FINE STRUCTURE OF THE ABSORPTION SPECTRA OF POLYCRYSTALLINE CdS FILMS

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N. V. PIROGOVA

FINE STRUCTURE OF THE ABSORPTION SPECTRA OF POLYCRYSTALLINE CdS FILMS

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As was established in (1), the absorption spectrum of polycrystalline cadmium sulfide films at room temperature in the region 460–507 mμ, depending on the conditions under which the specimens studied were prepared, may have one or two absorption maxima. As the temperature is lowered, these maxima behave differently. In particular, the long-wavelength maximum exhibits doublet splitting, while the short-wavelength maximum shifts toward shorter wavelengths and in some specimens splits into a triplet. In this connection, studies of the influence of the conditions of preparation of specimens on their absorption spectrum at low temperatures are of particular interest.

For this purpose, films were prepared by sublimating cadmium sulfide powder in different media. In our case, deposition of the films was carried out in vacuum at a pressure of 10^{-5} mm, and also in an atmosphere of argon and hydrogen sulfide at a pressure of 0.5–1 mm. The experimental apparatus in which the specimens were prepared prevented foreign impurities from entering the sublimate during its deposition.

In order to establish the relation between the number of absorption bands in the absorption spectrum of polycrystalline CdS films and the conditions of their deposition, it is first necessary to exclude the influence of the thickness of the specimens studied. In this connection, to avoid random results, the thickness of the films studied in our experiments was varied over wide limits from 10^{-6} to 10^{-4} cm.

The relation between the number of absorption bands of thin cadmium sulfide layers and the conditions of their preparation was established by us on the basis of a large body of statistical material.

As we found, all films deposited on substrates that had not been preheated, irrespective of the medium in which they were prepared, do not luminesce at liquid-nitrogen temperature and, in the region 460–507 mμ, have no absorption bands. At the same time, layers prepared in vacuum and in an argon atmosphere are low-resistance, with a specific resistance of 10^{-2}–1 ohm $\cdot$ cm. In addition, such films have no photoconductivity. Among films deposited in

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

an atmosphere of hydrogen sulfide on specially unheated substrates, there are both low-resistance and high-resistance specimens with a specific resistance of more than 10^6 ohm • cm. Specimens with a specific resistance of more than 10^2 ohm • cm, as a rule, showed photoconductivity. However, such layers also did not exhibit luminescence and had no absorption band in the spectral region studied.

Cadmium sulfide films deposited on substrates preheated to temperatures of 300, 350, 450, 500, and 550°, irrespective of the medium in which they were prepared, at liquid-nitrogen temperature in the region 460–507 mμ exhibit absorption bands and luminesce with green light. It is very important to note here that with increasing tempera-

the preliminary heating temperature of the substrate, the luminescence intensity of the samples increases.

A study of different parts of the specimens at 77.3° K showed that, when passing from one region of a sample to another, the number of absorption bands remains the same. The number of bands also does not change in the case when repeated immersion of the specimen in liquid nitrogen even led to its considerable destruction. This fact evidently indicates that there is no fundamental connection between surface, purely defect-related phenomena and the presence of absorption bands in the absorption spectrum of cadmium sulfide.

Fig. 1

Fig. 2

Figure 1 shows microphotograms of the absorption spectra of films obtained in vacuum at a substrate preheating temperature of 300°. As is seen from the figure, in layers prepared, it would seem, under identical conditions, the spectra are very different. Thus, in the absorption spectrum of sample No. 244 absorption bands are absent; in film No. 232 there is only a hint of a structural character of the spectrum; and specimen No. 234 reveals three clearly expressed absorption maxima, located at $\lambda\lambda$ 4880, 4840, 4731 Å. In addition, in the spectrum of the last sample there is also observed a fourth, very weak band at λ 4785 Å. These changes in the spectra of the indicated samples were not determined by the thickness of the absorbing layers. In the present case films Nos. 244 and 232 have practically the same thickness, $4 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ cm, while for specimen No. 234 the thickness is an order of magnitude smaller ($6.7 \cdot 10^{-6}$ cm) than for the first two. Nevertheless, clearly expressed maxima occur in its spectrum.

It should be noted that all the indicated samples possess photoconductivity. Luminescence, however, is observed visually only for specimen No. 234. As for the specific resistivities, they are different and, respectively, equal to: 8, 28, and $2 \cdot 10^6$ ohm • cm. From a comparison of the specific resistivities of the layers it may be concluded that, under the given conditions of preparation of the specimens, absorption bands appear only in high-resistance samples.

