NONELECTRONIC PROPERTIES OF SEMICONDUCTORS
(ATOMIC STRUCTURE, DIFFUSION)

Solubility of Oxygen in CdS Single Crystals and Their Physicochemical Properties

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Abstract—The specific features of oxygen dissolution in CdS using the example of single crystals grown by the gas-transport method with deviations from stoichiometry at 1100°C are considered. The effect of various types of intrinsic point defects in crystals of different composition on the form in the presence of oxygen is analyzed. It is shown that the most stable composition thermodynamically is that corresponding to nonstoichiometric "self-activated cadmium sulphide" stabilized with oxygen.

1. INTRODUCTION

The issue concerning the solubility of oxygen in $A^{II}B^{VI}$ compounds has many times been raised during the course of studies of these compounds [1–5]. An analysis of related publications over the past two decades makes it possible to remove existing contradictions related to the possible value of the solubility of this impurity and the role of intrinsic point defects. We study defect formation in CdS on the basis of the Schottky–Frenkel scheme, for which, its correspondence to the electrical properties of CdS in contrast to the antistructure model was previously demonstrated. Under the conditions of growth, oxygen behaves as a background impurity up to the saturation limit [2, 4].

2. EXPERIMENTAL

The calculated concentrations of point defects are correlated with the growth conditions of single crystals by the Markov–Davydov method at 1100°C within the limit of CdS homogeneity (Fig. 1). In Fig. 1, the conditions of single-crystal growth are mapped by a diagram on the P_{Cd} scale, which determines the composition of the crystal by the location of dashes on the P_{Cd} scale, while the length of dashes determines the content of oxygen in these crystals [4]. It can be seen that the solubility of oxygen in the case of the deviation of crystals from stoichiometry does not vary smoothly but passes through a maximum.

According to experimental data, the largest amount of oxygen corresponds to compositions in the central part of the diagram: from the point of stoichiometry $\delta = 0$ to the point P_{dis}. Crystals grown at a low sulfur-vapor pressure transition to the solid phase to the region of compositions with a slight cadmium excess. Such crystals contain positively charged intrinsic point defects $Cd_i^{\bullet}$, which can provide the volume and, partially, charge-related compensation of oxygen in the $A^{II}B^{VI}$ lattice. Within the limits of the entire region of homogeneity, these samples feature the crystalline-structure homogeneity described in [3, 4]. Previous studies [3, 4] revealed characteristic self-activated (SA) emission for compositions related to the central area of the diagram. The highest intensity of SA emission is observed when the concentration of singly positively charged $Cd_i^{\bullet}$ defects is equal to the concentration of doubly negatively charged V_{Cd}'' centers, which gives rise to the highest concentration of $\{V_{Cd}''-Cd_i^{\bullet}\}'$ complexes or A centers [1].

