

EFFECT OF DOPING ON FORMATION OF DISLOCATION STRUCTURE IN SEMICONDUCTOR CRYSTALS

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Numerous experimental data on the effects of dopants on the properties of dislocations and on the formation of dislocation structure in semiconductor single crystals grown from the melt are analyzed on the basis of model concepts derived from the results obtained in recent years (primarily by the authors of the present communication). Effects of dopants on generation, motion, and multiplication of dislocations are discussed in the high temperature range ($T \geq 0.7T_{\text{melt}}$), for the stress level typical for crystal growth $\tau/G \leq (10^{-5} - 10^{-4})$, dislocation density not exceeding $10^4 - 10^5 \text{ cm}^{-2}$, and dopant concentrations far from the solubility limit. Changes in the dislocation structure of crystals caused by the effects of dopants on the generation, motion, and multiplication of dislocations are discussed. It is demonstrated that the changes caused by doping in the dislocation structure of semiconductor crystals can be explained on the basis of the relationship obtained between the doping impurities and the dynamic properties of dislocations.

1. Introduction

In most cases the doping which is a traditional and most effective method of controlling electrophysical properties of semiconductors, also affects the perfection of the crystal structure. The problem of the effects of dopants on the properties of dislocations and on the formation of the dislocation structure of semiconductor single crystals grown from the melt has specific features. This specificity appears first of all because the microscopic processes of generation, motion, multiplication, and interaction of dislocations proceed at high temperatures ($T \geq 0.7T_{\text{melt}}$) and at stresses typical for crystal growth $\tau \leq (10^{-5} - 10^{-4})G$ (where τ is normalized shear stress and G is shear modulus) with a dislocation density usually not exceeding $10^4 - 10^5 \text{ cm}^{-2}$. As a result, the information extracted from numerous experiments on the effects of doping on dislocation mobility, and on the relations found from the macroscopic plastic strain in semiconductors at relatively low temperatures (below $0.7T_{\text{melt}}$), cannot be used for the analysis of the peculiarities of the formation of dislocation structures in doped crystals. Moreover, when we discuss formation of a dislocation structure in the course of crystal growth, we have to take into account the

non-equilibrium state of the ensemble of both intrinsic and extrinsic point defects, which itself depends on the specific mode of growth.

Inhomogeneity in the distribution of impurity is directly introduced in the course of crystallization of highly doped crystals from the melt (impurity substructures and second phase precipitates, facet-effect inhomogeneities). This inhomogeneity is known to constitute a source of additional disturbance of structural perfection. This aspect of the effect of doping on the dislocation structure of semiconductor crystals has been discussed in the literature in sufficient detail (see, for example, ref. [1]) and thus will not be touched upon in the present review.

Numerous experiments have established that doping may cause a substantial change in the concentration not only of extrinsic but also of the intrinsic point defects of the semiconductor lattice. Besides, the mechanisms of the additional generation of point defects in doped semiconductor crystals may be quite different. The interaction of intrinsic point defects among themselves, as well as with the atoms of doping or residual impurities, leads to the formation of complexes which are particularly diverse in semiconductor compounds [2, 3]. The individual nature of the doping elements is especially well

pronounced in the complex-formation processes. Consequently, doping produces changes in the ensemble of point defects (both in their number and in the types of defects); these changes are additionally modified by the growth conditions (ingot cooling rate, departures from stoichiometry in the case of compounds, etc.).

2. Effect of doping on the formation of the microdefects

From the standpoint of formation of the dislocation structure in crystals, the processes among the point defects must be treated as primary processes because they initiate the formation of microdefects in the course of crystal cooling. Microscopic defects may act as centers for heterogeneous generation of dislocations by stresses. This generation of macroscopically extended dislocations from microscopic dislocation loops was observed, for example, in the growth of initially dislocation-free silicon single crystals [4]. The microscopic defects may be either microscopic segregations or microscopic partial or perfect dislocation loops; they are generated mostly by heterogeneous mechanisms. And although the nature of the microdefect generation centers is mostly unclear, their latent presence in a growing crystal manifests itself by a specific distribution of microscopic defects found after various treatment procedures, including the cooling stage in the growth of crystals (for instance, swirl defects in silicon). The formation and growth of microscopic defects results from diffusion and condensation of non-equilibrium point defects (intrinsic or extrinsic point defects, depending on the nature of the microscopic defect) in the crystal. Hence, microdefects are observed in crystals free from dislocations which would play the role of effective sinks for point defects.