The fact that, among specimens deposited on substrates preliminarily heated to 300°, there are both films in which absorption maxima are observed and samples in which they are absent indicates that this substrate preheating temperature is a limiting one, i.e., near this temperature, in the formation of polycrystalline cadmium sulfide layers, changes begin to occur which cause the appearance of absorption bands in their absorption spectra.

Samples prepared at substrate preheating temperatures of 350, 450, 500, and 550°, regardless of the medium in which they were deposited, as a rule luminesce and have a complex absorption spectrum. The number of maxima in the spectrum at 77.3° K differs for different samples and depends on the preliminary heating temperature of the substrate at which the film was deposited. Thus, with preliminary heating

substrate heating to 350°, the samples are characterized by an absorption spectrum having three absorption maxima (Fig. 2, 1). The position of the indicated bands varies rather considerably from sample to sample. In films prepared in an atmosphere of hydrogen sulfide, the first maximum shifts from sample to sample by 9 Å (from 4873 to 4882 Å), the second by 17 Å (from 4832 to 4849 Å), and the third by 30 Å (from 4699 to 4729 Å). In samples deposited in an argon atmosphere, this shift is somewhat smaller: for the first band it is 5 Å (from 4873 to 4878 Å), for the second 13 Å (from 4838 to 4851 Å), and for the third 11 Å (from 4704 to 4715 Å).

Fig. 3
Fig. 3

Fig. 4
Fig. 4

However, at a substrate preheating temperature of up to 450°, the number of absorption bands depends on the medium in which the specimens are prepared. For example, for vacuum samples the number of bands remains the same as in the preceding case, i.e., equal to three (Fig. 3, 1). Their position from sample to sample varies: for the first from 4875 to 4878 Å, for the second from 4832 to 4849 Å, and for the third from 4705 to 4735 Å. In layers obtained in an atmosphere of hydrogen sulfide, the absorption spectrum consists of five bands (Fig. 2, 2), whose maxima occur at $\lambda\lambda$ 4878–4880, 4838–4851, 4800–4801, 4702–4731, and 4641–4676 Å. As our studies have shown, the absorption spectrum of films deposited in an argon atmosphere may have either three or five absorption maxima (Fig. 4, 1 and 2). In this case the position of the first varies from sample to sample within the limits from 4875 to 4882 Å, the second from 4832 to 4849 Å, the third from 4794 to 4798 Å, the fourth from 4701 to 4735 Å, and the fifth from 4650 to 4676 Å.

In samples obtained in vacuum, even with preliminary heating of the substrate to 500°, the number of maxima does not exceed three or four (Fig. 3, 2 and 3). Their positions correspond to $\lambda\lambda$ 4878–4882, 4838–4846, $\sim$ 4792, 4704 –4725 Å. The absorption spectrum of films deposited in argon at the same substrate-heating temperature reveals five absorption bands (Fig. 4, 3), and their positions are rather constant and are at $\lambda\lambda$ 4873–4878, 4834–4935, 4790 –4796, 4702–4704, 4641 Å.

Thus, we have experimentally established that the presence of absorption bands in the absorption spectrum of polycrystalline cadmium sulfide films, as well as their number at 77.3° K, depends on the conditions of preparation of the specimens and, above all, on the temperature of preliminary heating of the substrate. With an increase in temperature from 350 to 550°, the number of maxima increases–

from 3 to 5, and at the same time the intensity of the luminescence increases. These bands, as shown in work (1), are due to the absorption of cadmium atoms in excess of the stoichiometric composition. In this case, through the quantum of absorbed light, an electron from the normal level of an excess cadmium atom, ${}^1S_0$, is transferred to its excitation levels ${}^3P_1$ and ${}^3P_2$, of which the first is split in the electric field of the crystal lattice into a doublet, and the second into a triplet.

The influence of the temperature of the substrate during deposition of the semiconductor film on it may manifest itself, first of all, in a disturbance of the stoichiometry of the composition of the sublimate. In addition, a change in the temperature of preliminary heating of the substrate may also affect the crystalline structure of the deposited layer. Therefore, the differences we have found in the absorption spectra of samples deposited under different conditions should be attributed either to a change in impurity concentration–namely, the concentration of excess cadmium atoms–or to a change in the crystalline structure of the cadmium sulfide lattice. As follows from the theoretical work of Bete (3), in the lattice of the hexagonal modification the splitting of impurity electronic levels in the fields of the crystal should occur according to the law $j+1$. Thus, the fact that five absorption bands are observed in the CdS absorption spectrum only for preparations obtained at high temperatures of preliminary heating of the substrate evidently indicates that only under these conditions of film deposition do cadmium sulfide films possess a hexagonal lattice. In all other cases, deviations from this modification exist to one degree or another.

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