SOVIET PHYSICS JETP VOLUME 27, NUMBER 6 DECEMBER, 1968

EFFECT OF DISLOCATIONS ON THE ELECTRIC PROPERTIES OF INDIUM ANTIMONIDE

Yu. A. OSIP'YAN, Yu. I. FEDYAEV, and S. A. SHEVCHENKO

Institute of Solid State Physics, Academy of Sciences, U.S.S.R.

Submitted January 26, 1968

Zh. Eksp. Teor. Fiz. **54**, 1706–1714 (June, 1968)

The effect of dislocations on the concentration and mobility of charge carriers is investigated experimentally in p-type and n-type indium antimonide crystals. Up to 10^7 cm^{-2} excess α dislocations (terminating with a row of indium atoms) and β dislocations (terminating with a row of antimony atoms) were introduced by plastic deformation through four-point bending. The Hall e.m.f. is reversed at 120°K when α dislocations are present in n-type InSb crystals, and at lower temperatures p-type conductivity is observed.

INTRODUCTION

INDIUM antimonide belongs to the group of crystalline semiconductor compounds that are formed by IIIb and Vb elements. The equal numbers of different atoms alternate to form a diamond-type lattice with two different atoms per unit cell, i.e., a zincblende (or sphalerite) lattice.

Each III atom has one valence electron less, and each V atom has one more than the IV atoms that form semiconducting crystals (diamond, germanium, and silicon). Thus the average number of electrons per atom in III–V compounds is the same as in IV compounds; as a result they have similar crystalline structures and electronic properties. However the structure of InSb, like that of the other III–V compounds which crystallize in the zincblende structure, exhibits an important difference from the diamond structure. This difference, which is quite essential for our purpose, lies in the fact that the absence of a center of symmetry allows the ⟨111⟩ directions to form polar axes, so that the [111] and $[\bar{1}\bar{1}\bar{1}]$ directions are different, as well as the (111) and $(\bar{1}\bar{1}\bar{1})$ planes.

If we arbitrarily assume that the [111] direction goes from a III atom (In) to a V atom (Sb), with $[\bar{1}\bar{1}\bar{1}]$ as the opposite direction, then Fig. 1 shows that in the direction perpendicular to [111], the InSb structure appears as a series of double layers consisting of In and Sb atoms.

Utilizing the difference between the structure factors F(h, k, l) and F($\bar{h}$, $\bar{k}$, $\bar{l}$), by comparing the intensities of x-ray reflections from opposite surfaces of a crystal, we can distinguish the (111) and $(\bar{1}\bar{1}\bar{1})$ planes accurately.[1]

It has been found that the two aforesaid planes are affected differently by chemical etching.[2,3] This difference can be attributed to the different chemical activities of the atoms forming the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces. The $(\bar{1}\bar{1}\bar{1})$ surface, which consists of Sb atoms having three bonds with the crystal, possesses high chemical activity, because two of the five valence electrons of Sb are unsaturated. On the other hand, in $(\bar{1}\bar{1}\bar{1})$ surfaces, which consist of In atoms, all three valence electrons form crystal bonds. Chemical etching is a very simple means of differentiating surfaces formed out of different atoms.

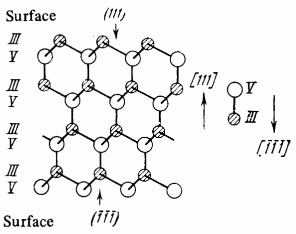

FIG. 1

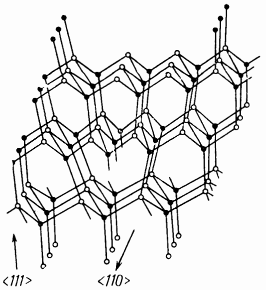

FIG. 2

FIG. 1. Projection of InSb structure on a (110) plane, illustrating the difference between the [111] and $[\bar{1}\bar{1}\bar{1}]$ directions.

FIG. 2. The dangling-bond model in a 60-degree dislocation of InSb structure.

DISLOCATIONS IN THE InSb STRUCTURE AND STATEMENT OF THE PROBLEM

It has been established[2] that in InSb crystals dislocations are observed lying in {111} planes and having ⟨110⟩ directions, according to the model shown in Fig. 2. Dislocations and their slip directions, which are different ⟨110⟩ directions, lie in {111} planes and form a 60° mutual angle. This 60-degree dislocation model, which was proposed by Read,[4] characterizes all diamond structures of either semiconducting elements (Ge, Si) or compounds (InSb, GaAs, etc.). An extra half-plane is terminated in a slip plane by a row of like atoms having only three lattice bonds. For (111) and $(\bar{1}\bar{1}\bar{1})$ slip planes the row would consist of In or Sb atoms, respectively.

