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Inverse defect formation during growth of epitaxial InAsSbP/InAs structures

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The laws governing plastic deformation during the growth of single-crystal gradient layers of solid solutions have been studied on the example of the $InAs_{1-x-y}Sb_xP_y$/InAs structure. The degree of plastic deformation of the crystals was evaluated by counting dislocation etch pits. The samples were bent during growth. The composition of the solid solution was varied smoothly in the direction of film growth and the lattice constant increased toward the surface of the layer. With decreasing thickness of the substrate the curvature of the structure and the dislocation density in the substrate increased. The dislocation density in the epitaxial layer was practically independent of the local thickness of the substrate. The results of this study are explained on the basis of the model of a crystal with a radially symmetric virtual lattice.

Epitaxial layers (epilayers) of solid solutions with a composition gradient or smooth heterojunctions are used extensively in modern semiconductor electronics to obtain built-in quasielectric fields in optoelectronic devices, in the fabrication of buffer regions between the substrate and the working layer of the heterostructure. Most of these materials are characterized by an appreciable lattice-constant gradient, which causes tilted dislocations to form in the layer[1] and these dislocations worsen the quality of the crystal, e.g., because of excess currents in the planar p–n junctions.[2]

Pseudomorphic (coherent) growth of an epilayer is known to occur in the initial stages until some critical thickness is reached. When this thickness is exceeded the elastic stresses relax owing to plastic deformation and the formation of misfit dislocations (MD) in the epilayer.[3,4] Even when the lattices match ideally at the heteroboundary, therefore, a dislocation density close to the value for the initial material of the substrate usually cannot be obtained in junction layers with a lattice-constant gradient.

At the same time, the choice of the optimal substrate thickness makes it possible to make mismatch dislocations form mainly in the substrate,[8] i.e., the part of the structure that is not usually the active region of the semiconductor device.

The aim of this work is to study the laws governing the plastic deformation of a heterostructure, occurring during the growth of gradient layers on substrates of various thicknesses, on the example on the InAsSbP/InAs structure.

The samples were grown by liquid-phase epitaxy in an open apparatus with forced cooling of a solution in a melt at 700-750°C. The substrates were n-type InAs (111) wafers, oriented by the method of Ref. 9, with a carrier density of (3-5)·10^{16} cm^{-3} and a dislocation density of the order of 10^4 cm^{-2}. A number of substrates were prepared as wedge-shaped wafers, whose inoperative surface formed an angle of ∿2°, and the thickness of the wedge varied within the limits 80-500 µm. Either the A-side or B-side of an InAs wafer served as the working side of the wedge-shaped substrates.

On the basis of x-ray data the composition of the solid solution in $InAs_{1-x-y}Sb_xP_y$ epitaxial films was varied smoothly in the growth direction (Fig. 1). Measurements by the method described

FIG. 3. Photomicrographs of the region near an InAsSbP/InAs heteroboundary, revealed by the "oblique section" method: a) cathodoluminescence photomicrograph, b) secondary-electron photomicrograph. The arrow points to the epilayer.

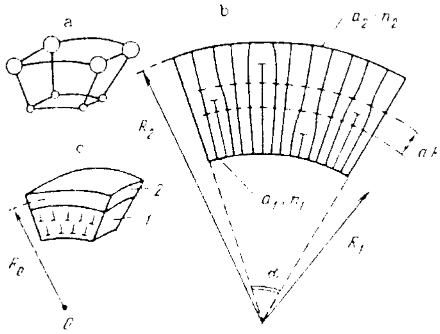

FIG. 4. Virtual unit cell of a gradient crystal (a) and the model of a plastically relaxed crystal with grad $\bar{a} > 0$ ($\bar{a}_2 > \bar{a}_1$) (b) and of the heterostructure (c): 1) deformed substrate, 2) epilayer when $R = R_0$.

