JOURNAL OF MATERIALS SCIENCE 11 (1976) 491–499

Surface features on zinc-diffused indium phosphide

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When zinc is diffused into indium phosphide, interesting features are sometimes observed on the surface of the semiconductor at the end of the diffusion. In the work to be described, the experimental conditions necessary to produce these feaures were investigated and the features were observed using the techniques of optical microscopy, scanning electron microscopy, and X-ray microprobe analysis. Two different types of feature were identified, one zinc-rich and the other indium-rich. Some experiments were carried out using radio-tracer zinc so that diffusion profiles of zinc in the indium phosphide could be plotted. It was found that experimental conditions that gave rise to surface features also produced very high surface concentrations of zinc. An attempt is made to explain the results using a proposed In/P/Zn phase diagram.

1. Introduction

Indium phosphide is one of the important group of semiconductors made from elements taken from groups III and V of the periodic table. The group includes, amongst others, the compounds GaAs, GaP, AlSb, InSb. In general these materials are originally prepared in the form of n-type single crystals and p–n junctions are made by diffusing in zinc. For this reason the diffusion of zinc in the III–Vs has been studied extensively by a number of workers, although it is probably true to say that less information is available on indium phosphide than most of the other semiconductors of the group. Some work has been carried out using radio-tracer zinc and plotting diffusion profiles [1, 2] and a tentative approach has been made attempting to explain the results using a ternary phase diagram [2]. Other workers have studied the electrical properties of zinc-diffused indium phosphide [3–6]. Very little seems to be known about the surface features that can appear during the diffusion process, however, and their relation to the various phases that exist in the diffusion ampoule during the experiment is not understood. Ryzhikov *et al.* [5], working at temperatures in the range 600 to 750° C reported the formation of a high-resistivity indium phosphide layer on the surface after diffusion. Underneath this layer was a layer of indium. They gave no information on how these layers were identified but stated that the introduction of phosphorus into the diffusion ampoule prevented the formation of both layers. Kundukhov *et al.* [4] found that when they diffused zinc into indium phosphide at temperatures in excess of 700° C, small droplets of indium appeared on the sample surface unless extra phosphorus was added. More recently, Hooper *et al.* [2] have described the diffusion process at 700° C. They discussed the different species of surface feature that can occur and attempted to explain them in terms of the condensed phases presumed to exist in the ampoule during diffusion.

In this paper, further information is given on the form and composition of the features that appear on the indium phosphide surface after zinc diffusion at 700° C. An attempt is made to relate them to the proposed In/P/Zn ternary phase diagram.

2. Experimental

The indium phosphide was n-type with carrier concentration in the range 6 to 8 × 10^{16} cm^{-3}. It was

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cut in (1 0 0) slices, about 0.5 mm thick. Typically, a sample of about 0.5 cm^2 area was used. For some of the diffusions, radioactive zinc was used so that profiles could be plotted. The remainder of the experiments used non-radioactive zinc: these diffusions were performed in order to observe any surface features.

A slice of indium phosphide was first chemically polished in a 1% solution of bromine in methanol and then put into a clean quartz ampoule with a small amount of zinc and sometimes, also, a small piece of phosphorus. The ampoule was evacuated to 10^{-4} Torr and sealed to a volume of 12.5 cm^3. It was then placed in a three-zone furnace set to 700° C. At the end of the diffusion the sample was removed and cleaned. In a case in which radioactive zinc had been used, the procedure was to plot the diffusion profile by removing layers with the bromine-methanol solution. The activity of the removed material was counted using standard techniques. Layer thicknesses were found by weighing before and after etching.

The specimens that had been prepared using non-radioactive zinc were inspected for surface features using both optical and scanning electron microscopy. Some of the features were further investigated using an electron-probe X-ray micro-analyser. This instrument scans across a specimen with an electron beam, causing X-rays to be emitted which are characteristic of the chemical elements making up the surface. By tuning the instrument to detect the characteristic radiation from just one element, a "map" of the surface can be produced, with areas containing the element showing up as regions of high intensity. Maps for indium, phosphorus and zinc were obtained. It was therefore possible to determine how the elements were distributed on the surface and to relate the distributions to the observed surface features.

