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REAL STRUCTURE OF CRYSTALS

Specific Features of the Formation of Dislocation Structure in Gallium Arsenide Single Crystals Obtained by the Czochralski Method

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Abstract—The influence of the deviation of seed orientation from the [100] direction on the formation of a dislocation structure of gallium arsenide single crystals grown by the Czochralski method has been revealed. The intensive multiplication of dislocations and formation of a block structure occur at deviation by an angle of more than 3° in the region that is radially shifted to one of crystal sides. The linear density of dislocations in the walls changes from 1×10^4 cm^{-1} in low-angle boundaries to 6×10^4 cm^{-1} in subboundaries.

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INTRODUCTION

Gallium arsenide (GaAs) is one of the most popular semiconductor materials (along with silicon). Due to some fundamental properties, GaAs and related solid solutions are widely used in optoelectronic and microwave devices, microelectronics, and power electronics. Along with the charge-carrier concentration, the dislocation density is one of the main parameters determining the suitability of material. This is due to the influence of dislocations on the device characteristics and the fact that the grown epitaxial layer inherits its substrate dislocations when GaAs is used as a substrate material. The main method for growing GaAs single crystals is the Czochralski method with liquid melt sealing. The reduction of the dislocation density is a relevant and difficult problem in the growth technology of these single crystals. Some specific features of Czochralski method limit the possibilities of obtaining crystals with a low dislocation density. This is due to the high temperature gradients (necessary to stabilize the growing ingot diameter); they lead to a high level of thermoelastic stress and, therefore, high dislocation density. In addition, the kinks in the curves of axial temperature distribution at the melt–flux and flux–gas interfaces also increase the thermoelastic stress. The complexity of growing GaAs with a low dislocation density is related to the low thermal conductivity and, accordingly, higher temperature gradients during crystal growth, as well as low critical values of dislocation formation stress τ_{cr} [1].

In this context, the questions of nucleation, motion, and interaction of dislocations in GaAs single crystals during crystal growth should be considered in more details.

EXPERIMENTAL

Te-doped GaAs single crystals with a diameter of 40 mm and the ⟨100⟩ orientation were grown by the Czochralski method with liquid sealing of melt by boric anhydride on a GaAs seed crystal with a square cross section, oriented exactly in the [100] direction, and on a seed with an axis deviated by 3°–6° from the [100] direction. Wafers were cut from different ingot regions oriented perpendicular to the growth axis in order to investigate the dislocation structure. The cut samples were ground by M14 and M7 powders, chemically polished in a sulfuric acid etchant, and then etched in a KOH melt at 350°C to reveal dislocation pits. The dislocation structure was analyzed first visually and then using an optical microscope with a magnification of 10–400.

The deviation from the orientation was determined based on the shape of etching pits. The deviation angle γ of the (100) plane from the wafer plane and the deviation angle of the [100] crystallographic direction from the seed axis were determined by the X-ray method using a nonstandard attachment to a GUR-8 goniometer of a DRON-3 diffractometer.

RESULTS AND DISCUSSION

The commercial GaAs single crystals, grown on exactly oriented seeds, have a dislocation density on

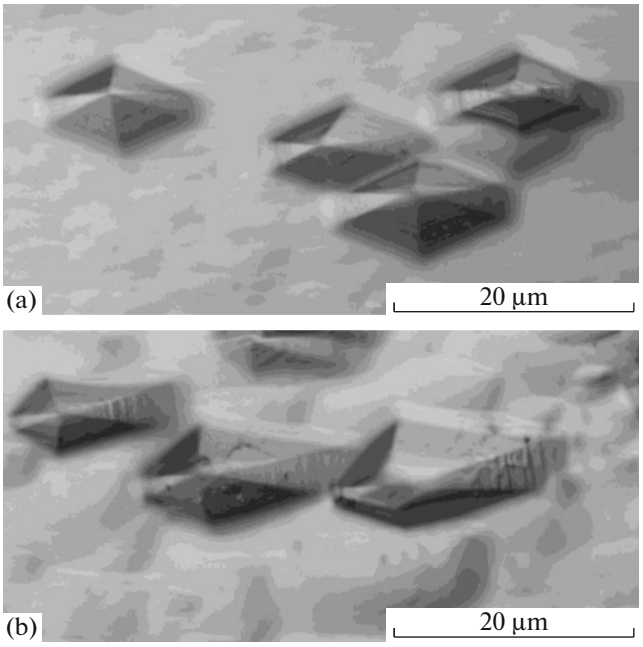

Fig. 1. Shape of dislocation etching pits on the GaAs wafer surface at an angular deviation of the wafer plane from the (100) plane by (a) no more than 1° and (b) more than 3°.

the order of (1–5) × 10^4 cm^{-2}. The dislocation density distribution along the crystal diameter is *W*-shaped, with a maximum dislocation density at the center and near the lateral wafer surface, with the expressed axis of symmetry of the fourth order. Extended low-angle boundaries with a linear dislocation density on the order of 1 × 10^4 cm^{-1} are often observed on the wafer surface.

