

# Increasing of dislocation mobility by heat treatment of deformed pure and doped InP crystals

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## Abstract

The influence of dopant impurity type on the dislocation mobility in InP crystals is investigated. It is shown that the dislocation mobility ( $\gamma$ ,  $\gamma_s$ ) under action of a concentrated load depends on impurity type and deformation temperature. The critical temperature ( $T_{cr}$ ) of dislocation activation for pure and iron doped InP is close to 600 K. The donor impurity (Sn) displaces  $T_{cr}$  towards low temperatures ( $T \approx 550$  K) and raises the  $\gamma$  and  $\gamma_s$  parameters. Acceptor impurity leads to increase of  $T_{cr}$  ( $> 800$  K) and decreases the  $\gamma$  and  $\gamma_s$  values. The nature of this phenomenon consists in change of the lattice parameter ( $a$ ) of the InP crystals —  $a$  is increased by doping with donor impurity and decreased by acceptor doping. The deformation (dislocation and twinning) mechanisms are concerned with the size of lattice parameter as well. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* InP; Impurities; Concentrated load; Heat treatment; Dislocation mobility; Deformation mechanism

## 1. Introduction

Dislocation mobility is an important characteristic of crystalline solids, which determines the material behavior under action of mechanical load [1]. The relaxation process in crystals after unloading and its time dependence under variation of exploitation temperature are governed by the mobility of dislocations.

If the dislocation mobility is high, the deformation of a crystal is defined almost completely by the dislocation mechanism. In cases when the dislocation mobility is hindered, some other processes become decisive, such as dislocation-interstitial or twinning mechanisms, the mechanism of phase transition, etc. [1–5].

The specific deformation mechanism realized in the material under action of external forces depends on resource of plasticity, the main criterion of which is the dislocation mobility. The dislocation mobility itself is not a constant, representing a function of many factors, such as crystal structure, impurity content, deformation temperature, etc. The investigation of interconnection

between the dislocation mobility and crystal parameters is an important problem for both the physics of strength and plasticity and the technical application.

In this context, the purpose of the present work is to study the dislocation mobility in InP crystals in dependence on the type of dopant impurity and temperature change, and to investigate the influence of these two factors on the mechanism of plastic deformation under action of a concentrated load.

## 2. Experimental procedure

Pure and doped InP single crystals were grown by the Czochralski technique. The elements Fe, Sn, Zn and ZnO complex were used as impurities. The density ( $N_D$ ) and distribution of as-grown dislocations were evaluated over the crystal ingot sections. The distribution of dislocations along the ingot diameter showed that in most cases,  $N_D$  was less at the ingot center than at the periphery. To obtain the comparable results, the samples were selected to have an approximately equal ( $N_D \approx (2-3) 10^4 \text{ cm}^{-2}$ ) density of as-grown dislocations. The brief characteristics of the investigated crystals are given in Table 1.

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Table 1  
Characteristic features of the samples

Crystal	$N_D$ (cm <sup>-2</sup> )	$n$ (cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> V s <sup>-1</sup> )	Conductivity type
InP, pure	$(2-3) \times 10^4$	$(1.9-4.1) \times 10^{16}$	3500–3900	n
InP:Sn	$(1-2) \times 10^4$	$(9.2-9.8) \times 10^{17}$	2080	n
InP:Fe	$(2-5) \times 10^4$	$2.07 \times 10^8-2.67 \times 10^9$	325–530	i
InP:Zn	$(2-3) \times 10^4$	$6.0 \times 10^{17}-2.0 \times 10^{18}$	50–80	p
InP:ZnO	$5 \times 10^3-1.5 \times 10^4$	$7.0 \times 10^{17}-5.6 \times 10^{18}$	46–90	p

The measurements were carried out at the (001) and (111) crystal faces, which, after preparation, were subjected to chemical polishing for elimination of the damaged surface layer. Deformation (microindentation and scratch generation) was performed with aid of a PMT-3 microhardness tester. The diamond pyramid with a square base (Vickers' pyramid) served as an indenter. The load  $P$  on the indenter varied in the limits 0.4–1.0 N (for microindentation) and 0.1–0.2 N (for the sclerometric method). The indentation ( $H$ ) and sclerometric ( $H_s$ ) microhardness were calculated by standard formulae [1].