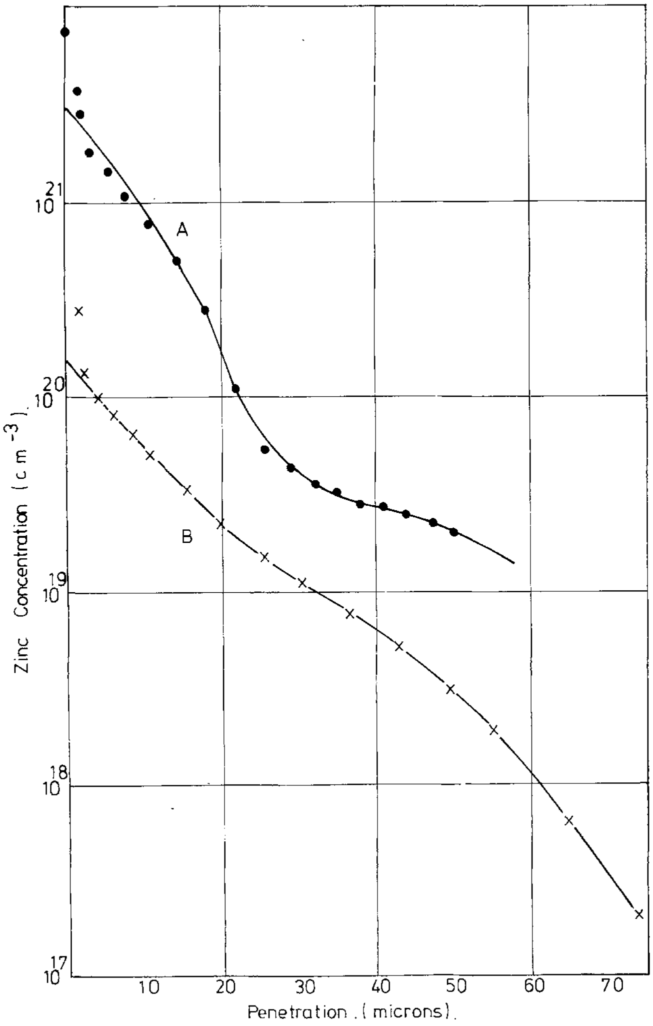


Figure 1 Diffusion profiles of zinc in InP at 700° C. Curve A is class 1, curve B is class 2. Both experiments used 520 μg zinc in the ampoule with no added phosphorus.

3. Results

3.1. Surface concentrations of zinc

The diffusion profiles plotted from the experiments using radioactive zinc fell into two distinct categories. Consider first those experiments in which no extra phosphorus was included in the ampoule. For zinc weights in excess of about 600 µg, profiles were obtained with extremely high surface concentrations, in the region of 4 x 10^{21} cm^{-3}. These were called class 1 diffusions, and an example is shown as curve A in Fig. 1. Some care must be taken when considering large surface concentrations such as this, because of the possibility of radio-tracer zinc condensing from the vapour on to the sample during cooling. Surface features, also, might consist of a phase containing a lot of zinc and cause the initial section to give a very high count. The high surface concentrations quoted for class 1 diffusions are genuine, however. They are obtained by extrapolating points from deep inside the crystal to the surface. If the count from the initial section was anomalously high, it was ignored. The conclusion

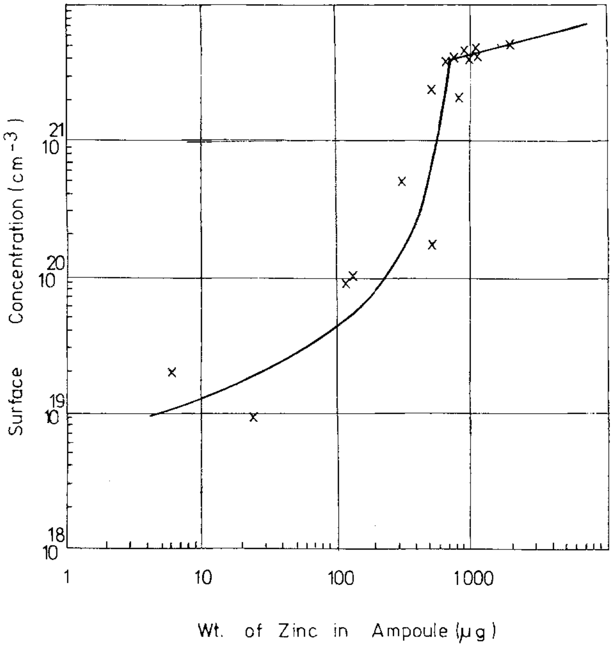


Figure 2 Surface concentration of zinc as a function of zinc weight in the ampoule, with no added phosphorus.

