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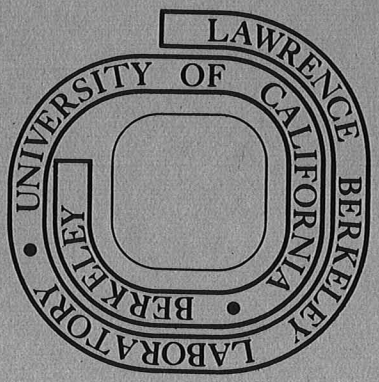

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THE MICROSTRUCTURAL LOCATION OF THE INTERGRANULAR METAL OXIDE PHASE IN A ZINC OXIDE VARISTOR

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ABSTRACT

High resolution electron microscopy of a commercial ZnO based varistor reveals that the Bi-rich intergranular phase is found at all three and four grain junctions and that the majority of ZnO grains are not surrounded by an oxide barrier film as hitherto believed.

1. Introduction

Metal oxide varistors are ceramic semi-conductor devices based on Zn O that exhibit very non-linear current-voltage characteristics. This non-Ohmic behavior, which may be expressed by the relationship $I=kV^{\alpha}$, makes the devices attractive as electrical circuit protectors against power and voltage surges.[1] However, the degree of non-linearity, α, is found to be highly dependent on both the minor additions of oxide constituents used in the device manufacture and the resulting microstructure.[1-4] For this reason considerable effort has been devoted to understanding the conduction mechanism and to relate it to the microstructure of the polycrystalline ceramic material. The intention of this paper is to contribute to this work by clarifying the nature of the microstructure and in particular the distribution and location of intergranular phases, if any.

Observations of varistor materials and the prototype ZnO - Bi_2O_3 system have suggested that they essentially consist of ZnO grains surrounded and separated by a thin continuous intergranular oxide phase.[3-6] This has led to the varistor behavior being widely interpreted as resulting from the series-parallel network formed by the ZnO-intergranular phase junctions.[4,5,7,8] The importance of the intergranular phase is substantiated by the effect that minor chemical additions have on the value of the exponent, α. For instance, the early ZnO based varistors such as those made from the binary ZnO-Bi_2O_3 exhibited low α values, typically $2 \leq \alpha \leq 6$, but by incorporating other oxides Matsuoka et al.[9] developed far superior varistors having α values in the range $30 < \alpha < 50$. A typical multicomponent varistor composition reported by Matsuoka comprises 97 mole % ZnO, 1 mole % Sb_2O_3, and 1/2 mole % each of Bi_2O_3, CoO, MnO and Cr_2O_3. The sensitivity of the exponent, α, to such small quantities of oxide additions has led to intensive efforts to determine the composition of the intergranular phase

in order to maximize the varistor performance. In order to do this two different varistor materials have been investigated by previous workers, one the simple binary system $ZnO-Bi_2O_3$ and the other multicomponent materials commercially produced and having compositions similar to those reported by Matsuoka.

In the $ZnO-Bi_2O_3$ materials the the two phases have been determined by Xray diffraction to be ZnO and the tetragonal Bi_2O_3[5]. By etching away the ZnO grains and subsequently examining the remaining Bi_2O_3 phase by scanning electron microscopy, Morris[3] has demonstrated that the Bi_2O_3 forms a three dimensional open network about the individual ZnO grains.

A similar etching experiment carried out on the multicomponent materials reveals the same intergranular morphology but there is an uncertainty as to its homogeneity and crystallinity.[7,11] By Xray diffraction of the ceramic there are found to be two crystalline phases present in addition to the ZnO, the spinel phase identified as being $Zn(Zn_{4/3}\ Sb_{2/3})O_4$ and a Bi_2O_3 rich pyrochlore phase, $Bi_2Zn_{4/3}\ Sb_{2/3}O_6$[7]. In the microstructure the spinel is seen as faceted octahedral crystals often situated at ZnO grain boundaries[7] whereas the pyrochlore appears by optical microscopy to fill the space at multiple grain junctions and occasionally to partially surround a ZnO grain. Attempts to identify the extracted network phase by Xray emission spectroscopy[7] indicate that it may be the pyrochlore phase doped with Co and Mn, but when examined by electron diffraction it is found not to be crystalline.[11] This has been rationalized as being chemically related to and derived from the pyrochlore phase itself.[11]

Despite these findings however, there is little <u>direct</u> evidence for a continuous intergranular phase separating the ZnO grains. Whilst observations by optical microscopy and scanning electron microscopy reveal the existence at multiple grain junctions of the oxide phase and indicate that it decreases in thickness away from the junctions, the techniques are incapable

of determining whether an intergranular film, deduced to be 100-500 Å thick, is present. Two transmission electron micrographs have been presented by Levinson and Philipp[4] (figures 8 and 9) illustrating an intergranular phase at two ZnO-ZnO grain boundaries, but no attempt was made to demonstrate that such a phase was present at all the ZnO-ZnO grain boundaries examined. Furthermore, measurement of the dihedral angles formed by the oxide phase at the multiple grain junctions in the $ZnO-Bi_2O_3$ binary system indicate that it would not wet the ZnO grains to form a continuous film.[12]

Therefore the present investigation was undertaken to observe directly whether the oxide phase does in fact lie between the individual ZnO grains as hitherto supposed, and to examine the dihedral angles formed by the minor phases.

