The anisotropy and the electrical properties of In$_2$Se$_3$ layered crystals and their lithium and hydrogen intercalates are studied in the temperature range 80-400 K. It is established that, with increase in the temperature, the electrical conduction and the mobility along layers decrease, whereas the free electron concentration remains practically invariable. The obtained temperature dependence of the electron mobility is explained by the interaction of electrons with homopolar optical phonons. A change of the electrical conduction of hydrogenated In$_2$Se$_3$ crystals depending on the annealing time is due to the formation of new levels in the forbidden band and the effect of intercalated hydrogen on the deformation potential of a crystal. The established decrease of the anisotropy for the Li$_1.5$In$_2$Se$_3$ intercalate as compared with that of In$_2$Se$_3$ in the temperature interval 250-400 K is caused by the prevailing reduction of the electrical conduction normally to layers over a slight decrease of the conduction in parallel to them.

1. Introduction

One of the layered compounds which are of interest both in the scientific and applied aspects is In$_2$Se$_3$ semiconductor. This crystal as well as intercalation compounds on its basis can be used to produce primary and secondary current sources with high specific characteristics and sensitive elements of strain gauges. The published results of studies of the physical properties of these crystals [1-3] considerably differ, which is explained both by the strong imperfection of the material structure and the presence of various ($\alpha$, $\beta$, and $\gamma$) crystal phases. The aim of this work is to study the electrical properties of In$_2$Se$_3$ layered crystals and their lithium and hydrogen intercalates.

2. Experimental Technique

In$_2$Se$_3$ single crystals were grown by the Bridgman technique from a stoichiometric melt at a temperature gradient at the crystalization front equal to 15 deg/cm and a growth rate of 1 mm/h. The obtained materials are characterized by a pronounced layered structure over the whole length of a sample. The performed X-ray analysis demonstrates that they have a structure of the $\alpha$-phase with the lattice parameters $a = 4.031$ Å, $c = 19.2$ Å. The In$_2$Se$_3$ layered crystals were intercalated by the electrochemical method using a 1M solution of LiClO$_4$ in propylene carbonate. The effect of the concentration of intercalated lithium ions on the properties of In$_2$Se$_3$ was studied on the same group of samples by means of the deintercalation. The process of intercalation of In$_2$Se$_3$ single crystals was realized within the the method of “pulling” electric field [4] in the galvanostatic mode. Lithium ions were intercalated into the layered crystal by allowing the passage of the electric current of the necessary magnitude through the electrochemical cell. The concentration of the intercalated impurity $x$ ($0.1 \leq x \leq 1.5$, where $x$ is the number of intercalated lithium ions per one formula unit of the crystalline matrix) was determined by the charge which has passed through the cell, i.e. the controlled parameters in the process of the intercalation reaction were the electric current density and the duration of the process. The use of the optimal technological parameters of the intercalation process (current density below 10 $\mu$A/cm$^2$) allowed us to obtain homogeneous intercalated samples.

The intercalation of hydrogen into In$_2$Se$_3$ (hydrogenation) was performed according to the thermal exposure method used for the intercalation of layered semiconductors with metals [5, 6]. For this purpose, the initial In$_2$Se$_3$ samples were placed in quartz ampoules evacuated to a residual pressure of $10^{-3}$ Torr through a nitrogen trap in order to prevent the formation of a vapor with carbon compounds. The evacuated ampoules were filled with hydrogen at the liquid-nitrogen temperature and then sealed off. Molecular hydrogen was introduced by keeping the samples in the hydrogen medium at a temperature of 600 °C and a pressure of $\sim 0.3$ MPa. Moreover, the first group of the samples was kept during 24 h, while the second one — during 48 h. According to the Sieverts law, in the case of diffusion of a diatomic gas decaying into separate atoms when entering a solid body, the amount of intercalated hydrogen is proportional to...
ELECTRICAL PROPERTIES OF In$_2$Se$_3$ INTERCALATED LAYERED CRYSTALS

Fig. 1. Temperature dependence of the layer-parallel electrical conduction $\sigma_{\perp c}$ for In$_2$Se$_3$ layered crystal (1) and intercalation compounds Li$_{0.1}$In$_2$Se$_3$ (2), Li$_{1.0}$In$_2$Se$_3$ (3), and Li$_{1.5}$In$_2$Se$_3$ (4), respectively.

