

DIFFUSION AND SOLUBILITY OF THERMALLY INDUCED ACCEPTORS IN INDIUM ANTIMONIDE

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The paper deals with physical properties of thermally induced acceptors in indium antimonide single crystals. The temperature dependence of their solubility was determined. The diffusion properties of thermally induced acceptors have been investigated on the basis of dissociation diffusion mechanism and the obtained results have been analysed with respect to their origin. The conclusion is that the occurrence of thermally induced acceptors is probably due to the diffusion of interstitial copper into indium antimonide and its resulting electric activation.

INTRODUCTION

It is known that by heating indium antimonide crystals in pure atmosphere at a certain higher temperature for a definite time and then their cooling down to room temperature (s. c. heat treatment) electrically active centres with acceptor activity are created [1], [2], [3]. The occurrence of such defects is undesirable for all technological operations connected with the heating of semiconductor materials.

The origin of thermally induced acceptors has not been explained yet, it may however be facilitated by the study of its physical properties.

The purpose of this paper is to determine the solubility and diffusion properties of thermally induced acceptors in indium antimonide crystals and to analyse the obtained results with respect to their origin.

GENERALLY ABOUT THE HEAT TREATMENT OF InSb

For experimental procedures samples of *n*-type InSb have been used, which were cut out of single crystals in the form of thin plates in the required size of about $0.6 \times 1.5 \times 7.0$ mm³. Heat treatment of samples was done in the vacuum or in pure hydrogen atmosphere at different temperatures (from

300 up to 500 °C), the time intervals ranging from several minutes to several days.

The influence of heat treatment on the electric properties of InSb samples can be determined by comparing concentrations of active impurities and specific electric conductivities of samples before and after the heat treatment and by calculating concentrations of thermally induced acceptors. The Hall constant and electric conductivity measurements were made on samples with standard techniques at 77 °K. Concentration of thermally induced acceptors may be defined as the increase of acceptor centres in the *p*-type that came into being as a result of the heat treatment, as compared to the concentration of acceptors in the original *n*-type, i. e.

$$N_{TA} = N_{Ap} - N_{An}. \quad (1)$$

For the electron and hole concentrations in InSb at 77 °K, assuming full ionisation of all impurities, we can write

$$n = N_{Dn} - N_{An}, \quad (2a)$$

$$p = N_{Ap} - N_{Dp}, \quad (2b)$$

where N_{Dn} , N_{Dp} are donor concentrations, N_{An} , N_{Ap} are acceptor concentrations in *n*-type and *p*-type, respectively.

The concentration of thermally induced acceptors in then

$$N_{TA} = n + p + N_{Dp} - N_{Dn}. \quad (3)$$

If we assume that the donor concentration is not affected by heat treatment, the last term of Eq. (3) can be neglected.

Figure 1 illustrates the dependence of electric conductivity of heat-treated InSb samples on heating time and temperature. Four InSb samples with approximately the same electric parameters ($n = 2 \div 3 \times 10^{14}$ cm⁻³, $\mu_n = 4.6 \div 4.8 \times 10^5$ cm²/Vs at 77 °K) and with the same dislocation density ($N_d \approx 10^2$ cm⁻²) were repeatedly heat-treated at different constant temperatures for a total time of 140 minutes. As can be seen, the sample that was heat-treated at 400 °C remains an *n*-type during this annealing and does not change its conductivity. With the increase of heating temperature changes of electric conductivity are observable. As a result of compensation of initial donor impurities by thermally induced acceptors the sample heat-treated at 500 °C is converted very rapidly from the *n*-type to the *p*-type, the conversion time t_c being about 6 minutes. It can also be seen from Fig. 1 that the steady level of electric conductivity increases with increases of heating temperature.

The influence of crystal perfection on the change of electrical parameters of heat-treated indium antimonide is very strong [4]. The velocity of thermally

induced acceptors increases with growing dislocation density. For example, the sample with dislocation density of 10^4 per cm^2 , when heated at 400°C , is converted to the p -type in about 12 minutes, while the sample with the same electric parameters but with the dislocation density of 10^2 per cm^2 does not change its electrical properties even when heated much longer and it requires heating for about 10 hours at the same temperature to be converted to the p -type.