The microhardness measurements were performed for two orientations of the indenter on each of the investigated planes, the diagonals  $d$  of the indentation pattern were parallel to the directions  $\langle 100 \rangle$  and  $\langle 110 \rangle$  for the (001) plane; and  $\langle 11\bar{2} \rangle$  and  $\langle \bar{1}\bar{1}2 \rangle$  for the (111) plane. At sclerometric testing the indenter moved along those crystallographic directions as well. The crystal deformation was made at room temperature ( $T_{\text{def}} = 293$  K). After that, the crystals were subjected to annealing at  $T_{\text{an}} = 600$  and 800 K to make fresh dislocations in the deformed zones more active. For comparison, some indentations and scratches were made at high temperature (450 and 600 K). The dislocation structures arising near indentations and scratches were studied by the selective etching technique. The solution of CrO<sub>3</sub> (0.01 N) in HCl (30 ml) was taken as an etcher. The examination of the deformed zones was made using optical and scanning electron microscopy with aid of the Amplival, Neophot and Tesla-BS340 microscopes. The parameters  $\gamma = l/d$  and  $\gamma_s = L/b$  were accepted as dislocation mobility characteristics. Here  $d$  and  $b$  are, the indentation diameter and the scratch width, respectively;  $l$  and  $L$  are the maximal removal of dislocations from indentations and scratches.

### 3. Experimental results

It was demonstrated by transmission electron microscopy [6–8] that dislocations in the semiconductor crystals can appear around indentations and scratches even at room temperature. However, chemical etching did not reveal the dislocations at the deformed places in

all of the investigated crystals deformed at  $T = 293$  K. This fact indicates rather low mobility of dislocations, which are concentrated in immediate proximity of the indentations and scratches and cannot be detected by chemical etching.

If the crystals deformed at room temperature are subjected to annealing at  $T = 600$  K for 2 h, then the deformed zones, mainly composed of dislocations, will be revealed near the indentations and scratches. The appearance of dislocation zones (in some cases, the twinning ones) after thermal treatment is conditioned by the increase of dislocation mobility and activation of the dislocations that have been formed under concentrated load action at 293 K.

The picture of dislocation structures around indentations and scratches correspond on the whole to the symmetry of the deformed plane and are in agreement with data in the literature [1,4,7]. Some dislocation rosettes, which appear on the (001) and (111) planes of doped InP crystals, are shown in Fig. 1. The typical dislocation zones in the neighborhood of scratches generated on the (001) plane of pure and doped (by Sn, Fe and Zn) InP crystals are presented in Fig. 2. The dislocation structures on the InP (pure), InP:Sn and

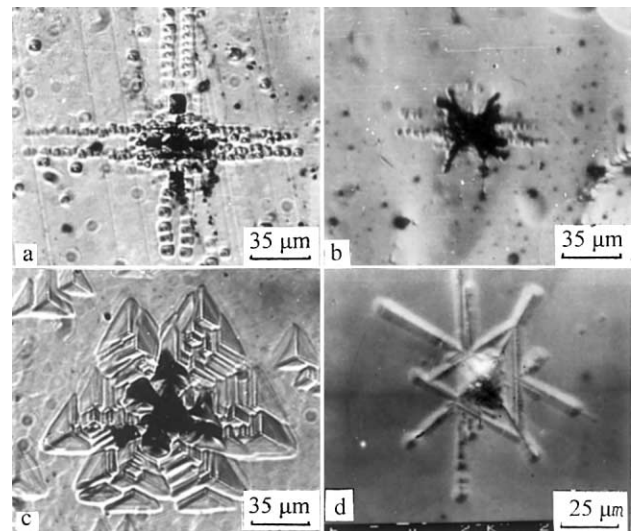


Fig. 1. Dislocation rosettes arising around indentations. a, b (001) face, InP:Sn (a); InP:Zn, (b); c, d (111) face, InP:ZnO (c); InP:Zn (d).  $T_{\text{def}} = 293$  K;  $T_{\text{an}}$ K, a, c, d, 600; b, 800.

