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DEFECTS IN EPITAXIAL MULTILAYERS

III. Preparation of almost perfect multilayers

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Almost perfect multilayers composed of epitaxial GaAs and $Ga(As_{0.5}P_{0.5})$ films have been prepared by chemical vapor deposition. The techniques used to enhance perfection were: (a) to use film thicknesses below that at which misfit dislocations are formed between layers; (b) to match the lattice parameter of the substrate to the lattice parameter of the multilayer taken as a whole; and (c) to use coherency, or misfit, strain to drive threading dislocations out of the sample. Specimens prepared using these techniques contained no dislocations to accommodate misfit between layers, and few dislocations to accommodate misfit between multilayer and substrate. The density of threading dislocations was $< 10^4/cm^2$. This is at least 10^4 times smaller than the density of threading dislocations in the multilayers described in Parts I and II. These results establish that multilayers containing few dislocations can be made from materials with rather different lattice parameters.

1. Introduction

In Parts I [1] and II [2] of this series of papers we described multilayers prepared by depositing a succession of GaAs and $Ga(As_{0.5}P_{0.5})$ films onto GaAs substrates. The multilayers were made for the "semiconducting superlattice device" proposed by Esaki and Tsu [3] and met many of the rather stringent requirements of this device. The films that made up the multilayers were accurately planar and their thickness uniform. The variation in thickness from one GaAs film to another, or from one $Ga(As_{0.5}P_{0.5})$ film to another, was also very small (less than 3%). However, the dislocation content of the multilayers was high. The dislocations can be divided into three groups [1, 2]. These are:(1) threading dislocations, (2) dislocations that accomodate misfit between individual layers, (3) dislocations that accommodate misfit between the multilayer and its substrate.

The aims of this paper are to suggest methods for avoiding these dislocations and to describe the perfection of the multilayers obtained when the methods are applied.

2. Methods for controlling dislocation density

2.1. *Dislocations that accommodate misfit between layers*

Dislocations that accommodate misfit between individual layers in a multilayer can be avoided by choosing layer thicknesses that lie below h_{crit}, the thickness at which it becomes energetically favorable for misfit dislocations to be made. An approximate value for h_{crit} is given by eq. (5) in Part I. The value predicted by this equation for multilayers composed of GaAs and $Ga(As_{0.5}P_{0.5})$ layers of equal thickness is 250 Å. The experimentally determined value is 350 Å. These results are encouraging. They show that the layer thickness at which misfit dislocations first appear in GaAs–Ga(As, P) multilayers is several times larger than the thickness required for the "semiconducting superlattice device" that Esaki and Tsu [3] have proposed. In addition, they suggest that it might be possible to construct devices that are free of misfit dislocations from materials whose stress-free lattice parameters differ by 4 or 5%.

2.2. Dislocations that accommodate misfit between multilayer and substrate

Part II described dislocation pile-ups, threading dislocations, slip lines and cracks generated as a result of the misfit between the multilayer and its substrate. One way of avoiding these defects is to match the lattice parameter of the coherently strained multilayer (see section 2.1) to the lattice parameter of its substrate. The condition for this is that the lattice parameter of the substrate be

$$a_A = a_B\,[1 + G_B h_B f/(G_B h_B + G_C h_C)]\,,$$

where G_B and G_C are the shear moduli of the films that form the multilayer, h_B and h_C are the thicknesses of these films, and f is the misfit between the stress-free lattice parameters of the film materials.

2.3. Threading dislocations

Between 10^4 and 5×10^4 dislocations terminated on unit area (cm^2) of the substrates used for the multilayers described in Parts I and II. The multilayers themselves contained about 10^8 threading dislocations per unit area. This 10^4 fold increase in dislocation density is thought to have resulted from the nucleation of half-loops during the growth of the first epitaxial layer and from the operation of dislocation sources. These processes are illustrated in fig. 8 of Part I and fig. 6 of Part II. Dislocation sources are not expected to operate in multilayers that satisfy the condition given in section 2.2. Dislocation half-loops may be nucleated during the growth of multilayers that satisfy the condition in section 2.2 but they are not expected to lead to threading dislocations; the half-loops will be closed to form complete ones by the process illustrated in fig. 9 of Part I. Thus, multilayers that satisfy the condition in section 2.2 are expected to contain significantly fewer threading dislocations than the multilayers described in Parts I and II.