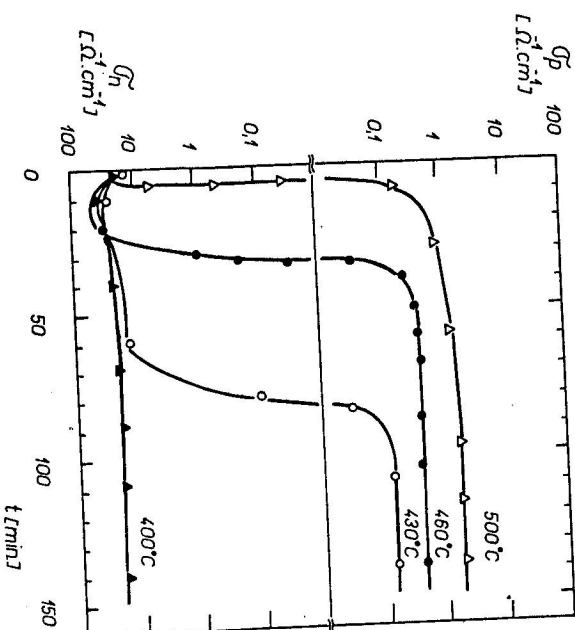


Fig. 1. Electric conductivity variation vs. time of heat treatment at fixed temperatures for four InSb samples.

Cooling velocity of heat-treated InSb samples has not essential influence on the occurrence of thermally induced acceptors. Electrical parameters of two heat-treated samples before and after heat treatment are plotted in Tab. 1. Heat treatment conditions were the same, the cooling velocity differed substantially and as can be seen, the difference in the resulting concentration of thermally induced acceptors is slight.

The kind of atmosphere used for heat treatment of InSb (vacuum, hydrogen, argon, Sb-vapours) has no influence on the occurrence of thermally induced acceptors either [5], [6].

Table 1
Influence of cooling velocity on the occurrence of thermally induced acceptors

Initial parameters	Cooling velocity	Final parameters	Concentration of thermally induced acceptors
$n = 5.5 \times 10^{14} \text{ cm}^{-3}$ $\sigma = 34.4 \Omega^{-1} \text{ cm}^{-1}$	2.5°C/min	$p = 2.2 \times 10^{15} \text{ cm}^{-3}$ $\sigma = 2.74 \Omega^{-1} \text{ cm}^{-1}$	$N_{TA} = 2.75 \times 10^{15} \text{ cm}^{-3}$
$n = 5.6 \times 10^{14} \text{ cm}^{-3}$ $\sigma = 24.1 \Omega^{-1} \text{ cm}^{-1}$	100°C/min	$p = 1.4 \times 10^{15} \text{ cm}^{-3}$ $\sigma = 1.24 \Omega^{-1} \text{ cm}^{-1}$	$N_{TA} = 1.96 \times 10^{15} \text{ cm}^{-3}$

$T = 455^\circ\text{C}$, $t = 24$ hours, vacuum.

SOLUBILITY OF THERMALLY INDUCED ACCEPTORS

The solubility of impurities in semiconductors depends on temperature, as

$$S = S_0 \exp\left(-\frac{W_s}{kT}\right), \quad (4)$$

where S_0 is the material constant and W_s is the activation energy of solubility.

To express the temperature dependence of solubility of thermally induced acceptors according to this relation, it is necessary to heat-treat the samples at different annealing temperatures for a certain time, the so-called time of setting the equilibrium value τ , within which the concentration of thermally induced acceptors becomes maximal at a certain annealing temperature. It can be expected that the time of setting the equilibrium value τ is exponentially dependent on temperature with a certain characteristic activation energy W_n . It can also be assumed that the time of setting the equilibrium value is indirectly proportional to the lattice vibration of atoms in substitutional sites, i. e. to the Debye frequency ν and also indirectly proportional to the dislocation density N_d , as

$$\tau = \frac{K}{\nu N_d} \exp\left(-\frac{W_n}{kT}\right), \quad (5)$$

where K is a constant.

For the purpose of determining the solubility of thermally induced acceptors, the InSb samples were heat-treated at certain temperatures ranging from

300 up to 500 °C for a sufficient period of time and the concentrations of thermally induced acceptors at a given heating temperature and time were determined according to Eq. (3). In view of a possible partial precipitation of thermally induced acceptors, the samples were cooled very quickly (about 100 °C/min) after the heating was finished.