$\sqrt{P}$ (where $P$ is the partial gas pressure in the system) [7]. The weak van der Waals bond between layer packets in In$_2$Se$_3$ and the strong ion-covalent bond inside the layers enable one to intercalate hydrogen into the interlayer space. The relation between the interlayer distance in In$_2$Se$_3$ (3.55 Å) and the gas-kinetic diameter of a hydrogen molecule (2.89 Å) testifies to the validity of such an assumption. An increase of the time of keeping the samples in the hydrogen atmosphere must result in a rise of the amount of introduced hydrogen and its ordering in the crystal system of the sample. The ampoules with samples were cooled in a switched-off furnace for 24 h. The described procedure yielded hydrogenated samples $\langle H \rangle$In$_2$Se$_3$.

Fig. 2. Temperature dependence of the free carrier mobility $\mu_{\perp c}$ for In$_2$Se$_3$ layered crystal (1) and intercalation compounds Li$_{0.1}$In$_2$Se$_3$ (2), Li$_{1.0}$In$_2$Se$_3$ (3), and Li$_{1.5}$In$_2$Se$_3$ (4).

The temperature dependences of the Hall coefficient $R_H$ (B $\parallel$ c), the electrical conductions in parallel and normally to layers ($\sigma_{\perp c}$ and $\sigma_{\parallel c}$, respectively), and the Hall mobility $\mu_{\perp c}$ were studied in the temperature range 80÷400 K. The experiments were performed at a constant current using the samples $10 \times 2.3 \times 0.6$ mm$^3$ in size in a magnetic field. Indium contacts were deposited in the classical configuration. The electrical conduction $\sigma_{\parallel c}$ was measured by the four-probe technique with contacts placed at the opposite cleaved surfaces: two of them were used as current ones and the other two — as probe ones. The electrical properties of the hydrogenated In$_2$Se$_3$ samples were investigated the next day after the completion of annealing, as there exist data [8] on the 15–20% decrease of the effect of intercalated hydrogen on the properties of layered crystals kept in air at room temperature during 80–100 days.

Fig. 3. Temperature dependence of the free carrier concentration $n$ for an In$_2$Se$_3$ layered crystal (1) and intercalation compounds Li$_{0.1}$In$_2$Se$_3$ (2), Li$_{1.0}$In$_2$Se$_3$ (3), and Li$_{1.5}$In$_2$Se$_3$ (4).

3. Results and Their Discussion

The electrical properties of an In$_2$Se$_3$ layered crystal and its intercalates were investigated in the temperature range 80÷400 K. Figures 1–3 show the temperature dependences of the electrical conduction $\sigma_{\perp c}$ and the electron mobility $\mu_{\perp c}$ in parallel to layers, as well as the free electron concentration $n$ for the initial In$_2$Se$_3$ crystal (curve 1) and its lithium intercalates (curves 2–4) with various lithium concentrations. Experimental data are also presented in Table 1. The temperature dependence of the electrical conduction anisotropy of the initial In$_2$Se$_3$ samples and the intercalation compound


377
Li$_{1.5}$In$_2$Se$_3$ are depicted in Fig. 4. The experimental dependences $\sigma_{\perp c}(T)$ and $n(T)$ for the hydrogenated In$_2$Se$_3$ crystals are depicted in Figs. 5–6.