Although the condition in section 2.2 is expected to reduce the density of threading dislocations to a low value it is worthwhile to consider methods of reducing their number still further. Three processes which reduce the density of threading dislocations are illustrated in fig. 1 : a, b, c, d, and e in part (i) of this figure are substrate dislocations that are replicated in an epitaxial and coherently strained (i.e., pseudomorphic) thin film. The dislocation lines are bowed as a result of the coherency strain present in the film [5]. Bowing increases as film thickness increases. Eventually, the threading dislocations move laterally and leave misfit dislocations in the interface as illustrated in part (ii) of fig. 1. Lateral motion may lead to the combination of two dislocations like a and b to form a third. One of the possible reactions is

$$\tfrac{1}{2}a\,[0\bar{1}\bar{1}] + \tfrac{1}{2}a\,[101] = \tfrac{1}{2}a\,[1\bar{1}0]\,.$$

Lateral motion may also lead to annihilation of dislocations of opposite sign as illustrated by c and d, and to escape at the specimen edge as illustrated by e.

Some of the conditions that are expected to favor the escape of threading dislocations, and reactions between them, have been outlined by Matthews et al. [5] and by Mader and Matthews [6]. Experimental evidence for the removal of threading dislocations during the growth of one III–V compound on another has been obtained by Saul [7], Rozgonyi et al. [8] and Olsen et al. [9]. Further evidence is given in section 3.5.

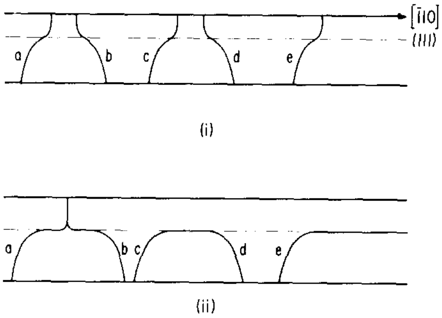

Fig. 1. Processes that lead to a reduction in the density of threading dislocations.

3. Almost perfect multilayers

3.1. Specimen preparation

Multilayers were grown by chemical vapor deposition and thinned for transmission electron microscopy as described in Part I. However, there was one important modification to the technique used earlier. A layer with gradually increasing GaP content was grown on the GaAs substrate before deposition of the multilayer began. This gave composition profiles

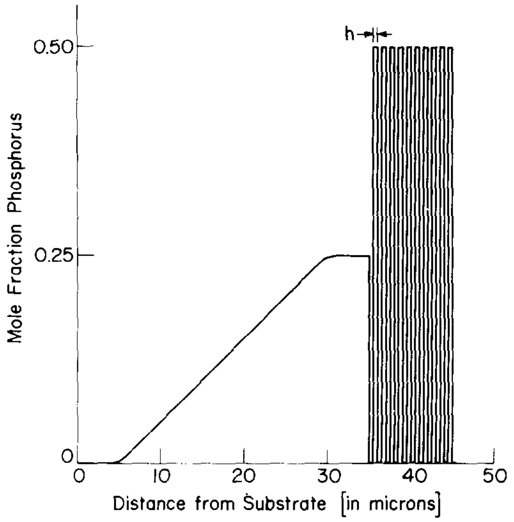

Fig. 2. The composition profile in GaAs–Ga(As, P) multilayers grown on matched substrates. The value of h shown is larger than that normally employed.

similar to that shown in fig. 2. The purpose of the graded layer was to give a substrate surface whose lattice parameter matched that of the multilayer. (See section (2.2.)

So far, six multilayers grown on matched substrates as described above have been examined by transmission electron microscopy. All of them were oriented with their interfaces inclined at a few degrees to (001). Rotation away from (001) was usually about one of the ⟨110⟩ directions in (001). The thicknesses of the GaAs and $Ga(As_{0.5}P_{0.5})$ layers were approximately equal in all specimens. The thicknesses (in Å) of individual layers in the specimens were 870, 325, 300, 190, 80, and 65. Thus, in one multilayer the layer thickness was much greater than h_{crit}, in two it lay between the measured and predicted values for h_{crit}, and in three it was below h_{crit}.