The actual influence that the time of setting exerts on achieving the equilibrium concentration is illustrated by Fig. 2, where concentrations of thermally

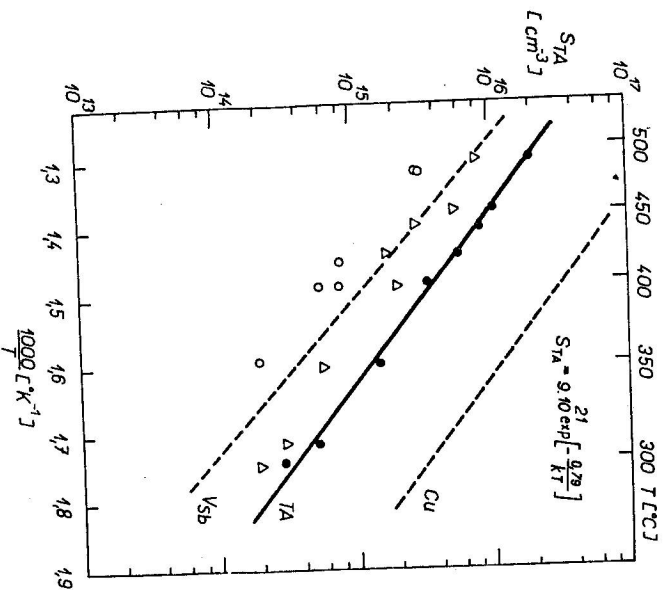


Fig. 2. Temperature dependence of solubility of thermally induced acceptors (experimental points are for time of heat treatment: \circ — from 1 up to 4 hours, \triangle — from 10 up to 40 hours, \bullet — more than 48 hours) in comparison with temperature dependence of solubility of copper and Sb-vacancies in InSb.

induced acceptors are plotted against the heating temperature. Experimental points are divided into three groups (according to designations) in dependence on the heating time. With increasing time of the heat treatment the values of concentration of thermally induced acceptors at a certain temperature increase, i. e. they approach the equilibrium value of concentration of thermally induced acceptors. Only the points corresponding to heat treatment for a pe-

riod of time longer than 48 hours (Fig. 2 — full circles) are the correct values of solubility of thermally induced acceptors.

Experimentally obtained temperature dependence of solubility of thermally induced acceptors in In Sb (Fig. 2 — full line) is according to (4)

$$S_{TA} = 9 \times 10^{21} \exp\left(-\frac{0.79}{kT}\right). \quad (6)$$

DIFFUSION PROPERTIES OF THERMALLY INDUCED ACCEPTORS

One possibility of determining the diffusion coefficient of impurities in semiconductors is by means of the depth of the p - n junction created by diffusion. At the point of the p - n junction, $x = x_c$, the concentration of diffusing impurities is equal to the impurity concentration before diffusion, $N(x) = N_b$. For the calculation of the diffusion coefficient we have, according to the 2nd Fick law (assuming that the diffusion coefficient is independent of the concentration of the diffusing atoms),

$$D = \frac{x_c^2}{4t \ln(N_0/N_b)}, \quad (7)$$

where N_0 is the surface impurity concentration.

The effective diffusion coefficient of thermally induced acceptors was derived from this relation by determining the conversion time t_c for a certain heating temperature (Fig. 1) and by determining the active distance x_c that equals half the thickness of the sample. The assumed value of the surface concentration is $N_0 = 3 \times 10^{16} \text{ cm}^{-3}$ [7].

Calculated values of the effective diffusion coefficient of thermally induced acceptors D_{TA}^H and D_{TA}^B at different heating temperatures in two crystallically different perfect materials are plotted in Fig. 3. The dislocation density in the material „H“ is $N_d^H = 8 \times 10^2$ dislocations per cm^2 , whereas in the material „B“ it is $N_d^B = 7 \times 10^4$ dislocations per cm^2 .

The temperature dependence of the diffusion coefficient, when assuming its independence of impurity concentration, is

$$D = D_0 \exp\left(-\frac{W_D}{kT}\right), \quad (8)$$

where D_0 is the material constant and W_D is the activation energy of the diffusion process.

According to this equation we can write for the effective diffusion coefficient of thermally induced acceptors in the two investigated InSb crystals

