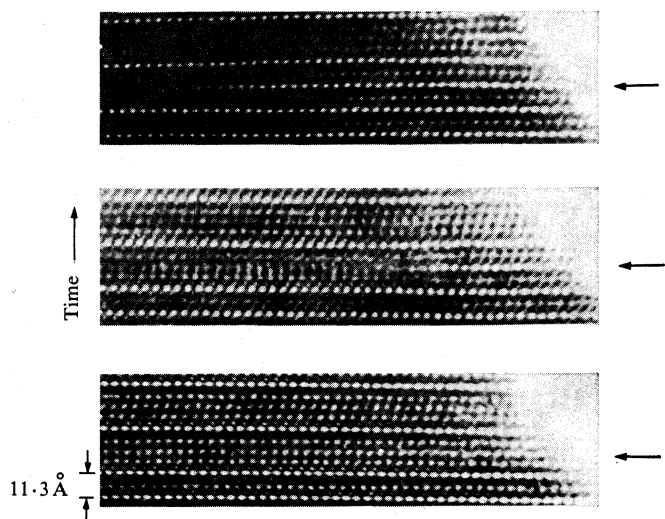


Fig. 7. Sequence of high resolution images at 15 s intervals and at 200 kV for the beam parallel to (11 $\bar{2}$ 0) in sodium β'' alumina, showing the collapse of conduction planes (visible as the brightest rows of spots). Arrows on the right identify a particular conduction plane. [Hull *et al.* (1981); Matsui and Horiuchi (1981).]

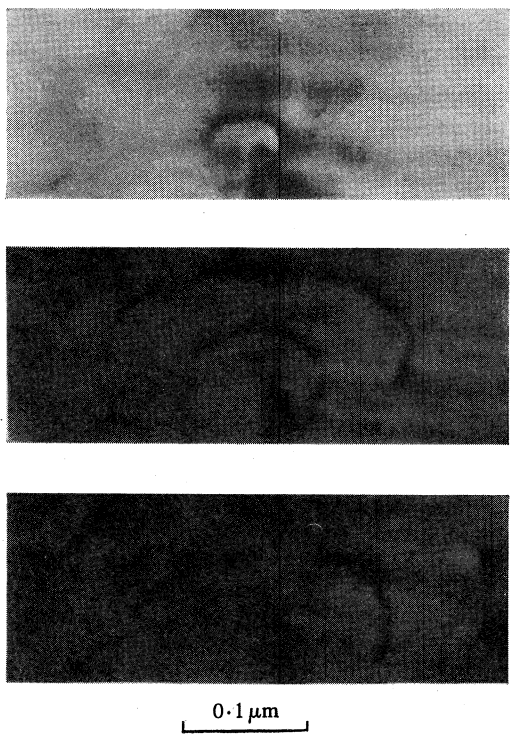


Fig. 8. Dislocation half loops expanding along the different conduction planes of Fig. 7. [Hull *et al.* (1981).]

4. Hydration and Strength of Cements

Although cement is a very important material (current world production is about 10^9 tonnes per annum), relatively few attempts have been made until fairly recently to increase its strength and toughness. High voltage electron microscope observations of the hydration of individual cement grains, using a 'wet' cell, provide support for the 'osmotic membrane' model for the development of the hydrate morphology (Double and Hellawell 1976; Double *et al.* 1978). The initial product of hydration of the calcium silicate grain is a hydrate gel, which acts as a semi-permeable membrane; water diffuses in, and Ca ions out, but silicate ions tend to be blocked. When the osmotic pressure has increased sufficiently, the membrane bursts and fibrils are formed as the silicate-rich solution is ejected. The model was suggested by analogy with the rather similar morphology found in silicate gardens. A similar model was proposed independently and at about the same time by Birchall *et al.* (1978).

