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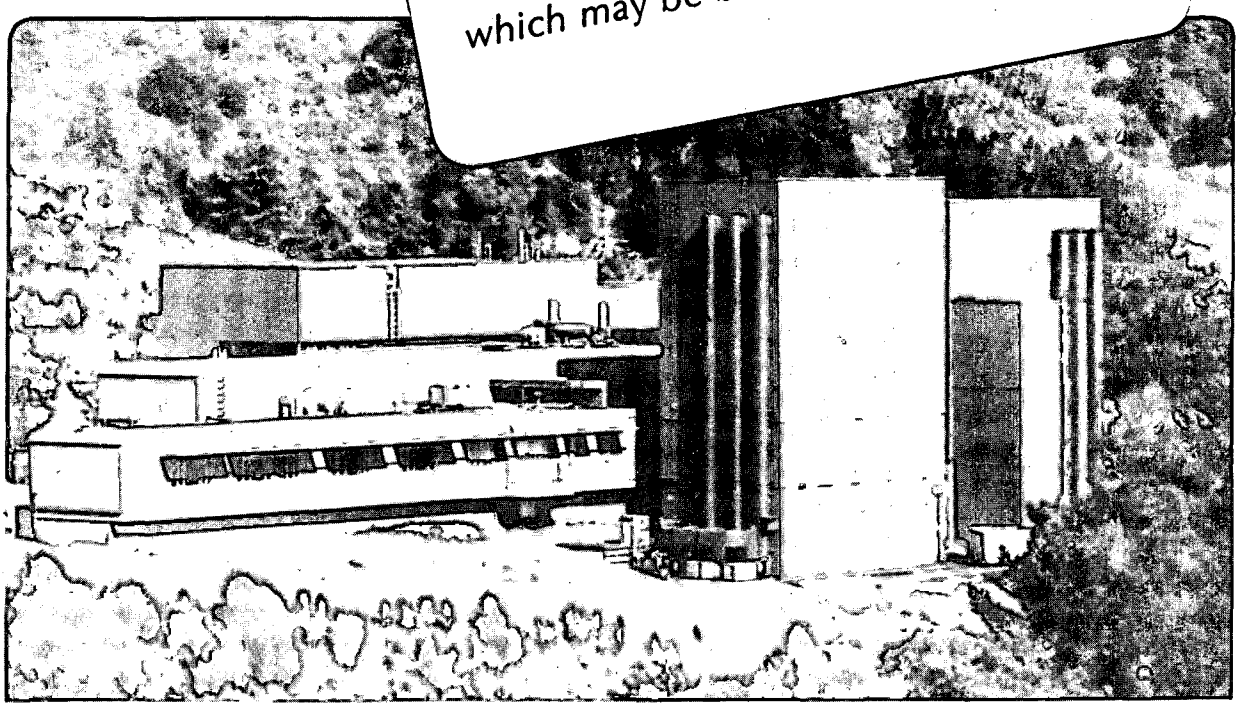

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THE USE OF HETEROEPITAXY IN THE FABRICATION OF BICRYSTALS FOR THE STUDY OF GRAIN BOUNDARY STRUCTURE

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1. Introduction

Experiments on grain boundary structure can be grouped into two categories - those that provide limited structural information on a large number of boundaries and those that give detailed structural information on a limited sampling of boundaries.

The first category is typified by the elegant Rotating-Sphere-On-Plate experiments pioneered by Gleiter and coworkers (1,2). In this technique single crystal spheres are placed in a random array on a single crystal plate and annealed to promote their relaxation into low-energy orientations. The resulting orientation distribution is recorded in an X-ray pole figure and, assuming all boundary planes are parallel to the plate surface, statistically significant data on misorientation and type of boundary (twist/tilt, symmetrical/asymmetrical) can be obtained rapidly. However, this macroscopic method does not give any direct information on the grain boundary structure.

