EFFECT OF SURFACE AND CONTACT PHENOMENA ON THE CONDUCTIVITY OF SINTERED SPECIMENS OF GALLIUM AND INDIUM PHOSPHIDES

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In recent years increasing attention has been focused on semiconducting materials prepared by powder metallurgy techniques. In addition to being relatively inexpensive and lending themselves to the manufacture of parts of various shapes and sizes, sintered polycrystalline semiconductors possess some unusual physico-chemical properties which occasionally make them superior to single crystals [1].

However, the basic laws governing the electrotransport phenomena in polycrystalline semiconductors have not yet been established and, consequently, no generally accepted methods have been evolved for their investigation, which accounts for the wide scatter of experimental data obtained by various investigators. A number of formulas have been quoted in the literature for the approximate calculation of the conductivity of porous materials [2, 3]. As in their derivation no allowance was made for contact or surface phenomena, they can yield really reliable results only for materials with the metallic type of conductivity. In the case of semiconductors of a size commensurable with the Debye length of surface charge screening such as film type structures or finely divided materials, surface phenomena may become of vital importance.

The present work was undertaken with the aim of studying the effect of surface and contact phenomena on the conductivity of two typical AIIIBV semiconductors, gallium and indium phosphides, prepared by powder metallurgy methods. As the first step, lamellar crystals of gallium and indium phosphides were obtained by cooling dilute solutions of GaP and InP in Ga and In, respectively [4]. All the crystals exhibited n-type conductivity. After the measurement of the electrical resistivity of the resultant single crystals by the Van der Pauw method, the latter were wrapped up in tracing paper and ground into powder, which was then fractionated by screening. To obtain a particle size of 1-5 μ, the powder which had passed through a 325-mesh sieve was subjected to further prolonged grind.

The powder was pressed into compacts 6-8 mm in diameter and 10-12 mm high. Sintering was performed in a phosphite atmosphere [5]. The grain size of sintered specimens was determined metallographically under an MIM-7 microscope. Ohmic contacts were produced by the technique of vacuum deposition of gold or tin, with subsequent shaping for 2-3 min at 600°C in a hydrogen atmosphere. To these contacts were bonded copper wires, using condenser discharges.

The resistance of low-resistance sintered contacts was measured by the dc two-probe compensation method, and that of high-resistance (ρ >10⁶ Ω·cm) contacts with an MOM-3 ohmmeter. Their density was determined by hydrostatic weighing. Table 1 presents experimentally determined values of electrical resistivity of the starting gallium and indium phosphide single crystals and sintered specimens of varying porosities.

The difference in electrical resistivity ρ between the nonporous material and the single crystals which were ground and sintered to give fine-grained specimens (for gallium phosphite, a discrepancy of nine orders was recorded) is linked with the effect of granular structure on the phenomena of current carrier electrotransport. A study of the dependence of ρ on grain size demonstrated that, as the latter increases from 5 to 400 μ, the electrical resistivity of sintered GaP and InP specimens decreases by a factor of 10-15. This is an indication of the influence exerted by the grain boundaries on the conductivity of specimens.


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An investigation of the effect of sintering temperature on the electrical resistivity revealed that the resistivity of GaP falls by several orders with rise in temperature (Fig. 1a). For indium phosphide, the resistivity at first decreases with rise in sintering temperature, but above 670°C sintering temperature has virtually no effect on the electrical resistivity of specimens (Fig. 1b).

To examine the role of surface charges in the mechanism of conductivity of gallium and indium phosphides, a study was made also of the effect of various sintering atmospheres on the resistivity of these materials. Measurements were made on three identical specimens, and the mean values of results were computed. Error in these determinations did not exceed 10–15%. The data yielded by this study (Table 2) show that sintering conditions, too, strongly affect the electrical resistivity of sintered GaP and InP specimens.

The results obtained may be elucidated by considering a diagrammatic cross section through a real sintered material and its model (Fig. 2). The dotted lines arbitrarily denote the space charge regions, of width $\lambda$. For the majority of semiconductors, $\lambda = 10^{-4}-10^{-5}$ cm. In a polycrystalline porous material, different types of connection may exist between different grains. Thus, grains 1 and 2 are separated by a pore whose size is commensurable with that of the grains; between grains 3 and 4 there is a small air gap whose width is of the order of atomic diameters; grains 2 and 3 are joined together only on their surfaces; grains 3 and 6 and also 3 and 5 are fully merged as a result of intergrowth to a considerable depth. In any sintered material, there will be varying numbers of contacts of each type. Predominance of any given type of contact depends on the nature of the material and sintering conditions.

The overall resistance of a sintered semiconductor is the sum of several components:

$$R_{\text{eff}} = R_m + R_{sl} + R_s + R_p + R_a,$$

where $R_m$ is the resistance of the semiconductor material itself, $R_{sl}$ the resistance of surface layers, linked with surface charge generation, $R_s$ the "screening" resistance of contacts, due to the concentration of current lines at the connections between the grains, $R_p$ the pore resistance, and $R_a$ the resistance of air gaps of the order of $5-100$ Å. Using the model of a sintered semiconductor illustrated in Fig. 2, we can obtain approximate analytical expressions for these components.

The contribution to the overall electrical resistivity of a specimen from the electrical resistivity of the semiconductor material is

$$\varrho_m = \frac{l - 2\lambda}{l(m\mu)}.$$