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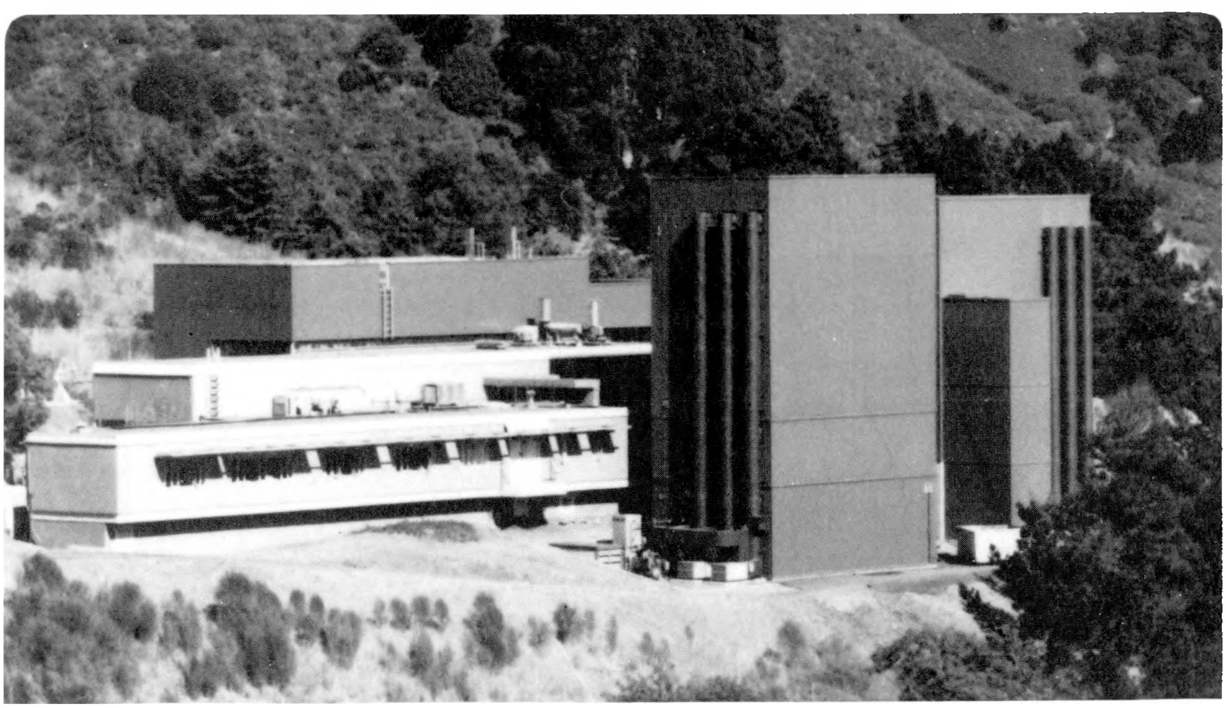

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TEM CHARACTERIZATION OF GRAIN BOUNDARIES IN MAZED BICRYSTAL FILMS OF ALUMINUM

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ABSTRACT

The structure and faceting behavior of near-90° <110> tilt grain boundaries in thin films of aluminum with a unique mazed bicrystal geometry is characterized by conventional, high-resolution and high-voltage electron microscopy. In this microstructure the absence of triple junctions allows grain boundaries to facet in optimum orientation (inclination) during annealing. The degree of anisotropy of the boundaries is expressed in the form of a rose plot. Small local deviations in misorientation are shown to be necessary to accommodate optimum boundary segments. The crystallographic symmetry inherent in this microstructure is apparent and utilized throughout the analysis.

INTRODUCTION

The study of grain boundaries by high resolution electron microscopy (HREM) is mostly limited to special boundaries with fixed inclination and misorientation. The connection between these special boundaries and the structure and behavior of polycrystalline materials is not straightforward. The present work is a step toward understanding this connection. By using heteroepitaxial deposition on a single crystal substrate it is possible to approximate a polycrystalline structure by a "mazed bicrystal" arrangement with interesting topological and crystallographic properties [1]. In the present work, the structural characteristics of interfaces in thin films of aluminum with the mazed bicrystal microstructure are investigated by transmission electron microscopy.

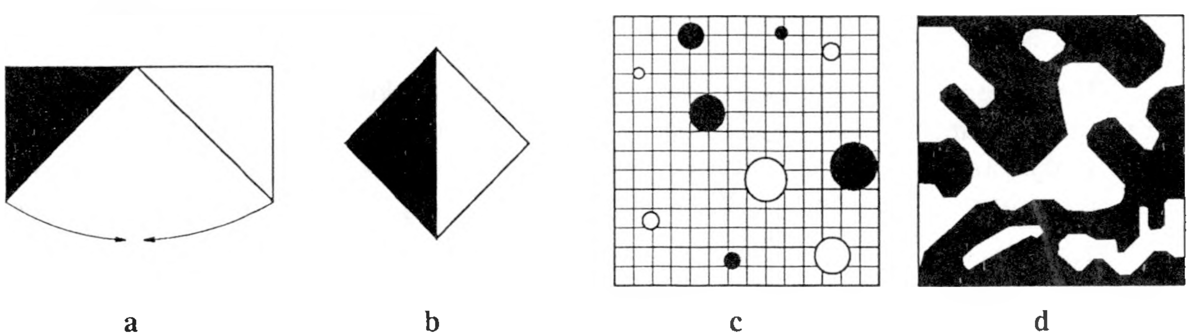


Fig. 1 Schematic comparison between conventional bicrystal (b) made by welding together two single crystals along the boundary plane (a) and mazed bicrystal (d) made from crystallographic orientation variants in heteroepitaxial growth (c). The two crystal orientations are indicated as black and white (XBL 914-844).

Conventional bicrystals are prepared by diffusion welding or melt growth from a bicrystal seed. Simplistically this method is described by the schematic in fig. 1: after removing a wedge from a single crystal (a) the two halves are joined together along a common interface (b). The axis and angle of misorientation and the plane of the boundary are all determined by the geometry of the wedge. The resulting bicrystal sample has a single grain boundary confined to a given plane and rigidly defined crystallography, i.e. it is a boundary with fixed inclination and misorientation. For comparison the mazed bicrystal structure is shown schematically in (d). An epitaxial thin film is grown with an orientation of lower symmetry on a substrate orientation of higher symmetry, in the present case (110) Al on an (001) Si substrate (c). Because the thin film has an axis of twofold symmetry parallel to the fourfold axis of the substrate surface there are two equivalent orientation variants. Both variants form with equal probability and where they impinge, a 90° grain boundary is generated. The resulting thin film has many grains but only two orientations.

Although at first glance this might appear similar to a polycrystalline film, the fact that only two orientations are present means that all grain boundaries have the same misorientation and there are no triple junctions [2]. During annealing the boundaries tend to orient themselves normal to the film surface, turning them into pure tilt boundaries [3]. As a result, the microstructure is that of a polycrystalline film with bicrystal character, where two grains form an intertwining arrangement of concave and convex shapes. All grain boundaries have near-90° <110> tilt character, and all possible inclinations are present in any single grain.

If the boundary energy were isotropic, i.e. independent of inclination, then at equilibrium all orientations would occur with equal probability, and random curvature would prevail. Any deviation from randomly curved boundaries is a sign of anisotropy which in turn indicates a preference for certain boundary inclinations. Such microstructural anisotropy is an important characteristic because it is a measure of preferred grain boundary inclination for a given misorientation. As such it could be a sensitive indicator of the effects of segregation or heat treatment. From this anisotropy it is also possible to determine on a mesoscopic scale which boundaries are significant, and concentrate on those boundaries for further structural characterization on a microscopic scale. The present study focuses on just such a connection between the microstructure on a scale of micrometers to the atomic scale.