cathodoluminescence regime (a) and in the secondary-electron regime (b). The dislocation density in the layer [round (black) etch pits] is seen to be lower than in the substrate (triangular pits). The individual dark lines in Fig. 3a are usually linked to nonradiative recombination on impurity atmospheric dislocations, lying parallel to the heteroboundary, i.e., misfit dislocations (MD). Figure 3 shows that the MD lines end primarily at dislocation etch pits, i.e., at places where tilted dislocations emerge. The relation between misfit and tilted dislocations is an important feature of gradient layers,[1] which allows selective etching to be used to evaluate the degree of relaxation of the stresses and plastic deformation of the epilayer.[5-7]

The above-described "inversion" of defect formation, i.e., a process in which misfit dislocations are formed mainly in the substrate and not in the epilayer, has been observed experimentally in "small-mismatch" structures,[8] i.e., structures in which the critical stresses for misfit-dislocation formation are reached for comparable thicknesses of the layer (t) and the substrate (c). In our case $t \ll c$, but the heterostructures possess the same property as did the samples in Ref. 8: the dislocation density is lower in the layer than in the substrate.

The data obtained can be explained by the fact that at the growth temperature of the solid solution InAsSbP is less plastic than is InAs. This may be due to the hardening action of isovalent "impurities" with a different tetrahedral radius than As atoms have (in the given case Sb atoms[14] and P atoms). The reduced plasticity inhibits the formation of misfit dislocations in the InAsSbP epilayer and is the reason why there is no high dislocation density in the epilayer, which according to calculation[1] is 10^6-10^7 cm^{-2}.

The "inverse" distribution of misfit dislocations in the heterostructures studied can also be described qualitatively within the framework of the model of a completely relaxed state of a system with a gradient epilayer.

For this purpose we consider the distinctive features of the crystal lattice of a solid solution with a composition gradient. To do so we used the model of Ref. 15, in which the linear size of the virtual unit cell increases continuously from the center of curvature in accordance with the variation of the lattice constant (Fig. 4a). A real crystal may contain dislocations that distort its shape[16,17] and in the case of a gradient crystal dislocations can either increase or decrease, depending on their sign. The second variant is of practical interest since epitaxial layers of the solid solutions are grown on initially planar orientation substrates. We consider a crystal with a "radial" unit cell (Fig. 4a), in which the planes undergo additional bending upon the introduction of edge dislocations with the sign opposite to the curvature of the unit cell (Fig. 4a). The crystal will be assumed to be in the free state ($\varepsilon = 0$); for simplicity we confine ourselves to the case when the dislocations are distributed uniformly in the sample and its linear size is much smaller than the radius of curvature.

The presence of dislocations causes a change in the number of atomic planes along the radius vector, $dn = -NR_\alpha dR$, where α is the angle delineating the crystal, N is the dislocation density, and R is the radius of curvature of the bent planes. Moreover,

$$n_2 = n_1 - N\frac{\alpha}{2}(R_2^2 - R_1^2),$$

where n_1 and n_2 are the numbers of atomic planes that emerge on the concave and convex surfaces, respectively, of the crystal and R_1 and R_2 are the radii of the concave and convex surfaces, respectively.

Taking into account the fact that the lattice constant varies linearly with the coordinate, $\bar{a}_2 = \bar{a}_1 + \text{grad}\,\bar{a}(R_2 - R_1)$, as well as the fact that

$$\frac{n_2\bar{a}_2 - n_1\bar{a}_1}{n_1\bar{a}_1} = \frac{R_2 - R_1}{R_1}, \qquad \alpha = \frac{n_1\bar{a}_1}{R_1},$$

we obtained

$$N = \left(\frac{\text{grad}\,\bar{a}}{\bar{a}_1}\left(\frac{2R_1}{R_1+R_2}\right) - \frac{2}{R_1+R_2}\right)\Big/\ \bar{a}.$$

We can assume that $\bar{a}_1 \approx \bar{a}_2 \approx \bar{a}$ and $R_1 \approx R_2 = R$ in real structures and, therefore, for the dislocation density in a gradient crystal we have

