NASA TECHNICAL MEMORANDUM

NASA TM-88431

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

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IN -18395

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546   MAY 1986

1. Report No. NASA TM-88431	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle PREPARATION AND OPTICAL PROPERTIES OF GA$_X$IN$_{1-X}$P ALLOYS		5. Report Date May, 1986
		6. Performing Organization Code
7. Author(s) H. Rodot, J. Horak, G. Rouy and J. Bourneix; National Center of Scientific Research, Hauts-de-Seine, Paris		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-4005
		12. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Use of the solution crystallization method to obtain Ga$_Z$In$_{1-X}$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).

17. Key Words (Selected by Author(s))	18. Distribution Statement Unlimited-Unclassified

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 7	22.

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

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It has been recently demonstrated that the semiconductor
$Ga_z In_{1-x} P$ 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 transi-
tions between bands of valence and of conduction. However, the re-
sults obtained [1, 2] are not in agreement, which may be due, in par-
ticular, 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 wave-
length 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 al-
lows crystallization of the solid at a constant temperature, depend-
ing on the concentration of the liquid in phosphorous at the inter-
face of crystallization. This is a favorable factor when the compo-
sition of the alloy depends very strongly on the temperature of crys-
tallization, as in the present case. An indium-gallium mixture is

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

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 ($\simeq 2 \cdot 10^{-4}$ 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 <u>/382</u> 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]).
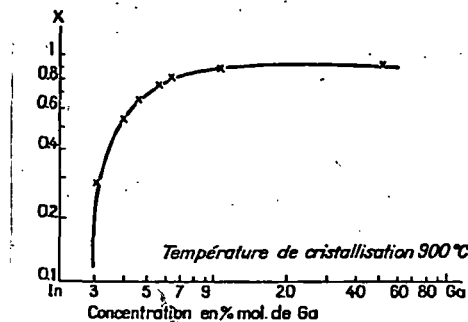

Figure 1.

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.
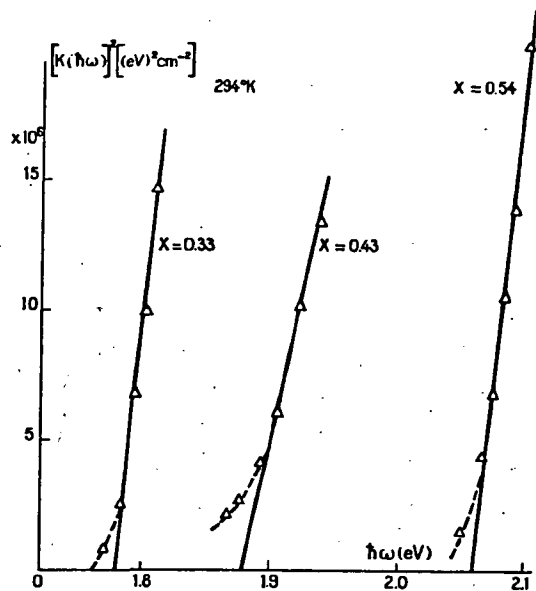

Figure 2.

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 10T0. 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 5·10^{-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 $Ga_z In_{1-x} P$ 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~ $(\hbar\omega - E_g)^2$ 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).
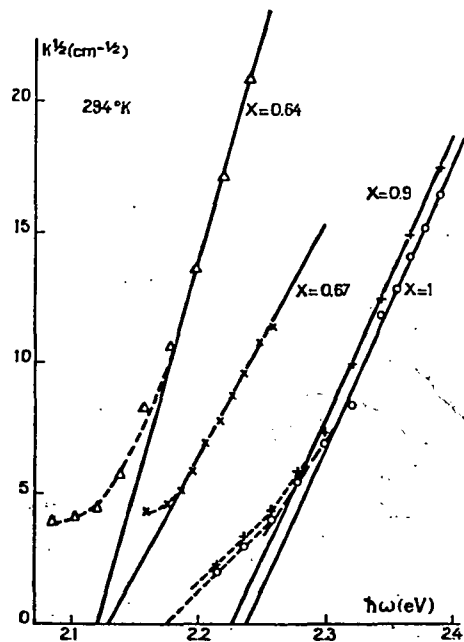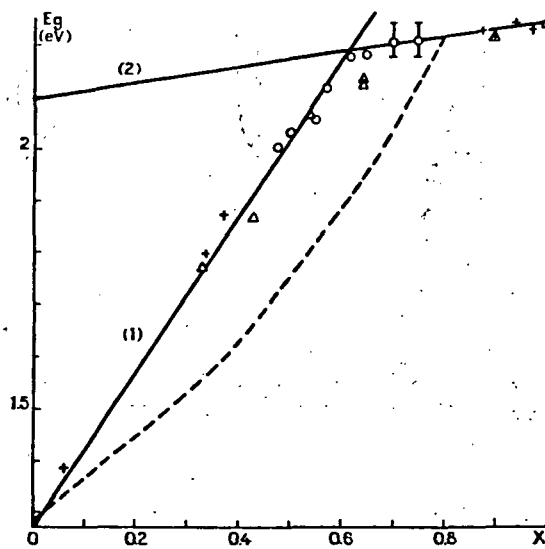
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Figure 3.

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

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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