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Abstract

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Preparation, Structure, and Some Properties of Single-Crystal Films of Lead Selenide

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It is well known that the physical properties of thin semiconductor films obtained by sublimation in vacuum differ strongly from the properties of single crystals. This applies first of all to such important parameters as carrier mobility and lifetime; in films these parameters are much lower than in single crystals obtained from the melt or from the gas phase. This difference is evidently connected with the small size of the crystallites forming the film, with the existence of intercrystalline boundaries, and with the presence in the film of a large number of defects, such as dislocations, stacking faults, voids, vacant sites, etc.

In connection with the above, the problem of obtaining single-crystal semiconductor films with a perfect structure and the required physical properties is very important and timely.

In an earlier work by one of the authors it was shown (^1) that, in the case of semiconductors of the PbS group, such films can be obtained by using the phenomenon of epitaxy, i.e., oriented crystallization of one substance on the faces of another. The present work gives data on the structure and some properties of single-crystal films of lead selenide, which belongs to this group of semiconductors.

It is known that in semiconductors of the PbS group rather considerable deviations from stoichiometry are possible; moreover, the presence in the specimens of excess lead atoms leads to electronic conductivity, while atoms of S, Se, or Te lead to hole conductivity. Accordingly, both alloys close in composition to stoichiometric* and alloys with an excess of one of the components (0.5 wt.% Se and 2 wt.% Pb) were taken for evaporation.

Evaporation was carried out from graphite and tantalum evaporators in a vacuum of $\sim 10^{-5}$ mm Hg. Crystals of NaCl, LiF, and glass plates were used as substrates. The temperature of the evaporator and of the substrates was measured by means of platinum–rhodium thermocouples and was varied in different experiments from 580 to 1050° and from room temperature to 550°, respectively.

The thickness of the resulting films was measured with an MII-4 microscope (in the case of sufficiently thick films) and was varied, depending on the purpose of the investigation, from hundreds of angstroms to 5-10 μ. The structure of the films was investigated with an EG electron-diffraction camera and with an MIM-8 microscope.

During sublimation of substances of complex composition, their gas phase may in principle consist of the most diverse particles; for example, in the case of PbSe, of Pb and Se atoms, Pb^{++} and Se^{--} ions, or $PbSe^{-}$ and $PbSe^{+}$, etc.

Porter' s mass-spectroscopic investigations (ˆ2) indicate that, in the case of lead selenide, the gas phase contains mainly PbSe molecules, whose dissociation energy into Pb^{++} and Se^{--} ions is 61.5 kcal/mol (2.7 eV).

When PbSe vapors condense on a substrate at room temperature, the same features are observed as in the case of PbS films.

At the initial stages of deposition the films have a mirror-like appearance, and no structure is visible on their surface at magnifications up to 1000 times. However, as the thickness of the films increases, their appearance changes sharply and eventually, instead of an even mirror-like film, a loose soot-like film ("black") is formed.

Electron-diffraction study of such films (Fig. 1, see insert, p. 1337) established that they are not amorphous or oxidized, as is sometimes assumed. The crystallites in such films are oriented with a cube face parallel to the substrate (independently of its nature), and are arranged randomly in azimuth; in other words, under these condensation conditions (room temperature of the substrate) plate textures of the first kind (according to A. V. Shubnikov) are formed. If deposition is carried out for a sufficiently long time, individual crystallites grow so large that they become visible in an ordinary metallographic microscope.

The formation of soot-like specimens was observed earlier in the preparation of lead sulfide films. Electron-microscopic studies (3) indicate that in such films the crystallites have the form of long thin needles, densely covering the entire surface of the substrate and forming a loose velvety structure. Such a surface absorbs all the light incident upon it, reflecting nothing, which accounts for the black velvety color of these specimens.

When the temperature of the substrate is raised, the specimens behave differently depending on the substrate material. On glass and LiF crystals, at a certain substrate temperature, a transition is observed from soot-like films to gray matte specimens with a rough surface resembling that of polished metal. Electron diffraction patterns from such specimens show a strong background and several sharp rings. Microscopic studies indicate the presence in the film of rather large crystallites ($\sim 1\,\mu$), arranged randomly with respect to one another.

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A completely different picture is observed when films are prepared on heated NaCl crystals. Here, at a certain substrate temperature, the film remains mirror-like and smooth throughout, despite the increase in its thickness. When viewed under a microscope, no structure is visible on the film surface even at 1000-fold magnification. Electron-diffraction studies indicate that such films are single-crystalline; however, depending on the substrate temperature and the deposition rate, electron diffraction patterns of various types are obtained, indicating different degrees of perfection in the structure of the films (Figs. 2 and 3).

At a substrate temperature of $\sim$ 350°, films were obtained whose electron diffraction patterns show many round reflections arranged at the nodes of a two-dimensional lattice (Fig. 2). Such photographs indicate a strongly pronounced mosaicity of the specimens. They contain reflections from the PbSe cube face up to the 12th order, which corresponds to a misorientation in the positions of individual crystallites of $\sim$ 1–3 degrees.