TABLE I. Compositions of Etchants for Revealing Dislocations

No. of etchant	Composition of mixture	Ratio of components	Type of surface where etch pits appear	
1	$HF+CrO_3+AgNO_3+H_2O$ (AB-etchant	2 mm:1 g:8 mg:1 ml	A and B	EL
2	$H_2SO_4+H_2O_2+H_2O$	1:1:1 vol. fraction	A	EL
3	$H_2SO_4+H_2O_2+H_2O$	1:1:1 vol. fraction	A	InAs
4	$HF+HNO_3+CH_3COOH$	5:3:3 vol. fraction	A	EL
5	$HF+HNO_3+CH_3COOH$	5:3:3 vol. fraction	A	InAs
6	$HCl+H_2O$	1:1 vol. fraction	B	InAs

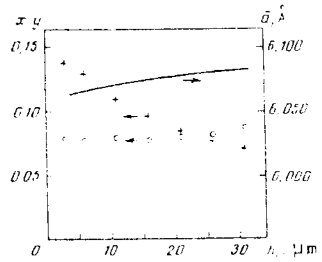

FIG. 1. Distribution of the composition (x, y) and the lattice constant ($\bar{a}$) over the thickness of $InAs_{1-x-y}Sb_xP_y$ in a B-sample: O) InSb content (x); +) InP content (y); the line represents the epilayer lattice constant obtained by linear interpolation.

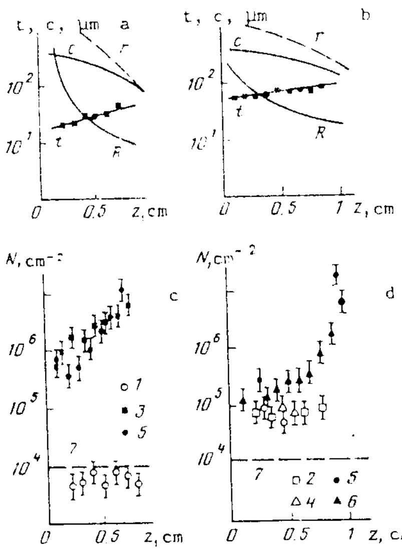

FIG. 2. Structural characteristics of wedge-shaped A-structure (c, d) and B-structure (a, b). The black symbols denote data for InAs and the white ones, for the epilayer; 1-6 correspond to the numbers of the etchants used to reveal the dislocations in Table I; 7 is the dislocation density in the initial InAs wafers.

in Ref. 10 showed that the lattice constant increased virtually linearly toward the surface of the layer (grad $\bar{a}$ = const). The lattice-constant gradient in the A-sample was smaller by a factor of 2 than in the B-structure ($2.3\cdot10^{-8}$ and $4.7\cdot10^{-8}$, respectively); the lattice mismatch at the heteroboundary was $\Delta\bar{a}$ = 0.014 Å (A) and $\Delta\bar{a}$ = 0.007 Å(B).

The samples were curved and the epilayers had a specular surface and were on the convex side of the structures. The radius of curvature depended on the layer/substrate $\frac{\text{thickness}}{\text{thickness}}$ ratio and the lattice-constant distribution in the InAsSbP. In Fig. 2a, b we give the data that characterize the local thickness (t) of the epilayer (EL) and of the substrate (c) and the radius of curvature (R) in wedge-shaped A- and B-structures. The z axis was directed along the surface of the wedge from the apex of its angle; N is the density of tilted dislocations.

In some of the experiments we etched off the epitaxial films: at the epitaxial-deposition temperature by fusing the In–As–Sb–P after its growth or at room temperature by using a selective etchant. In both cases the curvature of the substrates persisted after the films were etched away. The epilayers remained bent when the substrates were etched away.