At the other extreme, detailed investigations of the structure of individual grain boundaries have been carried out using transmission electron microscopy. High-resolution observations have revealed the atomic structure of special grain boundaries in semiconductors, (e.g. 3,4) and ceramics, (e.g. 5,6), but the difficulty of sample preparation has severely limited the number of experimental analyses of such boundaries. Until quite recently an additional problem hindering the study of the close-packed structure of metals has been the resolution limit of available microscopes (7). Thus only a few examples of the detailed grain boundary structure in metals have been reported (e.g. 8,9).

The purpose of the present note is to point out a new method for producing specimens that are particularly suitable for high-resolution observations of grain boundary structures. Unlike the bicrystals produced by conventional methods, the specimens contain boundaries that display a continuous variation in boundary orientation. The technique simply relies on heteroepitaxial growth as a means of controlling the misorientation between grains during thin film growth. For example if the substrate surface has fourfold rotational symmetry and epitaxial overgrowth occurs in an orientation with twofold rotational symmetry, then two orientation variants are equally probable. As illustrated schematically in Fig.1, the two variants will be at right angles due to the 90° rotation symmetry of the substrate. If nucleation occurs equally in both orientations, a random distribution of the two variants, or grains results. Wherever the two variants impinge a 90° grain boundary is formed. In a thin film the grain boundaries will tend to become perpendicular to the foil surface during annealing, leading to a preference for boundaries with tilt character. This makes them ideally suited for study by high-resolution electron microscopy.

2. Application

Fig. 2 shows a TEM micrograph of a thin film bicrystal structure formed in aluminum deposited on silicon. The {100} silicon single crystal substrate was removed to reveal more clearly the unique grain structure of the aluminum. The corresponding diffraction pattern (inset) shows two <110> patterns of aluminum rotated by 90°. This particular bicrystal structure was produced by ionized cluster beam deposition (10) and its structure has been investigated previously in the context of the problem of electromigration in aluminum metal contacts on silicon (11). Note the facetting of the grain boundaries to form planar segments on {100}||{110} and {557}||{557} planes, corresponding to an asymmetrical and symmetrical tilt boundary orientation, respectively.

A high resolution image of a symmetrical tilt boundary in this material is shown in Fig. 3. The boundary lies on the {557} plane in both grains and is viewed precisely edge-on. The periodic structure along the boundary due to atomic relaxations is clearly visible (see arrows). Image processing and simulations, currently underway, can provide an exact analysis of possible rigid body translations and structural relaxation units along the boundary. Because many boundaries are available in a single foil, detailed comparisons can be made between similar boundaries and between different boundary orientations.

The above example shows the importance of substrate symmetry and overlayer orientation in the final structure of a heteroepitaxial thin film. In order to exploit these concepts more systematically, it is necessary to understand the factors controlling a) the orientation relationship and b) the selection of variants. The two factors will be discussed briefly below.

3. Factors controlling the orientation relationship

Because of its importance in microelectronics the orientation relationship between two dissimilar crystals in the heteroepitaxial growth of metals on semiconductors has received much attention in recent years. However, many of the underlying principles were established in earlier work on the preferred orientation of metals on NaCl (12) or on other metal substrates (13). It was shown for example that bcc metals on fcc metal substrates (and vice versa) usually grow in orientations that minimize mismatch in the plane of contact. While this appears to be generally true for the simple structure and bonding of metals, other factors such as coordination number (12,14), surface reconstruction, bond directionality, charge neutrality, etc. come into play when nonmetals are involved. But even then the minimization of interfacial mismatch is one of the dominant factors. In this sense the problem is similar to that of plate- and lath-shaped particles of one structure precipitating in a matrix of a different structure, and indeed the observed orientation relationships are largely identical in precipitation and epitaxial growth. Hence while the prediction of optimum orientation relationships from first principles may be difficult, it is possible to use observations from bulk precipitation behavior as a guideline for predicting the expected orientation during heteroepitaxial growth.

Substrate surfaces are usually prepared in low-index orientations, e.g. cubic {100}, {110} or {111}, therefore the deposit usually grows in some low-index orientation as well. If the crystal structures are similar and the lattice mismatch is not too large, parallel epitaxy is preferred. A simple example is the parallel epitaxy of Au (a=4.078Å) on Ag (a=4.086Å) that is commonly used in the preparation of Au bicrystals.