3.2. Identification of interfaces

A crucial step in the assessment of almost perfect multilayers is the identification of interfaces between layers. This is because, in the absence of this identification it is difficult to distinguish between a perfect multilayer and the material above and below it. Also, if a dislocation is present, it is difficult to determine the interface it occupies. A feature of thinned multilayers that plays an important part in interface identification is their terraced surface. Terraces are formed because the solution (bromine in methanol) used to thin samples for electron microscopy does not dissolve Ga(As, P) as rapidly as GaAs. Terraces made during the dissolution of a multilayer composed of fifteen GaAs and fifteen Ga(As, P) layers are seen in fig. 3. This figure confirms a feature expected from a difference in dissolution rates. It is that one step is formed for each pair of layers. It means that two interfaces are associated with each step and that the change in surface elevation from a point on one terrace to an equivalent point on the next is $h_B + h_C$.

The contrast in transmission electron micrographs of steps has been considered by Weatherly and Sargeant [10]. Although the coherency strains at the steps discussed by them were rather different from those present at steps in thinned multilayers, their predictions are expected to hold qualitatively for our samples. Weatherly and Sargeant show that the coherency strain at steps gives rise to dark or light lines. The contrast at these lines reverses when the sign of the operating Bragg reflection is changed and when the sign of the step is changed. These features are visible in the curved lines in figs. 4a and 4b. The contrast reversal that accompanies a change in the sign of g is seen by comparing 4a and 4b. The reversal that accompanies a change in the sign of a step (with respect to g) [11] is seen at A and B in 4a or 4b.

The straight dark lines parallel to the ⟨110⟩ directions in fig. 4 are images of coplanar dislocation lines. The lines are in or very close to the interface between the multilayer and a deposit that was formed on the multilayer surface when the reaction chamber was cooled [1]. The geometry of the dislocations suggests that they were made to accommodate part of the misfit between the multilayer and the deposit formed on it. Evidence that the dislocations are coplanar and lie near the final surface of the multilayer is provided by stereo microscopy. Stereo microscopy also confirms our identification of steps and terraces.

A stereopair of a sample composed of layers 65 Å in thickness is seen in fig. 5. It is clear that if our interpretation of steps and terraces is correct then A is steeply inclined to the multilayer plane, and B_1 and B_2 are almost parallel to it. Examination of fig. 5 with a suitable viewer confirms that this is so. B_1 is a flat valley, A is a steeply inclined hillside, and B_2 is a flat