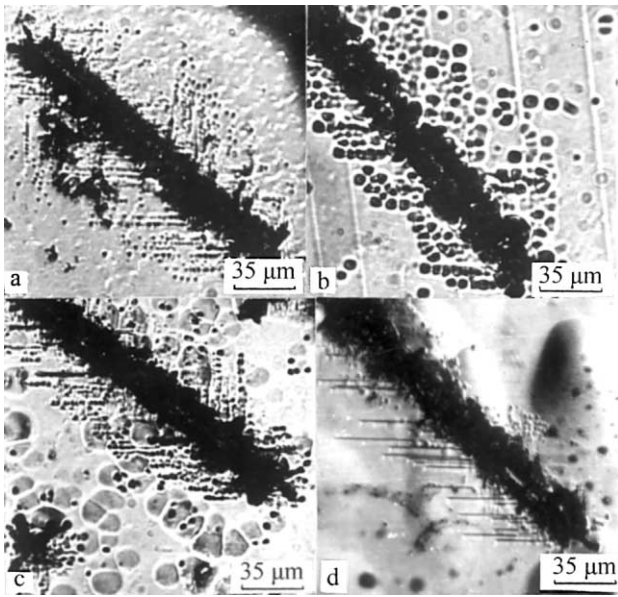


Fig. 2. The deformation zones of scratches generated along  $\langle 100 \rangle$ , face (001).  $T_{\text{def}} = 293$  K,  $T_{\text{an}} = 600$  K (a, b, c); 800 K (d). Crystals, a, InP, pure; b, InP:Sn; c, InP:Fe; d, InP:Zn.

InP:Fe crystals have been revealed after annealing at 600 K (Fig. 2a–c). Heat treatments at temperatures up to 800 K are needed to activate the dislocations in the InP:Zn crystals (Fig. 2b).

It is interesting to mention that size and structure of dislocation zones depend on the impurity type (Figs. 1 and 2). The zones with a little bit chaotic distribution of dislocations are characteristic for the InP crystals doped by donor impurity (Sn), that indicates the development of slip processes in the cross planes (Fig. 2b). The cross slip becomes retarded in pure and Fe doped crystals. As a result, clear dislocation rows and a few twins have been observed (Fig. 2a and c). In the InP crystals doped by acceptor impurity (Zn), the dislocations are located around the scratches. Besides, the well-defined twin rows can be seen in Fig. 2d as well.

The results regarding the dislocation mobility in the neighborhood of the indentations and scratches for  $d \parallel \langle 100 \rangle$  and  $d \parallel \langle 11\bar{2} \rangle$  orientations of the indenter are presented in Table 2. Similar data were obtained for two other orientations,  $d \parallel \langle 110 \rangle$  and  $d \parallel \langle \bar{1}\bar{1}2 \rangle$ . The quantitative estimation have shown that higher dislocation mobility is characteristic for crystals doped by Sn. Doping by the iron impurity in InP crystals reduces, approximately, twice the  $\gamma$  and  $\gamma_s$  value. The greatest hardening was reached in InP crystals with Zn impurity and, accordingly, this was accompanied by the greatest reduction of  $\gamma$  and  $\gamma_s$ .

However, as it follows from Table 2, the addition of some amount of oxygen to InP alongside with zinc results in essential increase of dislocation mobility. While the value of dislocation mobility is 0.5 for the InP:Zn crystals, it grows up to 3.5–4.0 for InP:ZnO.

Table 2

Parameters of dislocation mobility on the (001) ( $d \parallel \langle 100 \rangle$ ) and (111) ( $d \parallel \langle 11\bar{2} \rangle$ ) planes of pure and doped InP crystals at indentation ( $\gamma$ ) and scratch ( $\gamma_s$ ) testing<sup>a</sup>

Investigated plane and deformation direction	Crystal	$\gamma$	$\gamma_s$	$H$ (Mpa)
(001) $\langle 100 \rangle$	InP, pure	4.0	2.0	360
	InP:Sn	5.0	2.0	368
	InP:Fe	2.0	1.8	370
	InP:Zn	0.5	0.5	390
(111) $\langle 11\bar{2} \rangle$	InP, pure	–	5.0	330
	InP:Zn	0.5	0.5	360
	InP:ZnO	3.5	4.0	350

<sup>a</sup>  $T_{\text{def}} = 293$  K;  $T_{\text{an}} = 600$  K.