The effects of doping on the nature and density of microdefects in moderately doped silicon crystals (impurity concentration below 10^{18} cm^{-3}) is considerably masked by the effects of growth conditions. The mechanism by which dopants affect perfection remains therefore unclear [5].

However, in silicon and germanium single crystals heavily doped with donor impurity [6, 7], and in crystals of $A^{\text{III}}B^{\text{V}}$ compounds, an increase in the doping level brings about an increase in the concentration of microdefects; these defects are microscopic loops of partial and perfect dislocations of the interstitial type [8, 9]. Thus, although the problem is still unresolved to identify the atoms (intrinsic or extrinsic) which form these microdefects, it can be considered being proved that their formation in heavily doped crystals is related to a large extent to the decomposition of solid solutions both of doping impurities and (in the case of compounds) of excessive intrinsic components. The pattern of distribution of microscopic defects in dislocation-free $A^{\text{III}}B^{\text{V}}$ single crystals is often found to be swirl-shaped as in the case of Si. Since in many cases microdefects correspond to microscopic dislocation loops, we are justified in classifying crystals with micro-defects as dislocation-free crystals only in the sense of absence of macroscopically extended dislocations.

3. Effect of doping on the generation of dislocations

The secondary processes determining the formation of the dislocation structure in growing crystals are the generation of stable dislocation loops in the dislocation-free matrix and their multiplication. The formation of macroscopically extended dislocations in semiconductor crystals at high temperatures (close to the melting point) takes place at stresses (10^{-5} – 10^{-4}) G , approximately 10 times lower than the upper yield stress. Small values of these critical stresses determined by static load experiments are an argument in favor of a heterogeneous mechanism of dislocation generation [1, 10]. Studies conducted at a number of elementary semiconductors and semiconductor compounds demonstrated (see review paper [11]) that the critical stress of dislocation generation τ_{cr} is a well-defined characteristic of a material, and depends on temperature (fig. 1). It is therefore highly effective to use the value of τ_{cr} as a

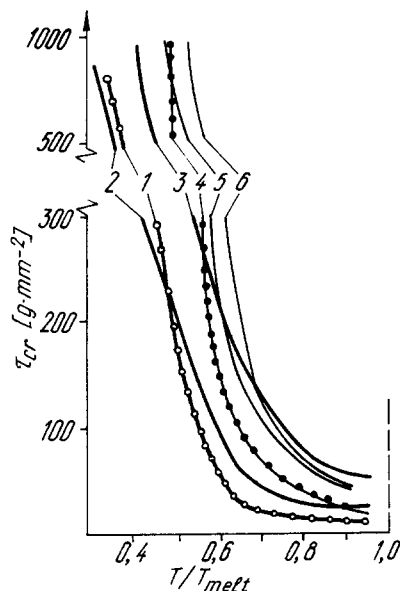


Fig. 1. Critical stress of generation of dislocations, τ_{cr} , as a function of temperature in Ge and GaAs crystals: (1) GaAs (undoped); (2) GaAs:Zn ($p = 7 \times 10^{19} \text{ cm}^{-3}$); (3) GaAs:Te ($n = 2 \times 10^{18} \text{ cm}^{-3}$); (4) Ge (undoped); (5) Ge:P ($n = 2 \times 10^{19} \text{ cm}^{-3}$); (6) Ge:Ga ($p = 3 \times 10^{19} \text{ cm}^{-3}$).

criterion of the limiting admissible level of stress when analysing thermal conditions of growth of perfect semiconductor crystals by taking into account specific properties of the material [12]. It is wrong to use the value of the upper yield stress as this critical stress τ_{cr} [10, 11]. Experiments carried out at moderate temperatures ($T \leq 0.7T_{\text{melt}}$) with Ge, Si, GaAs, and InSb have demonstrated that, depending on the electric behavior of the dopant in the crystal, the dopants may increase or reduce the dislocation mobility and, correspondingly, reduce or increase the macroscopic yield point. According to the existing theoretical concepts, this effect appears because doping shifts the Fermi level and therefore alters the frequency of generation of the thermal double kinks and the propagation rate of the kinks along the dislocation (for example, [13]).