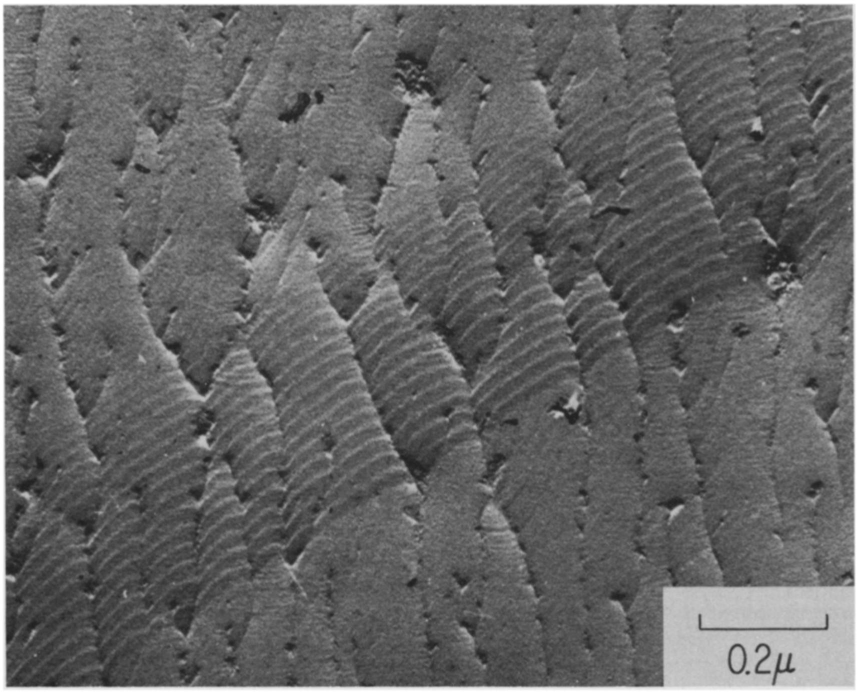

Fig. 3. Transmission electron micrograph of a carbon replica of an etched multilayer that contained fifteen GaAs and fifteen Ga(As, P) layers. Steps and terraces that resulted from a difference in the etch rates of GaAs and Ga(As, P) are discernible.

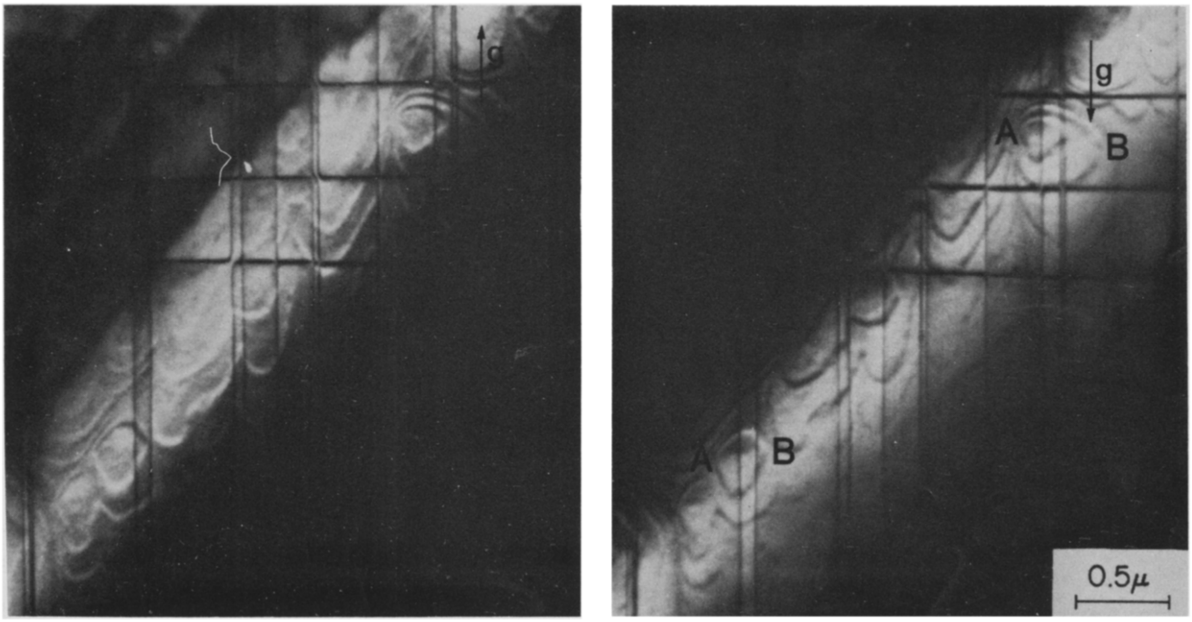

Fig. 4. Micrograph of terraces and curved steps in a multilayer composed of layers 65 Å in thickness. The dark lines parallel to the borders of the figures are dislocations in or very close to the boundary between the multilayer and a deposit grown on it.

