Title
DIRECT OBSERVATION OF LATTICE PLANES AT GRAIN BOUNDARIES IN SILICON NITRIDE

Author
Clarke, D.R.

Publication Date
1976-09-01

Presented at the NATO Advanced Study
Institute on Nitrogen Ceramics,
Canterbury, England, August 16 - 27, 1976

LBL-5435
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D. R. Clarke

September 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

LBL-5435

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D. R. Clarke

Department of Materials Science and Engineering, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

The rather dramatic decrease in the strength of hot pressed silicon nitride above about 1000°C has led investigators to postulate the existence of a glassy phase at the boundaries between the individual silicon nitride grains. The suggestion is that at these high temperatures the viscosity of the glassy phase rapidly decreases, flows and allows the grains of silicon nitride to slide past one another at unexpectedly low stresses.

Although recourse is frequently made to this explanation, the evidence is strictly circumstantial since no direct observation of the glassy grain phase between the boundaries has been made. Amongst the pertinent pieces of evidence suggestive of a glassy grain boundary phase are the following. The commonest sintering aid, magnesium oxide, used to hot press silicon nitride is known to form a magnesium calcium silicate with the silica invariably present on the surfaces of the silicon nitride powders used and the calcium impurities also present in the powder (1). Noncrystalline regions commensurate in size to the grain size have occasionally been observed by conventional electron microscopy, particularly at triple points (2,3). In addition internal friction measurements show that there is a viscous component present, which would be sufficient to form a glassy boundary phase perhaps 50-1000Å thick(4).

The purpose of this short contribution is to present, for the first time, direct observations of the crystal lattice planes up to, and on either side of, selected grain boundaries in silicon nitride. These observations show that there is no glassy phase at the grain boundaries at the paticular boundaries investigated in a 5% MgO hot pressed silicon nitride. The technique used is that of lattice fringe imaging with the transmission electron microscope.

Lattice imaging by transmission electron microscopy enables the structure of a crystalline material to be studied directly at an atomic level. This approach has already proven to be extremely valuable in investigating phase transformations in metallic alloys (e.g. 5,6) and the structure of a variety of minerals (7).

In the following pages lattice images of a number of grain boundaries are presented, but before describing them in detail it is appropriate to mention how they were selected. Essentially this was done at random, since the position of the specimen was shifted under the beam (in the diffraction mode) until one, or two adjacent, grains were found to be oriented such that the lowest index planes were parallel to the electron beam. This method was chosen because it was not possible to tilt the specimens in the microscope in order to bring a desired orientation into a strongly diffracting condition. The low index planes were chosen for imaging since the observing conditions are marginally less severe, so enhancing the probability of obtaining a lattice image.

Figure 1 is a lattice image of a low angle twist boundary in which the prism $(10\bar{1}0)$ planes on either side can be seen. Whilst it was not possible to determine whether the grains are of α or β, the long, waisted appearance of whole B grain suggests that it is typically β silicon nitride. Grain A is also probably β silicon nitride since its fringe spacing is identical to that of grain B. In the boundary three sets of fringes can be discerned; the prism plane fringes extending from either grain and the coarser Moire fringes. Together these demonstrate that there is no amorphous region between the two grains. The characteristics of the Moire fringes serve to confirm this conclusion since their spacing and inclination are precisely those expected from the plane matching theory of crystalline grain boundaries (8).

Figure 2 is of a very small part of a boundary between a silicon nitride grain in which the $(10\bar{1}0)$ prism planes can be clearly identified and an unidentified lower grain. Although the actual planes cannot be distinguished in the area of the lower grain the presence of the Moire pattern indicates that the grain boundary must almost certainly be devoid of any amorphous phase. The remarkable features of this micrograph, however, are the steps in the grain boundary which are indicated by the black arrows. These show that the grain boundary consists of a smooth crystal plane (which we are looking down) with unit cell high steps to accommodate the shape of the grain. They are also very suggestive of a ledge mechanism for grain growth during sintering of the material. In addition, the boundary appears to be formed by a low index plane indicating that the boundary was determined by a strongly anisotropic surface energy.

The stepped nature of the grain boundaries is also shown in the next figure, where the boundary plane is inclined to the (0001) planes in an α silicon nitride grain. (The irregular, stepped profile is most clearly seen by sighting along the boundary). In this figure the plane of the boundary is slightly tilted with respect to the electron beam, giving rise to the bright region at the boundary.