In virtue of the fact that a row of Sb atoms (a β-dislocation) has two unsaturated bonds per atom, while a row of In atoms (an α dislocation) has no unsaturated bonds, it is quite obvious that they should exhibit entirely different electrical activities in the crystal. Their behavior should resemble that of rows of donor (V) and acceptor (III) impurities in a Ge or Si (IV) semiconductor. There is a particularly interesting possibility of revealing one-dimensional bonded states because of the close proximity (a few angstroms) of these "impurities" and their clearly defined directional arrangement.

It is noteworthy that conflicting results are reported in the publications[5-7] concerning the effect of plastic deformation on the electric properties of indium antimonide. In view of the foregoing discussion we introduced controlled amounts of α or β dislocations into an InSb crystal and investigated their effect on the electric properties of the crystal (carrier concentration and mobility).

DISLOCATION INTRODUCTION TECHNIQUE

We investigated n-type and p-type InSb crystals grown by the Czochralski method. At 78°K the initial carrier concentrations were 2×10^{14} cm^{-3} and 5×10^{14} cm^{-3}, and the resistivities were 5×10^{-2} and 2.5 ohm-cm, for the n-type and p-type crystals, respectively. The initial dislocation density was under 10^{-2} cm^{-2}. Excess α or β dislocations were introduced through plastic deformation (bending). Since InSb crystals are brittle at room temperature, the plastic bending was performed at higher temperatures using the apparatus that is shown in Fig. 3.

An $18 \times 3.5 \times 1.8$-mm sample 1 was placed in the graphite holders 2, and was compressed from above by the quartz die 3, which was joined to the yoke 4 of a dc electromagnet. A gap was formed between the yoke 4 and the magnet core 6 by adjusting the stage 5. The size of the gap was registered on the pointer dial 7 having 10^{-3}-mm divisions. After the required gap had been provided the bending jig was placed in a vacuum chamber at 10^{-2} Torr. Here the sample was heated by passing a current through it; in all instances the temperature 200°C was reached, as measured with a KhA thermocouple. A current was then passed through the coil 8 of the electromagnet, the sample was bent, and its deflection was registered on the dial.

The density of like dislocations producing plastic bending is calculated from the relation

$$D_T = \frac{1}{rb\cos\theta}\cos\psi, \qquad (1)$$

where D_T is the dislocation density (cm^{-2}), r is the radius of curvature, b is the Burgers vector, θ is the angle between the neutral and slip planes, and ψ is the angle between the front edge of the sample and the plane cross section for which the dislocation density is being calculated.

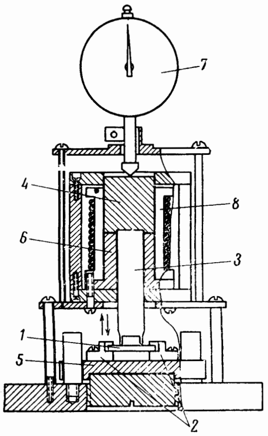

FIG. 3. Apparatus used for plastic deformation of InSb single crystals. 1–crystal, 2–graphite holders, 3–quartz die, 4–yoke of dc magnet, 5–adjustable stage, 6–magnet core, 7–pointer dial, 8–coil of dc electromagnet.

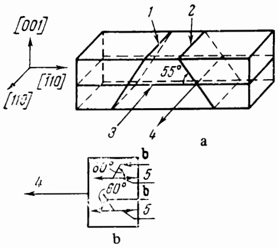

FIG. 4

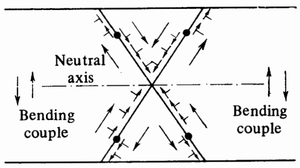

FIG. 5

FIG. 4. Sample orientation for bending about a [110] axis: a–locations of planes in the crystal, b–($\bar{1}$11) slip plane (plan view); 1–($\bar{1}$11) slip plane, 2–(111) slip plane, 3–neutral plane, 4–[110] bend axis, 5–⟨110⟩ dislocation, b–Burgers vector.

FIG. 5. Dislocation-generating mechanism in uniformly bent crystals. Shear forces acting on dislocation sources in the slip planes produce positive and negative dislocations, which move toward and away from the neutral axis, respectively.