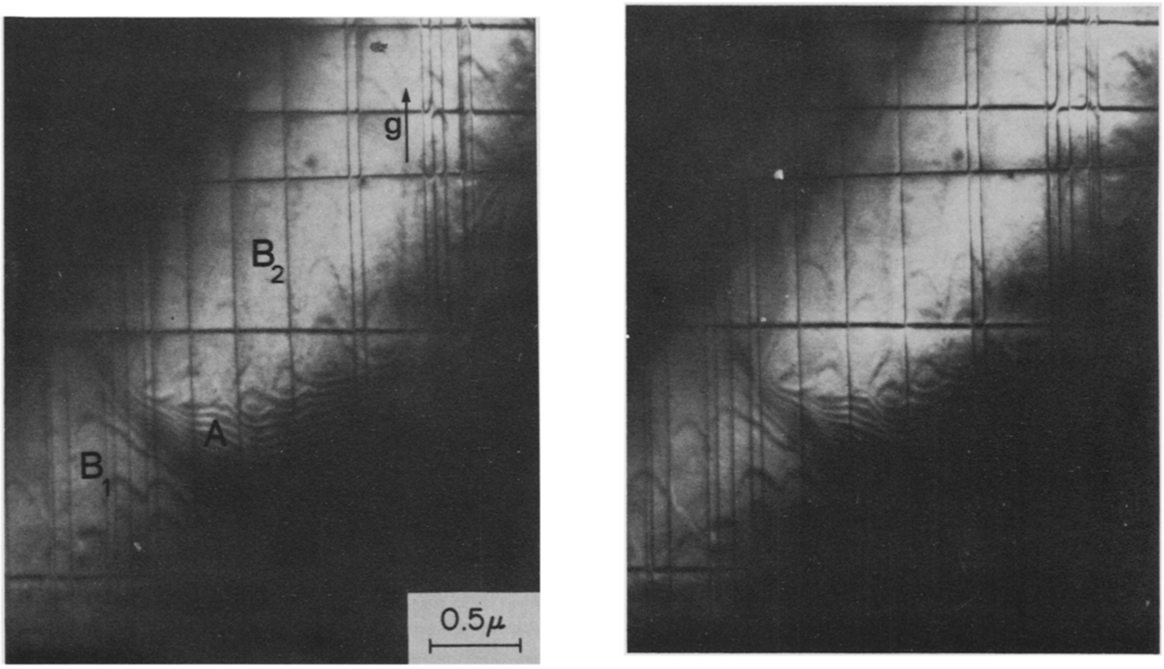

Fig. 5. Stereomicrographs of a multilayer composed of layers 65 Å in thickness. If a suitable viewer is used it can be seen that A is a steep hillside, B_1 is a flat valley, and B_2 is a flat top to the hill. The dark lines parallel to the edges of the figures are coplanar dislocations in an interface many layers above B_2.

top to the hill. The dislocation lines are coplanar and lie many layers above B_2.

3.3. Misfit dislocations between layers

Defects generated to accommodate part of the misfit between individual layers were described in Part 1. Some of the defects were pairs of long, straight, parallel dislocations with antiparallel Burgers vectors. Others were arrays of closely spaced dislocations in which the Burgers vectors of adjacent dislocations were opposite in sign. The Burgers vectors of paired dislocations and dislocations in arrays were $\frac{1}{2}a\langle 110\rangle$, and were inclined at about 45° to the interface plane.

The micrographs in figs. 4 and 5 were recorded under diffraction conditions that reveal all misfit dislocations of this type. The absence of dislocations that terminate on the steps, and the absence of dislocations that lie between the top of B_2 and the planar dislocation network in fig. 5, show that there were no dislocations present to accommodate misfit between layers.

This result is not surprising because the layer thicknesses in figs. 4 and 5 lay well below h_{crit}. Results which are more surprising at first sight were obtained from the sample in which layer thickness was above h_{crit}. This specimen did not contain any paired dislocations or dislocation arrays. Part of the evidence for this is present in fig. 6. The arrowed lines in this figure are steps 1740 Å in height. They are darker than the background in the area labelled Y and lighter than the background in that labelled Z. This difference in contrast is present because the sign of the steps (with respect to g) [11] changes between Y and Z. The change in contrast occurs at X and in this area the steps are invisible. The lower portion of the figure is darker than the upper because the sample thickness was greater in the lower portion. Sample thickness below the lowest arrow was over one micron. The Bragg reflection responsible for the contrast in fig. 6 was such as to reveal all paired dislocations and dislocation arrays. The absence of these defects from fig. 6, indicated that there were no dislocations present to accommodate misfit between layers.

