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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF TEMPERATURE ON THE OPTICAL ABSORPTION OF POLYCRYSTALLINE LAYERS OF CADMIUM SULFIDE

(Presented by Academician V. N. Kondrat' ev on 17 III 1960)

The present communication sets forth the results of investigations of the influence of temperature on the optical absorption of cadmium sulfide layers. At room temperature, the absorption spectra of polycrystalline CdS films have been studied by a number of authors ([1]-[3]). In paper ([3]) it was established that the absorption spectrum of thin CdS layers is complex and, in the region 300-550 mμ, has three absorption maxima at $\lambda\lambda$ 340, 420, 500 mμ.

Until now, similar investigations ([2], [3]) were carried out on an OF-4 instrument. We set ourselves the task of studying, by a photographic method, the structure of the long-wavelength absorption maximum of CdS films, using an instrument with sufficiently large dispersion. The spectra were photographed with the aid of the UF-84 camera of an ISP-51 spectrograph. In addition, it seemed to us of fundamental importance to establish whether changes occur in the structure of the maximum under investigation when the temperature is lowered from room temperature to the temperature of liquid nitrogen. Such experiments are of interest from the point of view of obtaining new additional information explaining the nature of the indicated absorption maximum and, what is especially important, may give a picture of the dynamics of the appearance of cadmium sulfide absorption bands at low temperatures, the nature of which remains controversial up to the present time ([5], [6]).

The layers studied by us were prepared by sublimation of cadmium sulfide powder in vacuum (10^{-5} mm), in an atmosphere of argon and hydrogen sulfide at a pressure of 0.5-1 mm. Deposition of the films was carried out on substrates that had not been specially preheated beforehand and at the beginning of evaporation were at room temperature, as well as on substrates preheated to temperatures of 300, 350, 450, 500, and 550°. The experimental apparatus in which the specimens for investigation were prepared was designed in such a way that the evaporator heater, as well as the substrate heater, remained outside the evaporation volume during the entire film-deposition process, and therefore the introduction of extraneous impurities into the semiconductor layer during

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Fig. 1. Microphotograms of the absorption spectra of CdS films deposited in an atmosphere of H_2S on substrates heated to 350 (A), 500 (B), and 550° C (V)

Figure 1: Fig. 1. Microphotograms of the absorption spectra of CdS films deposited in an atmosphere of H_2S on substrates heated to 350 (A), 500 (B), and 550° C (V)

its deposition was excluded. Glass and quartz plates were used as substrates.

Our experiments established that films deposited on preheated substrates, regardless of the medium in which they were prepared, in the region 460–507 mμ, both at room temperature and at the temperature of liquid nitrogen, do not exhibit absorption bands. Layers sublimed onto substrates preheated to not less than 300° C exhibit green luminescence and, in the region where on the SF-4 at room temperature one long-wavelength absorption maximum was observed ([2], [3]), with the spectrographic method of investigation they have one or two absorption maxima (Fig. 1). At a temperature of 77.3° K the absorption spectrum of such samples has a complex structure (Fig. 1).

In the present communication it is impossible to consider in detail such phenomena as the influence on the absorption spectrum of the medium in which the deposition took place—

and also the effect of the temperature of preliminary heating of the substrate. Here only the main regularities in the change of CdS absorption upon changing the temperature of investigation from room temperature to the temperature of liquid nitrogen will be discussed. Fig. 1 shows the most characteristic microphotograms of the spectra. In order to avoid confusion when considering the figures, the microphotograms have been arbitrarily displaced with respect to one another in height. However, as was established, when the temperature at which absorption was studied is lowered, there is in fact always a decrease in the background of continuous absorption, although not to such an extent,

Fig. 1. Microphotograms of the absorption spectra of CdS films deposited in an atmosphere of H_2S on substrates heated to 350 (A), 500 (B), and 550° C (V)

as follows from Fig. 1, but in some samples it is quite pronounced. It should be noted that this phenomenon is not connected with the thickness of the layer under study. At the same film thickness, some samples were transparent, while others were completely opaque in the region 4600–5070 Å. This indicates that the factor determining absorption in the indicated part of the spectrum varies from sample to sample. Therefore it cannot be attributed to fundamental absorption and is evidently due to the presence of absorbing centers, whose concentration is not the same in all specimens. In our experiments the conditions for preparing the layers under investigation excluded the introduction into the sublimate of extraneous impurities and, consequently, the impurity could only have been atoms of one of the components of the substance in excess of the

stoichiometric composition. In work (3) it was shown that, owing to the high volatility of sulfur, such an impurity consists of excess cadmium atoms. The absorption of these excess metal atoms above the stoichiometric composition determines the absorption of CdS in the spectral region under consideration.

