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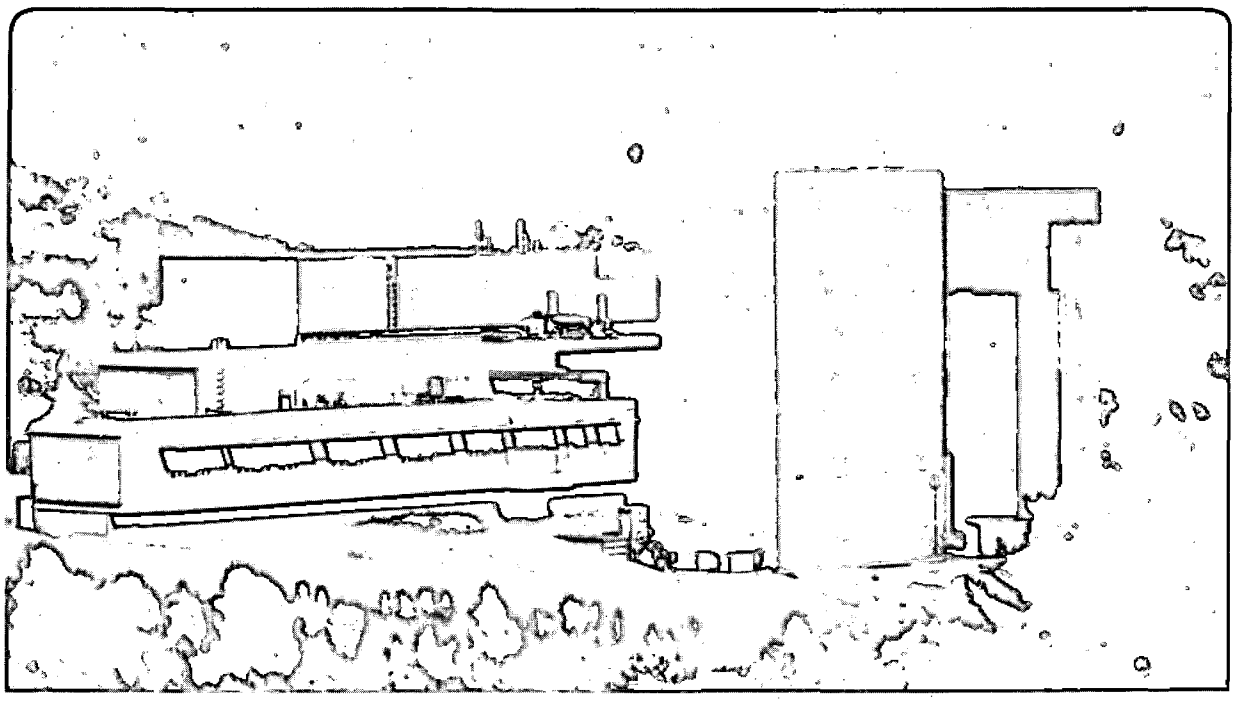

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Impurity Distribution in Polycrystalline AlN Ceramics

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Abstract

Convergent beam electron diffraction and diffuse dark field imaging in the transmission electron microscope have been used to obtain qualitative information regarding the distribution of impurities in polycrystalline AlN. Solutionized impurites are distributed homogeneously within the grains of a given ceramic but an amorphous grain-boundary phase on the order of 10 - 20 Å in thickness is observed between the AlN matrix grains.

Introduction

Aluminum nitride is of technological interest due in part to its high intrinsic thermal conductivity which makes it attractive for electronic packaging applications. The instrinsic thermal conductivity is degraded by the presence of very small concentrations of solutionized impurities such as oxygen which act as phonon scatterers. The accurate determination of impurity content is consequently important to the characterization of AlN ceramics for electronic applications.

Initial measurements of the influence of oxygen on AlN thermal conductivity were made by Slack using neutron activation to determine oxygen concentration.[1] In addition to the degredation of thermal conductivity Slack correlated oxygen content with the change in lattice parameter due to substitution of oxygen for aluminum. For high purity AlN

Slack found that oxygen impurities cause an isotropic (c/a remains constant) decrease in lattice parameter. Consequently, lattice parameter measurements can theoretically be used to determine oxygen content in high purity AlN powders and ceramics and this in turn correlated with thermal conductivity.