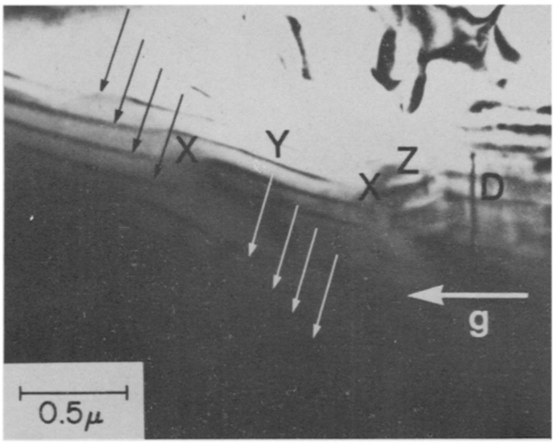

Fig. 6. Micrograph of steps and terraces in a multilayer made up of layers 870 Å in thickness. The steps are dark near *Y*, light near *Z*, and invisible near *X*.

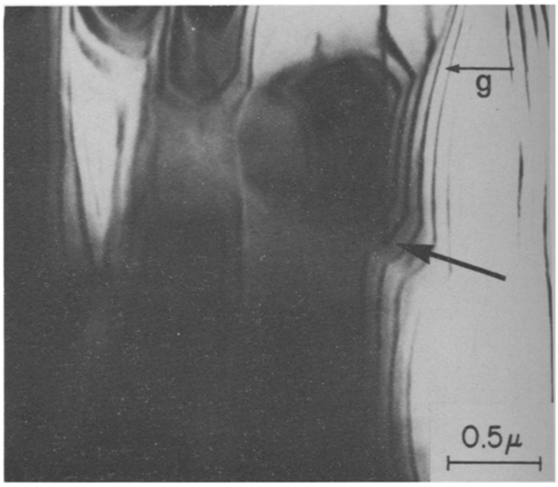

Fig. 7. Micrograph of steps that bound pairs of coherent interfaces in a multilayer composed of layers 190 Å in thickness. The arrowed dislocation was formed to accommodate misfit between the multilayer and its substrate.

The dislocation labelled D in fig. 6 lies in an interface between layers but is not paired or part of an array. A few dislocations of this type were found in matched multilayers and are discussed in section 3.4. The rarity of paired dislocations and dislocation arrays in the multilayer composed of thick (870 Å) layers is discussed in section 4.1.

3.4. Dislocations to accommodate misfit between multilayer and substrate

Isolated dislocations do not accommodate misfit between individual layers in a multilayer [2]. However they can accommodate misfit between a multilayer and its substrate. A few isolated dislocations that were probably formed to accommodate misfit between multilayer and substrate have been found. One is present in fig. 6 and was briefly discussed in the previous section. An example in the multilayer made up of layers 190 Å in thickness is seen in fig. 7. 190 Å is less than h_{crit}. The presence of an isolated dislocation in a sample with $h < h_{crit}$ is consistent with the suggestion that isolated dislocations are made to accommodate misfit between multilayer and substrate. It is not consistent with the suggestion that they are made to accommodate misfit between layers.

Dislocations that accommodate misfit between multilayer and substrate are not expected if the matching of the multilayer to the substrate is perfect (see section 2.2). Although we have attempted to match multilayers and substrates very accurately there is evidence, in addition to that provided by fig. 7, that matching was imperfect. Fig. 8 is a low magnification image of a hole in a multilayer. The fine white lines emerging from this hole are cracks on {110} planes perpendicular to the multilayer plane. Similar cracks were present in all the other matched multilayers we have examined. Thus, it seems that the lattice parameter of the top of the graded layers was always slightly larger than that of the multilayers grown on them. An explanation for this is given in section 4.2.

3.5. Threading dislocations

Figs. 4–7, and all other micrographs of matched multilayers that we have obtained so far, do not contain images of threading dislocations. This means that the density of threading dislocations was less than 10^4 per cm^2. Comparison of this result with that obtained earlier for multilayers grown on unmatched substrates shows that the use of matched substrates reduced the density of threading dislocations by a factor greater than 10^4.