II. Experimental Details

The material investigated was cut from commercially available varistors produced by General Electric under the trade name GE-MOV^{TM}. The exact varistor composition is proprietary information but is similar to that used in previous studies.

Thin foil specimens for transmission electron microscopy were prepared from thin sections by ion-thinning in the standard manner, with two additional steps to ensure comparatively large regions of very thin material. Firstly, the surfaces of the thin sections were diamond polished (0.25μm grit) prior to ion-thinning, and secondly the ion-thinning (4kV) was performed at a lower angle of incidence (~ 10°) than is usual.

To determine whether a very thin intergranular film is present at the grain boundaries the electron microscopy techniques of bright field imaging and lattice fringe imaging were used. The latter has recently been utilized to study the distribution of the intergranular phase in MgO fluxed and hot pressed silicon nitride [13,14] and to detect for the first time an intergranular film 5-70 Å wide in Y_2O_3 fluxed silicon nitride. [15] The method involves imaging the crystal lattice planes in adjacent grains up to and on either side of selected grain boundaries. In this way intergranular films, amorphous or crystalline, as thin as an interplanar spacing can be detected provided that the boundary plane is viewed edge on. Experimental details of the technique and image interpretation are described elsewhere. [16]

The lattice finge images were taken with a Philips EM 301 electron microscope fitted with a high resolution stage having a limited angle (±6°) of tilt and operated at 100kV.

III. Varistor Microstructure

The gross features of the microstructure as observed by both optical and scanning electron microscopy were found to be the same as have already been described by previous workers[3,6,7,9,10], namely ZnO grains, occasionally twinned, together with a small volume fraction of faceted octahedral spinel grains predominately located at ZnO-ZnO grain boundaries and the pyrochlore phase at some of the multiple grain junctions. In this section therefore attention is restricted to the morphology and crystallography of the phases at the multiple ZnO grain junctions as observed by transmission electron microscopy and to the detection of any intergranular film.

At low magnifications (figure 1) two phases are readily discernable, the ZnO grains and a grain junction phase that appears very dark in bright field except where located in the thinnest regions of the foil. The ZnO grains are rarely faceted and in general have smoothly curving boundaries indicating that they have an almost crystallographically isotropic surface free energy. The very dark phase is observed at every three and four grain junction and in every case it decreases rapidly in thickness away from the junction itself. Xray emission spectroscopy of the phase reveals the presence of Bi, Sb and Mn in agreement with that found by Wong[7]. The presence of these heavy elements having large electron scattering factors accounts for the phase being darker than the neighboring ZnO grains due to structure factor contrast.

There are a number of related observations that suggest that this junction phase is amorphous. Firstly, electron diffraction patterns obtained from the phase give characteristic ring patterns as in figure 2.

(The short row of spots are from an adjacent ZnO grain and were included for calibration purposes). Analysis of the patterns reveals that the rings correspond to spacings of 3.3. 2.3 and 1.3 Å for the three diffuse rings discernable on the negative. These are similar to those reported by Levinson and Philipp [4] also from a commercial varistor. Secondly, the contrast of the junction phase is insensitive to the angle of electron illumination, a characteristic of amorphous materials. Thirdly, and equivalently, they do not exhibit any extinction phenomena, such as variation in contrast with deviations from the exact Bragg condition as crystalline regions do. These findings agree with those made by Wong et al. [11] who studied the extracted network phase from a six-component analog of a commercial varistor by electron diffraction.

Nevertheless, it may still be argued that the crystalline pyrochlore phase identified by Xray diffraction is vitrified by both the extraction process used by Wong et al. and by the ion-thinning process used to prepare foils in this study. However, this does not seem to be the case in the foils examined. Ion-thinning at an oblique angle of incidence (~10°) with argon ions accelerated to 4kV should restrict the induced radiation damage to the upper and lower surfaces of the foil. This effect is seen in the ZnO grains in the thin foil regions, whereas the junction phase appears to be non-crystalline even in the thickest regions of the foils. Vitrification caused by heating of the pyrochlore phase during ion-thinning can also be ruled out since Wong [7] has shown that on heating above 1100°C the pyrochlore transforms to the crystalline spinel phase. It must therefore be concluded that the junction phase is structurally predominately amorphous.

Although it is widely believed that there is an intergranular film 100 - 500 Å thick separating the ZnO grains, examination by bright field transmission electron microscopy and lattice fringe imaging clearly shows that this is not the case. Out of thirty-five multiple grain junctions examined in this study the junction phase was seen to terminate abruptly in fifty cases and to form an intergranular film in only four cases. (Boundaries from grain junctions that were terminated by the edge of the foil or where the foil was too thick to determine whether the phase was present were not counted).