Additional work concerning AlN and its thermal conductivity is available (e.g. references 2-6) but there are several complicating factors in the analysis of polycrystalline ceramic material. To date, there has been no attempt to definitively correlate the thermal conductivity of polycrystalline AlN with factors other than bulk oxygen content, in effect neglecting several potentially important effects such as inhomogeneities in the internal distribution of oxygen and the presence of impurities other than oxygen. Furthermore, there may be serious difficulties with the established use of bulk measurements of oxygen applied to these materials.

The direct measurement of oxygen content in modern AlN ceramics by neutron activation as used by previous authors may be prohibited by the presence of minority oxide phases added to promote densification (e.g. yttrium-aluminum oxides). X-ray diffraction (XRD) measurement of lattice parameter shifts due to oxygen impurities may be complicated not only by secondary phases but also by the effects of thermal expansion anisotropy and differing grain sizes in polycrystalline AlN. Even if such bulk measurements of oxygen concentration are successful, they yield no information regarding the actual distribution of oxygen within the ceramic. For this reason, microanalytical methods for the measurement of oxygen content with high spatial resolution are desired.

A significant obstacle to the use of microanalytical spectral techniques such as thin-window energy dispersive x-ray spectroscopy and Auger spectroscopy in the measurement of oxygen is the presence of an amorphous oxygen-rich layer which forms rapidly on AlN in the presence of oxgyen.[7,8] Even should in-situ sputtering methods be used to remove such layers under examination in high vacuum it is doubtful that such techniques have the necessary energy resolution for accurate quantification of small amounts of oxygen. A far more promising method is the use of convergent beam electron diffraction (CBED) to measure fine lattice parameter shifts.[9,10]

Ideally, CBED determination of lattice parameter can be used in correlation with the data established by Slack in order to determine oxygen content with high spatial resolution. CBED has an additional advantage over bulk XRD in that any residual elastic strain from thermal expansion anisotropy during processing is expected to be relieved through the loss of matrix constraint in the thin foils.

A significant problem in the use of lattice parameter measurements for the quantitative analysis of impurity content in AlN is that oxygen may not be the only significant impurity.[1-3,7-8] In particular, carbon may also coexist with oxygen in solution with AlN; the Al_2OC stoichiometry maintains electroneutrality and the compound may exist in a virtually continuous solid solution range with AlN. As carbon is (nearly) as ubiquitus as oxygen, it is likely that any given AlN may contain carbon in solution as well as oxygen. Carbon in solution (as Al_2OC) is expected to increase the AlN lattice parameter whereas Al_2O_3 in solution decreases it.[1,7] These competing effects make quantitative measurements of impurity levels by lattice parameter measurement very difficult without independent microanalytical spectroscopy of carbon and oxygen content.

A final complication in methods of bulk oxygen characterization is that oxygen may not only be solutionized in matrix AlN but present as a majority consituent in aluminum oxynitride grain boundary phases. Such phases may result from the surface oxidation of AlN powder prior to sintering or from reaction with oxide additives, much as in the case of Si_3N_4. The many similarities between the Al-O-N and Si-O-N systems suggest that any oxygen rich grain-boundary phases in ceramic AlN are likely to be amorphous, similar to those commonly observed in ceramic Si_3N_4. Diffuse dark-field Transmission Electron Microscopy (TEM) imaging[11] is a particularly useful technique to identify such amorphous regions as has been shown in prior investigations of Si_3N_4 (e.g. ref. 12).