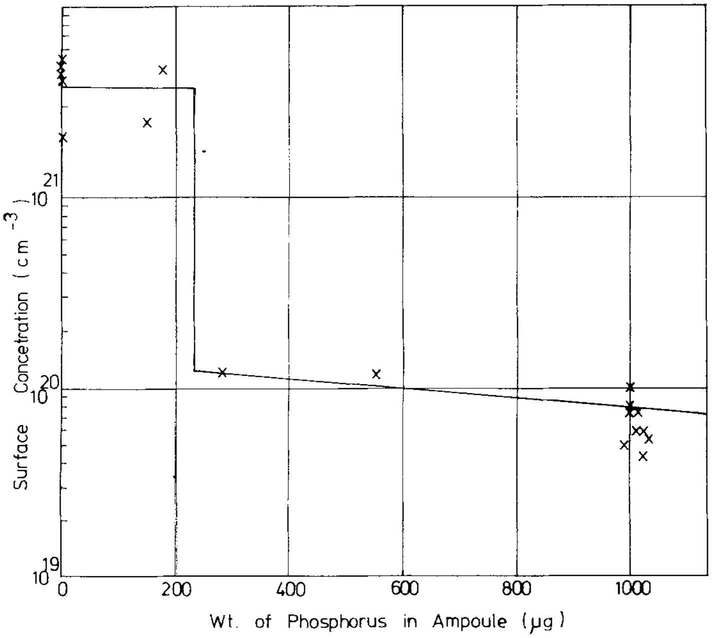


Figure 3 Surface concentration of zinc as a function of phosphorus weight in the ampoule. The ampoule contained 1 mg zinc in each case.

must be drawn that under certain circumstances the solubility of zinc in indium phosphide can be very high.

For zinc weights less than about 300 μg, profiles were obtained with surface concentrations at least a factor of twenty down on class 1 diffusions. These latter diffusions were designated class 2, and an example is given as curve B of Fig. 1. The change from class 1 to class 2 occurred quite abruptly, for a relatively small change in diffusion conditions. This is demonstrated in Fig. 2, in which surface concentration is shown as a function of the weight of zinc in the diffusion ampoule. From a practical point of view, it is worth noting that the sharpness of the change from class 1 to class 2 means that it is almost impossible to achieve reproducible profiles in this region. Fig. 1 illustrates the point rather well: both these curves were nominally for the same diffusion conditions, the only difference being that curve A is for a rather longer diffusion time.

For those experiments in which phosphorus was added to the ampoule, it was also possible to obtain two classes of profile. A series of diffusions was carried out in which the weight of zinc was kept constant at 1 mg for each diffusion and the amount of phosphorus was varied between zero and 1 mg. Fig. 3 shows the way in which the surface zinc concentrations varied as a function of the amount of phosphorus in the ampoule. For phosphorus weights less than about 230 μg, surface concentrations typical of class 1 diffusions were obtained. For phosphorus in excess of this amount, class 2 profiles were found.

3.2. Surface features

Discrete surface features were observed only after class 1 diffusions. Class 2 showed little or no sign of damage and the samples maintained their initial polished surface throughout. Class 1 diffusions produced crystals that were rough in appearance. Under closer inspection, this roughness proved to be caused by small deposits, metallic in appearance, on the surface. For long diffusion times, of the order of 4 to 5 h, the deposits took the form of hemispheres, ranging in size from a few microns to as much as $\frac{1}{4}$ mm in diameter. An example is shown in Fig. 4. For diffusion times in the region of 20 min, and for the same experimental conditions, the features generally took a rectangular form, with the rectangles lining up in a crystallographic manner, presumably following the (1 0 0) orientation of the crystal surface. A photograph of a number of these features is shown in Fig. 5. Also observed were the "maltese cross" features illustrated in Fig. 6. They appeared to be formed by a number of the rectangular features growing together. They were sometimes observed in clusters and were seen to line up in the same orientation, similarly to the way the rectangles line up in Fig. 5.

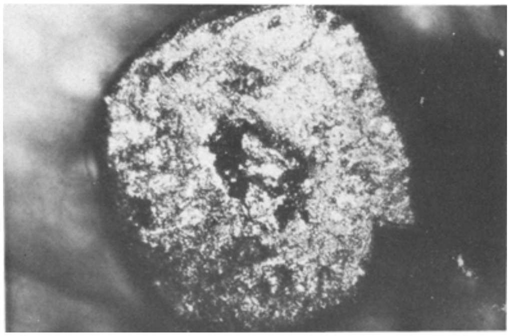


Figure 4 Hemispherical feature, × 200.