EXPERIMENTAL

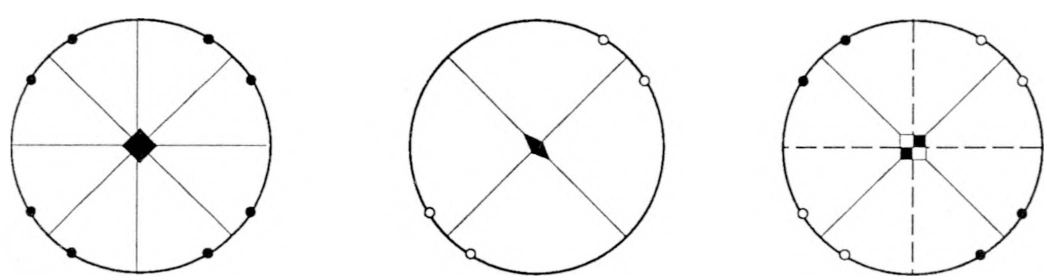
The Al films used in this work were prepared at Kyoto University by the ionized cluster beam deposition technique on a cleaned and 2x1 reconstructed (001) Si substrate [4]. The resulting thin films of approximately 80nm thickness were back-thinned to electron transparency from the Si substrate side by mechanical dimpling followed by ion beam thinning.

Recent work has shown that the same microstructure can be obtained by vapor deposition in ultrahigh vacuum and that the spatial distribution of the two orientation variants is related to the 2x1 reconstruction of the clean annealed Si surface before deposition [5]. It has also been demonstrated that Al deposited by either technique on a Ge (001) substrate takes on a different orientation which results in a single crystal film. Thus, to form a mazed bicrystal structure it is necessary to select an appropriate combination of substrate and thin film material.

Electron microscopy was performed on 200 kV microscopes, and high resolution images were obtained on the Berkeley ARM 1000 at an operating voltage of 800 kV. In-situ heating experiments were carried out on a Kratos 1500 kV high voltage microscope. The microstructural anisotropy was analyzed on digitized images using a specially developed code [6] to generate rose plots [7] describing oriented structures.

RESULTS

A selected area diffraction pattern showing the <001> Si and superimposed <110> Al orientation is seen in fig. 2a. The <001> Si pattern is clearly recognizable whereas the Al patterns are obscured by extensive double diffraction. When the Si substrate is removed by backthinning from the Si side, only the two <110> orientation variants of Al remain, as shown in fig. 2b. For clarity one of the variants, or grain orientations, has been marked with black dots. The symmetry relations that interchange the black and the white patterns (color symmetry) are the point symmetry elements of the substrate that are not shared by the deposit [8,9]. These color symmetry operations are the 90° rotation and the vertical and horizontal mirrors, whose traces are indicated as white lines. In contrast, the 180° rotation and the diagonal mirrors (also marked) are common to the substrate and the film. The first type of operations exchange the black and white crystal orientations whereas the second type returns each orientation to itself.



a b c

Fig. 3 Stereographic representation of 2-dimensional point groups of the substrate (4mm) (a), an Al orientation variant (2mm) (b) and the bicrystal (4'mm') (c). Black and white symbols, broken lines and primes indicate color symmetries.

The 2-dimensional point group of the bicrystal in this case is the square color symmetry group 4'mm' and its relationship to the rectangular group 2mm can be described as the following coset decomposition into color and non-color sets [10]:

$$4'mm' = 4^1\{2mm\} \cup \{2mm\},$$

where 4^1 is a 90° rotation, {2mm} is the set of symmetry elements that map each orientation variant onto itself, and $4^1\{2mm\}$ is the set of symmetry elements that exchange orientation variants (color exchange operations). This is illustrated in fig. 3 which shows the 2-dimensional point groups symbolically. The point group of the bicrystal 4'mm' is the union of the point group of the Al film 2mm and the color exchange set $4^1\{2mm\}$. Symmetry elements are denoted be the usual symbols. In the color-exchange set $4^1\{2mm\}$ the color symmetry elements are shown by broken or black and white symbols.

The actual microstructure is illustrated in a pair of bright field images in fig.4. Of the two grain orientations the dark one is in strong diffracting condition while the light one is not. Between a) and b) the diffracting conditions for the two grains were interchanged by a small tilt of about 1° across a color mirror plane whose trace corresponds to the vertical axis in this image. Note how the two grains form an interwoven "Holstein"-type structure. Although some grains have the traditional convex inclusion shape most grains have more convoluted shapes with regions of both concave and convex curvature.

It is also apparent from fig. 4 that considerable faceting has taken place. This is a result of an annealing treatment of 1h at 400°C. From fig. 4 and many similar observations of the annealed microstructure it is clear that facets tend to form parallel to the mirror planes of the bicrystal. A quantitative measurement of the faceting can be represented in a rose plot [11], a polar plot of total boundary length as a function of orientation (inclination). If all boundary inclinations were equally probable the polar rose plot would be a circle (a half circle if the sense of the boundary normal is not distinguished). The deviation from a circular rose plot is thus a direct measure of the anisotropy of the microstructure.

Fig 5. shows a micrograph recorded at an orientation near the thin film normal. Under this condition the contrast is less pronounced than in a tilted orientation such as that shown in fig. 4. However, in this orientation the projected microstructure reveals its full symmetry. As mentioned above, most boundaries tend to become perpendicular to the film surface and hence are of pure tilt character and are seen edge-on in this orientation. Due to diminished contrast under this condition the detection of the boundaries by automatic image analysis is difficult and some manual control is necessary.

Fig. 6a is a line trace of the boundaries in this area, only a section of which is shown in fig. 4, and the polar rose plot extracted from this image is given in fig. 6b. A pronounced anisotropy is clearly apparent from this graph as the deviation from a perfect circle, which would be seen for an isotropic microstructure. Notice that the preferred boundary inclinations lie at angles of 45° to each other. These preferred positions coincide with the mirror planes of the bicrystal. The degree to which the bicrystal symmetry is found in the rose plot is a measure of the statistical accuracy of the sample. In the absence of external effects such as preferred nucleation of one orientation variant, Curie's principle [12] demands that the symmetry of the bicrystal microstructure be at least that of its point group. As a result the rose plot should possess the bicrystal symmetry, and any symmetry lower than this indicates either insufficient sampling or an external influence on the distribution of variants and facets.

Although the rose plot shown in fig. 6b exhibits peaks on the mirror planes of the bicrystal, it must be considered preliminary because the tracing of the image was not sufficiently accurate to detect all facets and their orientations precisely. However, it is already clear that grain boundaries on the symmetry planes are preferred, even if the exact degree of preference remains to be determined. This observation is in agreement with the principle of symmetry constraints dictating extrema for interfacial properties which determine the symmetry of the Wulff plot [13].

The observed anisotropy clearly indicates a strong preference for grain boundary facets parallel to the mirror planes of the substrate. The significance and structure of these and other boundaries was characterized further by high resolution TEM observation. Fig. 7 illustrates a short segment of the 90° asymmetrical grain boundary that lies parallel to one of the diagonal mirrors in fig. 2. At the boundary a (100) plane in one grain faces a (110) plane in the other grain. Because the repeat periods of the lattice planes normal to the boundary are in the ratio of $1/\sqrt{2}$ they are not commensurate and hence the boundary cannot relax into a periodic structure. However, localized relaxations are clearly visible at the positions marked by arrows. It was found that facets such as that shown in fig. 7 are relatively short and stepped or tend to deviate slightly from the precise (100)/(110) position. Thus, even though its irrational geometry is simple, the question whether these boundaries are quasiperiodic [14] or just nonperiodic cannot be answered because sufficiently long segments are not observed.