Experimental Procedures

Three tape-cast AlN ceramics with varying amounts of yttrium-aluminum garnet additive† were examined by conventional

transmission electron microscopy and CBED to determine the distribution of impurities within the matrix AlN grains. Thin foil specimens were produced by standard thinning methods; specimens were cut and polished to 3 mm discs of widths below 200 μm, subsequently dimpled to less than 20 μm minimum thickness, and then ion milled to electron transparency. Electron microscopy was conducted on a Philips EM400T‡ transmission electron microscope operated at a nominal voltage of 100kV and with a spot size of approximately 100nm for CBED (compared to an average apparent grain diameter greater than 1μm). Higher order Laue zone (HOLZ) line patterns were simulated assuming the standard hexagonal wurtzite structure with c/a = 1.6004.[1]

Results and Discussion

The [1102] zone in AlN (Figure 1) was chosen for CBED examination due to the sensitivity of its first and second order Lause zone (FOLZ and SLOZ) deficiency line symmetries and the ease of locating the zone (an important practical criterion in the CBED examination of fine-grained non-cubic materials). If precise lattice parameter measurements were to be made without the benefit of an AlN standard, however, a much higher index zone would be used in order to minimize dynamical variation of the effective beam voltage.

The CBED central disk patterns from AlN specimens of different types exhibit noteable differences in both the FOLZ and the SOLZ deficiency line symmetries. These differences are shown in Figure 2 in sections of CBED patterns from the three ceramics examined. The three arrowed lines correspond to the (6334), (6514), and (3741) FOLZ deficiency lines. The two plain lines correspond to the (8805) and (8803) SOLZ deficiency lines. The relative placements of these lines illustrate that clear differences between the three AlN samples may be distinguished by CBED. These variations reflect processing differences which are known to result in differing thermal conductivity which in turn clearly relate to the differing matrix impurity concentrations.

Figure 3 contains diffraction patterns all taken from AlN-2. Figures 3(a) and 3(b) were taken at the center of different grains and Figure 3(c) was

taken at the edge of the same grain examined in 3(b). The important feature in these patterns is the similarity in HOLZ deficiency line features (e.g. the intersection of arrowed FOLZ deficiency lines) which indicates similarity in lattice parameter. These patterns are representative of the general finding that the HOLZ line symmetries do not vary across the width of a single grain or between two grains of the same AlN type. Since detectable differences in the HOLZ line symmetries correspond to a difference of approximately $2 \cdot 10^{-3}$Å (as determined by simulation‡‡), these patterns indicate internal lattice uniformity of approximately $\pm 2 \cdot 10^{-3}$Å on the c-axis. Regions directly adjacent to the yttrium-aluminum garnet precipitates were avoided due to the probable complications in interpretation resulting from residual strains induced by the differing thermal expansions of AlN and the garnet phase.

Figure 4 shows bright-field / diffuse dark-field micrographs demonstrating that a thin amorphous phase wets the AlN grain boundarys. Such amorphous layers were found at all grain boundaries examined. No substantial pockets (>100Å thick) of the amorphous phase were encountered in the specimens examined in this study; the lack of thicker amorphous regions prevents precise measurement of the boundary phase thickness from microdensitometer traces, but inspection of TEM images shows them to be on the order of 10-20 Å in width. As previously mentioned, such glassy regions are believed to be oxynitride phases very similar in origin to those found in sintered Si_3N_4 ceramics arising from reactions with the oxide sintering additives or oxide/oxynitride phases present on the powder surfaces due to exposure to air. The observation of significant concentrations of carbon in such surface phases[8] may also indicate residual carbon in solution at the grain boundary phases.

The very low volume fraction that these grain boundary glasses represent (on the order of 0.3v% for 10Å of glass wetting a 1μm diameter grain) should not significantly influence the bulk thermal conductivity relative to the pronounced effect of oxygen. In fact, it is unclear whether or not such regions might actually improve overall thermal conductivity by gettering impurities and promoting densification during firing. Studies by high resolution electron microscopy are planned for the near future in order

to more closely examine the crystalline matrix material adjacent to these amorphous grain-boundary phases.

Conclusions

CBED analysis of polycrystalline AlN shows internal uniformity of lattice parameter and hence uniformity of impurity content throughout the crystalline matrix. Distinct differences in HOLZ deficiency line symmetries are, however, apparent between the different AlN ceramics. The measurement of absolute difference in lattice parameter and hence oxygen content (or total impurity content in solid solution) may be complicated by the competing effects of oxygen and carbon in solution. Thin glassy phases (~10 Å) are found at all grain boundaries and are believed to be oxynitride phases of similar origin to those found in Si_3N_4.