The increase of  $\gamma_s$  in InP:ZnO is illustrated in Fig. 3a, where the dislocation zones can be seen around the scratches generated on the (111) plane along  $\langle 11\bar{2} \rangle$  at room temperature and subjected to annealing at 600 K (2 h). For the InP:Zn crystals, a great part of the deformed zone around the scratches obtained at the same conditions has twinning structure. The dislocations can be observed only in close proximity to the scratch (Fig. 3b).

The presented results show the following important regularity. A different mechanism, namely, the twinning one, is involved into deformation process when the

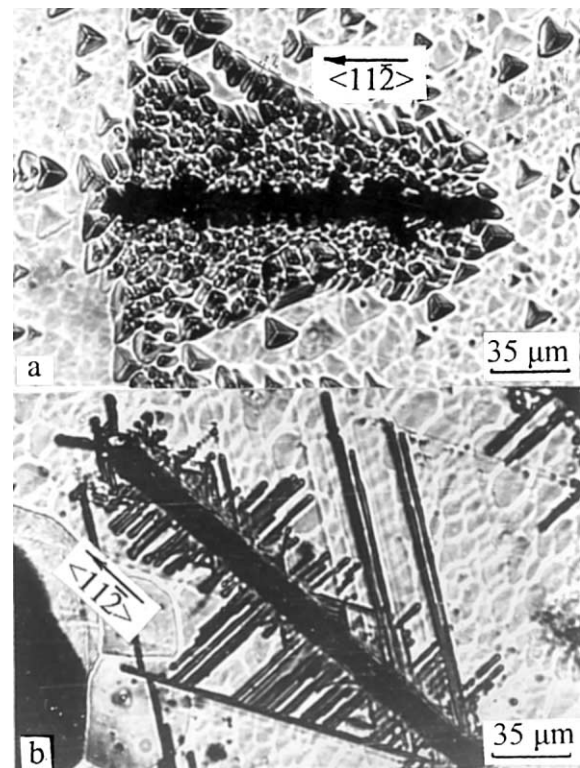


Fig. 3. Deformation zones of scratches generated along  $\langle 11\bar{2} \rangle$  direction, the surface (111).  $T_{\text{def}} = 293$  K;  $T_{\text{an}} = 600$  K. Crystals, a, InP:ZnO; b, InP:Zn.

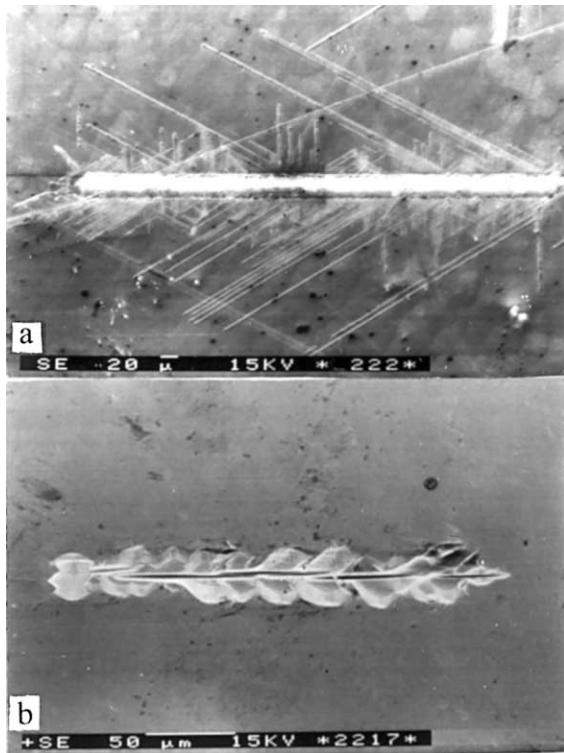


Fig. 4. Deformation zones of scratch generated on InP:Zn crystals; direction  $\langle 11\bar{2} \rangle$ ; the face (111);  $T_{\text{def}} = 450$  K; pattern, a, on surface; b, after polishing of  $\sim 10$   $\mu\text{m}$  depth.