An example of the exceptional cases, where a continuous intergranular phase does exist in the boundary, is presented in figure 3. Although the film is only 90A thick its presence is quite obvious even at relatively low magnifications. There are three striking features exhibited by this boundary phase. Firstly, the ZnO-ZnO grain boundary is very straight and selected area electron diffraction patterns taken from the grain to the right of the micrograph demonstrate that the boundary is parallel to the basal plane in this ZnO grain. Secondly, its contrast is insensitive to changes in orientation to the electron beam indicating that it is amorphous (Figure 4). Thirdly, the phase is of almost constant thickness along the entire length (~2μm) of the boundary.

To determine whether a thin intergranular film was present at a grain boundary two microscopy techniques were used. For those boundaries where both adjacent grains were in a strongly diffracting orientation the method of high resolution bright field imaging was the most appropriate technique since the junction phase being much denser

electron-optically than the ZnO appeared with high contrast. In general however the technique of lattice fringe imaging was preferred since it has the intrinsic advantage that films as narrow as one interplanar spacing may be resolved. In figure 5, the grain boundary region illustrated in figure 4 is shown in the lattice fringe imaging mode, and here the boundary phase can clearly be seen with the lattice plane fringes in the adjacent ZnO grains terminating at the edge of the phase. The contrast seen in the intergranular phase is due to variations in electron phase contrast and is characteristic of both an amorphous material and of carbon contamination on the sample.

The majority of grain boundaries were concluded to be free of any intergranular phase since the lattice plane fringes in adjacent ZnO grains were seen to be continuous right up to the plane of the boundary as in figure 6. Here the only discontinuity in the fringes occurs at the boundary line whereas if even a thin phase were present the discontinuity would not be a line but rather a band, as exhibited in figure 5. Careful examination of the boundary also reveals terminating fringes that accommodate the mismatch between the planes in the two grains. Whilst their separation is too small to carry out the dark field diffraction analysis necessary to determine unambiguously that they are grain boundary dislocations, they do have the fringe configuration expected of such dislocations. This further supports the conclusion that no intergranular film is present at the boundary.

Whether a continuous intergranular phase is present at a grain boundary is found to depend on the morphology of the triple grain junction phase which in turn is related to the crystallographic orientation of the grain boundary. The majority of grain junction phases have a morphology

as illustrated in figure 1 with concave profiles implying that the dihedral angles they form against the ZnO grain boundary become zero. This would allow the phase to penetrate along the grain boundary as a continuous film. However this is generally not the case, since the phase is seen by close examination in bright field to terminate abruptly. In addition away from the junction region no intergranular phase can be detected in the lattice fringe images.

In some cases the termination of the junction phase can be clearly seen allowing measurements of the projected dihedral angle to be made. An example of this is shown in figure 7, where the two angles are 46° and 72°. All the dihedral angles measured were in the range 12° to 85°, and since these values are non-zero the free energy of the interphase boundary must be greater than half the grain boundary energy. Penetration of the junction phase along the grain boundary would in these cases raise the total free energy at equilibrium.

In each of the four cases, in which a continuous intergranular phase does exist in the boundary, it is found that the grain boundary is parallel to the basal plane in one of the ZnO grains, as determined by selected area electron diffraction. In these instances the boundary is also extremely straight over distances of the order of microns and the boundary phase is of almost constant thickness over the same distance. Morris and Cahn [12] in their study of the binary $ZnO-Bi_2O_3$ system deduce from the non-zero dihedral angles that continuous intergranular films rarely occur, but have suggested that when they do they result from eutectic liquid flowing into gaps between grain interfaces created by anisotropic thermal contraction forces during cooling. The fact

that in each case here the boundary plane is defined by the basal plane in one of the grains however implies an alternative explanation with a crystallographic origin, possible due to a narrow cusp in the Wulff plot of the surface free energy of ZnO at the basal plane orientation.

Together, these findings suggest that the formation of a continuous intergranular phase is determined by the relative surface free energies of the junction phase having a higher surface free energy as evidenced by the non-zero dihedral angles, except when the boundary plane is bounded by a ZnO basal plane. This also accounts for the insensitivity of the varistor behavior to the exact molar fractions of Bi_2O_3 and other oxides used in manufacture, since they only affect how far the junction phase encroaches along the boundary by virtue of its volume rather than the thickness of any phase separating the ZnO grains.

In addition they add credence to the model proposed by Morris and Cahn [12], and Morris [10] that the non-linear conductance is due to segregation of Bi to the ZnO grain boundaries effectively forming an atomically thin absorption layer at the boundaries.