The deviation of the growth axis from the [100] crystallographic direction was registered based on the etching-pit asymmetry. When the orientation is exact, a dislocation etching pit has a boat-like shape with a sharp vertex at the pit center (Fig. 1a). The long and short pit axes are oriented along the $\langle 01\bar{1}\rangle$ and $\langle 011\rangle$ directions, respectively. This shape of etching pits on the surface of (100)GaAs single crystals is determined by a significant difference in the etch rates for the *A*(111) and *B*(111) planes, which limit an etching pit. Square pits are usually etched on the (100) surface of semiconductor materials (such as Si, Ge, and $A^{III}B^{V}$ compound). At a deviation from exact orientation, the pit vertex shifts, and the pit shape changes (Fig. 1b). The etching pit vertex shifts along the direction of deviation from the $\langle 100\rangle$ axis.

The dislocation density in each region of a grown crystal is the result of superposition of microscopic processes of nucleation, motion, multiplication, and interaction of dislocations, which successively occur at different temperatures in the alternating stress field [1].

Dislocations in single crystals can be formed either during crystallization as a result of capturing inclusions at the crystal–melt interface or due to the presence of efficient nucleation sources in the plasticity region of the growing crystal, where the thermoelastic stress exceeds the critical stress of dislocation nucleation and motion.

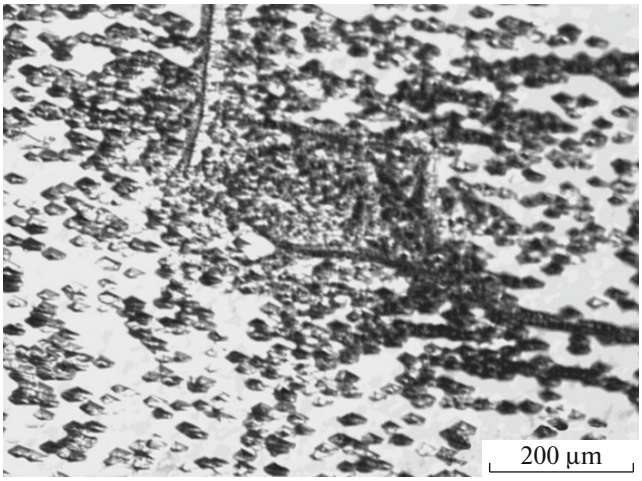

Fig. 2. Dislocation "knot" observed in GaAs single crystals.

The formation of a dislocation "knot" (a typical pattern of which is shown in Fig. 2) in the upper portion of the crystalline boule confirms the fact that the sources of dislocation nucleation are inclusions captured at the crystal–melt interface. The dislocation "knot" is a region with an enhanced dislocation density, surrounded by dense dislocation walls. The linear dislocation density in these walls is about 6 × 10^4 cm^{-1}. In the crystals grown on exactly oriented seeds, this "knot" disappears during growth, leaving a region with a slightly increased dislocation density. This is indicative of the fact that dislocations annihilate rather intensively during crystal growth. However, the pattern of the dislocation structure development during the growth for crystals grown on seeds with angular deviation γ of the seed axis from the [100] direction is significantly different. A typical example of the change in the dislocation structure during crystal growth is shown in Fig. 3.

The crystal dislocation structure evidently changes during crystal growth. There are several "knots" with dense dislocation walls and low-angle boundaries in the close vicinity of the crystal center (the region is indicated by letter *a*) in the wafer cut from the region where the growing-cone base diameter reaches the specified value of 40 mm (cross section *1*). In addition, extended slip bands are observed. The simultaneous occurrence of "knots" and slip bands in the same localized crystal region indicates that dislocations nucleated in the crystal not only near the crystal–melt interface ("knots") but also far from it (slip bands).