Additional evidence for the rarity of threading

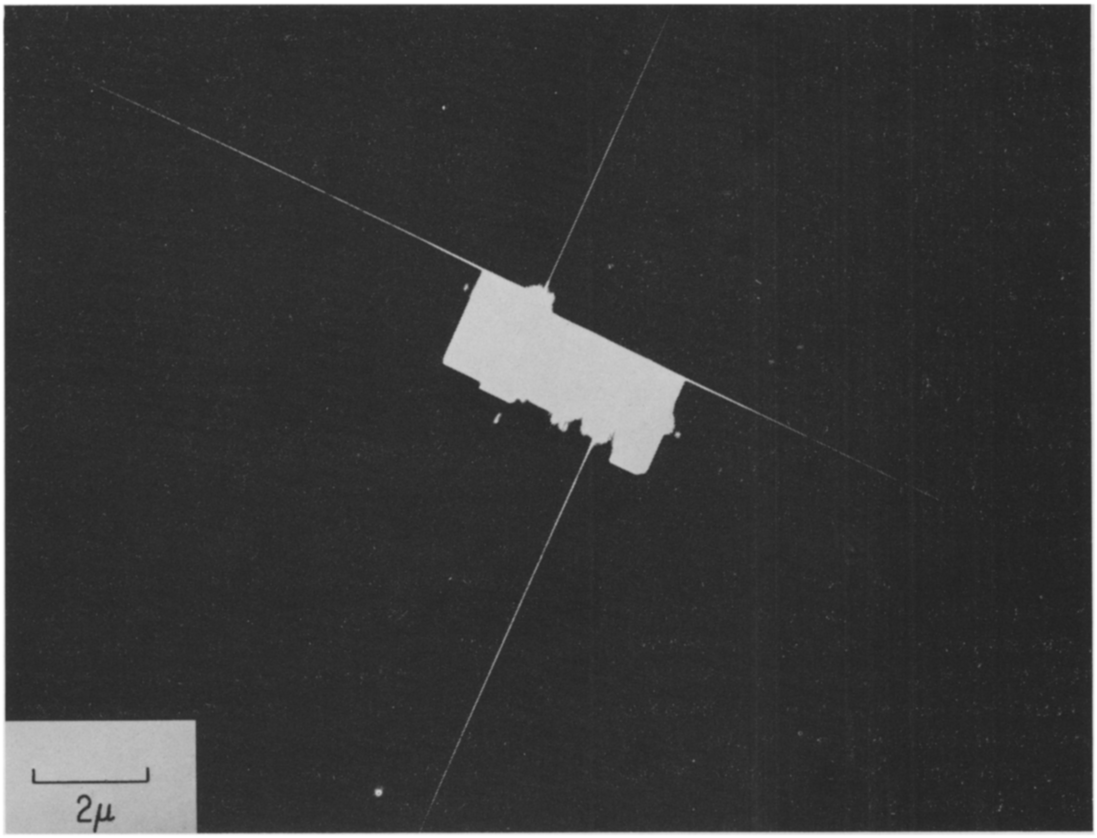

Fig. 8. Micrograph of cracks radiating from a hole in a thinned multilayer. Individual layers were 190 Å in thickness.

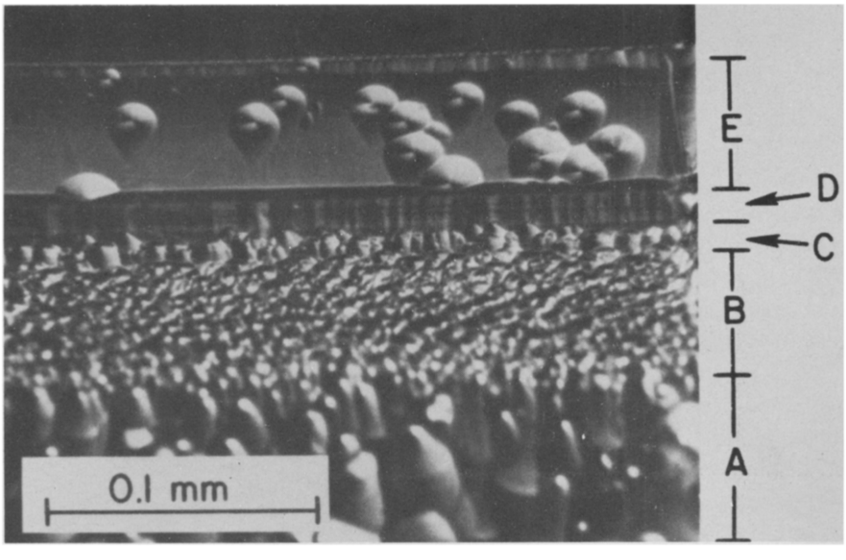

Fig. 9. Optical micrograph of an etched surface cut at an oblique angle to the multilayer plane. The letters are identified in the text.