IV. Conclusions

This microstructural investigation shows that the non-Ohmic behaviour of the varistors cannot be attributed to a three dimensional junction barrier network formed by a continuous thin film of insulating phase separating semiconducting grains of ZnO as hitherto believed, since the majority of the ZnO-ZnO grain boundaries are devoid of any intergranular phase. The bismuth rich phase is located principally at three and four ZnO grain junctions and exhibits non-zero contact angles with the ZnO grains. Those few grain boundaries that do contain an intergranular phase are "special" boundaries. They are formed by the basal plane of one of the adjacent ZnO grains resulting in a straight boundary and an intergranular phase of constant width over several microns.

Acknowledgements

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FIGURE CAPTIONS

FIG. 1. Low magnification bright-field electron micrograph of an intergranular phase, P, located at the three-grain junction. The intergranular phase appears dark since it contains a high concentration of elements, e.g. Bi and Sb, having large electron scattering factors.

FIG. 2. A thin three-grain junction phase, P, together with its ring-shaped selected area electron diffraction pattern characteristic of a non-crystalline material. The short row of spots are from one of the adjacent ZnO grains and were included for calibration purposes.

FIG. 3. A continuous intergranular phase present as a thin film, F, between two ZnO grains and leading from the three-grain junction, P.

FIG. 4. The same intergranular phase film as in Fig. 3, but observed at three different orientations to the incident electron beam, a) -6°, b) 0° and c) +6°. The relative insensitivity of the contrast in the film to changes in orientation indicates that it is probably amorphous.

FIG. 5. A portion of the grain boundary region of Fig. 4, observed by the technique of lattice fringe imaging. The lattice plane fringes in the adjacent ZnO grains can clearly be seen, together with the broad band discontinuity between them identifying the intergranular phase P. The spacings of the (100) and (101) planes in ZnO are 2.81 and 2.47Å respectively.

FIG. 6. A lattice fringe image of a grain boundary devoid of an intergranular film. The boundary plane is seen edge on and lies along the line joining the two arrows. The (002) lattice fringes in adjacent grains are seen to be continuous right up to the plane of the boundary. Terminating fringes may be seen in the boundary

indicative of the presence of grain boundary dislocations. (These may be seen most easily by viewing the figure obliquely).

FIG. 7. Bright field electron micrograph of a junction phase close to the edge of the foil. In this case the abrupt termination of the phase may be seen together with the non-zero dihedral contact angle. The measured angles are 46 and 72 degrees.