Fig. 8 illustrates the other commonly observed facet, the symmetrical boundary parallel to the horizontal or vertical color mirror in figs. 2 and 3. As with all symmetrical tilt boundaries, this boundary coincides with a color mirror plane of the bicrystal. The periodic relaxation into structural units with a relatively short repeat distance is clearly apparent in this micrograph. The boundary is parallel to a {557} plane in both crystals, demanding a misorientation of not precisely 90° but 89.4°. Only through this small deviation from the precise 90° misorientation originally dictated by the substrate can the boundary become periodic with a short repeat distance. Crystallographically, this boundary is described as a $\Sigma 99$ {557} 89.4° <110> symmetrical tilt boundary. It was the most frequently found boundary segment, and its structure has been investigated in some detail. A detailed comparison with models simulated by molecular statics methods has shown excellent agreement and given the first evidence that the structure of high-Σ boundaries can be accurately predicted from known potentials [15].

The two types of facet shown in figs 7 and 8 are the most prominent and easily identifiable boundary segments in the annealed bicrystal. However, not all boundaries exhibit such pronounced faceting. As seen in the conventional micrographs in figs 4 and 5, curved sections or straight boundary segments on irrational planes occur frequently. One curved segment is shown at high resolution in fig. 9a. Close scrutiny of this image reveals that the curvature is composed of short segments of the two types of boundary shown in figs 7 and 8. The same is true for the straight boundary in fig. 9b in which the zigzag appearance due to its decomposition into many nanometer-sized segments of the asymmetrical and the symmetrical type is emphasized by marking the trace of the interface. Occasionally, deviations from the pure tilt position were found when boundaries had twisted into an orientation where the interface plane was no longer parallel to the tilt axis.

Note that the two types of preferred segment described above require a slightly different misorientation. This means that the lattice must rotate locally to adjust the misorientation for a given segment. Although required difference in misorientation is not more than ± 0.6° in most cases, it is still very significant because it can make the difference between an irrational (90°), a rational $\Sigma 99$ 89.4° or a rational $\Sigma 99$ 90.6° CSL boundary.

At facet junctions where two such segments of different inclination and slightly different misorientation meet there will be considerable strain. No such strain is apparent in fig. 9b where the individual segments alternate and are of nanometer size. In this stepped structure the closeness of opposite junctions is likely to result in the cancellation of long-range strains.

However, when larger segments meet in the convex shape of a fully enclosed grain, long-range strains are clearly apparent. This is illustrated in fig. 10 which shows a small convex grain during in-situ shrinkage in a high voltage electron microscope. Large lattice strains are visible as bend contours converging on the grain. After such small grains disappeared during in-situ annealing it was frequently observed that the residual stress generated dislocations or microtwins [3]. These strains are sufficiently large to become an important part of any considerations concerning equilibrium shapes and the driving force for coarsening.

The small grain in fig. 10 is seen to have the shape of a truncated square with well-defined facets rather than a smoothly curved boundary. This is in full agreement with the anisotropy displayed in the rose plot shown fig. 6b. The absence of triple junctions permits relatively easy migration of boundaries into low-energy configurations.

DISCUSSION

The connection between the mazed bicrystal geometry and a general polycrystalline structure is best understood by thinking of the mazed bicrystal as a polycrystal film with only two allowed grain orientations. This is illustrated schematically in fig. 11. In fig. 11a a polycrystalline film is idealized as a hexagonal tiling, with each grain in a different orientation and all grain boundaries random in inclination and misorientation. If the same hexagonal grain tiling is occupied at random by only two orientation variants, indicated by horizontal and vertical cross hatching, the microstructure in fig. 11b results. The similarity with the experimentally observed microstructure is immediately apparent. Its particular characteristics are: 1) triple junctions are absent because only two grain orientations exist; 2) there are small convex grains, fully enclosed by the other grain orientation; 3) most grains are convoluted in shape with both convex and concave regions; 4) grain boundaries exhibit facets on preferred planes.

Because of the nature of thin film growth the geometry of this structure is essentially two-dimensional. The hexagonal tiling in the idealized model shown in fig. 11 was chosen as the simplest representation of a polycrystalline grain structure. Binary occupation of such a tiling is a standard problem of percolation theory. The percolation threshold for a hexagonal tiling or honeycomb structure is 0.6962 for site percolation and 0.6527 for bond percolation [16]. For either type of percolation it is necessary to have a fraction of more than 65% for one orientation to become continuous. At an average fraction of 50% for each of the two grain orientations it is thus clear that, although the bicrystal itself is continuous, the two individual grain orientations will be discontinuous across the film.

Carrying the honeycomb analogy further, the convoluted shapes of the individual grains may be considered lattice animals, and probabilities for the occurrence of particular shapes and orientations could be calculated. However, it must be kept in mind that the honeycomb analogy is a greatly simplified model of the microstructure. In reality, a range of grain sizes exist and the observed faceting is not due to impingement of growing nuclei. As a result the faceting is not of a hexagonal type but of a type that qualitatively reflects the symmetry of the underlying (001) Si substrate and quantitatively represents the relative magnitudes of different boundary energies. The optimum grain shape that could be deduced from the rose plot would be a truncated square. This is not included in the number of space filling polygons, and it would be impossible to devise a direct analogue to the hexagonal tiling.

The topology of this structure is of considerable interest. It should be noted that such binary microstructures are not limited to this particular case of (110) aluminum on (001) silicon. Analogous situations arise in many different circumstances. Other combinations of thin film and substrate could lead to a mazed bicrystal with different crystallography. For example two (111) orientation variants on a substrate with hexagonal symmetry would lead to a bicrystal with different symmetry but the same topology. Any surface reconstructions that lower the symmetry of the surface will lead to orientation variants. For example , $NiSi_2$ on (001) Si surfaces forms in two orientation variants related to the two variants of (001) surface reconstruction. Any two-dimensional binary domain structures resulting from a group-subgroup transition are subject to the same considerations. This includes ordered [17], ferromagnetic, ferroelectric, ferroelastic and other domain structures [18].

Apart from its topological properties this structure shows some other interesting features. Because it is not locked by triple junctions, the microstructure is unusually flexible. It was shown that during thermal annealing it relaxes into a faceted intertwining grain structure with all facets corresponding to near-90° <110> tilt boundaries of low energy. Because all boundary inclinations are possible and can form without hindrance from triple junctions the observed facets are a direct result of anisotropy in grain boundary energy. However, in addition, a small degree of freedom also exists for the local misorientation. This allows a boundary not only to take on its optimum inclination but also to adjust its misorientation locally by a small amount. This flexibility is similar to that observed in sphere-on-plate experiments where the crystal orientation is free to change but the inclination is fixed. The rearrangement of this structure during thermal annealing should therefore be analyzed in terms of both types of torque, that due to inclination (Herring torque) and that due to misorientation (Shewmon torque) [19] and the interaction between the resulting strain fields.