A centers can be formed with the involvement of oxygen, which possesses an effective negative charge O_S^*. In addition, oxygen located at the sulfur lattice site (O_S^*) as an isoelectronic substitutional impurity (with a large difference in terms of properties from the S_S of the main lattice), due to the forces of volume compensation ($-\Delta V$) and effective negative charge (*), interacts with the closest cadmium atom. Such representations were developed for alkali-halide and $A^{II}B^{VI}$ crystals [6–9]. In this case, a Cd atom shifts from the lattice site (the center of a tetrahedron) in the direction [111] to oxygen until stable equilibrium is attained. The shift of the cadmium atom $Cd_{Cd} \rightarrow Cd_i^{\bullet}$ under the impact of the isoelectronic oxygen impurity can be considered as the formation of a V_{Cd}'' vacancy and of cadmium in an interstitial position $Cd_i^{\bullet}$. In this
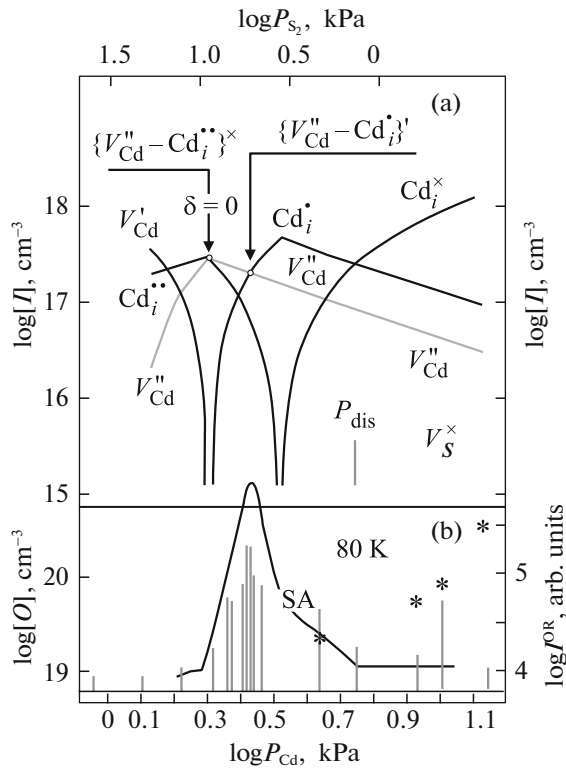
Fig. 1. Diagram of equilibrium for intrinsic point defects in gas-phase CdS at 1100°C; a variation in the composition of crystals with oxygen and the intensity of self-activated (SA) and orange (OR) (asterisks) emissions at 80 K. Charge states of defects (−, − −, 0, +, and ++) are designated as (', ", ×, •, and ••), respectively. The model of an A center with the inclusion of oxygen for an example of CdS is represented below.

case, the A center corresponds to the $\{V_{Cd}''{-}Cd_i^\bullet O_S^*\}'$ complex, which is stabilized by oxygen. A luminescence center can have a more complex structure than that of an A center [4]. The model assumes the inclusion of oxygen in the composition of the center. The results of experiments shown in Fig. 1 confirm that a variation in the intensity of SA emission reproduces the variation in the concentrations of oxygen and the A centers, with the maximum in the intensity of SA emission corresponding to the largest number of A centers in the crystals.
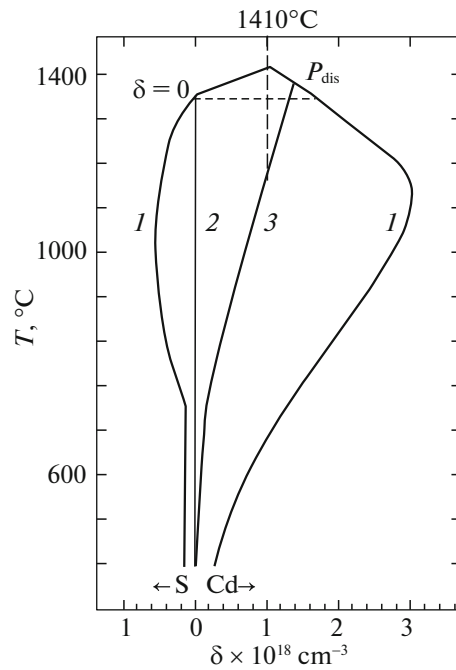

Fig. 2. Dependence of the melting temperature for cadmium sulfide on the composition within the homogeneity region [10]. The curves determine the deviation from stoichiometry (*1−1*), stoichiometry (*2*), and the dissociation pressure (*3*).

Comparison of our results with the data obtained in studies [10], restricted to the region of CdS homogeneity, shown in Fig. 2 makes it possible to obtain additional information on the compositions in the central region of the diagram of defect-formation in CdS from δ = 0 to the P_{dis} point.

As can be seen from Fig. 2, these compositions are specific in the fact that they feature a higher melting temperature compared to other compositions corresponding, in particular, to stoichiometric CdS. The region of compositions under consideration includes a point with the largest amount of oxygen A complexes, which stabilize the structure, and also points coinciding with the above one: the points of highest SA-luminescence intensity and the point of highest CdS melting temperature.