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FIG. 1

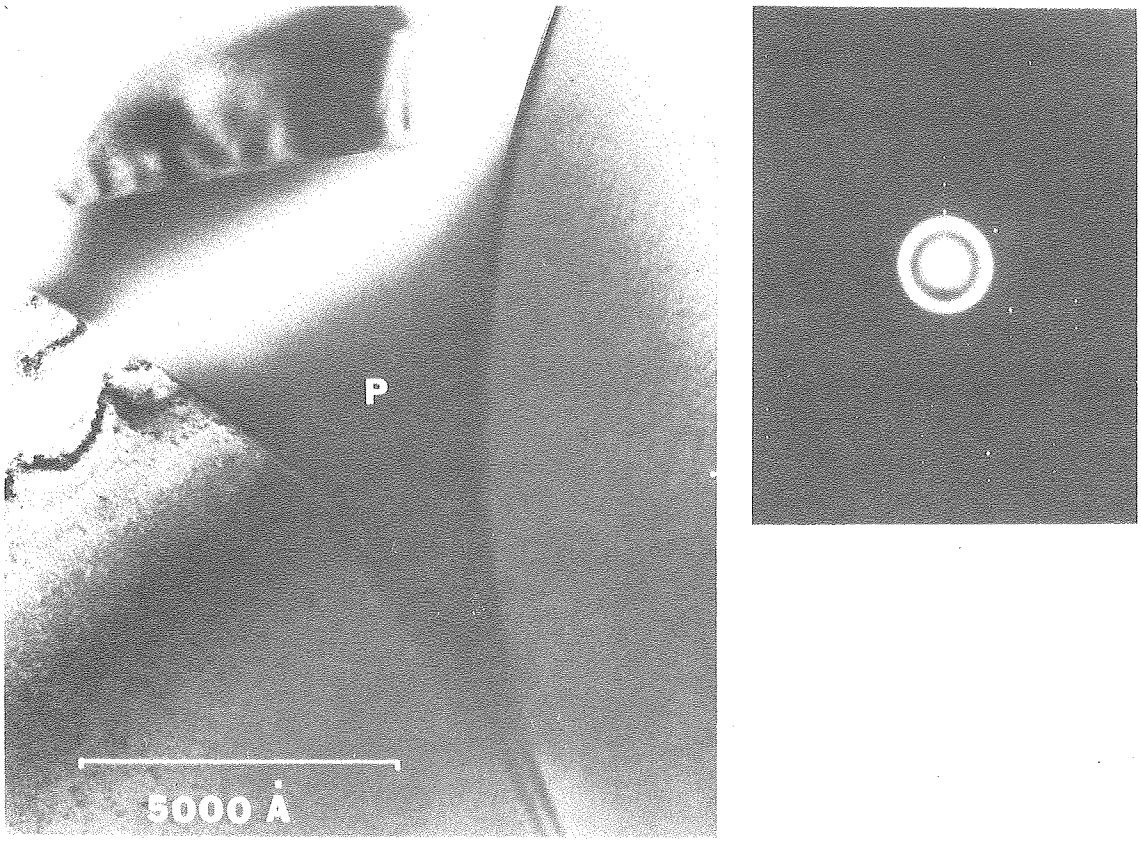

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FIG. 2