Our studies have demonstrated [14, 15] that the effect of dopants on the high-temperature plasticity in semiconductors (at $T \geq 0.7T_{\text{melt}}$) is essentially different. Regardless of the electric behavior in the crystal, in the high-temperature

range all dopants (including the electrically neutral ones) produce a qualitatively identical effect: they increase τ_{cr} and decrease the intensity of a multiplication of dislocations. Quantitatively, this strengthening depends substantially on concentration and nature of the dopant. As an example, fig. 2 plots τ_{cr} in Ge at $T = 900^\circ\text{C}$ as a function of dopant concentration.

This effect of dopants appears because high temperature and relatively low stress are favorable kinetic conditions for the formation of a stable impurity atmosphere surrounding moving dislocations. Estimates taking into account elastic interaction [14, 15] show that in the case of thermal stress in real crystals grown by the Czochralski techniques ($10\text{--}10^2 \text{ g/mm}^2$), most dopants form stable atmospheres on dislocations in Ge at temperatures $T \geq 800^\circ\text{C}$ and in GaAs at $T \geq 800\text{--}1000^\circ\text{C}$, depending on the impurity. Therefore, dislocation mobility is limited by dragging exerted by the impurity atmospheres. As the prevailing effect in these conditions is the elastic interaction of impurity atoms with dislocations, the efficiency of dragging is mostly determined by the difference in tetrahedral radii of the impurity and matrix atoms, and also by the diffusion mobility of the impurity; the dragging efficiency is essentially independent of the electric nature of the impurity. Specific effects of a number of impurities on the value of τ_{cr} in germanium (fig. 2) and an essential difference in the effects of Te and Zn on τ_{cr} in GaAs [15] are

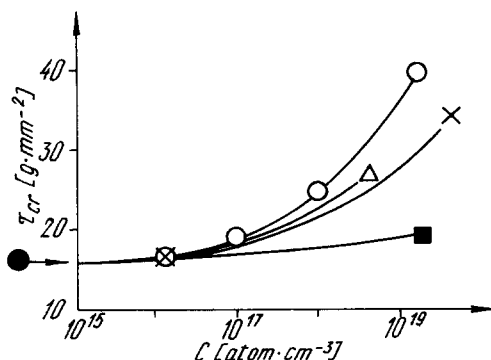


Fig. 2. Critical stress of generation of dislocations, τ_{cr} , in Ge crystals, as a function of dopant concentration, at 900°C : (Δ) Sb, (\circ) P, (\blacksquare) As, (\times) Ga, (\bullet) undoped.

successfully interpreted in terms of the above concepts.

Our initial assumption is that changes in the dislocation mobility caused by doping produce appropriate changes not only in the intensity of dislocation multiplication (it is proportional to the dislocation velocity [16]), but also in the critical stress of generation of stable dislocation loops. The difference between the dynamic and electrophysical properties of "grown-in" dislocations formed in the course of growth at high temperatures, on the one hand, and of "fresh" dislocations, that are introduced by plastic deformation at $T \leq 0.5T_{\text{melt}}$, on the other hand, is determined precisely by the difference in the density and composition of point defect atmospheres (both extrinsic and intrinsic point defects).

Fig. 3 plots the fraction of mobile (i.e. displaced by the fixed load) dislocations in germanium crystals doped at $T = 900$ and 400°C to different concentrations, as a function of stress (displaced dislocations were determined by the double-etching technique). We find that at concentrations of $\sim 10^{19}\text{ cm}^{-3}$, "grown-in" dislocations remain mostly fixed even at stresses at which the mobile "fresh" dislocations start multiplying intensively. This fixation of "grown-in" dislocations is enhanced if precipitates have

formed on them previously; an effect that is typical for highly doped crystals. At times these precipitates are revealed by specific features in the morphology of dislocation etch pits [17]. As the tendency to form precipitates along the dislocation is weakened as the dislocation formation temperature diminishes, the presence of such precipitates can be used to estimate the temperature range of formation of "grown-in" dislocations.

4. The dislocation structure of doped single crystals

The above-described effect of dopants on generation, propagation, and multiplication of dislocations at high temperatures determines the corresponding changes in the dislocation structure of crystals in the course of doping because this structure is mostly formed (see ref. [18]) in a relatively narrow region of the growing ingot in the vicinity of the crystallization interface. An analysis of typical features of the dislocation structures in doped semiconductor single crystals and $A^{\text{III}}B^{\text{V}}$ single crystals enables us to draw a number of general-type conclusions on the effect of doping. Among them, the following are considered as the most important.