This work provided a framework for the subsequent development of relatively strong cement. In particular, the group at ICI has developed a 'macrodefect free cement' with tensile strengths of $\sim 50 \text{ MN m}^{-2}$, compared with the usually accepted strengths of $\sim 5\text{--}10 \text{ MN m}^{-2}$ (Birchall *et al.* 1981). The increase in strength is obtained by refining the pore size distribution. In this case electron microscopy led to a model, which in turn stimulated further work, although the means by which the strength increase has been achieved so far are not related to the microscopic studies.

Further developments are likely to depend on improvements in the fine scale microstructure, and to depend more directly on electron microscope observations. Groves (1981a) has recently reported a number of interesting structural observations on the original and hydrated clinker material. The various phases in the complex Portland cement can be identified by electron diffraction. The formation of the gel coating as in the initial hydration state is readily observed, even without an environmental stage. A twinned martensite-type structure is present in some types of grains, and leads to the possibility of a toughening mechanism by martensitic phase transformations. The microstructure of calcium hydroxide, which is an important product of the hydrated Portland cement, is in the form of microcrystals in the macrodefect free cement paste, quite different from its usual form in normal cement paste, and may have a toughening effect (Groves 1981b). Observations can also be made readily on the effects of retarding agents on the hydration process.

5. Radiation Damage

Electron microscopy plays an important role in the elucidation of the nature of irradiation damage. The reason for this is that the nature (dislocation loops, voids) and scale of the damage ($10^{-10}\text{--}10^{-6} \text{ m}$) are such that no other technique is available. Electron microscope observations on void formation are important in relation to the question of suitability of particular alloys in fast reactors. A recent study on the effect of alloying additions on the nature and density of dislocation-type defects in ion-irradiated copper solid solution is typical of the type of information which can be obtained (Stathopoulos *et al.* 1981). It is found that alloying additions of any type result in an increase in yield (i.e. the number of observable defect clusters per number of incident ions). Furthermore, the increase in yield tends to correlate

with increasing size factor, and it is concluded that the effect is due to dechannelling of the ions by solute atoms or interstitial-solute clusters.

6. Catalysis

Electron microscopy and analysis is being used increasingly to characterize the microstructure and composition of catalysts, and to identify the microstructural parameters important for reactivity and selectivity. With an environmental cell, particularly in a high voltage microscope, it becomes possible to study reactions under conditions approaching those applicable to industrial practice (Gai 1981; Gai and Goringe 1981). In a recent study of the behaviour of α - Te_2MoO_7 catalysts used in the ammoxidation of propylene to acrylonitrile, a number of different techniques were used to identify the nature of the reduction product of the catalyst when used under reducing conditions. The *in situ* studies showed the crystals to break up, forming a new phase with an orthorhombic unit cell derived from electron diffraction patterns. Energy dispersive X-ray analysis was used to obtain an approximate composition of the new phase from areas less than 1000 Å in diameter, using a STEM with a field emission gun. A more accurate analysis was possible by comparing the spectra observed from the reduced crystallites with those from samples prepared under similar conditions outside the microscope and analysed using an electron probe X-ray microanalyser. Finally, X-ray structural analysis was used on bulk samples with the same composition and diffraction patterns of the microcrystals observed in the *in situ* experiments to determine the crystal structure (Gai *et al.* 1982).

7. Conclusions

In this paper we have tried to illustrate the use of electron microscopy for characterizing materials and for establishing composition/microstructure/property relations. The information obtained is important for technological developments; in many cases electron microscopy provides scientific 'underpinning' of technological problems solved in some other way, and in others it provides unique information leading to new models or pointing the way for further developments. The examples have been chosen deliberately to emphasize the variety of techniques available, and the need to use different and often several techniques for specific problems. Electron microscopists have sometimes a tendency to become 'hooked' on a particular technique, usually because some of the techniques require considerable specialist expertise. A broad appreciation of the various different techniques available is clearly important. Finally, it should be noted that this is an area in which collaboration between industry and academic institutions can be very effective.

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