The full page micrograph, figure 4, is of a high angle boundary between two α silicon nitride grains, looking almost straight down the boundary plane. The fringes can be followed right up to the boundary from either side demonstrating to a high degree of confidence the absence of any intergranular amorphous layer. The details of the Moire pattern once again confirm this interpretation. A striking feature of the micrograph is the smoothness and straightness of the boundary plane, again suggesting a very anisotropic surface energy. In this micrograph, as well as in the previous three, it is noticeable that the fringe spacing does not measureably alter in the vicinity of the grain boundaries suggesting that the unit cell and the composition do not change appreciably right up to the atomic planes forming the boundary.

A number of important conclusions concerning an amorphous intergranular phase can be drawn from these observations. Firstly, there is no such phase at the particular grain boundaries studied, to a resolution of one unit cell. Secondly, the amorphous material detected by indirect methods must be inhomogeneously distributed throughout the material. Taken with the clear evidence from Auger analysis that fracture surfaces contain a glassy layer, this conclusion suggests that silicon nitride fractures intergranularly between only those grains which are separated by an amorphous region. A failure model in which the material is taken to be a composite of elastically deformable grains glued together in a softer viscous matrix would thus be most appropriate. Thirdly, the fact that the fringe spacings do not alter in the vicinity of the boundaries is striking confirmation that if silicon nitride is capable of taking into solid solution those elements not forming a glassy phase it does so by forming a uniform solid solution.

ACKNOWLEDGEMENTS

This work has been supported by the National Science Foundation and by the U.S. Energy Research and Development Agency, through the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory. I am grateful to Dr. R. N. Katz of the Army Materials and Mechanics Research Center for the supply of the silicon nitride materials.

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FIGURE CAPTIONS

Fig. 1. A low angle (10.5°) twist boundary in silicon nitride. The $(10\bar{1}0)$ prism planes on either side of the boundary have been imaged together with the grain boundary Moire fringes.

Fig. 2. $(10\bar{1}0)$ lattice image showing unit cell high steps in the grain boundary of a β-silicon nitride grain.

Fig. 3. Irregularly stepped grain boundary at a α silicon nitride grain revealed from the (0001) lattice image.

Fig. 4. Micrograph of a high angle boundary between two α silicon nitride grains.