For several samples the dislocation density in the (111) plane was determined experimentally after the bending process from etch figures, using the SR-4A etchant.[8] We observed satisfactory agreement with the dislocation density calculated from the bend radius, as in [9]. Even at the maximum density of 10^7 cm^{-2} the discrepancy did not exceed one-half an order of magnitude; the experimental value always exceeded the calculated dislocation density, because the calculation took

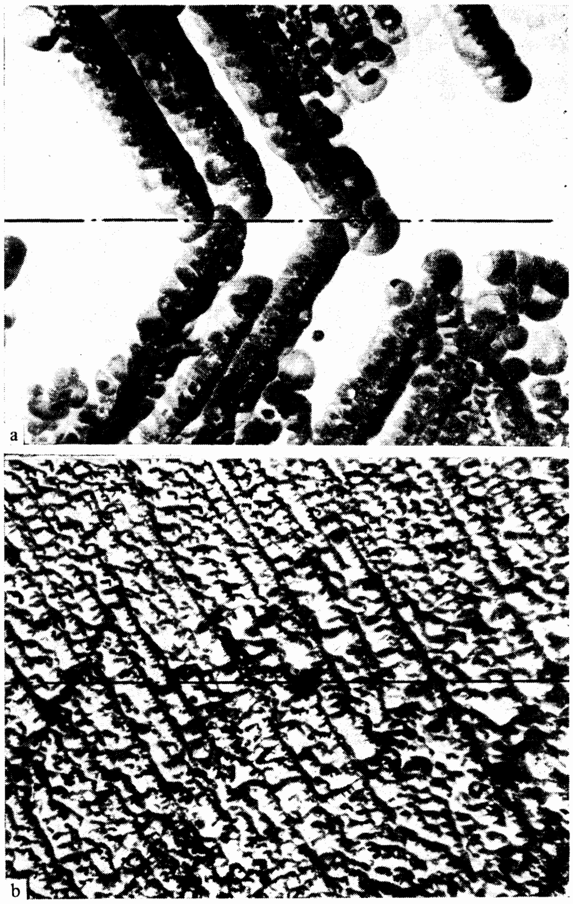

FIG. 6. Dislocation etch pits generated by SR-4A etchant near the neutral axis. a–for a deficiency of α dislocations, b–for an excess of α dislocations.

into account only the excess dislocations of a single type, whereas etching will reveal all dislocations of a given type. Subsequently only the bend radius was determined and the dislocation density was calculated.

Figure 4 shows the orientation of the samples, which was such that both active {111} slip planes were symmetrically located and forming angles of 45° with the maximum shear. It can be shown[2] that for this orientation and depending on the polarity of the sample, the direction of the bending axis, and the bending moment, the crystal will acquire either extra α or extra β dislocations; this is illustrated in Fig. 5.

When shear stresses activate sources of positive and negative dislocations in a crystal, then in the case of uniform bending the positive dislocations will move toward the neutral axis and the negative dislocations will move toward the surface of the crystal. Some of the negative dislocations will emerge to form a step on the surface and an excess of positive dislocations will remain inside the crystal. Depending on the sample orientation, the direction of the bending axis, and the bending moment, either the α or the β type can become the positive dislocations and thus constitute the excess after bending. Figure 6 illustrates the etch patterns in both instances.

Following bending, smaller samples ($9 \times 3.0 \times 6$ mm) were cut from the middle of the sample. A balance method was used to measure the temperature dependence of the electric conductivity and Hall constant in the range 78°–300°K. The maximum magnetic field used in measuring the Hall constant was 4400 Oe. To allow for possible evaporation of some components and stoichiometric imperfections as a result of heating preparatory to bending, undeformed control samples were also heated and were kept at the same 200°C temperature.

ELECTRIC PROPERTIES

The semilog figures 7 and 8 show the temperature dependences of the Hall constant R_H and electric conductivity σ for three typical n-type InSb samples: a control sample, a sample containing an α-dislocation excess, and a sample containing a β-dislocation excess. The deformed samples were oriented with the current flow direction either parallel or perpendicular to the bend axis. For the same samples Fig. 9 shows the temperature dependence of the product σR_H, which determines the Hall mobility for a single type of carriers. 100°K the donor electron concentration determined from the Hall constant for the control sample was 2×10^{14} cm^{-3}; the concentration of intrinsic holes at this temperature was two orders of magnitude lower. With increasing temperature the thermal ejection of electrons is enhanced, and at $T > 160$°K the crystal becomes an intrinsic semiconductor. Nevertheless, even in the region of intrinsic conduction the InSb samples behave like n-type semiconductors because of the large electron/hole mobility ratio ($\mu_n/\mu_p \sim 100$ at 300°K[10]). Therefore the σR_H vs. $1/T$ curve of the control sample determines the temperature dependence of electron Hall mobility in InSb, in agreement with [10]. The introduction of excess β dislocations does not change the Hall constant or electric conductivity significantly. The temperature dependence of the Hall constant and of the electric conductivity are affected significantly by the introduction of α dislocations. Then at $T \approx 120$°K the sign of the Hall constant is reversed, and with de-