SUMMARY

This paper describes the characterization of the structure and behavior of $\Sigma 99$ and other near-90° <110> tilt boundaries in bicrystals of aluminum. The geometry of the mazed bicrystal structure employed in these studies is unique and displays interesting topological and crystallographic properties. It maintains several of the characteristics of general grain boundaries, including high angle misorientation near 90°, faceting, elastic strains and defects. Although most boundaries are curved or microfaceted, they are of pure tilt type and their atomic structure can be characterized by HREM.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 2 Selected area diffraction patterns showing the observed orientation relationships. The pattern in (a) was obtained from a region of overlapping Al film and Si substrate. Note square <001> Si symmetry and extensive double diffraction. The pattern in (b) is from an area of freestanding Al film and shows the two 90° rotated crystal orientations. For clarity, one of the two patterns has been marked with black dots. Mirror plane traces are indicated by white lines. (XBB 915-3873)

Fig. 4 Complementary images of Al film with the mazed bicrystal structure, recorded under mirror-related bright field conditions interchanging the Bragg condition for the two orientation variants. Annealing for 1h at 400°C has resulted in extensive faceting. (XBB 880-10325)

Fig. 5 Annealed Al bicrystal film viewed along film normal. In this orientation most boundaries are on edge, and faceting is clearly apparent (XBB 915-3872).

Fig. 6 Digital tracing of an image, including the area in fig. 5, showing outlines of grain boundaries (a). Polar rose plot in (b) displays total boundary length as a function of inclination. The deviation from a circle is a measure of the anisotropy of this microstructure. (courtesy B. Tierney and W. Johnston) (XBB 915-3871)

Fig. 7 High resolution image showing asymmetrical 90° <110> (100)/(110) tilt grain boundary segment. This boundary lies parallel to mirror planes in both grains and is non-periodic due to incommensurate spacing of lattice planes crossing the interface. Unit cells outlined to illustrate 90° misorientation (XBB 915-3876).

Fig. 8 High resolution image of Σ99 {557} 89.4° <110> symmetrical tilt boundary segment. This boundary lies on a mirror plane of the bicrystal and has a relatively short repeat period (projected repeat period marked by black dots). The near-90° misorientation between grains is apparent from the outlined unit cells (XBB 915-3875).

Fig. 9 High resolution images of curved boundary (a) and straight segment along high-index plane (b). Both boundaries are seen to be constructed of short segment of the two types of boundary illustrated in figs 7 and 8 (XBB 915-3874).

Fig. 10 Micrograph taken during in-situ annealing at 400°C showing bend contours around enclosed convex grain. Note its faceted shape of a truncated square. (Micrograph by A. Schwartzman) (XBB 915-3877)

Fig. 11 Schematic representation of polycrystal as hexagonal tiling (left). With binary occupation by only two orientation variants the tiling takes on the mazed bicrystal structure (right) (XBL 914-843).