dislocation mobility decreases. From the photographs, we notice that the deformation zones are practically free of twins in the InP:Sn (Fig. 2b) and InP:ZnO crystals (Fig. 3a), while some contribution of twinning process can be observed in the InP:Fe crystals together with dislocation one (Fig. 2c). In the InP:Zn crystals, the entire zone around the scratch is consisting basically of twins (Fig. 3b).

At the same time, it is of interest to point out that contribution of the twinning mechanism is not accompanied by an increase of crystal brittleness. On the contrary, the scratches, generated on the InP:Zn crystals, are more plastic then those generated on the InP:ZnO crystals (Fig. 3). This is evident in Fig. 4a, where the scratch prepared at  $T = 450$  K on the deformed face is rather plastic though the dislocations are practically absent in the deformed zones.

One more interesting feature is worth to notice. The deformed zone consisted of twins, which spread not deeply into the crystal (Fig. 4a), i.e. deformation by the twinning mechanism has a surface character. The chemical polishing of a 10- $\mu\text{m}$  layer removed the deformed zone. Several longitudinal twins and subsurface cracks are observed only in central part of the scratch (Fig. 4b). Similar results have been observed before in bismuth type semimetals at local load action [2].

#### 4. Discussion

It was shown by our earlier researches [9–12] on crystals with different type of chemical bond (ionic, ionic-covalent, covalent) that variation of deformation temperature is the principal factor resulting in modification of deformation mechanisms. Amplification of contribution of the thermoactivated processes, increasing of dislocation mobility and intensification of cross slip have been observed at the increase of deformation temperature. The start (critical) temperatures for activation of these processes ( $T_{\text{cr}}$ ) depend on the crystal type,  $T_{\text{cr}} \sim 0.3T_{\text{ml}}$  ( $T_{\text{ml}}$ -melting temperature) for ionic crystals;  $T_{\text{cr}} \sim 0.5T_{\text{ml}}$  for covalent ones. The crystals with ionic-covalent bonds occupy an intermediate position.

As the InP crystals have some ionic character ( $f = 0.421$ , where  $f$  is ionic part) [13],  $T_{\text{cr}}$  for them may be  $\sim 0.45 T_{\text{ml}}$ . Considering that the InP melting temperature is equal to 1346 K,  $T_{\text{cr}}$  for them will be about 600 K. Hence, activation of dislocation movement and formation of the developed dislocation structures around indentations and scratches are expected at temperatures of deformation or annealing greater than 600 K. That has really been confirmed by the above results.

The data obtained in this work correlate with the results presented by other authors [14,15], who have also shown that a sharp increase of the dislocation mobility and, accordingly, the diminution of hardening parameters (microhardness, yield stress, etc.) are significant in the InP crystals at  $T_{\text{def}} \sim 0.45T_{\text{ml}}$ . However, different type of impurities brings various contribution in braking of dislocations in InP crystals. Acceptor impurities (Zn) hinder very much the generation and movement velocity of dislocation. The influence of donor impurity (S) on these parameters is weaker than that of acceptor. In some cases, the donor impurities can even stimulate the dislocation motion. As it is shown in [15], isovalent impurities (Ga) weakly influence the velocity and generation of dislocations.

We suggest that the change in the lattice period ( $a$ ) of the doped InP crystals in comparison with undoped ones is responsible for the alteration of the velocity and mobility of dislocations. Actually, as it was shown in [14], doping by Zn (acceptor impurity) reduced the  $a$  value in accordance with the Vegards' law. In opposite to that, the donor impurity (S) extended the lattice period  $a$ , and isovalent impurity (Ga) does not influence this parameter. The authors [14] consider that it is connected with the variation of homogenous area of the solid solution, and not with change in radius of impurity elements. The acceptor impurities increase the homogenous region, while the donor dopant reduces it. That alteration results in modification of the process of interstitial indium precipitation ( $\text{In}_i$ ) in the solid solution. It is shown that donor impurities intensify this process and bring the  $a$  to increase.

