PREPARATION AND OPTICAL PROPERTIES OF $GA_XIN_{1-X}P$ ALLOYS

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16. Abstract

Use of the solution crystallization method to obtain $Ga_zIn_{1-x}P$ alloys for all values of x desired between zero and 1. The method of preparation makes it possible to crystallize the solid at a constant temperature. The points obtained by cathodoluminescence are nearly in straight lines. The optical absorption thresholds are confirmed in the results and make it possible to define the nature of the transitions except when x is in the neighberhood of 0.65. These determinations agree with those of Hilsum and Porteus (1968), but are not in agreement with those obtained by Lorenz et al. (1968).

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It has been recently demonstrated that the semiconductor $Ga_zIn_{1-x}P$ alloys existed for all the values of x. Different optical measurements have been accomplished on these materials in order to know the energy and the character (direct or indirect) of the transitions between bands of valence and of conduction. However, the results obtained [1, 2] are not in agreement, which may be due, in particular, to the difficulty of obtaining, by the standard methods for elaboration, of homogeneous crystals.

The utilization of the solution crystallization method, already experimented with for gallium phosphate [3], has allowed these alloys to be obtained for all the values of x desired between 0 and 1. On the crystals obtained, the value of x has been measured by electronic microanalysis, while also estimating by cathodoluminescence the wavelength of the light emitted by the sample. In order to locate with more precision the boundary zone between the direct transition and indirect transition alloys, measurements of optical absorption have been carried out.

The method of elaboration in solution that has been utilized allows crystallization of the solid at a constant temperature, depending on the concentration of the liquid in phosphorous at the interface of crystallization. This is a favorable factor when the composition of the alloy depends very strongly on the temperature of crystallization, as in the present case. An indium-gallium mixture is

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*Numbers in the margin indicate pagination of the foreign text.

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utilized as a base, in which the phosphorous is made to diffuse according to the process described in [3]. For a given concentration of the liquid solution in gallium, the free energy of the liquid phase at the solid-liquid interface depends on the temperature; the free energy of the solid being equal to that of the liquid, the composition of the solid depends on that of the liquid.

The composition of the alloy obtained has been determined experimentally, as a function of the concentration in gallium of the base, for a temperature of crystallization T_C=850 to 950°C. Figure 1 illustrates the case of T_C=900°C. When T_C<850°C, the speeds of diffusion of the different molecules at the interface of crystallization becoming very low, the segregation of the base is incomplete and inclusions are observed in the alloy if the speed of crystallization is too great. For this speed to be low, the solution must be fed under a very reduced pressure of phosphorous ($\approx 2 \cdot 10^{-4}$ atm) and the temperature of the surface of the base must be very low, approximately 1050°C, in order to decrease the solubility of the phosphorous in the /382 In-Ga mixture. The temperature of the coolest point of the cell is adjusted as a function of the temperature gradient of the liquid column, so that the speed of crystallization is on the order of 0.10 mm/h and even possibly lower (c.f. [3]).
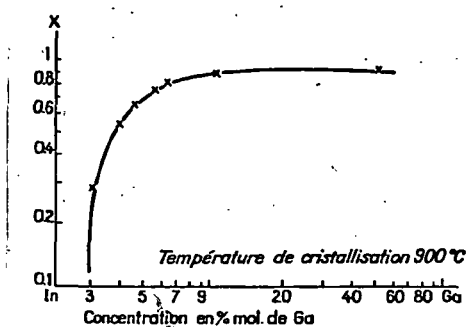

Figure 1.

Key: 1-Temperature of crystallization 900°C 2-Concentration in % mol. of Ga.

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The InP compound presents, at 300°K, a grounded band E_g from 1.27 eV with direct transition and toward 2.1 eV an indirect transition. At 300°K, there are found in GaP direct transitions at 2.75 eV and indirect transitions at 2.25 eV. In the systems of alloys, E_g frequently varies linearly with the composition which, for $Ga_z In_{1-x} P$ leads to straight lines (1) and (2) (figure 2) respectively for the direct and indirect transitions.
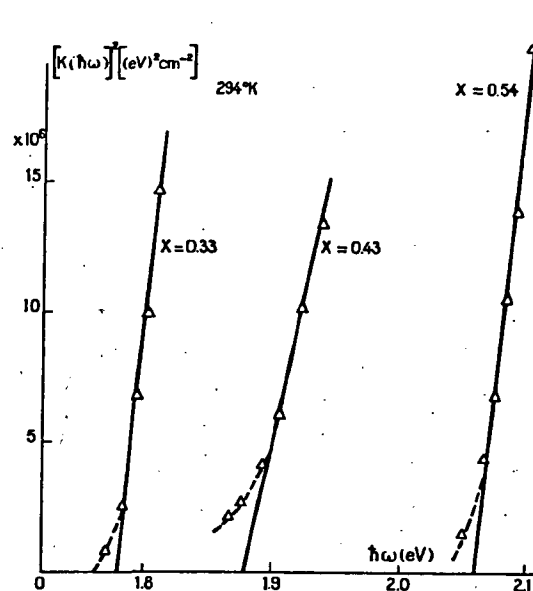

Figure 2.