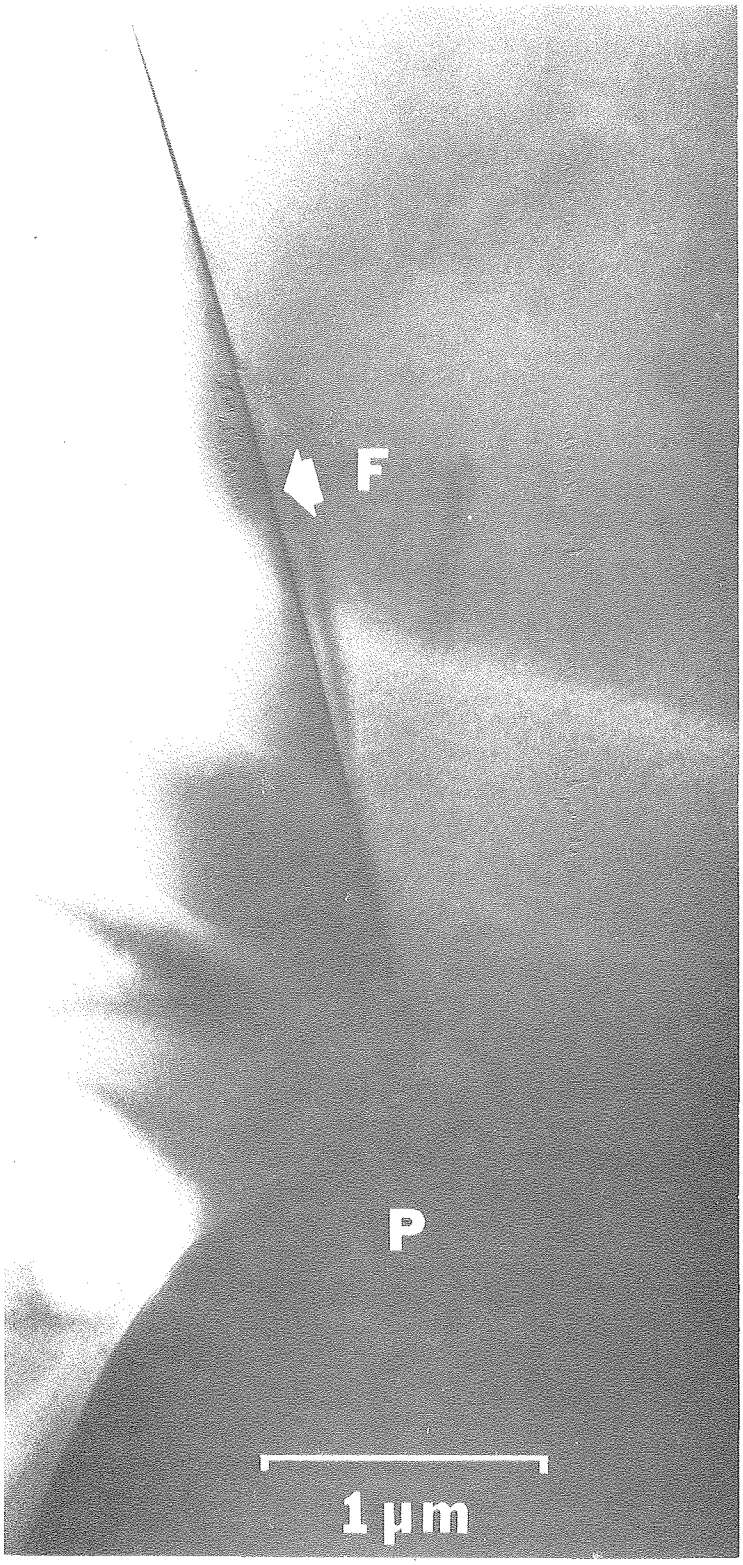

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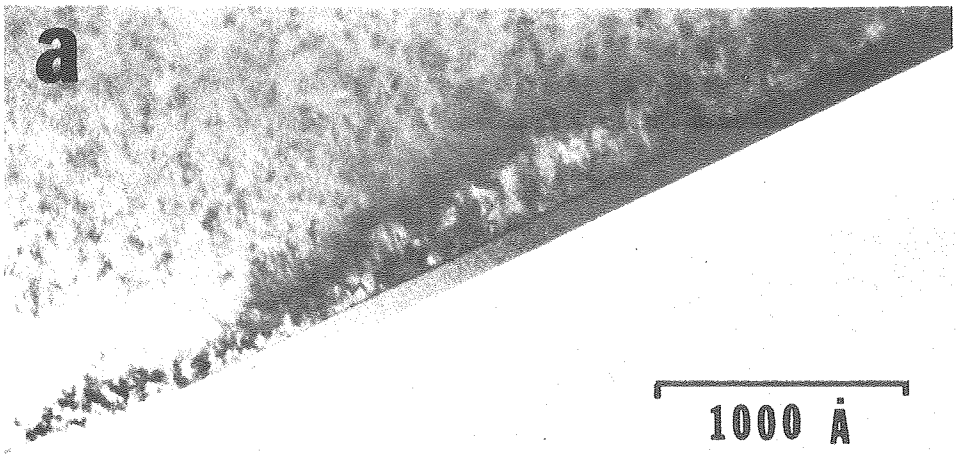
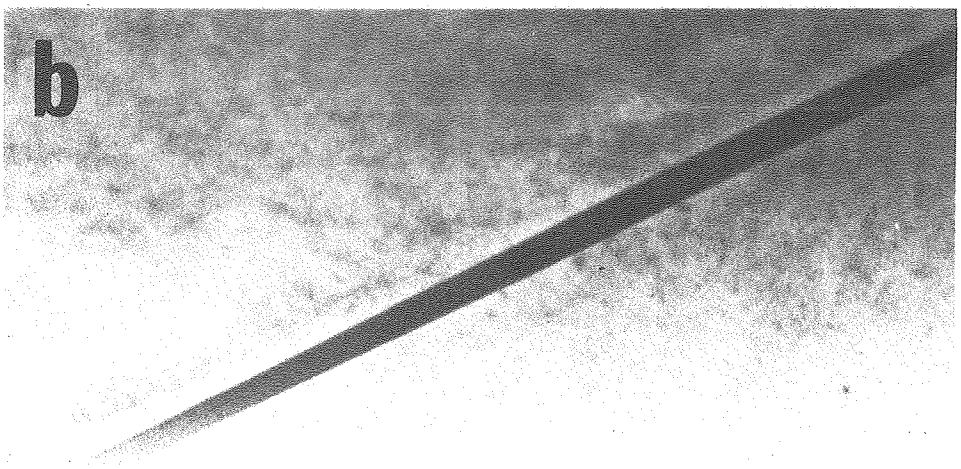
Fig. 3





