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Abstract

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A METHOD FOR DETECTING CRYSTALLITES IN GLASSES HAVING ELECTRONIC ELECTRICAL CONDUCTIVITY

(Presented by Academician V. N. Kondrat’ ev on 16 III 1962)

It is known that, in the volume of any glass, there are regions with a disordered arrangement of atoms in the lattice and with an ordered arrangement (crystallites) (^{1}). According to electron-microscopic investigations, the sizes of crystallites reach values of $\sim$ 300 Å (^{2}). The present work describes a method that makes it possible to detect crystallites in semiconductor glasses having electronic electrical conductivity (chalcogenides, etc.). The idea of the proposed method is based, on the one hand, on the conclusions of the quantum theory of electronic semiconductors and, on the other, on the specific features of a contactless method for measuring electrical conductivity that uses a rotating magnetic field (^{4},^{5}).

According to the conclusions of the quantum theory of electronic semiconductors (^{6}), regions of one and the same volume of a semiconductor that have different degrees of order in the arrangement of atoms in the lattice possess different values of specific electrical conductivity, determined mainly by the mobility of the current carriers: high in regions with a regular crystalline lattice, and low in regions with a disordered lattice. It follows from this that crystallites existing in the volume of a semiconductor glass must have a higher value of specific electrical conductivity than the disordered regions. In addition, there is yet another reason that determines, first, a higher absolute value of the conductivity and, second, a completely different temperature dependence of it in regions with an ordered lattice—crystallites—as compared with disordered regions.

To explain this fact, let us note the following. As numerous measurements of the conductivity σ of chalcogenide semiconductor glasses by the ordinary contact method have shown (^{3}), they do not exhibit impurity conductivity, although crystallized glass does have it; moreover, in measurements by the ordinary contact method it is impossible to distinguish highly conducting crystallites from the total volume of the glass, since what is determined is the conductivity of successively connected poorly conducting regions and well-conducting crystallites, i.e., in essence, the intrinsic conductivity of the disordered regions is determined.

These experimental data suggest that, in measurements of the conductivity of semiconductor chalcogenide glasses by the ordinary contact method, the impurity conductivity present in the crystallites does not manifest itself. Thus, the disordered regions of the glass manifest only intrinsic conductivity, whereas the ordered regions—crystallites, just like crystals—must manifest both impurity and intrinsic conductivity. Of course, for one and the same volume of semiconductor glass the intrinsic conductivity of the ordered and disordered regions is the same; moreover, at lower temperatures the concentration of impurity current carriers in the crystallites must be considerably higher than the concentration of intrinsic current carriers in the disordered regions. But with increasing temperature the difference in the values of the concentration

of the carriers and the conductivity of the different regions will decrease because the activation energy of the intrinsic carriers, equal to the band gap of the semiconductor, is higher than the activation energy of the impurity centers.

It follows from the foregoing that crystallites existing in a semiconductor glass must have, first, a higher absolute value of conductivity and, second, a different temperature dependence than the disordered regions.

In order for the crystallites to reveal their properties, it is necessary to measure the conductivity of one and the same semiconductor glass not only by the usual contact method, but also by a contactless method, which, unlike the former, makes it possible to measure the conductivity of a highly conducting material consisting of separate pieces separated from one another by an insulating medium.

Comparison of the data obtained by two different methods, contact and contactless, will make it possible to detect crystallites.

The validity of the proposed method for detecting crystallites in glasses follows from the results, presented in Fig. 1 as an illustrative example, of measuring the temperature dependence of the conductivity of one and the same semiconductor glass $3As_2Se_3 \cdot As_2Te_3$ by two methods: contactless and contact (^{7}). The sharp difference observed in Fig. 1 in the experimentally found absolute values of the conductivity and in its temperature behavior indicates that the different methods of measurement determine the conductivity of different regions of one and the same volume of glass: the contactless method determines the impurity conductivity of the crystallites in solid and liquid glass (at 100° the glass $3As_2Se_3 \cdot As_2Te_3$ is solid, at 300°—liquid), while the contact method determines the intrinsic conductivity of the disordered "glass-like" regions.

Fig. 1. Temperature dependence of the conductivity of the glass $3As_2Se_3 \cdot As_2Te_3$.
1 —contactless method;

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Figure 1: Fig. 1. Temperature dependence of the conductivity of the glass $3As_2Se_3 \cdot As_2Te_3$. 1 —contactless method; 2 —contact method

2 —contact method

It should be pointed out that the difference in the values of σ of semiconductor glasses measured by two different methods is absent in measurements of polycrystalline semiconductors. As shown in (^{5}), measurement of σ of polycrystalline semiconductor materials by the two methods gave complete agreement of the values.

It is known (^{4}, ^{5}) that the sensitivity of the contactless method of measuring σ is 20 orders of magnitude lower than that of the contact method. Therefore, at values of σ of crystallites lying below the sensitivity limit of the contactless method, they cannot be detected by direct measurement of their conductivity. But this can be done if the σ of the crystallites is artificially and substantially increased, without changing the structure of the glass, by introducing into the glass impurities that create impurity levels in the forbidden band. The substance introduced into the glass must be such that the impurity levels are located at a small energy distance from the edge of the valence band or the conduction band. In this case the concentration of impurity current carriers can be made sufficient for the appearance of appreciable conductivity, which will make it possible to detect the crystallites by the contactless method.

The artificial procedure described makes the crystallites of any organic and inorganic glasses highly conducting semiconductors, which are detected by a contactless method. At the same time, the introduction of impurities will have absolutely no effect on the values of σ of the glass measured by the contact method, i.e., the glass, being a dielectric before the introduction of impurities, will remain so after their introduction. As noted by B. T. Kolomiets (^{3}), the introduction of foreign impurities, even in large quantities, into chalcogenide semiconductor glasses does not change at all the values of σ obtained by the contact method. Thus, the method proposed in the present work makes it possible to detect crystallites in any organic and inorganic glasses in the solid and liquid states.

In conclusion, the author expresses deep gratitude to Academician V. N. Kondrat' ev for his interest in the present work and to Prof. B. T. Kolomiets for the opportunity provided to carry out measurements in his laboratory at the A. F. Ioffe Physico-Technical Institute of the Academy of Sciences of the USSR.

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