As one can see from the data presented for the Li$_2$In$_2$Se$_3$ (Fig. 1) and H$_2$In$_2$Se$_3$ (Fig. 5) crystals, an increase of the temperature results in a monotonous decrease of $\sigma_{\perp c}$. It is worth paying attention to the nonmonotonous character of the temperature behavior of $\sigma_{\perp c}$ for the Li$_{1.0}$In$_2$Se$_3$ and Li$_{1.5}$In$_2$Se$_3$ intercalated samples in the temperature range 250–400 K. Thus, the performed measurements testify to the fact that the electrical conduction along layers decreases from 63.2 Ohm$^{-1}$cm$^{-1}$ (“pure” In$_2$Se$_3$) to 14.6 Ohm$^{-1}$cm$^{-1}$ (Li$_{1.5}$In$_2$Se$_3$) at $T$ = 80 K and from 25.3 Ohm$^{-1}$cm$^{-1}$ (“pure” In$_2$Se$_3$) to 9.5 Ohm$^{-1}$cm$^{-1}$ (Li$_{1.5}$In$_2$Se$_3$) at $T$ = 400 K. A somewhat opposite picture is observed in the hydrogenated intercalates (H)In$_2$Se$_3$: the electrical conduction of the samples hydrogenated during 24 h increases approximately sevenfold as compared to the initial In$_2$Se$_3$ sample. With the following twofold increase of the time of keeping (which is expected to induce an increase of the amount of introduced hydrogen), the electrical conduction decreases thrice.

Fig. 4. Temperature dependence of the electrical conduction anisotropy for a In$_2$Se$_3$ layered crystal (1) and the intercalation compound Li$_{1.5}$In$_2$Se$_3$ (2)

As follows from the temperature dependence of the Hall mobility of electrons along layers $\mu_{\perp c}$ (Fig. 2), curves 1–4 monotonously decrease in the temperature interval 80–400 K without any changes of the slope angle with respect to the temperature axis. Analyzing the obtained data (see Table), one can see that the parameter $\mu_{\perp c}$ at $T$ = 80 K decreases from 1050 cm$^2$/(V·s) (“pure” In$_2$Se$_3$) to 413 cm$^2$/(V·s) (Li$_{1.5}$In$_2$Se$_3$), while, at $T$ = 400 K, the Hall mobility along layers decreases from 325 cm$^2$/(V·s) (“pure” In$_2$Se$_3$) to 155 cm$^2$/(V·s) (Li$_{1.5}$In$_2$Se$_3$).

According to the temperature dependence of the free carrier concentration $n$ for Li$_{1.5}$In$_2$Se$_3$ (Fig. 3) and (H)In$_2$Se$_3$ (Fig. 6), the given parameter undergoes insignificant changes (see Table). That is why the temperature behavior of $\sigma_{\perp c}$ must be mainly determined by that of $\mu_{\perp c}$.

Analyzing the dependence $\sigma_{\perp c}(10^3/T)$ for In$_2$Se$_3$ and its lithium intercalates (Fig. 1), one can see that $\sigma_{\perp c}$ decreases, as the temperature increases, which testifies to the partially “metal” type of conduction of these compounds. The nonmonotonous behavior (partial growth) of $\sigma_{\perp c}$ for the Li$_{1.0}$In$_2$Se$_3$ and Li$_{1.5}$In$_2$Se$_3$ intercalation compounds in the temperature interval 250–400 K is possibly related to the activation of a shallow donor level [9, 10], which is also confirmed by a partial increase of the free carrier concentration on the experimental dependence $n(10^3/T)$ (Fig. 3, curves 3, 4). A decrease of $\sigma_{\perp c}$ and $n$ at a fixed temperature with increase in the lithium concentration (Figs. 1, 3) is due mostly to the fact that the intercalation of lithium ions can result in the formation of deformation defects that induce, in turn, the generation of acceptor levels in the forbidden band of the In$_2$Se$_3$ crystal.