If the crystal structures are different, the optimum orientation is often continuously variable to minimize the mismatch in the interface and thus depends on the lattice parameters as well as substrate surface orientation and crystal structures involved (15). Hence by a small change in lattice parameter the situation depicted in Fig. 1 might change to that shown in Fig. 4 where the orientation relationship has been changed by an angle ß. It can be seen that three types of grain boundary misorientations can be found, 90° boundaries between variants 1/3 and 2/4, 2ß° boundaries between variants 1/2 and 3/4, and 90°+2ß boundaries between variants 1/4 and 2/3.

4. Factors controlling the selection of variants.

Given the orientation relationship and substrate surface orientation it is a simple matter to predict the number of orientation variants and the resulting grain boundary crystallography. The method has been described in different contexts by several authors (16,17,18,19,20) and can be summarized as follows: the number of orientation variants during epitaxial growth depends on the symmetry of the substrate crystal surface, the deposit crystal and their orientation relationship. If the substrate crystal has symmetry G_S, its surface lowers the symmetry to $G_O = G_S \cap \infty m$. The deposit crystal symmetry is G_1, and the orientation relationship has symmetry $G = G_O \cap G_1$ which is the set of symmetry elements shared by substrate, surface and deposit. Variants (sometimes called domains) are due to symmetry elements not shared by substrate and deposit. If orientation variants only are considered, their number is n=(order of G_O)/(order of G).

Each boundary between variants has a characteristic set of symmetry operations, called its coset. For example, the 90° boundaries in Fig.1 are generated by

90° and 270° rotation as well as the two mirror planes at 45° to the square net of the substrate lattice (the mirror planes parallel to the square net are shared by the deposit and do not generate new variants). In Fig. 4, variants 1/3 and 2/4 are related by rotation, 1/2 and 3/4 by the mirrors parallel to the square net, and 1/4 and 3/2 by the mirrors at 45° to the square net. Similarly, translations lead to antiphase boundaries, inversions to inversion boundaries and mixed elements of symmetry, such as screw axes and glide mirrors result in translation-rotation or translation-reflection boundaries, each with their own characteristic defect geometry (21). All of these have become important in the recent development of heteroepitaxy of compound semiconductors, oxides and intermetallics. However, while the objective in these cases is usually to eliminate such boundaries, the present method seeks to exploit their formation to study their atomic structure. The selected or combined use of broken symmetry in producing thin films with controlled texture and grain structure offers many possibilities for basic experimentation as well as materials engineering.

The example in Fig. 4 illustrates the difference between those boundaries generated by rotation and those formed by reflection. Rotation boundaries separate grains that are always misoriented by precisely 90°, while the reflection boundaries separate grains misoriented by an angle 2ß or 90°+2ß. The former are independent of lattice parameter, while the latter vary continuously with the mismatch between substrate and deposit. It is thus possible to make detailed comparisons between identical rotation boundaries in materials with different lattice parameter on the same substrate. But the continuously variable reflection boundaries can be compared only for the same mismatch. Due to the limited number of crystallographic rotation symmetries, only 60, 90, 120 and 180° boundaries of fixed misorientation can be produced and compared for different materials.

On the other hand it will be possible to compare mobilities, propensity for facetting, segregation or mechanical behavior for rotation and reflection boundaries in the same foil. One advantage of this technique is that because of the large number of grain boundaries available for analysis in a single foil it is now possible to obtain a sufficient number of observations to collect quantitative data, characteristic of a particular misorientation. This is useful for high resolution observations of atomic boundary structure as well as in-situ experiments on the behavior of well-characterized grain boundaries in thin films. A systematic investigation of these aspects of thin film bicrystal structures grown by heteroepitaxy is in progress.

