ON A NEW FIELD OF APPLICATION OF CERTAIN SEMICONDUCTOR COMPOUNDS

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Abstract

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ON A NEW FIELD OF APPLICATION OF CERTAIN SEMICONDUCTOR COMPOUNDS

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Advances in the technology of semiconductor compounds that possess a noticeable homogeneity range are based on the investigation of the relationship between the composition, structure, and properties of these crystals and on the resulting possibility of programming the conditions for obtaining a material with the required properties. In such investigations it is necessary to measure the partial vapor pressure of chemical elements over semiconductor compounds directly in the course of technological processes.

There exist a number of methods for determining the partial vapor pressure (p.v.p.) of components over complex systems ([1]), for example, over decomposing semiconductor compounds. The indicators of vapor pressure are optical transmission, volume, weight, activity (when radioactive isotopes are used), etc. In most cases, to determine the p.v.p. it is necessary to interrupt the experiment, dismantle the apparatus, carry out the corresponding measurements, and then perform approximate calculations. The principal drawback of the existing methods is that none of them has found application directly in real technological processes (for example, in the preparation of decomposing semiconductor compounds), where rapid monitoring and regulation of the process itself are required on the basis of continuous and fast measurements of the value of the component p.v.p.

In the present work a new type of sensor is described that makes it possible to measure the p.v.p. of a component directly in the volume in which the technological process is being carried out. In this case the value of the p.v.p. of a chemical element is determined with the aid of a sample of a semiconductor compound containing this element. The basic condition for the suitability of a compound as a sensor is the existence of a dependence of its electrical properties on the p.v.p. of the element.

For simplicity, let us consider a binary compound AB possessing a homogeneity range with respect to its constituent components A and B. The composition of such a nonstoichiometric crystal AB, placed in a closed volume, will be determined by its temperature and by the partial pressures of components A and B—

p_A and p_B, respectively. At a fixed temperature the composition of the crystal will be established in accordance with the partial vapor pressures of components A and B present in the closed volume. Changes in the values of the p.v.p. will cause a change in the composition of the AB crystal within its homogeneity range. In turn, a change in the composition of compound AB will manifest itself in a change of its properties. Since the solid phase-vapor equilibrium for compound AB is described by the equation $p_A p_B = K_{AB}$, where K_{AB} is a constant, the p.v.p. of one of the elements, for example B, is independent. For a definite crystal temperature and p.v.p. of component B, an equilibrium concentration of intrinsic point defects is established in the lattice of compound AB, and these defects determine its properties. The quasochemical theory of point defects (^{2}) indicates that, for example, the concentration of charge carriers, and consequently the specific electrical conductivity σ_{st}, in such crystals under equilibrium conditions is proportional to the quantity

partial pressure of the corresponding element p:

$$\sigma_{\text{st}} \sim p^{\pm\gamma}, \tag{1}$$

where the value of the exponent γ ($\gamma \leq 1$) is determined by the type of prevailing defect. Changing the value of p above the crystal causes the establishment of a stationary value σ_{st} defined for the given temperature.

A crystal AB and the pure component B are placed in a common closed volume, and the dependence of σ_{st} on the saturated vapor pressure of component B is investigated experimentally. Under such conditions, a sample of a nonstoichiometric compound AB can already be used as a sensor of the partial pressure of component B. For this purpose, a calibrated sample—the sensor—is placed in the volume in which the technological process for obtaining the compound AB in the presence of a complex vapor phase of the elements A and B is being carried out, and, by measuring the value of σ_{st}, the partial pressure of component B over the compound AB is determined.

A partial-pressure sensor based on the compound AB makes it possible to measure p at various points of the volume (probing), to obtain information on the kinetics of the change in p when the parameters of the technological process are varied (in the case of a low-inertia sensor), etc. By monitoring p only by the temperature of the vapor source T_{source}, it is impossible to record changes in pressure not associated with fluctuations of T_{source}. Thus, for example, a reaction may proceed in the system as a result of which the value of p will change, or a crack may appear in the system during the process and vapor B may leak out. In the course of prolonged high-temperature processes of growing and purifying crystals, the use of a sensor based on the compound AB is especially valuable.

The realization of the possibility described above for measuring the partial pressures of components over crystals of semiconductor compounds requires the detection and quantitative study of the dependence of the electrical properties of the compound on the magnitude of the partial pressure. In the direction of the experimental study of dependences (1), a number of works have already been carried out on compounds A_2B_6 and on certain oxides (^{3}, ^{4}), and therefore even now it is possible to make some choice of a compound for use as a sensor for the element of interest to us. For the time being, the range of such materials is highly limited, but the advantages noted above of using nonstoichiometric phases as partial-pressure sensors may stimulate investigations of this kind.

Our studies of the dependence of σ_{st} of cadmium telluride crystals on the partial pressure of cadmium p_{Cd} have made it possible to establish that $\sigma_{\text{st}} \sim p_{\text{Cd}}^{\gamma}$, where $\gamma \approx 0.5$ in the crystal-temperature interval $600 \div 1000°$ and $p_{\text{Cd}} = 10 \div 2000$ mm Hg (^{4}). Thus, by placing a CdTe crystal in a volume with an unknown cadmium vapor pressure, it is possible, by measuring σ_{st}, to obtain information on p_{Cd}. A cadmium partial-pressure sensor offers broad possibilities for developing the technology of obtaining CdTe crystals with the required properties.

In conclusion, we note that volume changes in CdTe crystals upon variation of p_{Cd} proved to be quite rapid (diffusion coefficient $D \approx 10^{-4} \div 10^{-5}$ cm^2/s in the temperature range $600 \div 1000°$), and because of this, sensors of the new type possess one more important property—low inertia.

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Note: Figure translations are in progress. See original paper for figures.