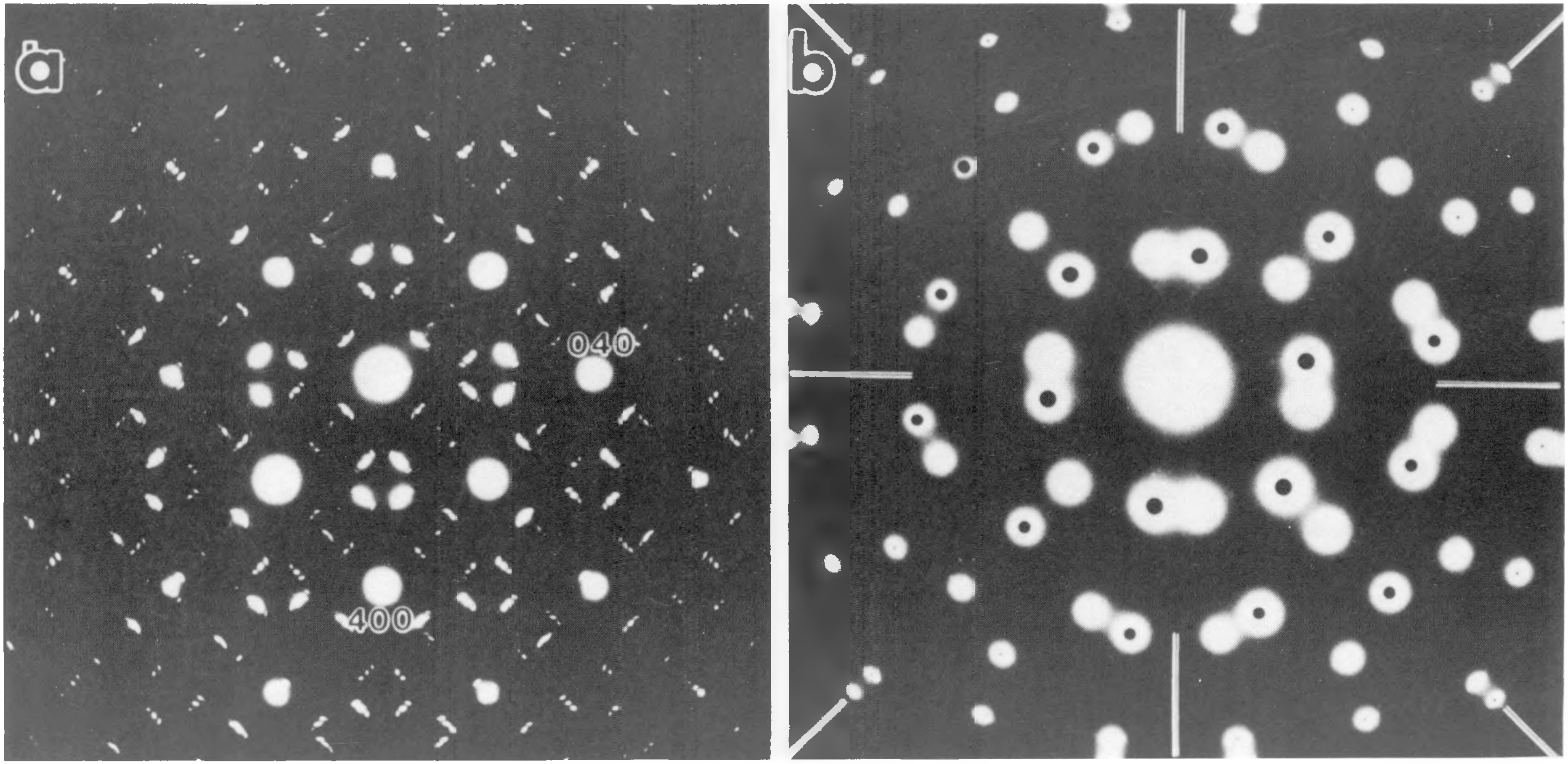

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Figure 2

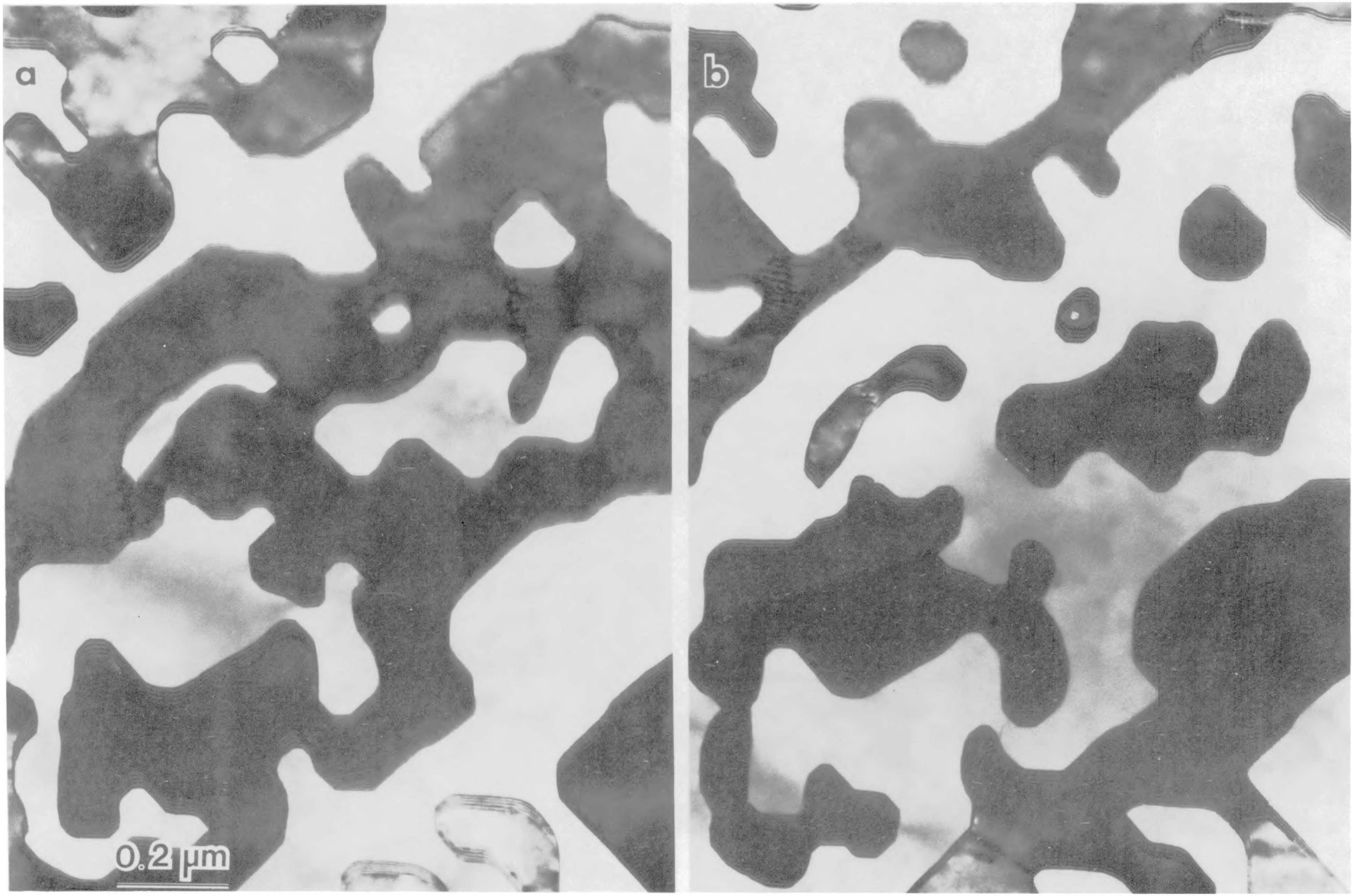

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Figure 4

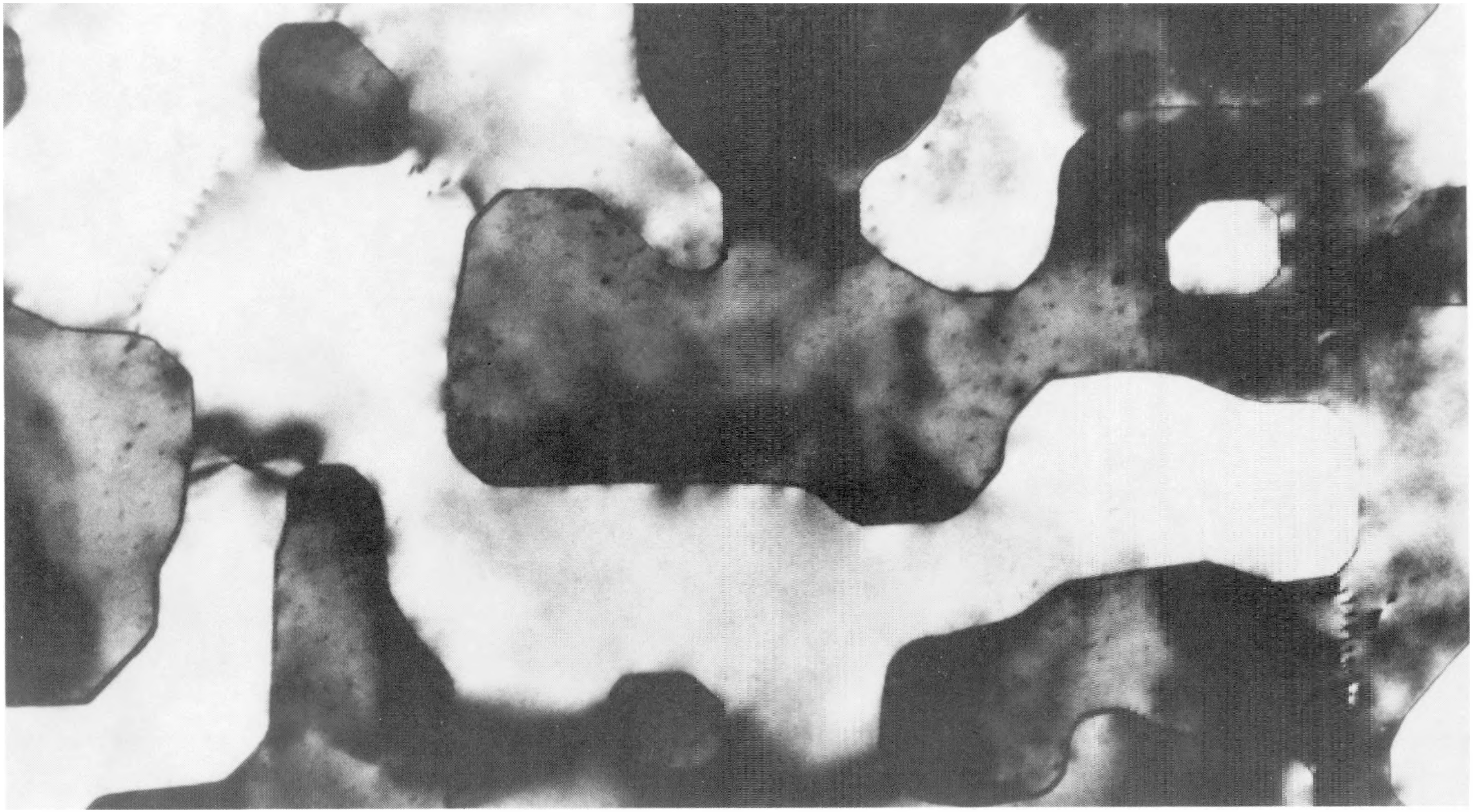