$$D_{TA}^H = 10^3 \exp(-1.80/kT), \quad (9a)$$

$$D_{TA}^B = 10^5 \exp(-1.19/kT). \quad (9b)$$

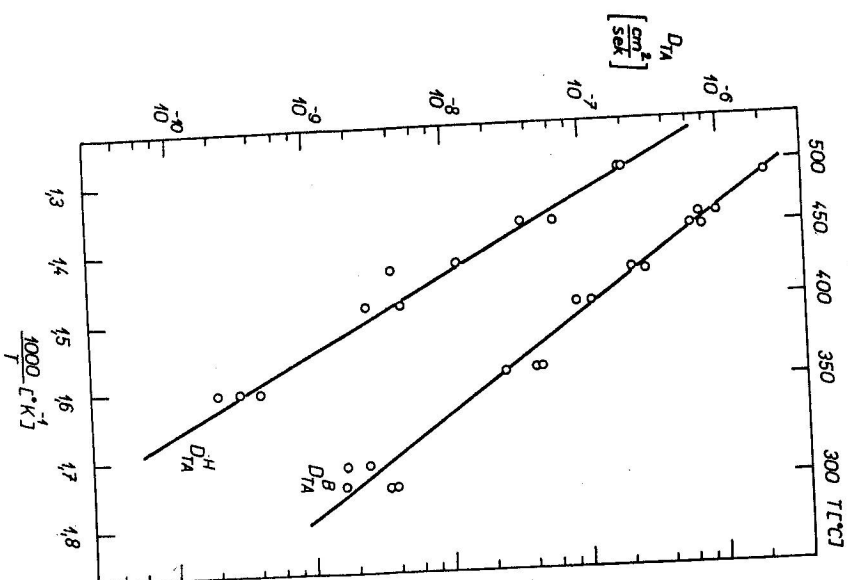


Fig. 3. Temperature dependence of effective diffusion coefficient of thermally induced acceptors in two crystallographically different perfect materials ($D_{TA}^H \rightarrow$ dislocation density $N_D^H = 8 \times 10^2 \text{ cm}^{-2}$, $D_{TA}^B \rightarrow N_D^B = 7 \times 10^4 \text{ cm}^{-2}$).

DISCUSSION

In view of the strong influence of crystalline perfection upon the formation of thermally induced acceptors in InSb, the analysis of their properties is

made on the basis of the dissociation diffusion mechanism, described by the equation



where TA_s and TA_i are the thermally induced acceptors in the substitutional or the interstitial position, respectively, and V is the vacancy.

The activation energy of the diffusion processes W_D equals the sum of the activation energy of the dissociation processes W_d and the activation energy of the substitutional position formation W_s , i. e.

$$W_D = W_d + W_s. \quad (11)$$

The value of the activation energy of the substitutional position formation $W_s = 0.79 \text{ eV}$ which was derived from the solubility of thermally induced acceptors, can well be compared with the value of the substitutional formation positions of copper in InSb $W_s^{\text{Cu}} = 0.76 \text{ eV}$, as determined by Stocker [8]. The absolute values of the solubility of Cu in InSb are greater (Fig. 2 — dashed line) than the solubility values of thermally induced acceptors in InSb at certain diffusion and heating temperatures, respectively.

One of the possible causes of thermally induced acceptors may be the activation of crystal defects due to heating. With respect to the acceptor action it may be caused by Sb-vacancies. The temperature dependence of the solubility of Sb-vacancies, determined by Pagnia [3] (Fig. 2 — dashed line), is smaller than the obtained values of solubility of thermally induced acceptors.

For the purpose of comparison Tab. 2 lists the activation energies of thermally induced acceptors in InSb, determined from Eqs. (6), (9) and (11) and activation energy values corresponding to Cu diffusion into InSb [8] and vacancy

Table 2
Activation energies of diffusion processes of thermally induced acceptors, copper and vacancies in InSb

	TA	Cu	V
Activation energy of diffusion processes W_D [eV]	1.80	1.84	
Activation energy of solubility W_s [eV]	0.79	0.76	1.02
Activation energy of dissociation process W_d [eV]	1.01	1.08	0.82

in InSb [3]. It follows from this comparison that there is a better accordance of thermally induced acceptors with copper than with vacancies.

The assumption that the occurrence of thermally induced electric activation, according to Eq. (10), is supported by the fact that the diffusion of Cu into InSb also corresponds to the dissociation diffusion mechanism and this diffusion is strongly dependent on the structural perfection of the material. The transition of Cu atoms from the interstitial, electrically inactive state, into the substitutional one takes place in the presence of vacancies, the origin of which may be different. There are vacancies in the crystal that have been there since its preparation, or they may be caused by diffusion from the surface and part of the vacancies is created in cooperation with dislocations. Dislocations can operate as capture centres for vacancies formed during the crystal preparation as well as a transport medium for diffusion of vacancies from the surface.