The crystal growth is accompanied by not only the change in the configuration of the "knots" containing region but also a shift of this region from the crystal axis to the ingot edge (cross section *2*, region *a*). Fur-

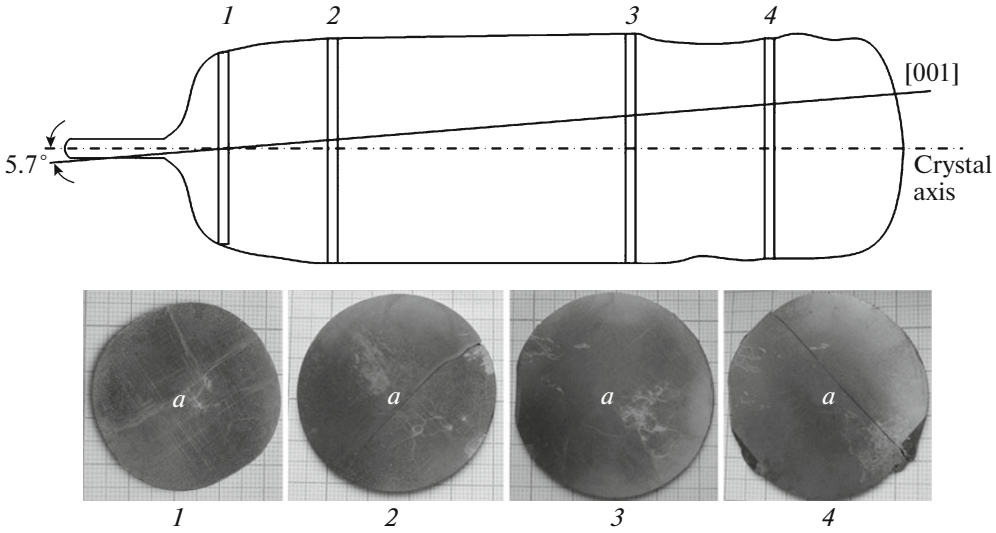

Fig. 3. Schematic of the crystal and macrophotographs of the surfaces of wafers cut along the GaAs crystal axis and corresponding to cross sections *1*, *2*, *3*, and *4*, respectively.

ther crystal growth is accompanied by intense multiplication of dislocations and formation of a network of dislocation subboundaries (cross section *3*, region *a*). A typical pattern of this substructure is shown in Fig. 4.

As the crystal continues to grow, dislocations are intensively multiplied and the region with a cellular substructure undergoes expansion and shift to the lateral crystal surface (cross section *4*, region *a*).

Thus, a difference was revealed in the dislocation multiplication rates for the exactly oriented crystals and the crystals grown on a seed deviated from the [100] direction. A more intensive multiplication of dislocations in the latter is observed in the peripheral region of crystal (from one side).

Several mechanisms of dislocation multiplication have been considered in the literature. The most popular is the Frank–Read mechanism, according to which dislocations are multiplied under stress as a result of bending of a dislocation fixed at two points [2]. In the model discussed in [3], dislocations are multiplied during the motion (i.e., an expanding dislocation loop leaves a "trace" of new dislocations). Haasen [4] proposed a dipole mechanism of dislocation multiplication. According to this model, the newly formed dipoles of dislocations with opposite signs can overcome their attractive force under stress and form a dislocation loop. According to the dipole mechanism, dislocation multiplication occurs on the steps with heights h exceeding the critical value:

$$h \geq Gb/[8\pi(1-\nu)\tau],$$

where G is the shear modulus, b is the magnitude of the Burgers vector of a perfect dislocation, ν is the Poisson ratio, and τ is stress. The Haasen model was experimentally confirmed in [5–7] when studying the processes of high-temperature statistical loading. These issues were considered in detail in [1].

The more intensive dislocation multiplication in GaAs single crystals grown on a seed with angular deviation γ can be understood by considering the influence of the deviation angle γ on the height of macrosteps formed at the crystal–melt interface, which is bent into the melt. These macrosteps arise due to the curvature of the crystal–melt interface. The step bases are oriented in the (100) plane. With an increase in the crystal–melt interface steepness, the linear size of the steps decreases, while their height increases (Fig. 5a).