4.1. The mean density of dislocations

As the level of doping increases, the mean density of macroscopically extended dislocations, N_D , is observed to decrease. This effect is a direct result of the above-discussed effects of dopants on the critical stress of dislocation generation and on the intensity of multiplication of dislocations. It has been shown previously (see review paper [1]) that doping to high concentration often facilitates growth of dislocation-free crystals of Ge, Si, GaAs. Fig. 4 plots N_D as a function of concentrations of a number of dopants (Te, Sn, Zn, In) in GaAs crystals grown by the Czochralski technique. The dislocation density begins to be reduced at certain concentrations. This lower bound of the doping concentration corresponds to the formation of

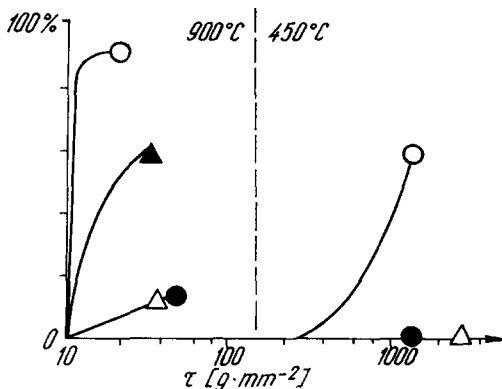


Fig. 3. The fraction of mobile "grown-in" dislocations in Ge as a function of the normalized shear stress τ , under the conditions of static loading: (○) undoped Ge; (▲) Ge:P ($n \approx 1 \times 10^{18}\text{ cm}^{-3}$); (△) Ge:P ($n \approx 2 \times 10^{19}\text{ cm}^{-3}$); (●) Ge:Ga ($p \approx 3 \times 10^{19}\text{ cm}^{-3}$); positions of symbols on the plot correspond to the critical stress for generation of dislocations.

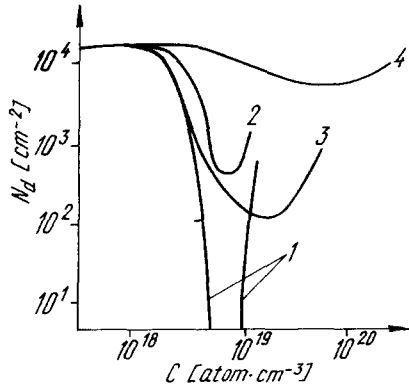


Fig. 4. Mean density of "grown-in" dislocations in GaAs single crystals (20–25 mm in diameter) grown by the Czochralski LEC technique, as a function of dopant concentration: (1) Te, (2) Sn, (3) In, (4) Zn.

sufficiently powerful impurity atmospheres on dislocations (the threshold on the strength of interaction between impurity atoms and the dislocation). However, at very high density of impurities, the mean dislocation density in crystals begins to grow again, owing to the above-mentioned effects caused by the formation in crystals of the specific impurity-based inhomogeneities. Hence, an optimum range of dopant concentration can be ascribed to each impurity; in this range the impurity has maximum efficiency for reducing N_D .

Doping with Te diminishes the dislocation density in GaAs much more effectively than doping with Zn (fig. 4). This fact is directly related to the effect of doping on τ_{cr} [11]. This difference in the behavior of Te and Zn in GaAs can be understood on the basis of the above-presented model concepts on the effect of dopants on the mobility of dislocations at high temperatures. The energy of elastic interaction of impurity atoms with dislocations, U_{int} , is proportional to the relative change in the atomic volume

$$\epsilon = (r^3 - r_0^3)/r_0^3,$$

where r_0 and r are tetrahedral radii of the solute and interstitial impurity atoms, respectively. According to refs. [14, 15], the efficiency of dislocation blocking by atmospheres is described by