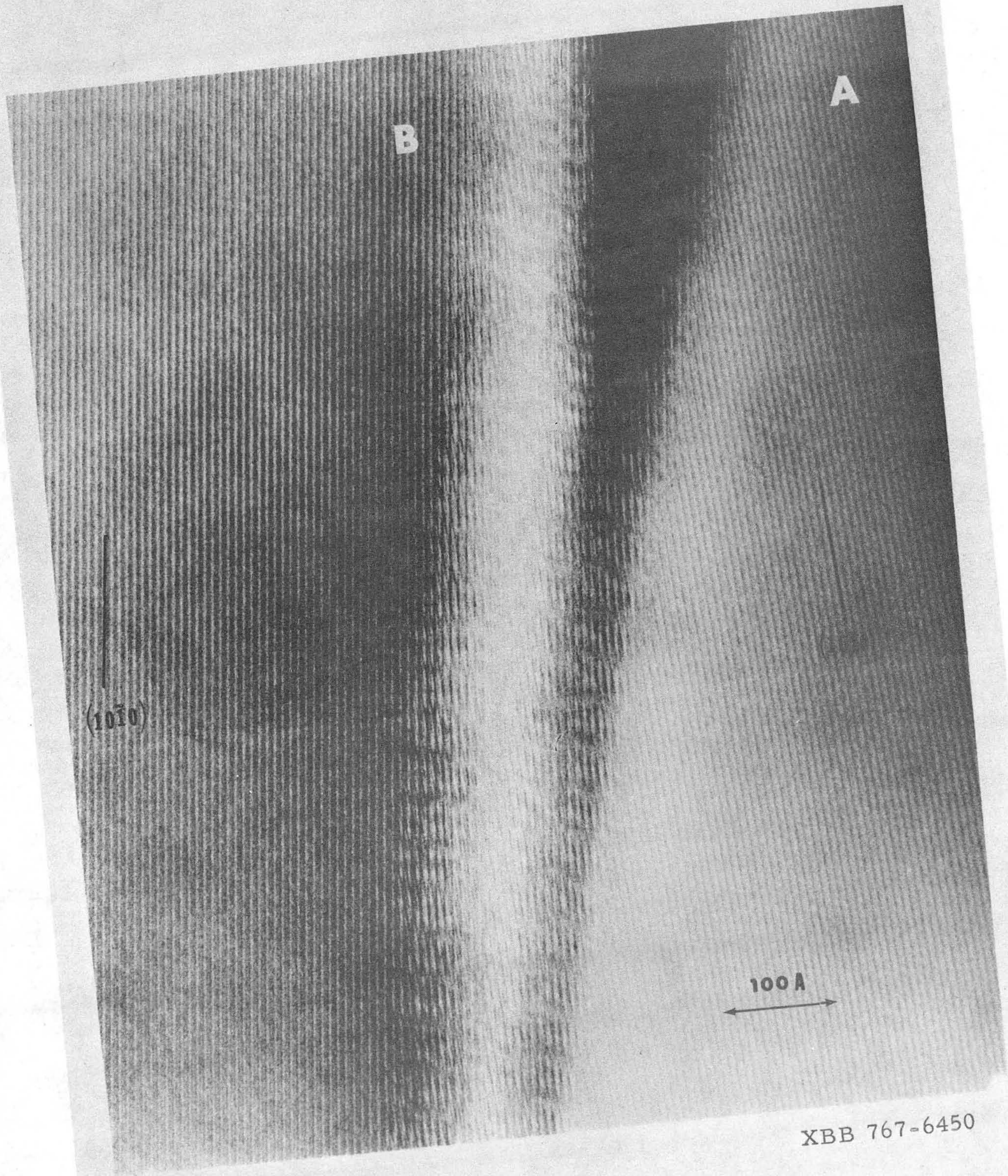

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Fig. 1

0 0 0 0 4 6 0 3 0 2 1

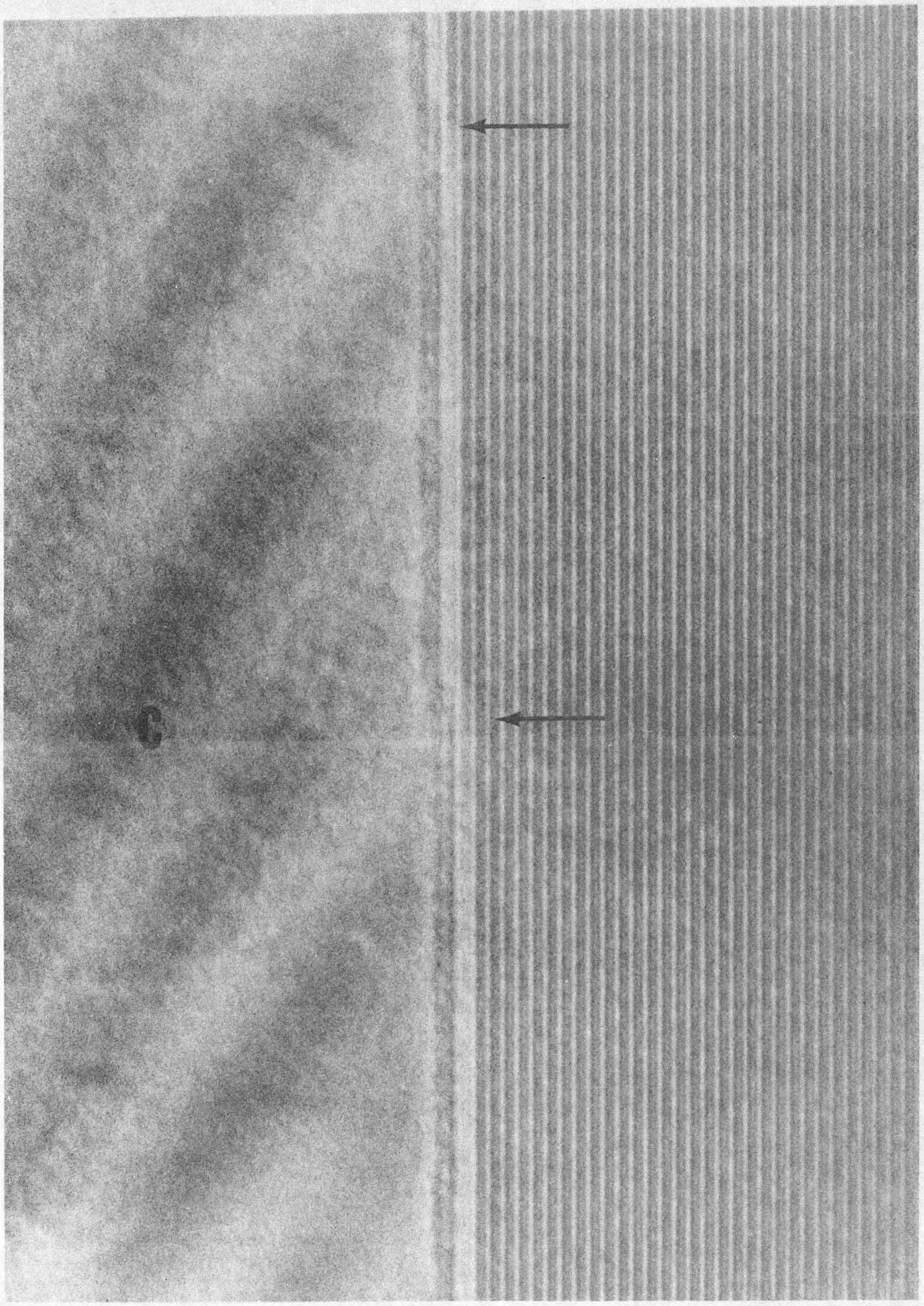