In its turn, the increase of the lattice parameter influences the process in mode similar to temperature leading to amplification of fluctuation processes and downturn of potential barriers for overcoming of obstacles by dislocations. It facilitates their movement and promotes the increase of mobility. For this reason, a critical temperature necessary for the dislocation activation is less in the InP crystals doped by donor impurities as compared with acceptor ones. The results obtained in the present work support the above. Then, the critical temperature ( $T_{cr}$ ) is equal to 550–600 K for the InP:Sn crystals, and  $T_{cr} > 800$  K for the InP:Zn.

The modification of the strength characteristics of a material is also connected with the dislocation mobility variation. The microhardness measurements of the pure and doped InP crystals revealed the following results (Table 2). It can be seen that the greatest hardening is caused by the acceptor impurity. The donor and transition element impurity (Fe) render a weaker strength action. Thus, the crystal hardening degree is a function of the braking of dislocation activity; the greatest hardening is observed when dislocation mobility is hindered to a greater extent.

The mechanisms responsible for plastic deformation at action of a concentrated load are also a function of dislocation mobility. When the low dislocation mobility is unable to ensure the necessary deformation velocity, the other mechanisms become included in deformation process. The twinning mechanism is one of them for the InP crystals.

For this reason, already at 600 K the deformation is realized due to the dislocation mechanism if crystals are doped by donor impurity (Sn), what promotes the motion and cross-section-slip of dislocations. Otherwise, the crystals require thermal treatment at higher temperature ( $T > 800$  K) for activation of dislocation mobility and substitution of the twinning mechanism by the dislocation one when doped by acceptor impurity (Zn).

A special attention deserves the InP doping by a complex (donor–acceptor) impurity (ZnO). In this case, the impurity contribution is different. We have mentioned above that the acceptor impurity Zn sharply brakes the dislocation mobility. However, that process is blocked by opposite effect of the donor impurity (O). As a result, the mobility and cross slip of dislocations are intensified as compared even with pure InP and InP:Sn, and the deformation mechanism becomes mainly the dislocation one.

## 5. Conclusions

Firstly, the influence of dopant impurity type on the dislocation mobility, as one of the main parameters of plasticity, is investigated in InP crystals.

Secondly, it is shown that the dislocation mobility under action of a concentrated load depends essentially on the impurity type and the deformation temperature. Noticeable activation of dislocation motion in pure InP begins at  $T_{def} \sim 0.45T_{ml}$  that corresponds to  $T \sim 600$  K.

Thirdly, doping by diverse impurities can shift the position of  $T_{cr}$ , donor impurities (Sn) increase the  $\gamma$  and  $\gamma_s$  parameters and displace  $T_{cr}$  in the low temperatures direction; acceptor impurities, on the contrary, hinder the dislocation motion, reduce the values of  $\gamma$  and  $\gamma_s$  parameters and increase  $T_{cr}$ . The nature of this phenomenon consists in change of lattice parameter of InP crystals being connected with the process of  $In_i$  precipitation. The lattice parameters grow at introduction of donor impurity and decrease by doping with acceptor one.

Fourth, the deformation mechanism is also connected with the size of lattice parameters. Dislocation mechanism realized in InP crystals containing the donor impurity (Sn) is observed at  $T > 550$  K. In InP:Zn crystals, this mechanism takes place only at  $T > 800$  K.  $T_{cr}$  for Fe impurity (transition element) is situated between those two temperature values. Below them, the twinning mechanism has a great (and, in some cases, predominant) contribution.

Fifthly, it is noticed that the replacement of the dislocation mechanism by the twinning one is not accompanied by increase of brittleness.

Lastly, the double doping by a complex impurity ZnO can render an appreciable plastification effect increasing  $\gamma$  and  $\gamma_s$  parameters and the deformation process to the dislocation mechanism. This particular property may be used for heterostructure growing technology in order to diminish the thermal stress between the substrate and the layer.

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