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Footnotes

* Member, the American Ceramic Society
†Toshiba Corp., Japan.
‡Philips Gloeilampenfabrieken N.V., Eindhoven, The Netherlands
‡‡Diffract 1.1, Microdev Software, Evergreen, Co.

Figure Captions

Fig. 1 Central disk (1-102) CBED pattern from a high-purity AlN

(AlN-2).

Fig. 2 (1-102) CBED patterns from three types of polycrystalline AlN; arrowed lines indicate three FOLZ dificiency lines; plain lines indicate two SOLZ deficiency lines.

Fig. 3 (1-102) CBED patterns from polycrystalline AlN (AlN-2) with arrowed FOLZ deficiency lines; (a) grain center; (b) center of a differenct grain in the same sample; (c) grain boundary of previous grain.

Fig. 4 Bright-field (BF) and diffuse dark-field (DDF) micrographs of the grain boundary phase in AlN (AlN-3).

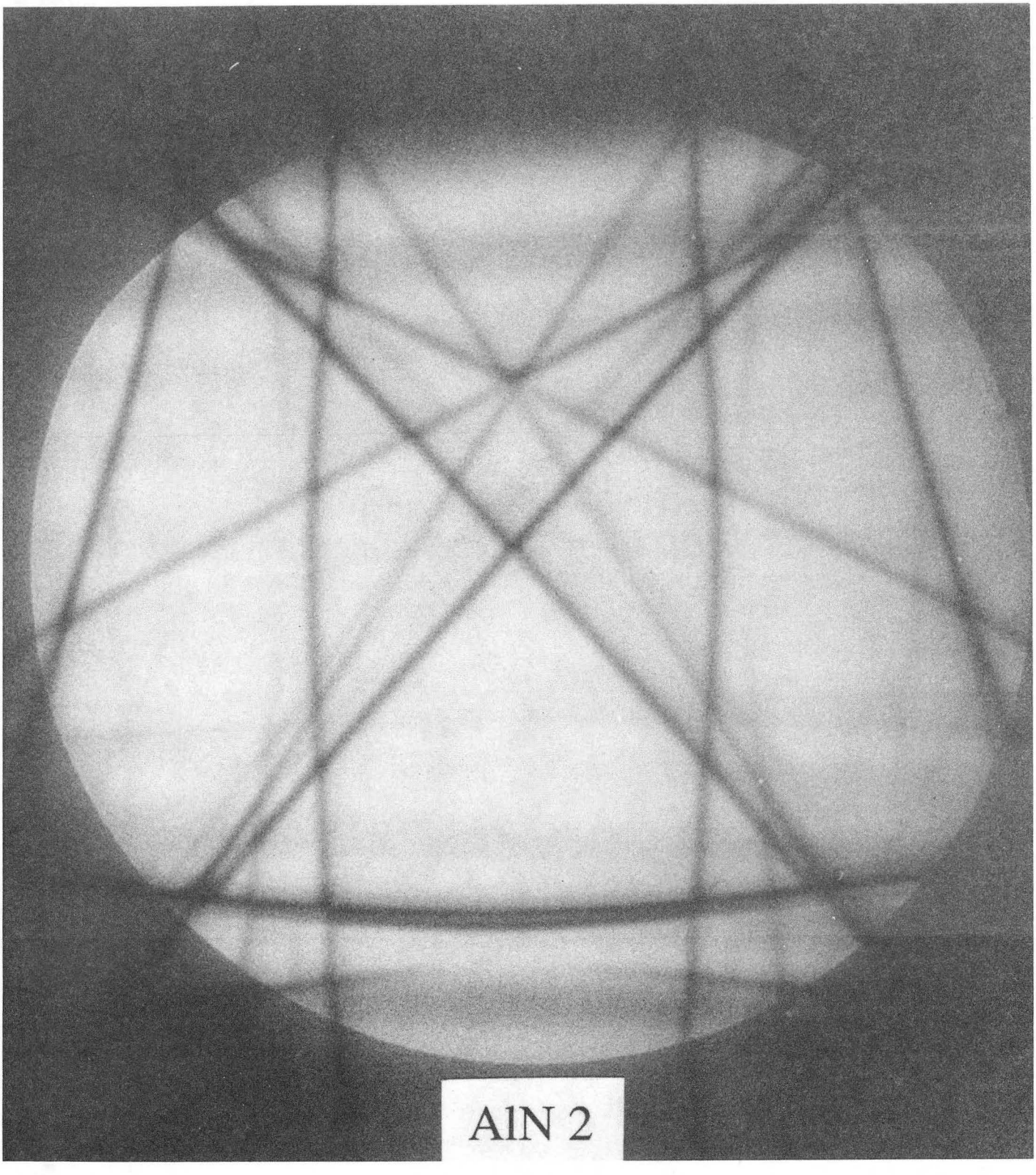

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Fig. 1

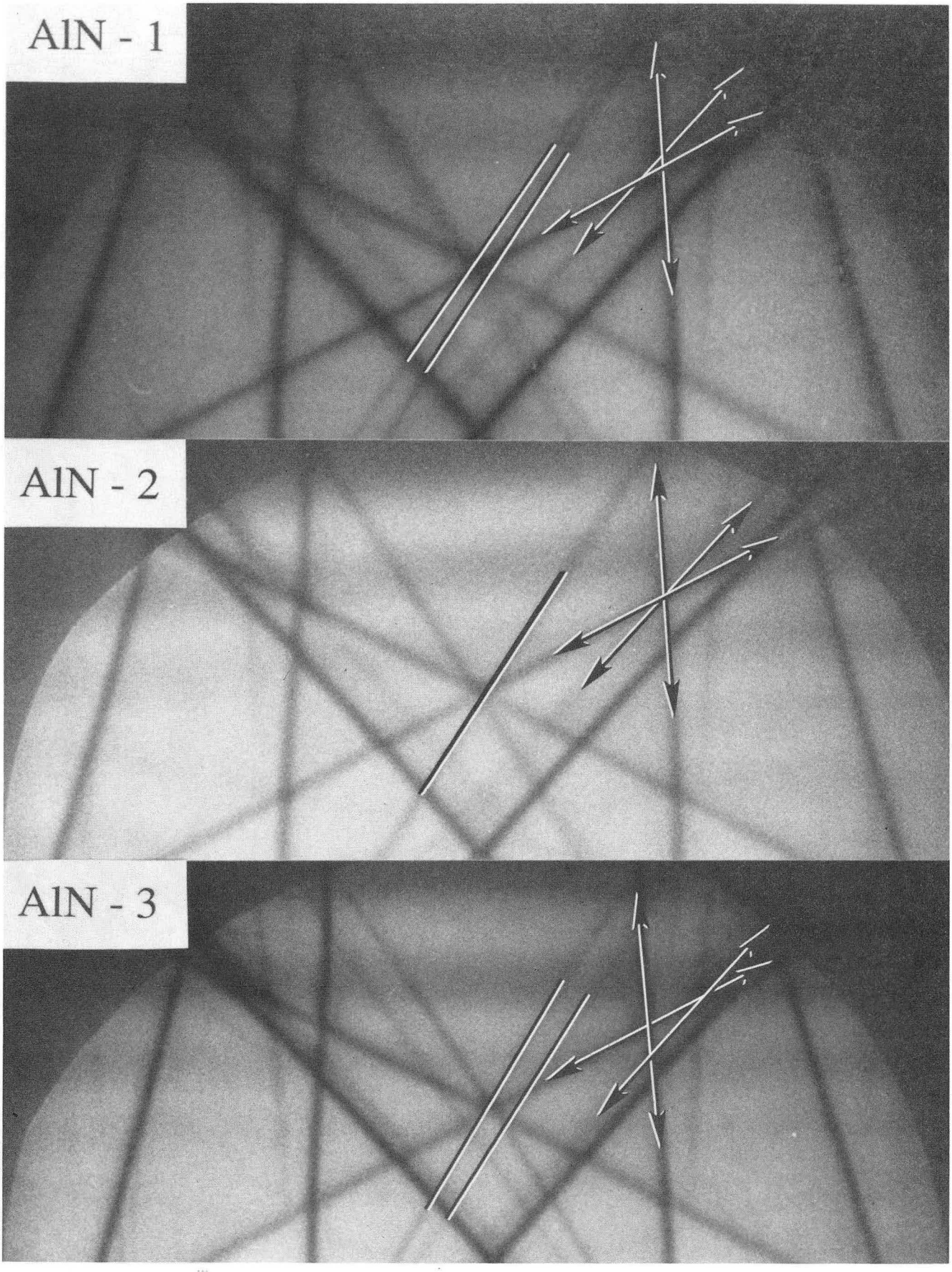