The dependence of the effective diffusion coefficient of copper into InSb on the dislocation density at the diffusing temperature 350 °C, as determined by Stocker [8], is illustrated in Fig. 4. For the sake of comparison this picture

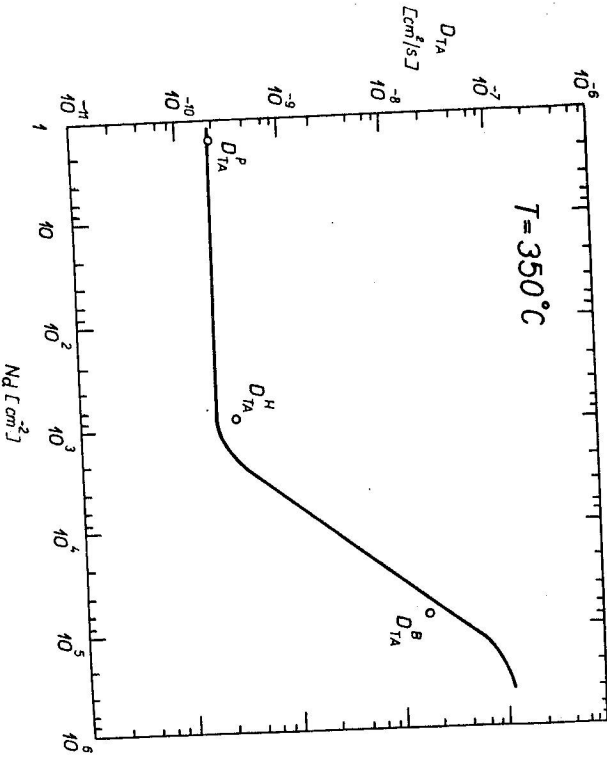


Fig. 4. Diffusion coefficient values of thermally induced acceptors D_{TA} in comparison with the dependence of effective diffusion coefficient of copper on the dislocation density in InSb at 350 °C.

contains diffusion coefficient values of thermally induced acceptors D_{TA}^H and D_{TA}^B , determined for the same diffusion temperature from Eq. (9). The value of the diffusion coefficient D_{TA}^P , corresponding to a perfect, dislocation-free crystal, was determined with respect to the maximal value of self-diffusion activation energy of In in InSb $W_{D_{In}} = 1.82$ eV, according to Eisen, Birchenall [9]. The agreement among these three values with copper diffusion into InSb is good. For a detailed verification of the agreement it would be necessary to obtain more diffusion coefficient values with different dislocation densities of the investigated crystals.

The assumption that the occurrence of thermally induced acceptors is caused by Cu diffusion into InSb is supported also by other experiments, first of all by the possibility of its extraction by heating in contact with liquid metals [7]. This so-called solvent extraction method is in semiconductor technology used for the re-diffusion of rapidly diffusing impurities (Li, Cu, Ni).

To obtain unambiguous evidence about the fact that the Cu diffusion causes thermally induced acceptors it would be necessary to answer the question where the Cu gets into the semiconductor crystal from. The segregation coefficient of copper in InSb is $k = 6.6 \times 10^{-4}$ [10], i. e. the copper can be removed from the crystal by zone refining. When preparing InSb single crystals by the zone refining technique [11], it was observed that only 1/9 of the crystal length was of the acceptor type when the crystal was prepared (compounding of In and Sb and zone refining) in a „closed“ system of gas or high vacuum, but as much as 1/2 of crystal length was of the acceptor type when the crystal was temporarily removed from the system. The surrounding atmosphere causes an increase of the acceptor impurities in the crystal, which, due to zone refining are concentrated at one end of the crystals. Judging by this experiment the cause of thermally induced acceptors is very probably oxygen. However, no information is available on the physical properties of oxygen in InSb. The fact that oxygen occupies donor states in germanium, in which heating also gives rise to electrically active centres with acceptor activity, contradicts the assumption that oxygen is the cause of thermally induced acceptors.

CONCLUSION

We have determined the temperature dependence of the solubility and diffusion coefficients of thermally induced acceptors in indium antimonide and analysed the cause of their origin. It follows from analyses of the properties of thermally induced acceptors that their occurrence is probably due to the diffusion of copper into InSb and its following electric activation. A definite

conclusion regarding their origin could be obtained by using more sensitive methods of determination of foreign atom concentrations in semiconductors, first of all by using radioactivation analysis. With respect to the concentration of thermally induced acceptors in InSb, the sensitivity of the method has to be higher than 0.1 ppm.

The author is grateful to Mr. K. Měřinský for his helpful comments and advice and to Mr. V. Beně and Mr. M. Morvíc for providing the InSb single crystals.

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Received April 10th, 1970

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