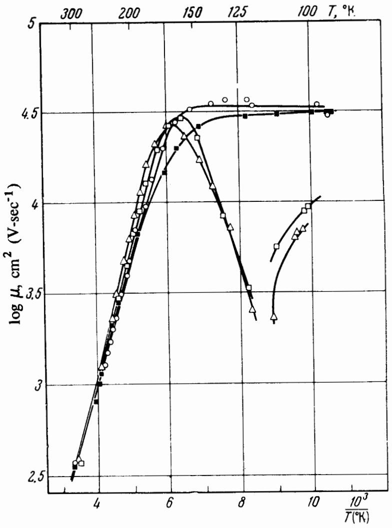

FIG. 7. Temperature dependence of the Hall constant for the n-type control sample and plastically deformed samples. ■—control sample, donor electron concentration 2×10^{14} cm^{-3}; ○—with excess of β dislocations, current flow perpendicular to bend axis; □—with excess of α dislocations, current flow perpendicular to the bend axis; ▲—with excess of α dislocations, current flow parallel to the bend axis.

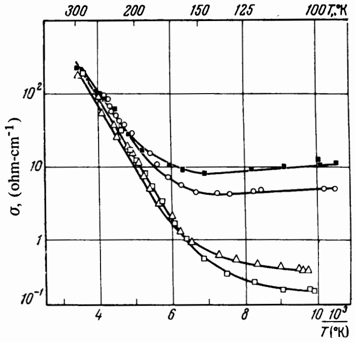

FIG. 8. Temperature dependence of conductivity for the control sample and plastically deformed samples (notation as in Fig. 7).

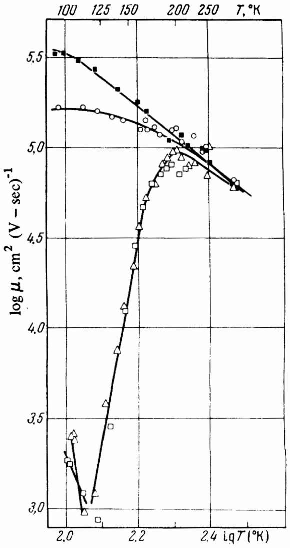

FIG. 9. Temperature dependence of carrier mobility for the control sample and plastically deformed samples (notation as in Fig. 7).

creasing temperature beginning at this point the conductivity becomes almost two orders of magnitude lower than that of the control sample.

Figures 10 and 11 show similar measurements for p-type samples. Above 160° K, in virtue of the aforementioned large mobility ratio the Hall constant is negative in p-type samples, where the introduction of either α or β dislocations reduces somewhat both the conductivity and the Hall constant. At about 100°K this reduction leads to a value about one-half order smaller than for the control sample (Fig. 11).

DISCUSSION OF RESULTS

The measurements show a clear reduction of carrier mobility in all instances, for n-type and p-type crystals containing α and β dislocations. This effect is accounted for satisfactorily by Read's simplest model, where a charged dislocation along with the space wherein its charge is screened can be regarded as a scattering cylinder.

We believe that our most important observation is the strong acceptor action of α dislocations in n-type crystals up to the sign reversal of the Hall constant. We believe that this effect requires principal attention in a discussion of the results, and we shall now discuss different versions of its cause.

1. In the direct acceptor action of dislocations each indium atom lying in a dislocation line can become a direct acceptor and trap either a donor electron or an intrinsic electron, thus leaving a hole in the valence band. When the density of dislocations is 10^6–10^7 cm^{-2} the total number of acceptor centers in them is at most 10^{13}–10^{14} cm^{-3}. When Coulomb repulsion is taken into account, then even when f (the fraction of occupied dislocation sites) = 0.1[9] the number of effective acceptor centers cannot exceed 10^{12}–10^{13} cm^{-3}. The concentration 2×10^{14} cm^{-3} of donor electrons in our purest crystals could not be neutralized directly by such a small number of acceptor centers. If we nevertheless consider this mechanism to be operative, we must seek conditions that would yield $f > 1$.