Acknowledgments

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References

1. G. Herrmann, H. Gleiter and G. Bäro, Acta Met. 24, 353 (1976)
2. R. Maurer, Acta Met. 35, 2557 (1987)
3. M.D. Vaudin, B. Cunningham and D.G. Ast, Scr. Met. 17, 191 (1983)
4. A. Bourret. L. Billard and M. Petit, Proc. 4th Oxford Conf. Microsc. Semicond. Mat.,
5. H. Ichinose, Y. Inomata and Y. Ishida, Proc. "Ceramic Microstructures '86, Role of Interfaces", A. Pask and A.G. Evans, eds., Materials Science Research, vol. 21, 255
6. K.L. Merkle and D.J. Smith, Ultramicroscopy 22, 57 (1987)
7. R.W. Balluffi, M. Rühle and A.P. Sutton, Mat. Sci. and Eng. 89, 1 (1987)
8. W. Krakow. J.T. Wetzel and D.A. Smith, Phil. Mag. A53, 739 (1986)
9. A. Bourret and J.-M. Penisson, JEOL News 25E, 2 (1987)
10. I. Yamada, H. Inokawa and T. Takagi, J. Appl. Phys. 56, 2746 (1984)
11. M.C. Madden and B.M. Tracy, Proc. 45th EMSA Meetg., 362 (1987)
12. L.E. Collins and O.S. Heavens, Proc. Phys. Soc. 70B, 266 (1957)
13. L. A Bruce and H. Jaeger, Phil. Mag. A36, 1331 (1977), *ibid* A37, 337 (1978), *ibid* A38, 223 (1978)
14. U. Erb, W. Abel and H. Gleiter, Scr. Met. 16, 1317 (1982)
15. C.R.M. Grovenor, A.P. Sutton and D.A. Smith, Scr. Met. 18, 939 (1984)
16. G. vanTendeloo and S. Amelinckx, Acta Cryst. A30, 431 (1974)
17. D. Gratias, R. Portier and M. Fayard, Acta Cryst. A35, 885 (1979)
18. J.W. Cahn and G. Kalonji, Proc. Int. Conf. Solid-Solid Phase Transf., H.I. Aaronson, D.L. Laughlin, R.F. Sekerka and C.M. Wayman, eds., Pittsburgh (1981), p.3

19. V.K. Wadhawan, Mat. Sci. Forum 3, 91 (1985)

20. U. Dahmen and K.H. Westmacott, MRS Proc. 62, 217 (1986)

21. R.C. Pond, "Line Defects in Interfaces", in series on "Dislocations in Solids", F.R.N. Nabarro, ed., in press

Figure Captions

Fig. 1. Schematic illustration of the two orientation variants resulting from the deposition of a film with twofold rotational symmetry on a substrate with fourfold rotational symmetry.

Fig. 2. TEM micrograph of aluminum deposited by the ionized-cluster-beam technique on {100} silicon in two {110} orientations misoriented by 90°. (XBB 886-6529)

Fig. 3. High resolution micrograph of 90° <110> symmetrical tilt boundary in thin film aluminum bicrystal shown in Fig. 2. Boundary plane parallel to electron beam. Arrows point to periodic structure along boundary plane. Recorded at 800kV on ARM. (XBB 886-6528)

Fig. 4. Schematic illustration of four orientation variants resulting from the same geometrical situation as in Fig. 1 with an orientation relationship that is slightly rotated by an angle ß due to greater lattice mismatch.