Fig. 5. Temperature dependence of the layer-parallel electrical conduction $\sigma_{\perp c}$ for In$_2$Se$_3$ layered crystal (1) and In$_2$Se$_3$ crystals annealed in the hydrogen atmosphere during 24 (2) and 48 (3) h

Based on the obtained temperature dependences, we determined the anisotropy of the electrical conduction $N = (\sigma_{\perp c}/\sigma_{\parallel c})$ for initial In$_2$Se$_3$ crystals and their intercalates Li$_{1.5}$In$_2$Se$_3$: $N_{\text{In}_2\text{Se}_3} = 620$, $N_{\text{Li}_{1.5}\text{In}_2\text{Se}_3} = 525$ at $T$ = 80 K and $N_{\text{In}_2\text{Se}_3} = 5.7$, $N_{\text{Li}_{1.5}\text{In}_2\text{Se}_3} = 35$ at $T$ = 400 K. In other words, the anisotropies of the elec-
Experimental data on the electrical conduction, free carrier mobility, and concentration of a In$_2$Se$_3$ layered crystal and Li$_x$In$_2$Se$_3$ intercalation compounds obtained at 80 and 400 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_{\perp,c}$, Ohm$^{-1}$cm$^{-1}$</th>
<th>$\mu_{\perp, c}$, cm$^2$/V$\cdot$s</th>
<th>$n$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80 K</td>
<td>400 K</td>
<td>80 K</td>
</tr>
<tr>
<td>In$_2$Se$_3$</td>
<td>63.2</td>
<td>25.3</td>
<td>1050</td>
</tr>
<tr>
<td>Li$_{0.1}$In$_2$Se$_3$</td>
<td>36.1</td>
<td>17.2</td>
<td>802</td>
</tr>
<tr>
<td>Li$_{0.0}$In$_2$Se$_3$</td>
<td>16.2</td>
<td>9.8</td>
<td>597</td>
</tr>
<tr>
<td>Li$_{0.5}$In$_2$Se$_3$</td>
<td>14.6</td>
<td>9.5</td>
<td>413</td>
</tr>
</tbody>
</table>

Fig. 6. Temperature dependence of the free carrier concentration $n$ for In$_2$Se$_3$ layered crystal (1) and In$_2$Se$_3$ crystals annealed in the hydrogen atmosphere during 24 (2) and 48 (3) h
The electrical properties and the anisotropy of In\textsubscript{4} layered crystals, their lithium intercalates Li\textsubscript{x}In\textsubscript{2}Se\textsubscript{3} \((0.1 \leq x \leq 1.5)\), and In\textsubscript{2}Se\textsubscript{3} crystals annealed in the hydrogen atmosphere are investigated. It is established that, with increase in the temperature, the electrical conduction and the mobility along the layers decrease, whereas the free electron concentration remains practically constant. The reduction of the anisotropy parameter for the Li\textsubscript{1.5}In\textsubscript{2}Se\textsubscript{3} intercalate as compared with In\textsubscript{2}Se\textsubscript{3} in the temperature range \(250 \div 400\) K is related to the prevalence of the decrease of the layer-normal electrical conduction over the insignificant decrease of the layer-parallel one.

The growth of the electrical conduction for the In\textsubscript{2}Se\textsubscript{3} crystals hydrogenated during 24 h is explained by the rise of the free carrier concentration (a part of hydrogen intercalated into the crystal occupies the H\textsuperscript{+} state) and the formation of new levels in the forbidden band of the layered crystals at small amounts of intercalated hydrogen. An increase of the annealing time results in a growth of the interlayer pressure and a deformation of the crystal structure due to the intercalation, which significantly decreases the mobility of charge carriers, as well as the value of \(\sigma_{\perp c}\).

Thus, the intercalation allows one to control certain electrical parameters of In\textsubscript{2}Se\textsubscript{3} layered semiconductors depending on the nature, amount of intercalated impurity, and the way of intercalation. It is worth noting that the studied compounds represent effective model objects for fundamental investigations and are promising for their possible use as elements of energy and strain-sensing devices.


Translated from Ukrainian by H.G. Kalyuzhna

ELEКТРИЧНІ ВЛАСНІСТІ ІНТЕРКАЛЬОВАНИХ ШАРУВАТИХ КРИСТАЛІВ In\textsubscript{2}Se\textsubscript{3}