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Figure 5

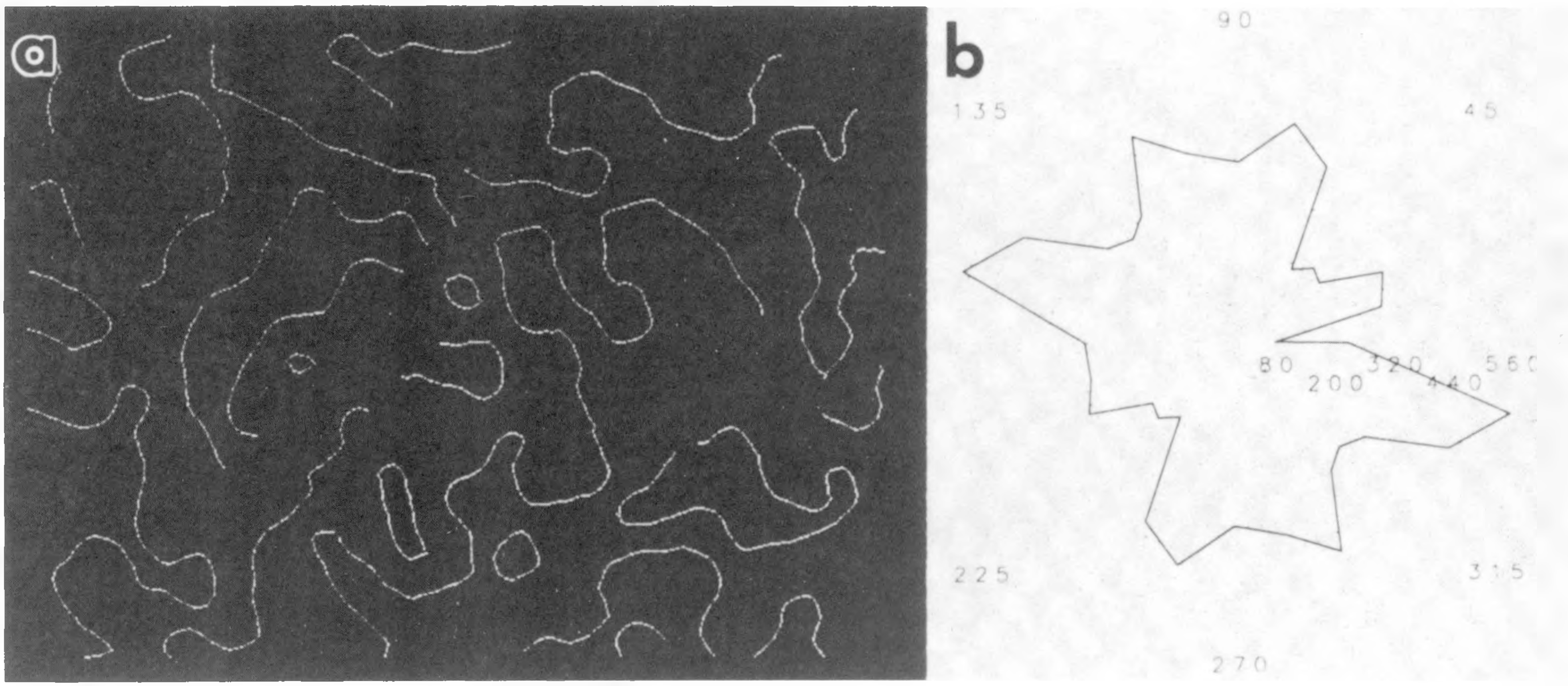

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Figure 6

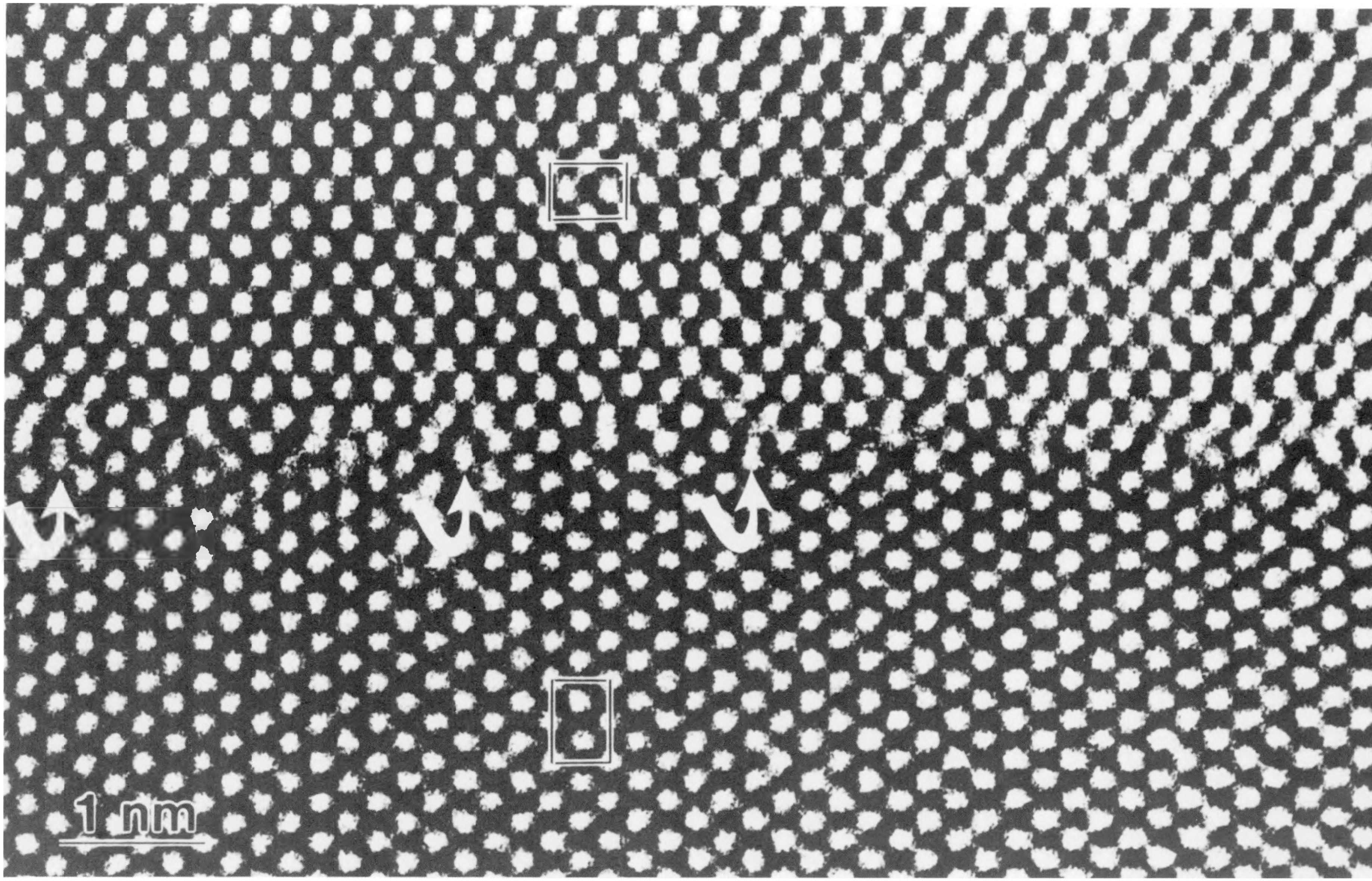

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Figure 7