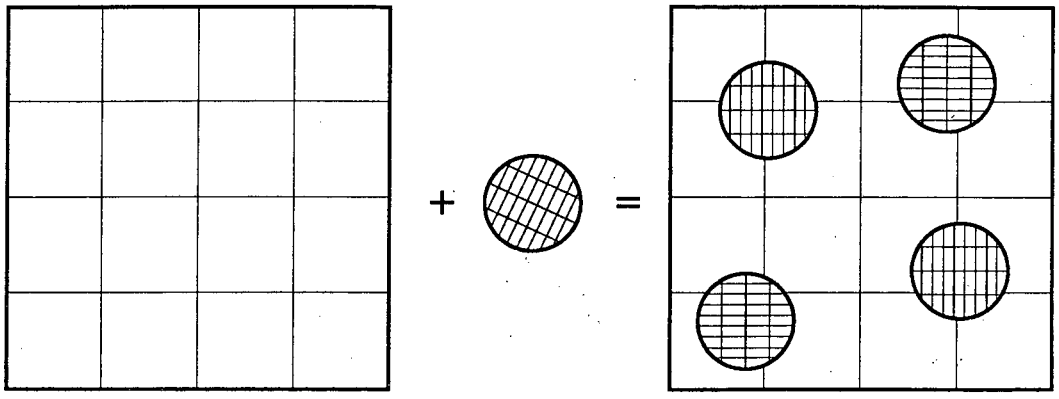

Figure 1

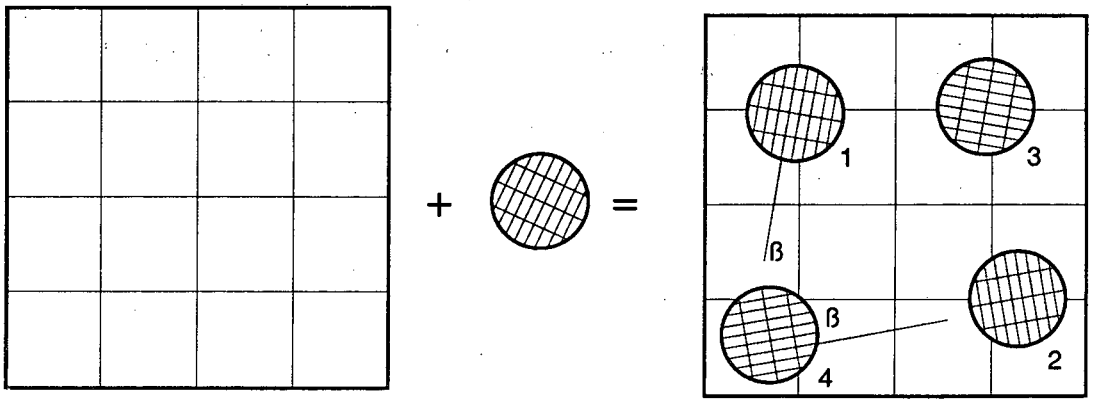

Figure 4

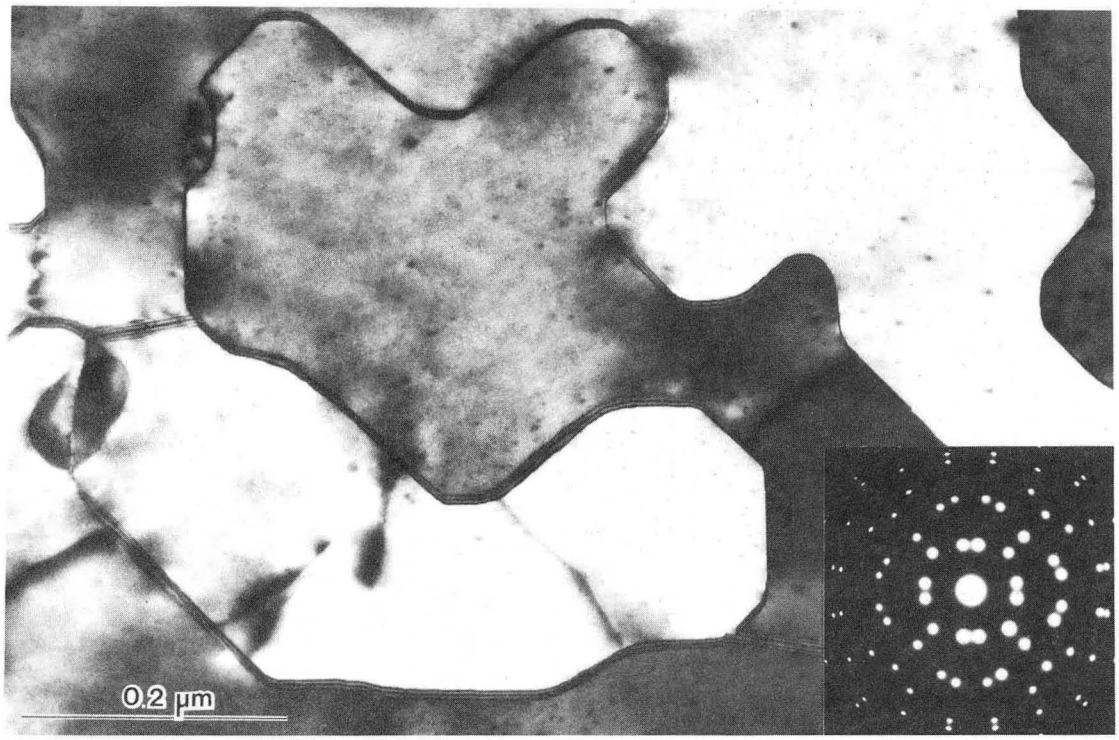

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Figure 2