a factor U_{int}^2/D (where D is the impurity diffusion coefficient); hence, the quantity ϵ^2/D is more convenient for comparative evaluation of the efficiency of different doping species. In GaAs and at $T = 1100^\circ\text{C}$, this quantity is $8 \times 10^{10} \text{ s/cm}^2$ for Te and $1.5 \times 10^7 \text{ s/cm}^2$ for Zn. From the point of view of dislocation density reduction, doping of GaAs with Sn is only slightly less effective than doping with Te (see fig. 4). This is in agreement with the quantity $\epsilon^2/D \approx 2 \times 10^{10} \text{ s/cm}^2$ for Sn-doped GaAs. We should note also that doping of GaAs with electrically neutral (isovalent) impurities, such as In, produces a considerable reduction of N_D . This result confirms the previously drawn conclusion that the effect of dopants on the high-temperature plasticity of semiconductor crystals is practically independent of their electric behavior in the crystal. There are no data in the literature on the rate of diffusion of In in GaAs. However, the relative change of the atomic volume ϵ for In is comparable to the corresponding values of ϵ for Te and Sn in GaAs. Hence, the behavior of In is also understandable within the framework of the model concepts described. Similar effects of a substantial decrease of N_D in GaAs are observed for doping with an isovalent impurity, Sb, with one of group VI, S and, also, with group IV impurities, Ge and Si.

A sharp reduction of N_D in the InP crystals was observed in the case of doping with Zn, S, and Te [19]. The dislocation density N_D was also predictably decreased by doping GaAs and InAs crystals with a number of impurities.

As a result, doping with high concentrations of certain impurities makes it possible to grow nearly dislocation-free crystals without resorting to special technological procedures, for example the thin-neck formation. This is especially significant for growth of single crystals of those semiconductors in which high plasticity of the matrix makes it very difficult to grow crystals with low dislocation density (this is true, first of all, in the case of semiconductor compound crystals). For example, it becomes possible to grow heavily doped dislocation-free GaAs [10] and InP [21] single crystals by the Czochralski LEC technique. It must be noted that micro-

scopic defects formed in highly doped crystals of $A^{III}B^V$ compounds do not act, under the usual growth conditions, as sources of macroscopic dislocations, that is, they do not prevent the growth of a dislocation-free crystal. This is so because such microdefects are mostly produced by decomposition of the supersaturated solid solution at temperatures $T \sim (0.6-0.8)T_{\text{melt}}$. Under these conditions the values of τ_{cr} are sufficiently large ($\sim 10^2 \text{ g/mm}^2$), both because of doping and as a result of strong dependence of τ_{cr} on temperature. As a result, new dislocations in practice cannot be generated in this temperature range in the course of crystal growth.

4.2. Macroscopic distribution of dislocations

When the concentration of the dopant is high (the crystal is effectively strengthened) and the level of thermoelastic stress is also sufficiently high, the non-uniformity of the macroscopic distribution of dislocations over the ingot cross section is enhanced. As an example, fig. 5 represents the macroscopic distribution of N_D in a GaAs crystal highly doped with Te, and the corresponding radial distribution of thermoelastic stress in the ingot, in the process of growth and at a short distance from the crystallization interface. The predominant part of the ingot cross

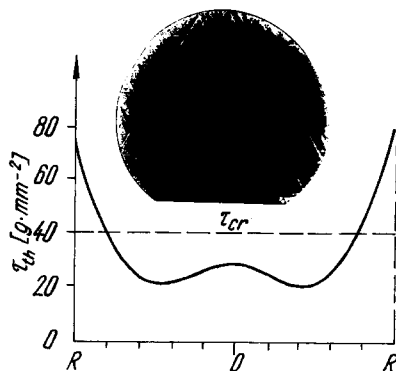


Fig. 5. Macroscopic distribution of "grown-in" dislocations over the cross section (III) of a Te-doped GaAs single crystal ($n \approx 3 \times 10^{18} \text{ cm}^{-3}$, diam. 30 mm) grown by the Czochralski technique, and the distribution of thermoelastic stress along the ingot diameter, in the course of growth (dashed line gives the level of critical stress for generation of dislocations).

section is practically dislocation-free, and the dislocation density reaches $\sim 1 \times 10^4 \text{ cm}^{-2}$ only in a narrow peripheral area where the thermoelastic stress exceeds τ_{cr} . Dislocation density in undoped GaAs crystals grown under similar thermal conditions changes over the crystal cross section by a factor of 3 to 5, and the mean dislocation density is approximately $2 \times 10^4 \text{ cm}^{-2}$. This effect occurs both because of a sharp increase in τ_{cr} due to doping, and because of the blocking by impurity atmospheres which hinder the redistribution of dislocations from the peripheral regions to the central area.