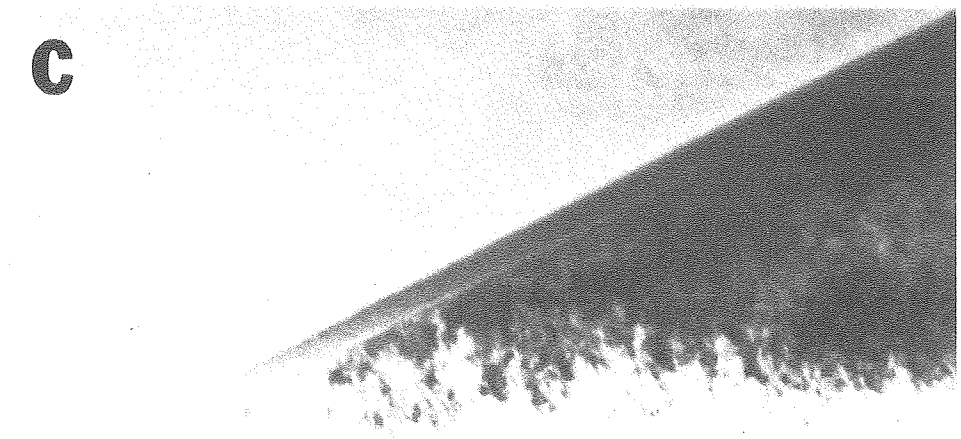


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FIG. 4

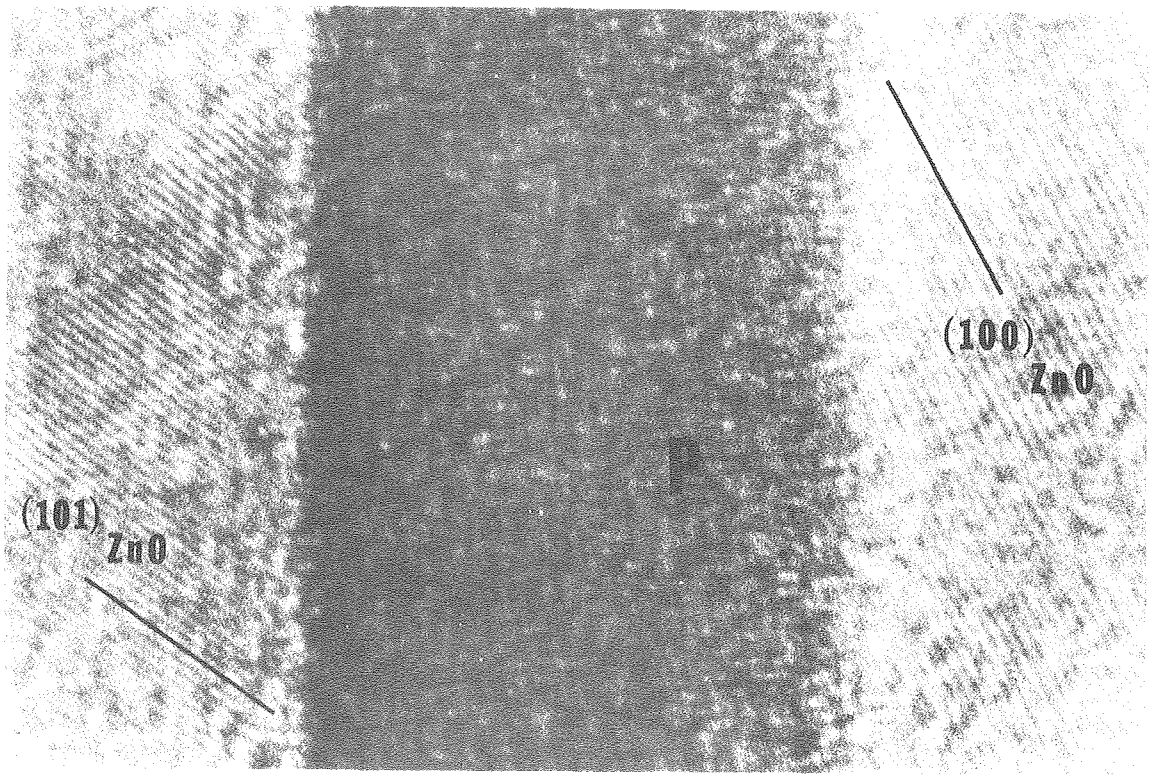

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FIG. 5

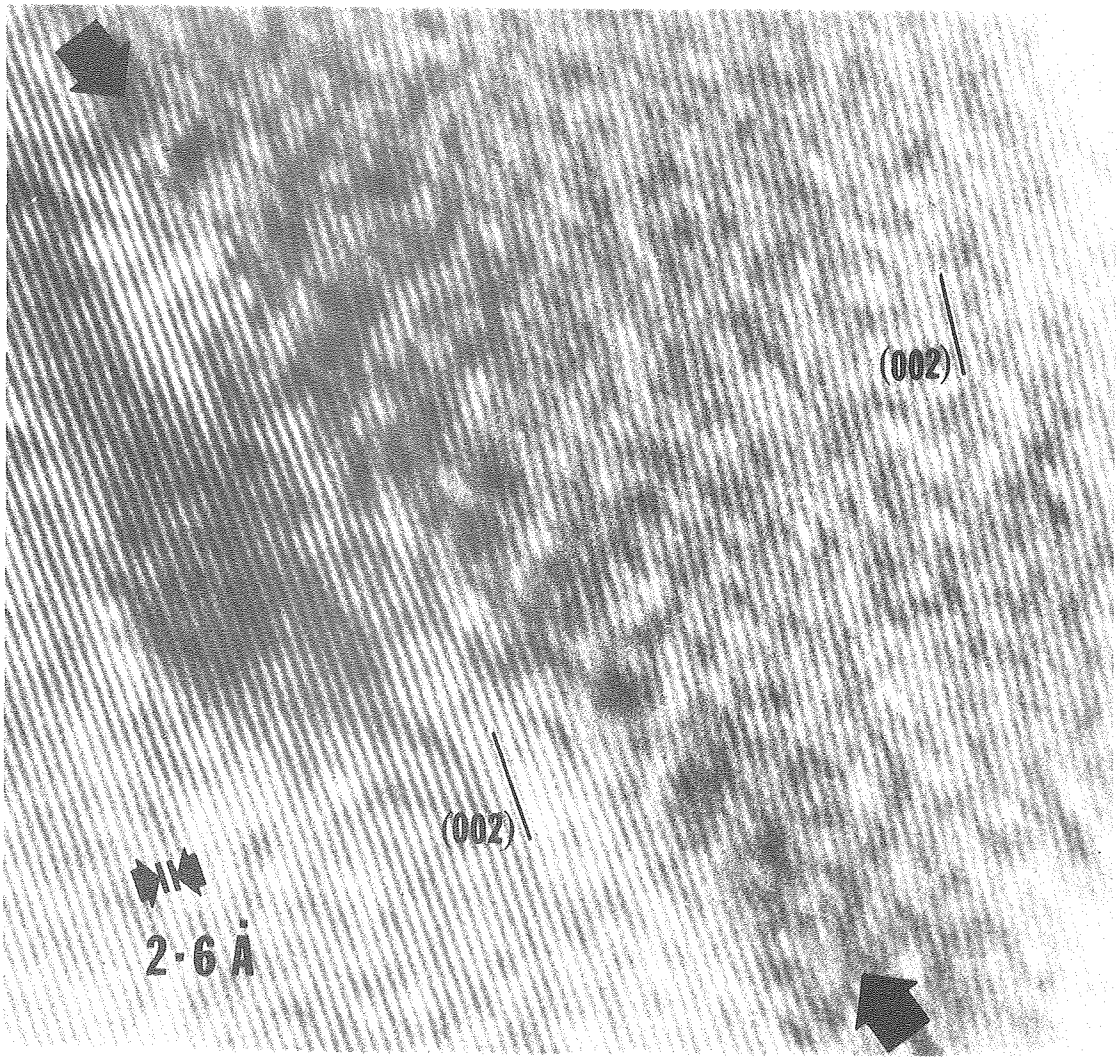