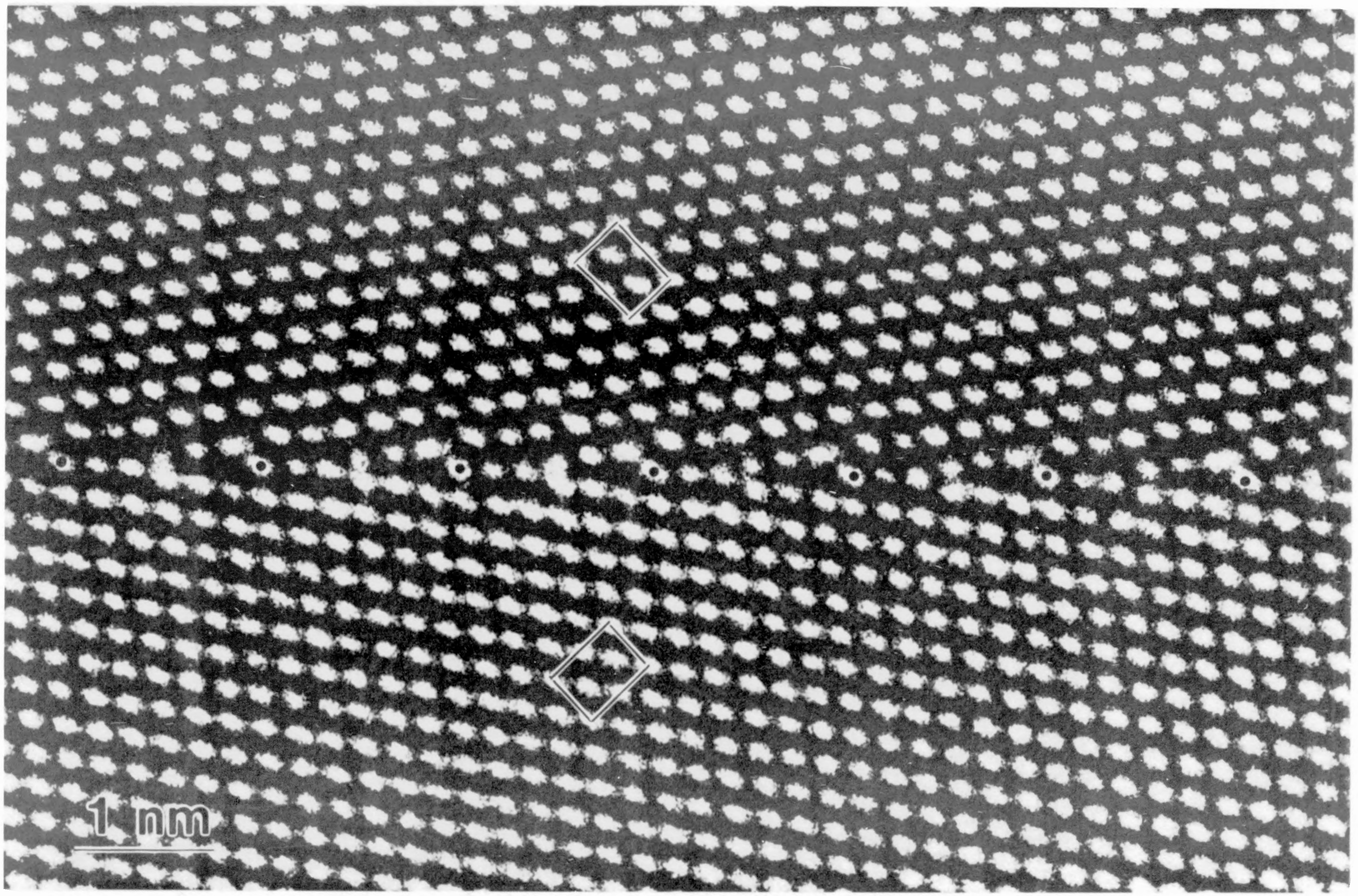

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Figure 8

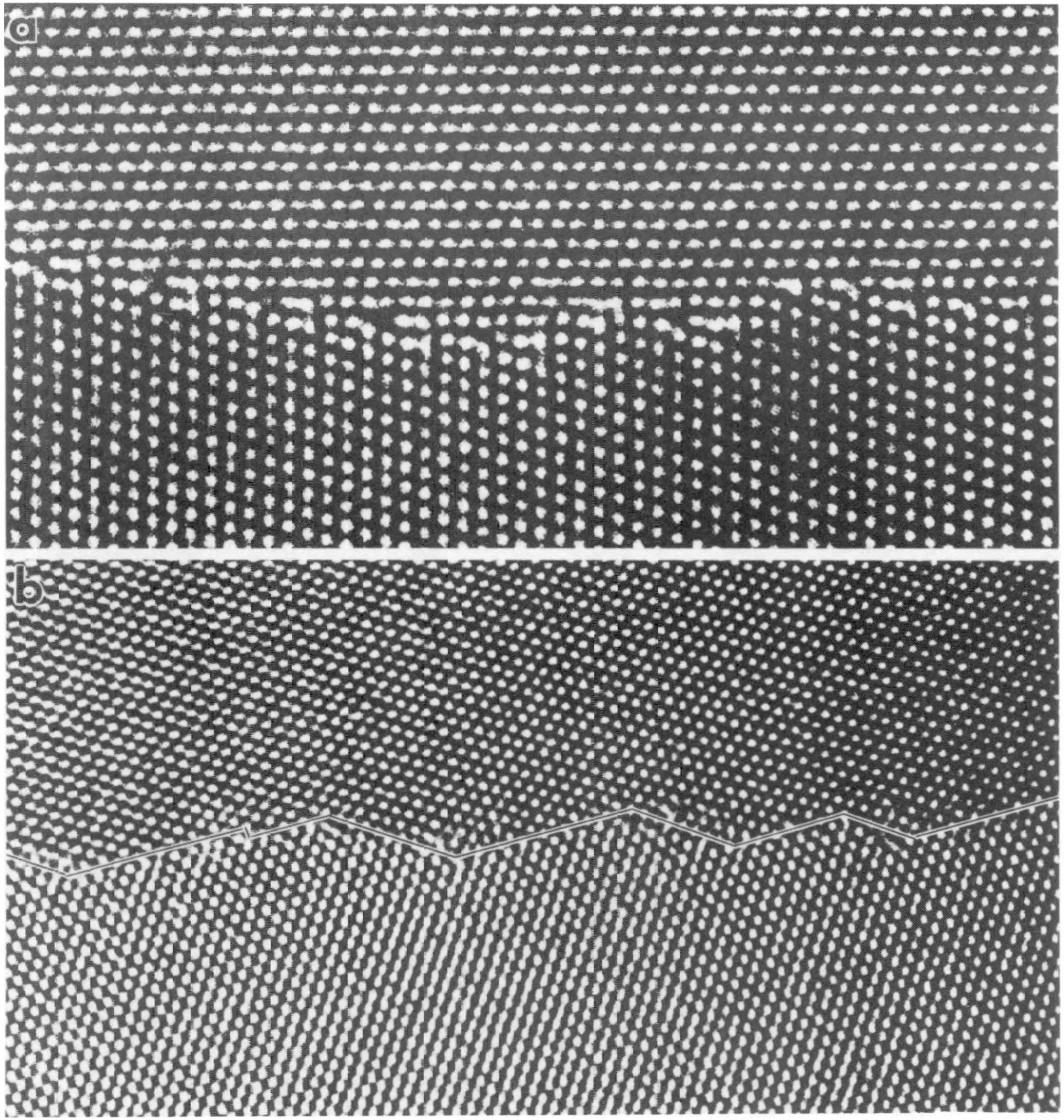

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Figure 9