The density of tilted dislocations and the degree of plastic deformation in InAsSbP and InAs were evaluated from the etch pits on the A- and B-surfaces of the samples. Table I shows the compositions of the etchants used and the type of surfaces on which etch pits are reliably revealed.

From Fig. 2c, d we see that the substrate thickness and curvature increased in both types of structure and, hence, so did the local dislocation density in the InAs substrate. At the same time, the dislocation density in the epilayer virtually did not change along the surface and was lower than in the substrate. The experiments also showed that the dislocation density in both the substrate and the epilayer varied little with depth but changed discontinuously at the heteroboundary.

DISCUSSION OF EXPERIMENTAL RESULTS

Let us compare the experimental results in Fig. 2a, b with the radius of curvature of an elastically stressed system,[11] which had the same parameters as the heterostructure that we studied (i.e., the same thickness and the same values of $\bar{a}$ and grad $\bar{a}$). The experimental values of the radius R are smaller than the calculated value of r by a factor of 5-10, which is indicative of plastic relaxation of stresses in the heterostructure, mainly in the substrate. The plastic nature of the substrate bending is also indicated by the fact that the dislocation density in the InAs wafers increases in comparison with the initial value (Fig. 2c, d) and that the curvature of the substrates persists when the epilayers are etched away,[12] as well by x-ray diffraction measurements on bent InAsSbP/InAs heterostructures.[13]

At the same time, the dislocation density data in Fig. 2 show that the degree of plastic deformation of the epilayers is small. As an illustration Fig. 3 shows photographs of the layer-substrate interface taken on an "oblique section" of a B-sample in an electron microscope in the

$$N = \left(\frac{\mathrm{grad}\,\bar{a}}{\bar{a}} - \frac{1}{R}\right) \Big/ \bar{a} \qquad (1)$$

As $R \to \infty$ relation (1) takes on the form of the dependence of the dislocation density on the lattice-constant gradient in a planar relaxed heterostructure[1] and when grad $\bar{a}$ = 0 it coincides with the well known Nye formula for a plastically deformed crystal[16] (the minus sign denotes that the crystal curvature, due to the extra half-planes shown in Fig. 4b, changes sign when grad $\bar{a}$ = 0). Making allowance for other types of dislocations that make their contribution to the total curvature of the crystal[16,17] complicates relation (1) but does not change the tendency in the dependence of N on R. An important consequence of the expression obtained for N is that when the condition R_1 = $\bar{a}$/grad $\bar{a}$ is satisfied, the gradient crystal does not have any misfit dislocations (in this case N = 0 and ε = 0).

The model representations obtained here are consistent with the conclusions of the linear theory of the deformation of epitaxial structures, containing films with a varying lattice constant. Thus, upon setting the substrate thickness equal to zero in the formula for the radius of curvature of the structure,[18] we obtain for the radius of the free layer the value that is obtained by substituting N = 0 in formula (1). The data in Fig. 2 are in qualitative agreement with this conclusion. For a layer where grad $\bar{a} \neq 0$, the dislocation density should be lower than in the substrate, which is also consistent with the data from metallographic analysis of the samples.

In conclusion, we point out that the above laws governing the growth of gradient layers and the "inversion" of defect formation was also observed in our studies of other systems [GaAsSbP/GaAs (Ref. 19) and InGaAsSb/GaSb] and optimization of the process of growing low-dislocation InAsSbP/InAs p–n structures made it possible to obtain effective sources of radiation in the middle IR region of the spectrum, which are appropriate for practical application in absorption gas analyzers.[20]

To sum up, during the experiment we detected the phenomenon of inverse defect formation, which consists in substantial plastic deformation of the substrate while at the same time a gradient epitaxial layer grows with a more perfect crystal structure than that of the substrate. As a result we have demonstrated that InAsSbP can be obtained with a lower density of tilted dislocations than the values published for the given material.

In our study we have obtained indirect data that support the assumption that the natural form of a gradient crystal is a spherical layer with a curvature that depends on the lattice-constant gradient.

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