When the substrate temperature is raised to 400°, continuous lines with points located on them appear in the corresponding photographs; this indicates an increase in the size of the blocks and a decrease in mosaicity. Finally, at a substrate temperature of about 500°, specimens are obtained whose electron diffraction patterns contain only vertically arranged "rods," which indicates the absence of noticeable mosaicity in the specimens (Fig. 3).

The indicated temperature intervals are relative, since the structure of the films, as noted above, depends strongly also on the deposition rate and on the crucible temperature; the substrate-temperature values given above were obtained at an evaporator temperature of 690–700°.

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Fig. 1. Electron diffraction pattern from a spherulitic PbSe film obtained on the cube face of an NaCl crystal at room temperature. Film thickness $\sim 2\,\mu$.

Fig. 2. Electron diffraction pattern from a single-crystal PbSe film obtained on the cube face of an NaCl crystal heated to 350°. Film thickness $5\,\mu$.

Fig. 3. Electron diffraction pattern from a single-crystal PbSe film obtained on the cube face of an NaCl crystal heated to 500°. Film thickness $6\,\mu$.

The single-crystal structure of PbSe films is more clearly manifested in their mechanical properties, in particular in the microphotograph of a cracked and broken film (Fig. 4). This microphotograph was obtained from a PbSe film exposed after dissolution of the NaCl crystal onto a glass plate. During the exposure process the specimen cracked and was partially destroyed; as can be seen from the figure, cracks formed in the specimens along directions of the type [100], i.e., along cleavage planes.

Fig. 4. Microphotograph of a cracked single-crystal PbSe film (540×). Film thickness ~ 3 μ.

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Figure 1: Fig. 4. Microphotograph of a cracked single-crystal PbSe film (540×). Film thickness ~ 3 μ

In some places the film cracked into many narrow (~5 μ) strips passing through the entire specimen. It is possible that such cracking is associated with the presence in the film of elastic stresses arising from the large difference in the coefficients of thermal expansion of the substrate ($4 \cdot 10^{-5}$) and the film ($2 \cdot 10^{-5}$). Electron-diffraction data on the dependence of the perfection of the film structure (mosaicity) on the substrate temperature were fully confirmed in measurements of the electrical conductivity and Hall effect of the films. These measurements were carried out in a magnetic field of 7000 oersted using a conventional potentiometric circuit. To eliminate error in determining the film thickness, the mobility was determined in the usual way (as the product $R\sigma$) and by the formula

$$\mu = \frac{V_x 10^8 l}{V_\rho H a} \, \frac{\text{cm}^2}{\text{V} \cdot \text{sec}}.$$

Here V_x is the Hall emf in volts, V_ρ is the voltage drop across a film of length l, and a is the film width.

The results of measurements on several specimens are presented in Table 1. From this table it is clear that, with increasing substrate temperature, the carrier mobility increases, which is evidently associated with improvement of the film structure, as discussed above. The mobility has its highest value in films obtained at 500-525°, and approaches values characteristic of the best single crystals grown from the melt (800-1000 cm^2/V · sec—*see*(4)).

For the carrier concentration in single-crystal films, values are also obtained that are characteristic of ordinary PbSe single crystals (10^{18}—10^{19} cm^{-3}). Attention is drawn to the change in the type of conductivity of the films that occurs when the substrate temperature is increased. This change in the sign of the carriers occurs in the region 480—500°.

Table 1

Results of measurements of the electrical conductivity and Hall effect of single-crystal PbSe films

Sample No.	Conductivity type	Substrate temp., °C	Thickness, μ	R_x, cm^3/C	σ, cm^{-1} · Ω^{-1}	μ, cm^2/V· s	n, 10^{18} cm^{-3}	Annealing temp., °C
144	n	250	2.2	1.0	292	315	5.7	760

Sample No.	Conductivity type	Substrate temp., °C	Thickness, μ	R_x, cm^3/C	σ, cm$^{-1}\cdot\Omega^{-1}$	μ, cm^2/V$\cdot$s	n, 10^{18} cm^{-3}	Annealing temp., °C
158	n	300	3.0	1.2	345	425	5.2	740
152	n	350	2.4	2.6	231	635	2	760
157	n	400	2.2	2.3	329	766	2.7	760
160	n	450	2.7	1.4	244	355	4.2	760
139	n	480	2.2	5.6	70	395	1	980
155	p	500	3.9	2.0	482	971	3	810
145	p	525	3.9	2.6	386	1014	2	1050
162	p	525	3.3	1.7	595	970	2.8	1050

Thus, the main parameters of the single-crystal PbSe films obtained in this work practically do not differ from the parameters characteristic of ordinary single crystals. In this connection, let us note that in polycrystalline films the carrier mobility is only 0.5—40 cm^2/V $\cdot$ s (^{5}).

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