It can be seen that the macrostep height changes symmetrically along the crystal radius with respect to its axis in the case of exact seed orientation. For a seed with axis deviated by an angle γ, the macrostep height

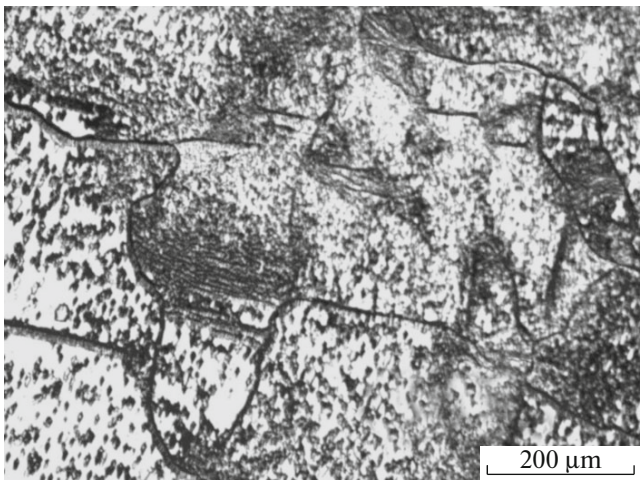

Fig. 4. Dislocation substructure in the GaAs crystal grown on a seed with an axis deviated from the [100] direction by an angle of more than 3°.

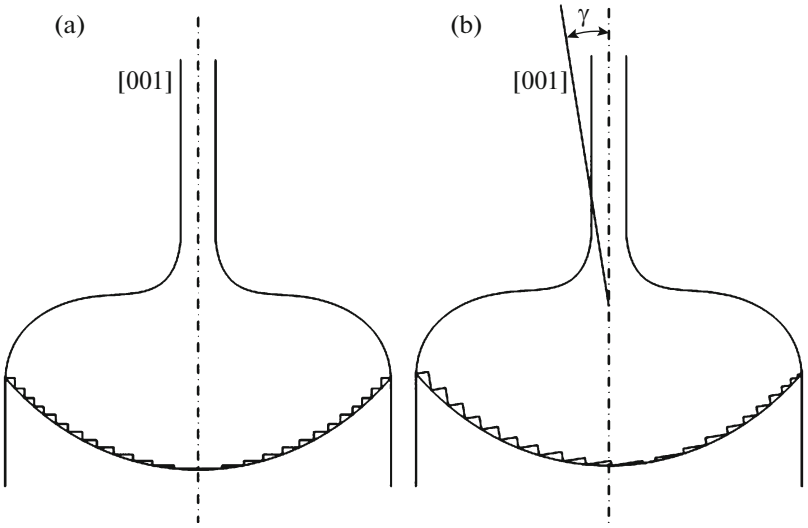

Fig. 5. Schematics of macrosteps at the crystal–melt interface for (a) exactly oriented seeds and (b) seeds deviated by angle γ.

decreases on the right of the crystal axis and increases on the left of it (Fig. 5b). The steps make some angle with the crystal axis. The defect region shifts to the crystal edge (specifically, to the region where the macrosteps are higher) (Fig. 5b).

The dislocation multiplication according to the Haasen mechanism depends on the step height (the process becomes more intensive with an increase in the step height). Indeed, dislocations are multiplied not so intensively when a "knot" is observed near the crystal center (Fig. 2, cross sections *1, 2*). When the dislocation boundaries threading at the crystal–melt interface shift towards higher steps during crystal growth, dislocations are multiplied intensively (Fig. 2, cross sections *3*, *4*). The intensive dislocation multiplication in GaAs single crystals is also related to the high growth temperature (1240°C), which provides a high dislocation mobility.

Three mechanisms of dislocation substructure formation were considered in [8]. The first mechanism corresponds to polygonization, which occurs at dislocation slip as a result of elastic interaction of dislocations of the same sign in parallel slip bands. The second mechanism is the substructure formation as a result of transverse slip. The third (polygonization) mechanism is based on the dislocation creep, which occurs at high temperatures and high concentrations of intrinsic point defects.

The presence of a volatile component (arsenic) in GaAs and the wide homogeneity range provide conditions for accumulation of intrinsic point defects in a high concentration in this material. In turn, this property ensures intensive dislocation creep and, consequently, intensive formation of dislocation walls. The linear dislocation density changes from 1×10^4 cm^{-1} in low-angle boundaries to 6×10^4 cm^{-1} in subboundaries.

Dislocation walls, leaving the front crystallization are inherited by the growing crystal. On subgranular happens peristerition of dislocations, which can lead to the disappearance dense dislocation walls.

CONCLUSIONS

The significant influence of the seed-axis deviation from the [100] direction on the formation of the dislocation structure of Czochralski-grown GaAs single crystals was revealed. The deviation from orientation was found to increase the intensity of dislocation multiplication and form a block structure with a high density of dislocation walls. The linear dislocation density turned out to change from 1×10^4 cm^{-1} in low-angle boundaries to 6×10^4 cm^{-1} in subboundaries.

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