In order to determine experimentally the width of the grounded band of the alloys as a function of their concentration x in gallium, the Castaing probe has been utilized, on the one hand by electronic microanalysis and, on the other hand, for a visual determination of the cathodoluminescence. This gives the possibility of estimating the width of the optical grounded band exactly at the site of the measurement of concentration. The micro-probe (Canseca, MS 46) was utilized with an excitation voltage of 15 kV and a probe current of 30 to 100 nA. The gallium content was determined by means of the $K\alpha_1$ radiation with a quartz spectrometer 11$\overline{2}$0 or 10$\overline{1}$1; for indium, the

Lα_1 radiation was utilized and a quartz spectrometer 10TO. The sample was made from GaP and InP compounds.

For the visual estimation of the luminescence under electron beams, operations have proceeded in the following manner. It is found that, for 0.3<x<0.7, the luminescence of the alloys possesses easily identifiable zones of wavelength, which are the red-orange transition at 2.00 eV, orange-yellow at 2.06 eV and yellow-green at 2.18 eV. The concentration of the samples emitting in these zones is reported on figure 2, as well as the mean values of concentrations obtained on thematerials emitting the yellow and in the orange. It is observed that the change of slope appears to be situated at the transition from yellow to green and for a value of x=0.63 to 0.65.

In order to refine these results, the optical absorption of samples of different thicknesses (d=15 to 500 µ) has been measured. In order to attain a great power of resolution, the slit of the spectrometer was very narrow (3 to $5 \cdot 10^{-2}$ mm). The absorption coefficient K has been calculated according to the formula:

$$K = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T}\right]^2 + R^2}\right].$$

The values of the reflexion coefficient R have been determined for the pure GaP and InP compounds. In order to calculate the value of K for the $Ga_zIn_{1-x}P$ alloys, there has been taken R=0.27 for 0.6<x <1, R=0.28 for 0<x<0.6. The low variations of the value of R in the range of the wavelengths situated below the threshold of absorption of the alloys influence little the value of K.

For 0.62<x<1, figure 3 demonstrates that the relationship $K \sim (\hbar\omega - E_g)^2$ is respected, the transitions allowed are thus indirect.

For the concentrations 0<x<0.60, there have been found, in the range of high absorptions, direct transitions (figure 4).
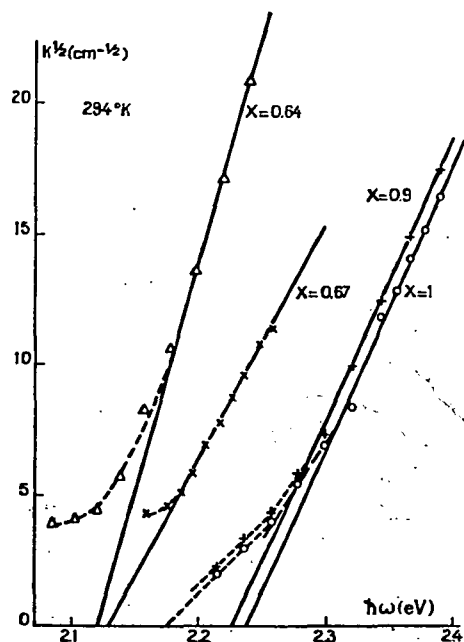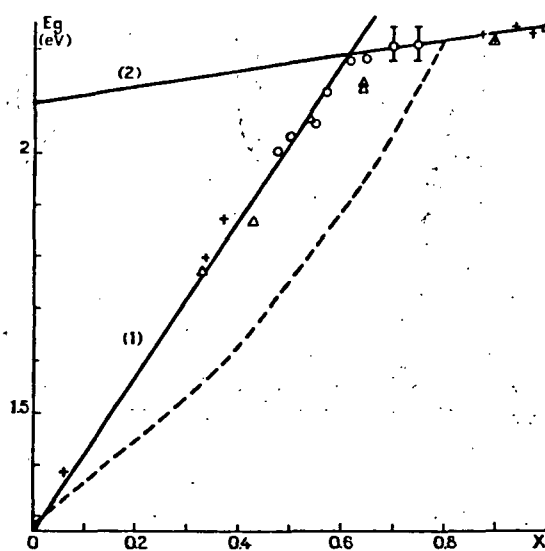
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Figure 3.

Figure 4.

The values of E_g measured by absorption are presented on figure 2 (triangles). It is observed that, for x near 0.65, these values are lower than those obtained with cathodoluminescence. This appears to be connected to the fact that there is found a zone of transition where it is difficult to interpret the curves of optical absorption.

Conclusions

First of all, it is possible to observe that the points obtained by cathodoluminescence are close to straight lines (1) and (2). The thresholds of optical absorption confirm the assemblage of these results and allow precise definition of the nature of the transitions, except for x close to 0.65. These determinations are in agreement with the results obtained by [1], which are shown on figure 2 (crosses) and are also situated close to straight lines (1) and (2). On the contrary, the results obtained by [2], represented on figure 2 (dotted curve), do not agree with the authors', particularly for the alloys with direct transitions. The method for determination and the

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quality of the alloys are perhaps responsible for such a difference in the results. The authors' method for elaboration in solution is demonstrated to be particularly effective in the case of these alloys.

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