When the temperature is lowered from room temperature to that of liquid nitrogen, as our investigations have shown, there is observed for all films (Fig. 1) a shift of the absorption maxima into the short-wavelength region of the spectrum and a doublet splitting of the long-wavelength band. The short-wavelength band at room temperature is not present in all samples. In cases where it is observed, lowering the temperature down to 77.3° K does not cause its splitting. In addition, depending on the conditions of preparation of the specimen, one or two further absorption bands may appear in the investigated part of the spectrum at low temperatures.

As follows from Fig. 1, the splitting of the long-wavelength maximum occurs differently in different samples. Fig. 1A shows microphotograms of the absorption spectra of a cadmium sulfide film prepared in an atmosphere of hydrogen sulfide with preliminary heating of the substrate

up to 350° C. For it, the long-wavelength maximum splits in the temperature interval 127–161° K. In this case the splitting is preceded by a considerable narrowing of this band. It is interesting that the absorption intensities in the bands arising as a result of the splitting are different, and the short-wavelength maximum of the doublet splitting is substantially greater in intensity than the long-wavelength one. Taking into account the splitting at liquid-nitrogen temperature, the spectrum of such a film consists of three clearly expressed maxima at $\lambda\lambda$ 4876, 4849, 4723 Å.

Microphotograms of the absorption spectra shown in Fig. 1B, for a film prepared in vacuum with preliminary heating of the substrate to 500° C, reveal an entirely different splitting pattern. First, at room temperature there is only one absorption maximum in the investigated spectral region. In comparison with the corresponding maximum of Fig. 1A, it is shifted into the long-wavelength region by approximately 30 Å. It should be noted that such a shift was not caused by a change in the temperature of the specimen under investigation. The short-wavelength maximum appears only at a temperature below room temperature —approximately at 230° K. It is comparatively small even at liquid-nitrogen temperature. First, in this case the fairly broad long-wavelength absorption maximum splits into two maxima of approximately equal intensity, and as the temperature is lowered the magnitude of the first of them becomes greater than that of the second. For such films the splitting effect is observed in the temperature interval 167–193° K, i.e., at a higher temperature than in the preceding case. As follows from Fig. 1B, at a temperature close to that of liquid nitrogen one more absorption band appears, located between the principal absorption maxima. Thus, in this case at 77.3° K the absorption spectrum of the polycrystalline CdS film in the region studied has four maxima at $\lambda\lambda$ 4882, 4838, 4730, and 4707 Å.

Figure 1C shows microphotograms of the absorption spectrum of a film prepared in an argon atmosphere with preliminary heating of the substrate to 550° C. At room temperature the absorption spectrum of the specified film consists of two bands. Splitting of the long-wavelength maximum is observed in the temperature interval 223–193° K, i.e., at a higher temperature than in the two preceding cases. In this case the magnitude of the short-wavelength doublet of the splitting is considerably greater than that of the long-wavelength one. However, with a further decrease in temperature the intensity of the long-wavelength doublet of the splitting also becomes significant. In addition, at a temperature lying in the interval 223–193° K a fourth absorption band appears, and in the temperature interval 161–135° K a fifth band is also observed. At liquid-nitrogen temperature the positions of the absorption maxima of this film correspond to $\lambda\lambda$ 4878, 4838, 4807, 4706, and 4637 Å.

Thus, the results obtained indicate that the presence of absorption bands in the absorption spectrum of cadmium sulfide in the region 4600–5070 Å depends on the conditions of preparation of the specimens. In addition, the presence of these bands is most closely connected with the luminescence of the films at low temperatures. Our spectrographic investigations showed that cadmium sulfide layers at room temperature in the region of 5000 Å may have one or two absorption maxima, depending on the technology used to obtain the specimens.

As was noted, absorption in the indicated part of the spectrum in our case as well was not determined by the thickness of the specimens studied. This fact is in complete agreement with the conclusion ([3]) concerning the impurity character of the absorption of cadmium sulfide in the region 460–507 mμ.

It is evident from the figures presented that the absorption spectrum at low temperatures consists of several bands. This indicates that the absorption of light by the impurity center occurs by transition of the electron from the normal impurity level to its excitation levels. Our investi-

···studies showed that the long-wavelength and short-wavelength absorption maxima behave differently when the temperature is lowered from 293 to 77.3° K. Consequently, they are due to different optical transitions in the cadmium impurity atom. On the basis of the energy scheme of the excited states of this isolated atom, such transitions may be: ${}^1s_0$—${}^3p_1$ and ${}^1s_0$—${}^3p_2$.

It is known from the works ([6]) that, under the action of the intracrystalline field, the energy level of the activator ${}^3p_1$ may undergo doublet splitting, and the level ${}^3p_2$, triplet splitting. In our case this effect is observed only at sufficiently low temperatures. This is evidently explained by the fact that the energy interval between the split levels is small. As a result, at room temperature, because of thermal vibrations, such splitting will most likely not be detected experimentally. With decreasing temperature, i.e., as thermal vibrations diminish, optical transitions from the normal state to the split levels of the ${}^3p_1$ and ${}^3p_2$ states begin to appear as independent absorption bands, which is what we observe experimentally.

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