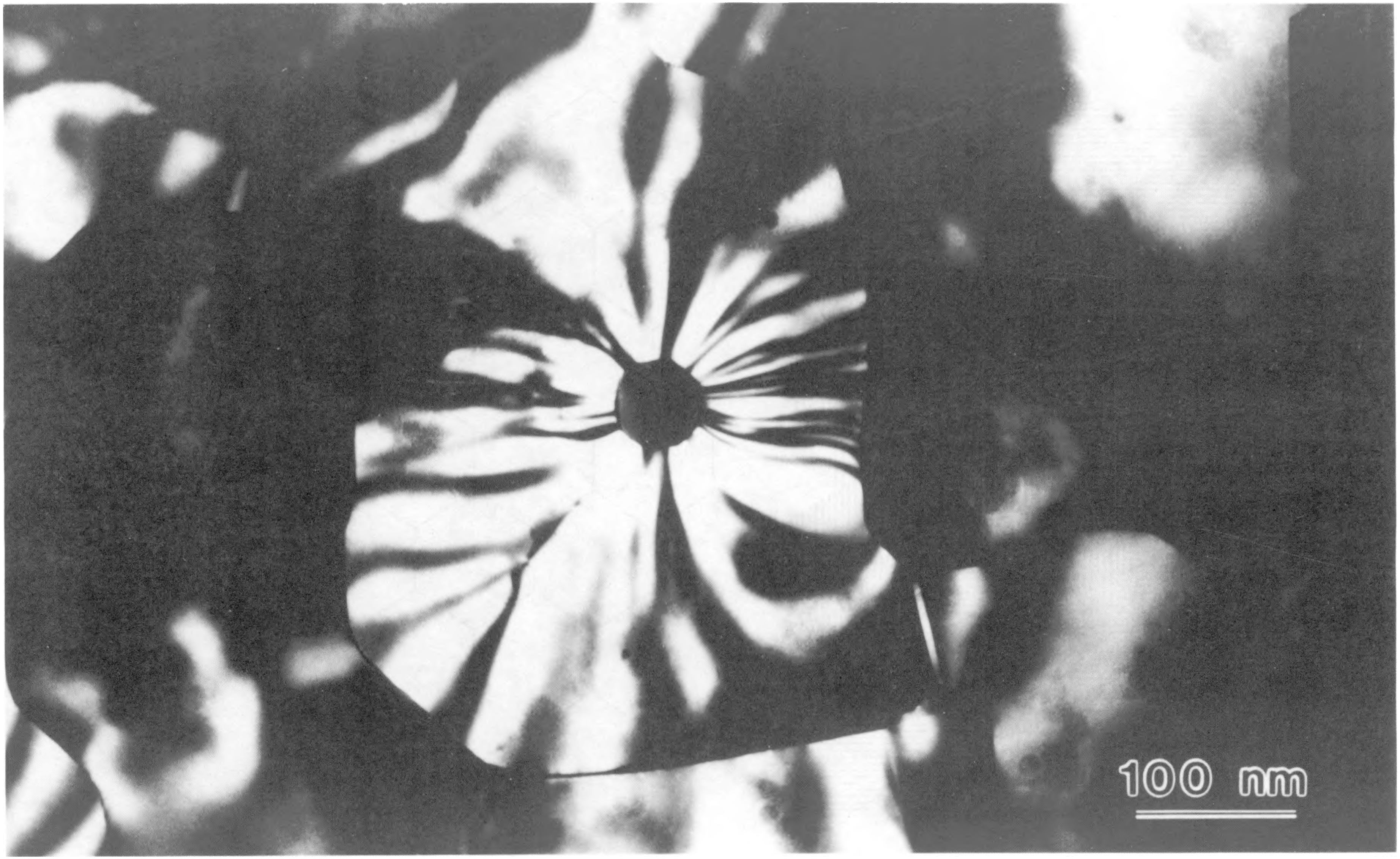

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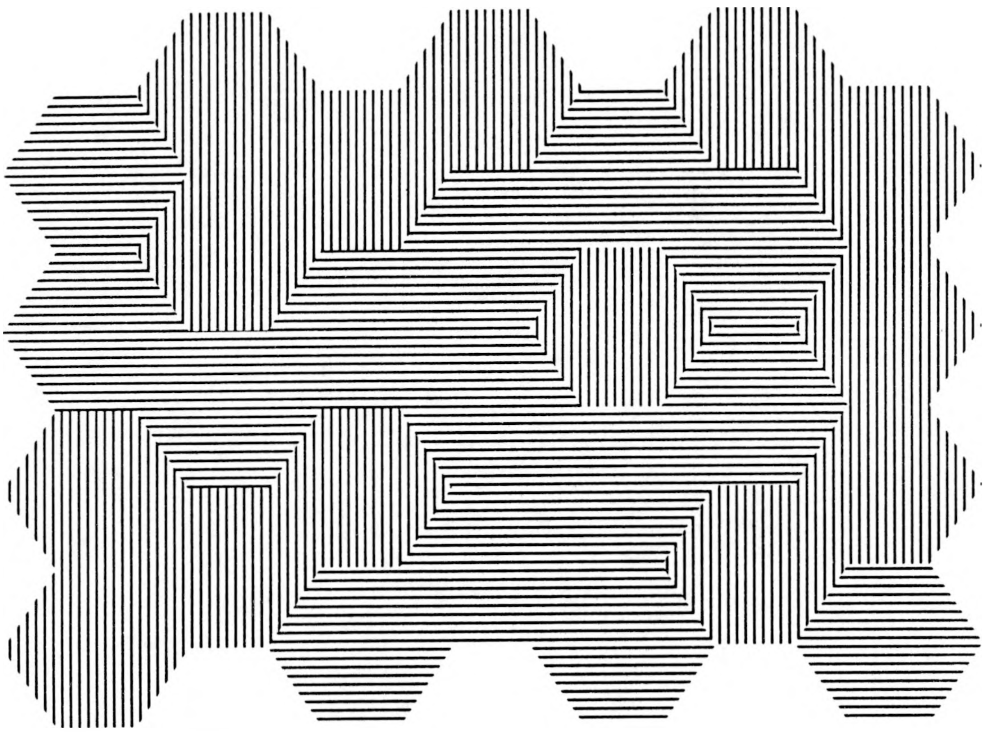
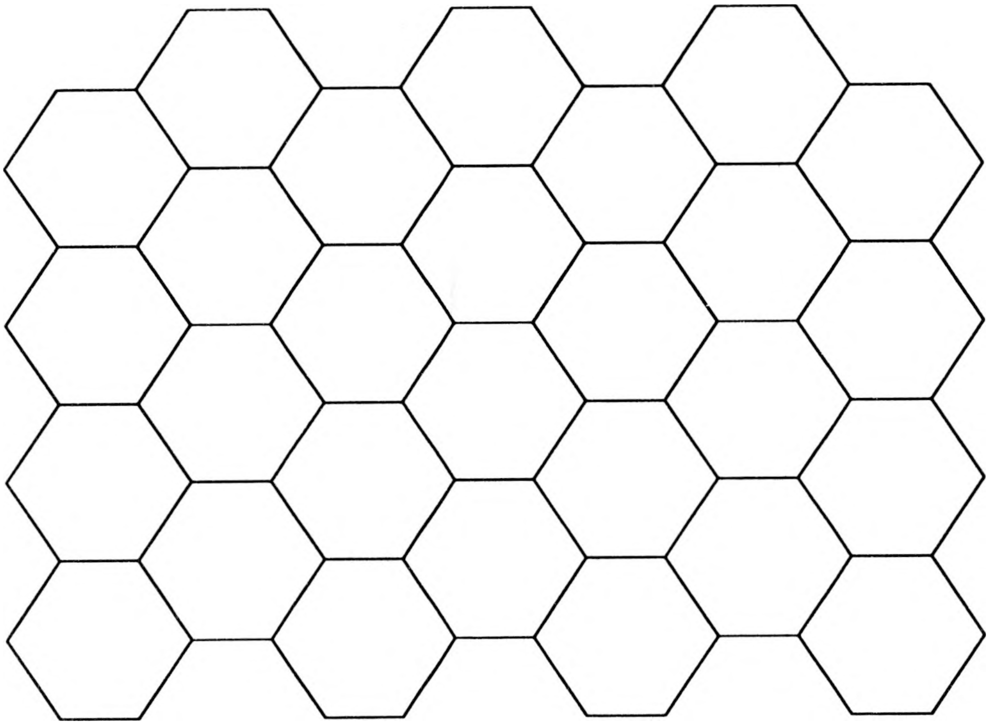
Figure 10





XBL 914-843

Figure 11

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