The sum of data makes it possible to compare the composition of the thermodynamically most stable nonstoichiometric CdS (Fig. 2) with that of "self-activated cadmium sulfide" (Fig. 1). It is stabilized due to oxygen. The notion of "self-activated" compound is widely used in available publications; however, the essence of it has thus far not been adequately determined.

3. OXYGEN IN CdS WITH AN EXCESS OF SULFUR AND IN STOICHIOMETRIC CRYSTALS

This range of CdS compositions from the point of stoichiometry δ = 0 to an excess of sulfur is poor in

oxygen (Fig. 1). In such compounds, there are no intrinsic defects, which can interact with oxygen and compensate the O_S^* centers. In fact, oxygen located at a lattice site gives rise to local compressive strains ($-\Delta V$) such as those produced by all other vacancies. The $Cd_i^{\bullet\bullet}$ defects ($+\Delta V$) only slightly compensate the volume incompatibility of vacancies since the size of the $Cd_i^{\bullet\bullet}$ defects and their concentration are much smaller than those of $Cd_i^{\bullet\bullet}$ in the central region.

A significant decrease in $[O]$ is observed already at the stoichiometry point $\delta = 0$ (Fig. 1). This point corresponds to the equality of the concentrations of defects $Cd_i^{\bullet\bullet}$ and V_{Cd}'' and their complexes $\{Cd_i^{\bullet\bullet}-V_{Cd}''\}^\times$. It was shown previously [3, 4] that the acceptor level of such a neutral complex is related to a center giving rise to another emission (the SAL emission), the highest intensity of which corresponds to the point $\delta = 0$. In addition, intensification of the SAL emission and its peak at the point of stoichiometry do not correlate with the oxygen concentration in the crystals. Evidently, oxygen is not involved in the composition of the $\{Cd_i^{\bullet\bullet}-V_{Cd}''\}^\times$ complex, which includes the same defects as those described above for the region with a sulfur excess.

Trends in variations in the composition of CdS crystals with deviations from stoichiometry in the case of the interaction of a gaseous phase containing oxygen are determined by CdS–CdSO$_4$–CdO equilibrium [11]. According to this equilibrium, in the case where a constant ratio of Cd/S is maintained, a significant increase in the concentration of the oxygen dopant in the growth atmosphere leads to transition to the region of stability of cadmium sulfide rather than to an increase in the solubility of oxygen in the CdS(O) solid solution.

According to experimental data, the limiting content of solved oxygen in the CdS crystals under study does not exceed 1 mol % (2×10^{20} cm^{-3}). Such concentrations are typical of impurities of the HMAs type but are significantly lower than was previously assumed in [5]. The obtained data on variations in the oxygen concentration within the homogeneity region for CdS make it possible to explain the mirror run of the curve characterizing a decrease in the lattice parameter of these crystals as a function of composition [12]. The largest amount of oxygen, which can be introduced into the lattice of the gas-phase-grown cadmium sulfide at a temperature close to that of melting is ⩽3 mol % [4].

In this context, it is not clear whether it is possible to obtain samples of the CdS(O) solid solution in the region of intermediate compositions in the CdS–CdO system since an increase in the amount of oxygen in the gas phase during the course of growth transfers the crystal to the region of stability of other equilibrium phases of cadmium sulfide or oxide. Such data were reported previously [13, 14]. However, recently there have appeared publications, which contain the first experimental data on the possibility of forming such systems of solid solutions under nonequilibrium conditions with the use of radio-frequency magnetron sputtering [19].