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FIG. 6

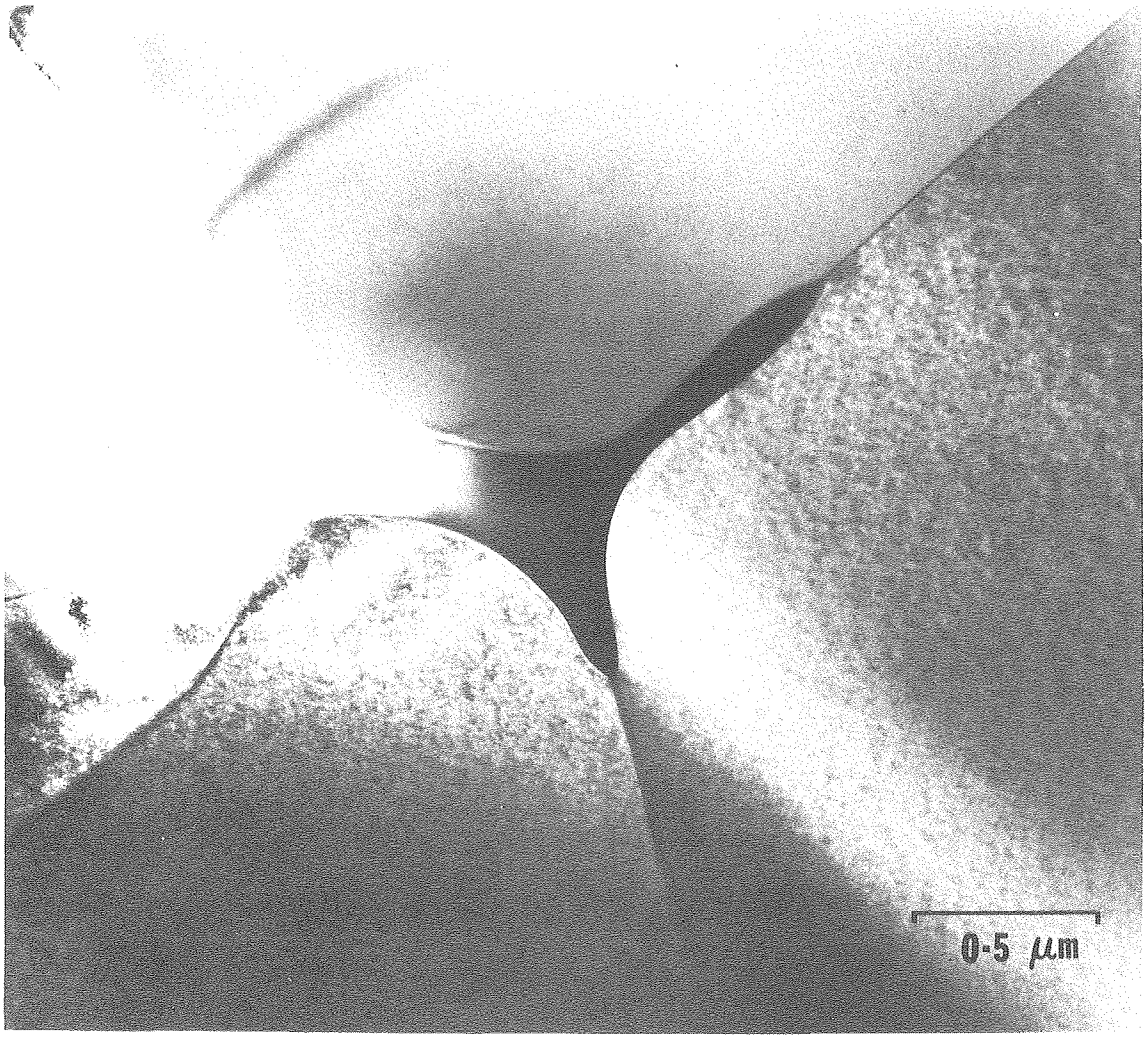

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FIG. 7

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