dislocations in matched multilayers has been obtained from an examination of etch pits. A multilayer was cut and polished on a {111} plane inclined at ~55° to the interface. It was then etched in an $HF-HNO_3-AgNO_3$ solution and examined by optical microscopy. One of the micrographs obtained is seen in fig. 9. The region labelled A is the GaAs substrate, B is the graded layer, and C is a thin layer of uniform composition that was grown on top of the graded layer (cf. fig. 1). D is the multilayer, and E is the layer grown on top of the multilayer. E in fig. 9 differs from the layer grown on the sample in figs. 4 and 5 in that it was deposited at the growth temperature and an attempt was made to match its lattice parameter to that of the multilayer. The dislocation densities (per cm^2) in the labelled regions were approximately: 10^4 to 10^5 in A, 10^8 in B, 2×10^6 in C, less than 10^4 in D, and 2×10^5 in E.

The decrease in perfection from A to B is a well-known phenomenon in graded layers and is discussed by Abrahams et al. [12]. The increase in perfection from B to D is thought to arise from the removal processes described in section 2.3. The small decrease in perfection from D to E may have been due to the formation of new dislocations to accommodate misfit between D and E. [Although we tried to match the lattice parameters of D and E it is probable that matching was not perfect (cf. sections 3.4 and 4.2).]

4. Discussion

4.1. Absence of misfit dislocations in multilayers composed of thick layers

Many of the misfit dislocations present in the unmatched multilayers were made as a result of the nucleation of dislocations during the growth of the first and subsequent $Ga(As_{0.5}P_{0.5})$ layers. This indicates that the 1.8% misfit between GaAs and $Ga(As_{0.5}P_{0.5})$ is sufficient to nucleate new dislocations at the substrate temperature (750°C) used.

The absence of paired dislocations and dislocation arrays from the matched multilayer with $h > h_{crit}$ indicates that the misfit strain present in this sample was too small to nucleate dislocations at 750°C. The misfit between GaAs or $Ga(As_{0.5}P_{0.5})$ layers and a perfectly matched substrate is 0.9% [or half the misfit between GaAs and $Ga(As_{0.5}P_{0.5})$]. Thus, the observations described in Part I and section 3.3 of this paper suggest that the elastic strain needed for dislocation nucleation in GaAs or Ga(As, P) at 750°C lies between 0.9 and 1.8%. This result agrees with the predictions of Frank [13] and Hirth [14].

4.2. Origin of the tensile stress in matched multilayers

A possible explanation for the imperfect matching of the substrates to the multilayers grown on them is imperfect control of the composition of the vapor. An alternative explanation is as follows. We attempted to match the lattice parameter of the graded layers to the lattice parameter of the multilayers by making the chemical composition of the upper surface of the graded layers equal to the average chemical composition of the multilayer (see fig. 1). Although this method seems satisfactory at first sight it does assume that the misfit between the graded layer and its substrate is accommodated by dislocations and not by coherency strain. The calculations of van der Merwe and others [5, 15] show that this assumption is approximate. Part of the misfit is accommodated by coherency strain. The magnitude of the coherency strain depends on the misfit between the graded layer and its substrate, on the thickness of the graded layer, on the geometry of the misfit dislocations, and on processes that impede the creation of misfit dislocation lines [5, 16]. Coherency strains in graded GaAs–Ga(As, P) layers would be expected to give rise to tensile stresses in chemically matched GaAs–Ga(As, P) multilayers. This agrees with observation. The cracks present in the chemically matched multilayers show that they were stretched.

Acknowledgements

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