4. FEATURES OF THE INCORPORATION OF OXYGEN INTO CRYSTALS WITH A LARGE CADMIUM EXCESS

An area of the diagram of defect equilibrium for such samples corresponds to the crystals grown in the case where cadmium vapors with increasing $P_{Cd} > P_{dis}$ in the growth zone. In general, for all crystals grown with a large cadmium excess, the oxygen concentration was on the order of 10^{19} cm^{-3}. Oxygen has an effective negative charge and interacts less actively with neutral defects $Cd_i^\times$ and $V_s^{\,x}$, which are dominant in these samples, and number of SA complexes decreases almost to zero (Fig. 1).

However, in addition to the general pattern, the content of oxygen in some samples of this group could be much higher, e.g., as high as ~10^{21} cm^{-3}. As we already noted, the crystals cannot be classified as CdS(O) solid solutions at such oxygen concentrations. The assumptions were confirmed by studies of the cathodoluminescence spectra of these crystals [13], in which the exciton bands of cadmium oxide were observed. The spectral positions of these bands refine the value of the direct band gap of CdO (2.45 eV at 80 K and 2.37 eV at 300 K). The possibility of the simultaneous formation of CdO and CdS phases is most probably related to the introduction of cadmium vapors during growth since the growth region in this case is ultimately close to the CdS/CdO phase boundary [11].

Additional information is provided by analysis of the crystal structure for crystals with a large cadmium excess. Previous studies [3, 4] showed that, in the case of such crystals, there is partial decomposition of the CdS(O)Cd solid solution during the course of cooling from the temperature of growth, which manifests itself in scanning electron microscopy as a layered inhomogeneity of the bulk. This inhomogeneity is related to precipitations of cadmium on the (0001) planes. The structure is unstable upon aging or annealing and under the effect of irradiation [4, 15].

The oxygen in such crystals is not bonded in complexes. Apparently, this induces a large increase (compared with that calculated) in the concentration of sulfur vacancies in CdSCd as a result of the possible removal of sulfur with volatile SO$_2$. At the surface, a layer depleted of oxygen with a thickness to 0.2 μm and nanocrystals of oxygen-free CdS are formed [4, 9, 14].

A study of the optical properties of the group of crystals under consideration with a cadmium excess reveals unusual orange emission with a peak at 630 nm (see Fig. 1, asterisks). The intensity of emission increases with excess cadmium but does not correlate with the oxygen concentration in the crystals.

Orange emission appears at the surface of crystals since the luminescence spectra (Fig. 1, arrows) were measured using a method, which involved a small information-layer depth [4, 3, 9]. Initially, the nature of the orange band was erroneously related to emission from F^+ centers [3, 4, 7, 16]. Subsequently, it was shown [17] that the intracenter transitions from an excited level to the ground level of an F^+ center occur nonradiatively. However, orange emission from sulfur vacancies in CdS was found to be typical, especially, in studies of the optical properties of CdS nanocrystals (see, e.g., [18]). The surface of such samples is a source of multiple sulfur vacancies. However, the nature of emission with a wavelength of 630 nm from V_S has attained a new interpretation. This emission is related to the transitions of excited-band electrons to the V_S surface recombination levels [18]. According to the works [15, 16], the orange emission is induced by an electron beam in the studies, using scanning electron microscopy, of CdS crystals with a cadmium excess.

5. CONCLUSIONS

The performed studies refined our notions of the interaction of oxygen with CdS intrinsic point defects of various types and made it possible to substantiate the agreement of the experiment with the Schottky–Frenkel scheme of defect formation.

For CdS compositions ranging from stoichiometric to those highly enriched with sulfur, there are no intrinsic point defects, which can contribute to a significant solution of oxygen.

The concentration of solved oxygen is highest for "self-activated cadmium sulfide" CdS(O). This composition is the most-stable thermodynamically and, as a result, is fundamental for the use of undoped CdS in optoelectronics.

Due to the volatility of SO_2 and the HMAs effect, oxygen is removed from cadmium sulfide during growth and determines the appearance of an oxygen-depleted layer with a thickness as large as ~0.2 μm,

which can significantly differ from the oxygen content in the volume [15].

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