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Fig. 2

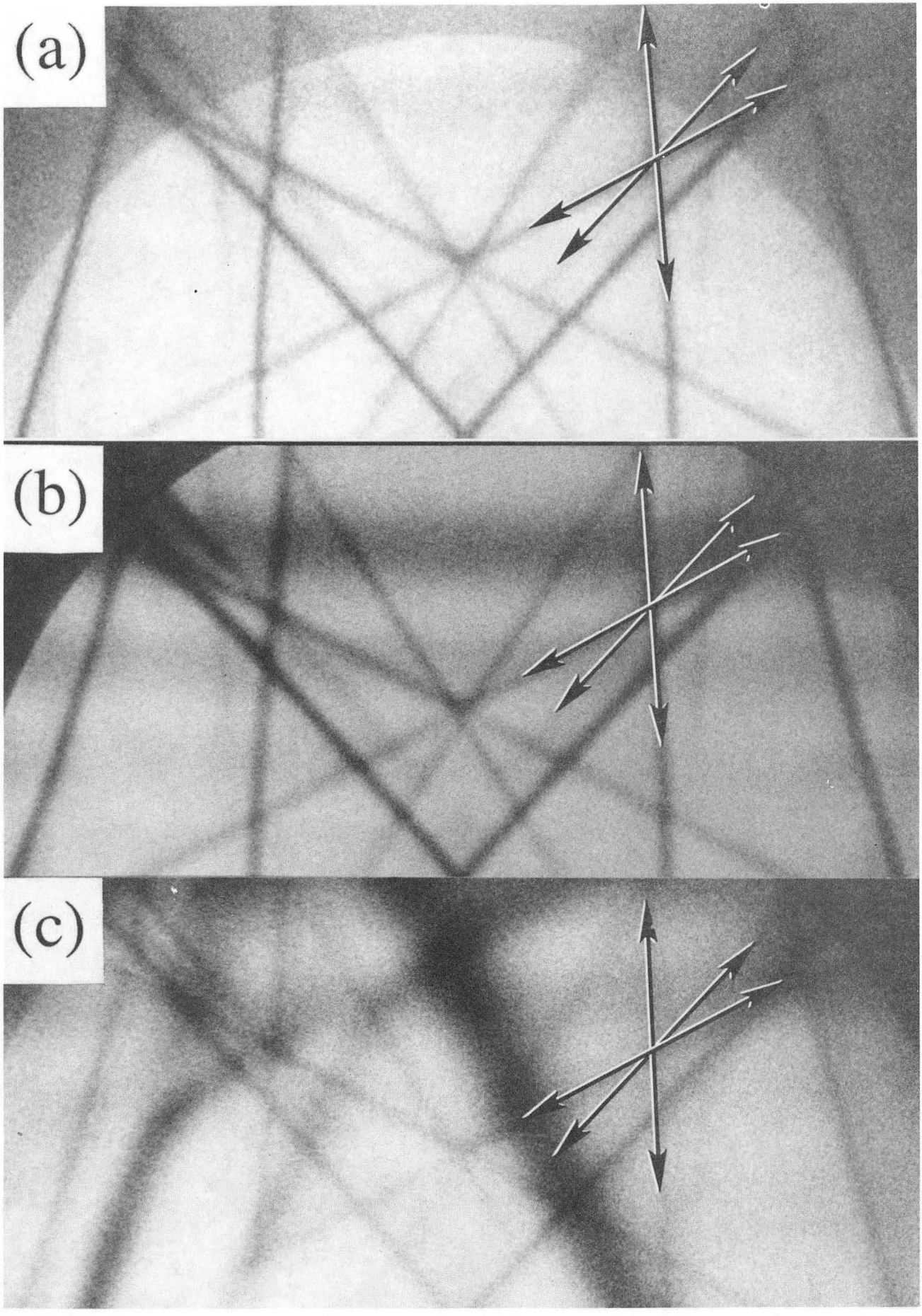

Fig. 3

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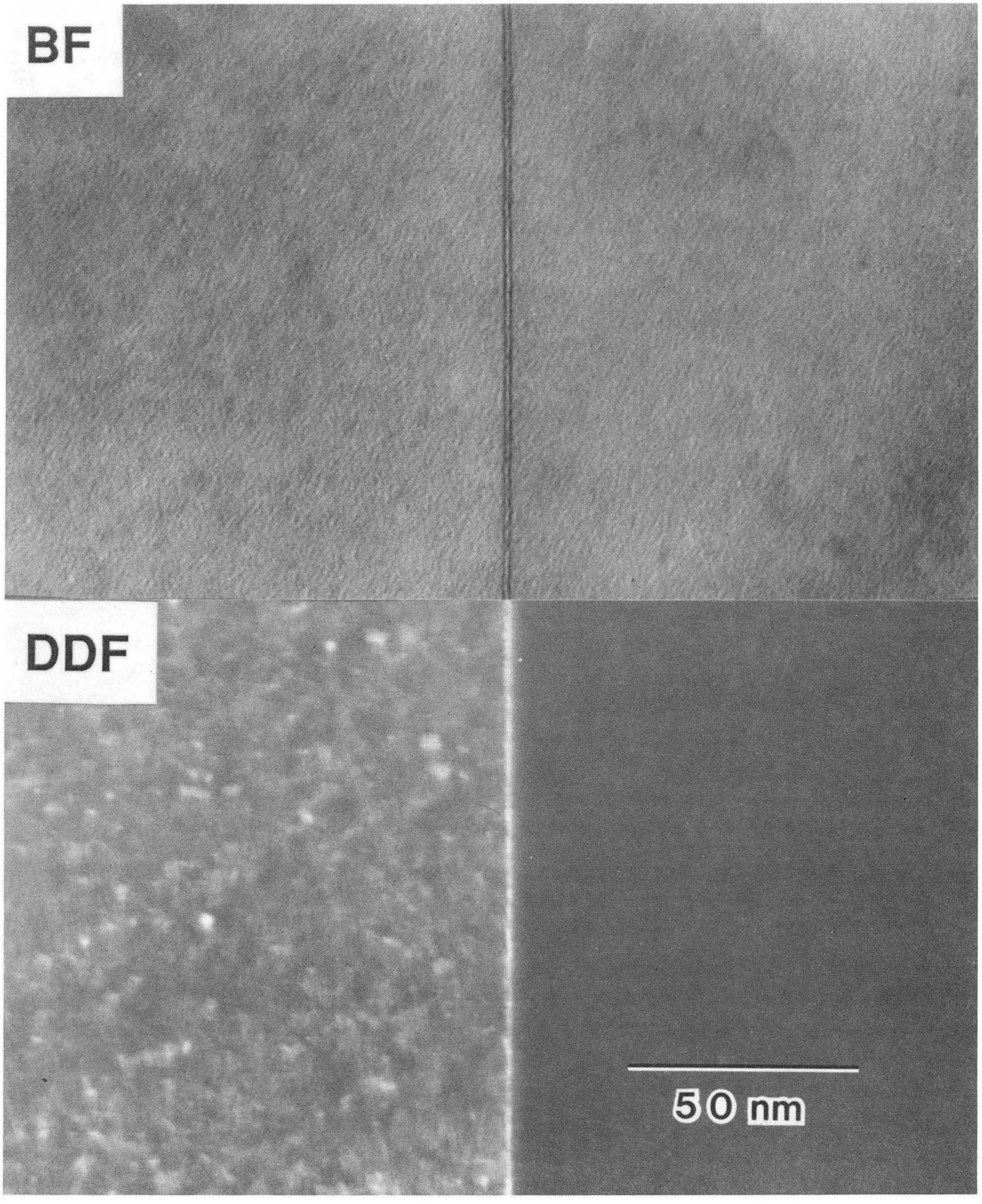

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Fig. 4

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