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Fig. 2

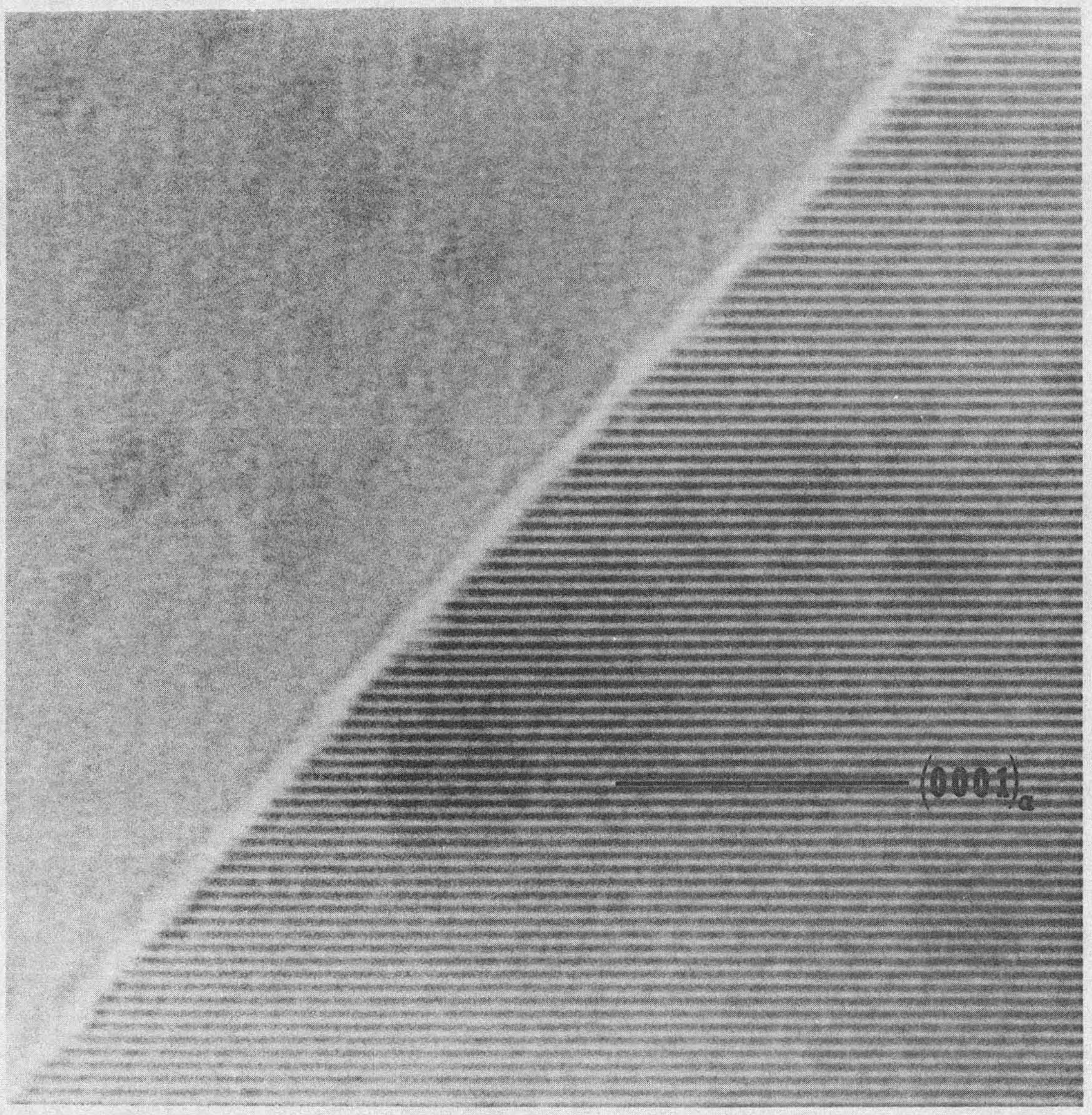

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Fig. 3

0 0 0 0 4 6 0 3 0 2 2