2. The acceptor action of the α dislocations can be accounted for in another way if we assume that the dislocations do not affect the mobilities of holes and electrons to the same extent. When both kinds of carriers are present, the carrier concentrations n and p and the respective mobilities appear in the expression for the measured Hall constant:[10]

$$R_H \sim \frac{n\mu_n^2 - p\mu_p^2}{(n\mu_n + p\mu_p)^2}. \qquad (2)$$

The electron mobility in InSb exceeds the hole mobility by about two orders of magnitude. Therefore even a crystal having some excess of holes will exhibit negative Hall voltage. If we assume that the α dislocations strongly reduce the electron mobility without appreciably affecting the hole mobility, we can account for the reversed sign of the Hall voltage at temperatures where the intrinsic carrier concentration remains sufficiently high. If this is the true mechanism we can expect to observe a second reversal of sign as the temperature is further reduced.

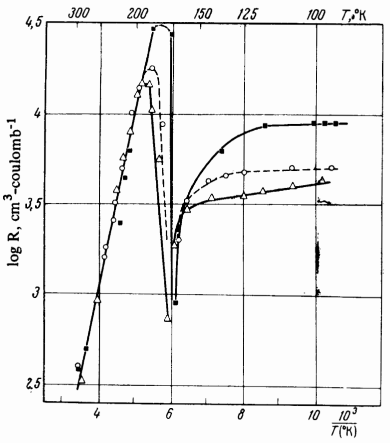

FIG. 10. Temperature dependence of Hall constant for the p-type control sample and plastically deformed samples. ■—control sample, hole concentration 5 X 10^{14} cm^{-3}; □—with excess of α dislocations, current flow perpendicular to the bending axis; Δ—with excess of β dislocations, current flow direction perpendicular to the bending axis.

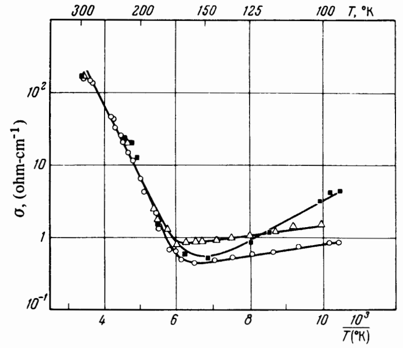

FIG. 11. Temperature dependence of conductivity for the p-type control sample and plastically deformed samples (notation as in Fig. 7).

3. Still another possible cause of R_H sign reversal would be a change in the band structure of the crystal resulting from stresses generated by dislocations and propagating to fairly long distances from the dislocation nucleus. It is known[11] that InSb is very sensitive to elastic stresses. However, in this case we cannot account for such a difference between the actions of α and β dislocations, whose elastic stress fields should be identical.

4. We must not fail to mention that plastic deformations not only increase the dislocation density but also increase the concentration and change the state of point defects in the lattice. The lattice could thus acquire a large number of indium and antimony vacancies and interstitial atoms. We can then assume that the interstitial indium atoms and the antimony vacancies will act as acceptor centers. It is also possible that the diffusion of dissolved donor impurities will be greatly accelerated in the dislocation field. Impurity atmospheres would form around the dislocations and the concentration of active donors would be reduced.

Our future experimental work will aim at obtaining more detailed information concerning the aforementioned possible mechanisms of the acceptor action of α dislocations in InSb crystals.

We are indebted to V. Ya. Kravchenko and V. L. Pokrovskiĭ for valuable discussions, and to L. G. Fedyaeva for experimental assistance.

[1] E. P. Warekois and P. H. Metzger, J. Appl. Phys. **30**, 960 (1959).

[2] J. P. Venables and R. M. Broudy, J. Appl. Phys. **29**, 1025 (1958).

[3] H. C. Gatos and M. C. Lavine, J. Appl. Phys. **31**, 743 (1960).

[4] W. T. Read, Phil. Mag. **45**, 775 (1954).

[5] H. C. Gatos, M. C. Finn, and M. C. Lavine, J. Appl. Phys. **32**, 1174 (1961).

[6] R. L. Bell, R. L. Latkowski, and A. F. W. Willoughby, J. Materials Sci. **1**, 66 (1966).

[7] B. A. Dvorkin, A. F. Kravchenko, A. M. Palkin, and F. L. Edel'man, Izv. vyssh. uch. zav., ser. fiz. No. 1, 93 (1967).

[8] J. W. Allen, Phil. Mag. **2**, 1475 (1957).

[9] E. A. Malinova, P. L. Petrusevich, and E. S. Sollertinskaya, Kristallografiya **11**, 896 (1966) [Sov. Phys.-Crystallogr. **11**, 760 (1967)].

[10] C. Hilsum and A. C. Rose-Innes, Semiconducting III–V Compounds, Pergamon Press, New York, 1961 (Russ. transl., IIL, 1963).

[11] G. L. Bir and G. E. Pikus, Fiz. Tverd. Tela **3**, 3050 (1961) [Sov. Phys.-Solid State **3**, 2221 (1962)].

Translated by I. Emin
198