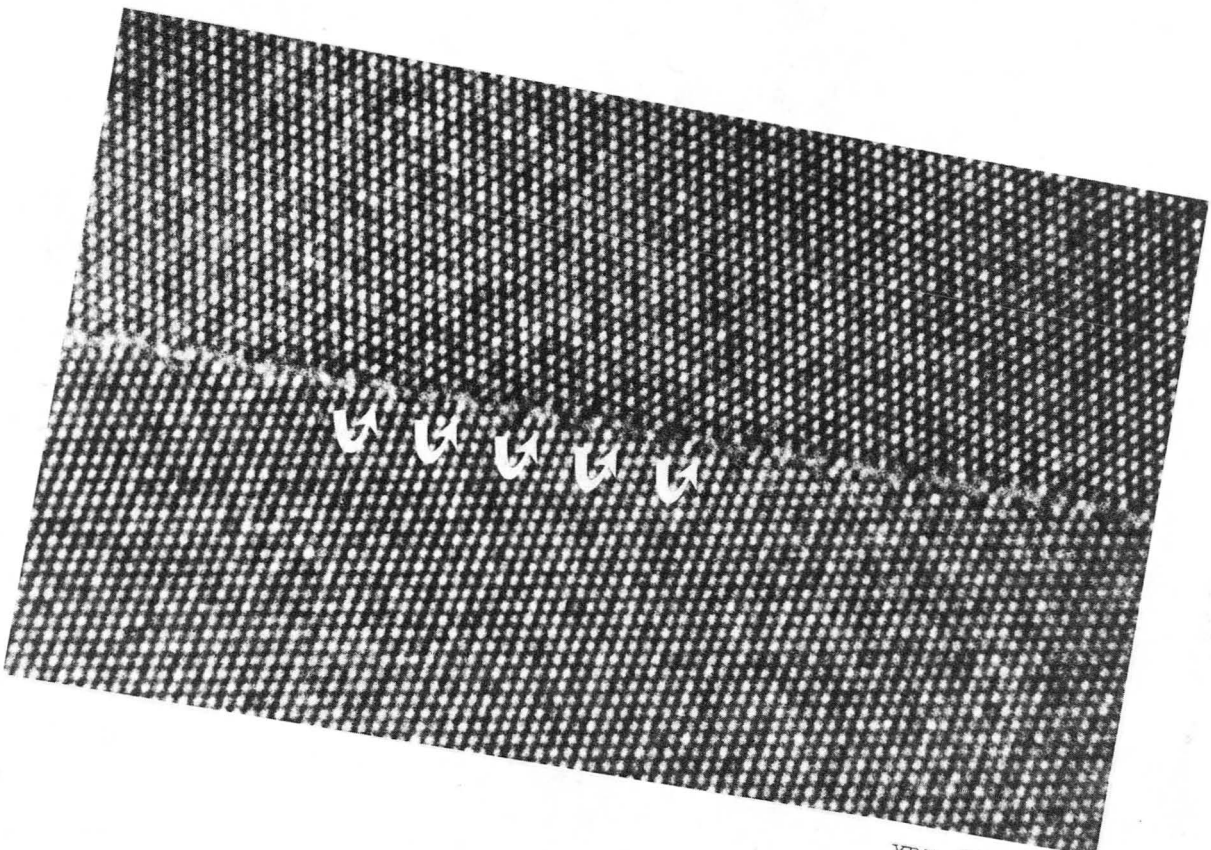

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Figure 3

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