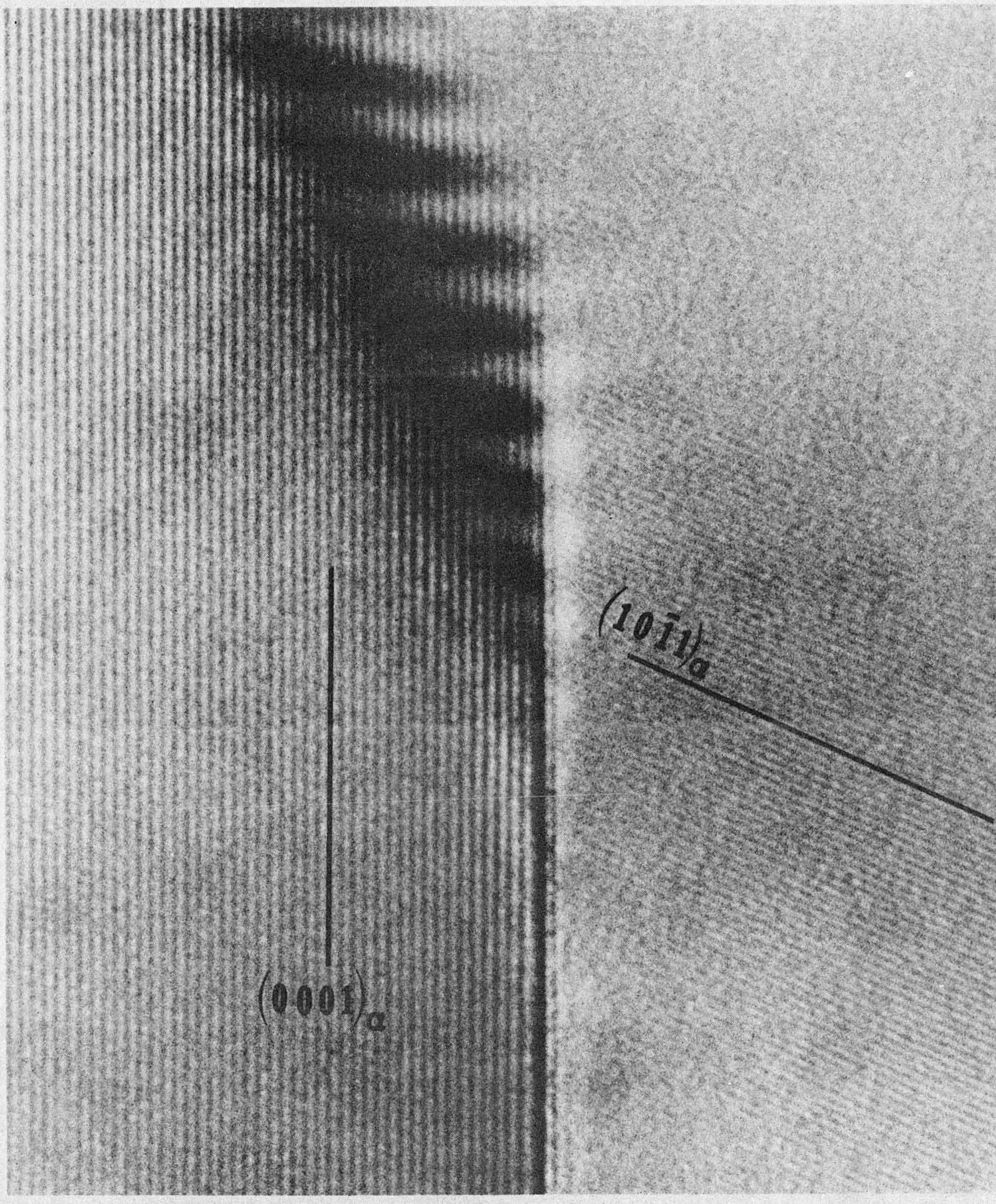

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Fig. 4

0 0 0 0 4 6 0 0 0 2 3

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