4.3. The microscopic distribution and geometric configuration of dislocations

As the dopant concentration is increased, typical features are observed in the microscopic distribution and in the geometric configuration of dislocations. These effects are caused by the interaction of dislocations with point defects. Dragging and blocking of dislocations by point-defect atmospheres and by precipitates hinders their displacement and, first of all, their slip motions. This suppresses the tendency to "spreading" of the primary slip bands, to the formation of a cellular distribution of dislocations and stable dislocation walls (in the form of extended small-angle boundaries) [22]. "Sharply defined" slip bands (see fig. 5) against a background of a low dislocation density are characteristic of highly doped crystals. In addition, blocking of dislocations concerns their preferred orientation along $\langle 110 \rangle$, while in undoped crystals dislocations are, as a rule, highly bent (see fig. 6).

In the high-temperature range, in which mobility of point defects is comparatively high, effects due to creep of dislocations may be observed. On a macroscopic scale, climb results in the formation of typical polygonal walls [17]. On a microscopic scale, climb disturbs "smoothness" typical for dislocations in undoped crystals: steps, very often of quite complicated shape, are formed on dislocations, and in some cases dislocations undergo helicoidal twisting [18].

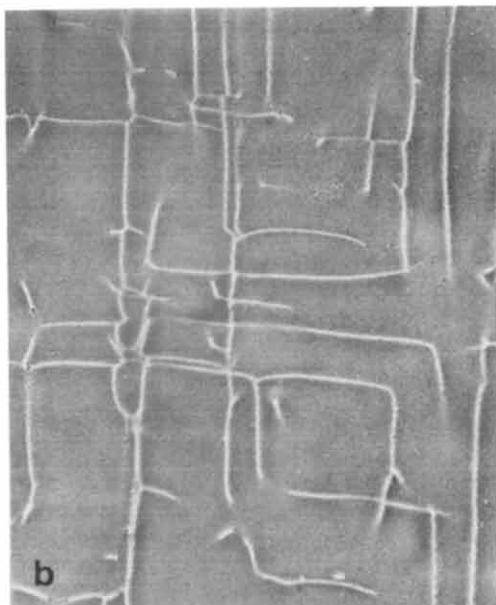
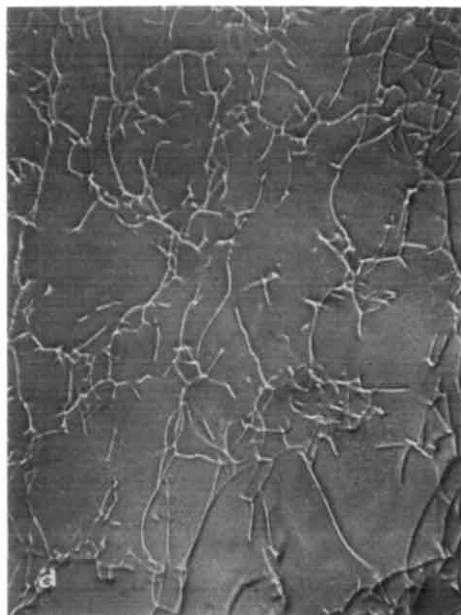


Fig. 6. "Grown-in" dislocations in GaAs single crystals revealed by the "projective" etching of (100) surface: (a) undoped crystals, (b) In-doped, 2×10^{19} atoms cm^{-3} ; magnification $\times 100$.

Note that, in addition to the temperature range of formation and blocking of dislocations, another significant factor is the state of the ensemble of point defects related to the specific nature of the doping species. For example, a high density of helicoidal dislocations is observed in Te-doped GaAs crystals with Te concentration above $2 \times 10^{18} \text{ cm}^{-3}$ but not in Sn-doped GaAs crystals.

5. Conclusion

The results given above demonstrate that in most cases the effects of dopants on the dislocation structure of semiconductor crystals can be interpreted by using the model concepts described. This approach to an analysis of phenomena caused by doping promises a possibility of effective control of structure and properties of crystals, by selecting appropriate (in combination, if required) dopants, taking into account their individual characteristics. Thus, it becomes possible to change independently the structure and the electrical properties of crystals, and also to grow low-dislocation-density and dislocation-free semiconductor crystals without microdefects.

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