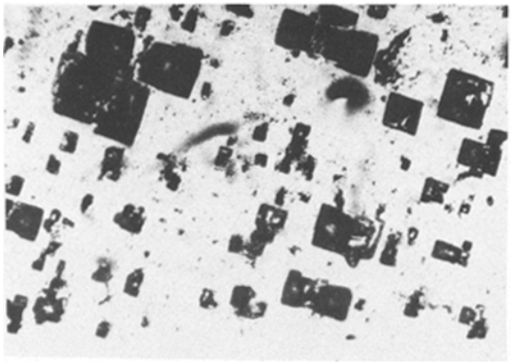
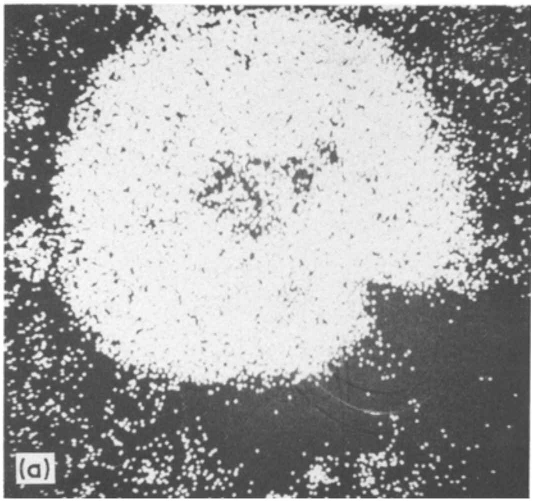
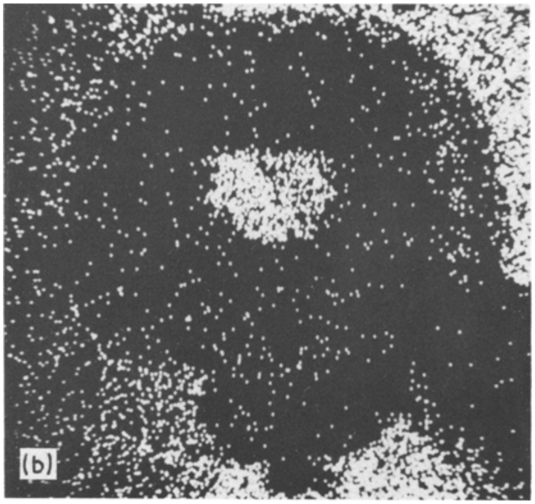


Figure 5 Rectangular features, × 250.

Figure 6 Maltese cross feature, × 760.

Use of the microprobe analyser indicated that the composition of the hemispherical features was quite different to that of the rectangular and





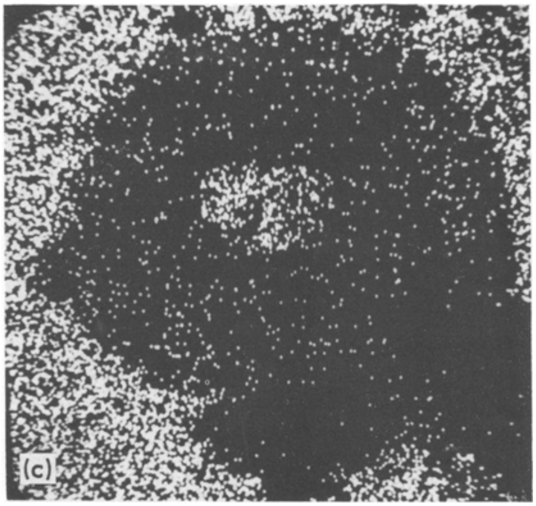


Figure 7 Elemental distribution for the hemisphere shown in Fig. 4. In each case the light areas correspond to the named element, × 240. (a) Indium, (b) phosphorus, (c) zinc.

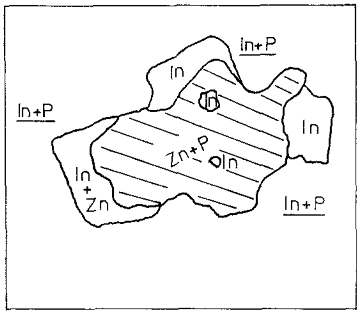


Figure 8 Elemental distribution for a maltese cross feature. The information was obtained from three separate X-ray probe micrographs, × 240.

maltese cross features. The hemispheres were largely composed of an indium-rich phase while the rectangular features were found to be rich in zinc. Fig. 7 shows the distribution of the three elements for the feature shown in Fig. 4. It can be seen that at the centre of the feature is a phase containing zinc and phosphorus, but that the rest of the hemisphere is composed of the indium-rich material. It is interesting that the central portion shows up quite clearly in the scanning electron micrograph of Fig. 4.

The most extensive work carried out on a rectangular feature was for one of the maltese crosses. A map derived from three microprobe photographs is shown in Fig. 8. Once again, the existence of two separate phases is clear but, in this case, the one consisting mostly of zinc and phosphorus is predominant. The indium-rich phase appears at the edges of the cross.

Some microprobe pictures were also taken of samples after class 2 diffusions. A uniform cover of indium and phosphorus was observed with a small amount of evenly distributed zinc, as would be expected from the general lack of surface features.

4. Discussion

4.1. Surface concentrations of zinc

The outstanding feature of this part of the work is the way in which small changes in experimental conditions could bring about large changes in surface concentration. Similar results were found by Shih *et al.* [7] when they diffused zinc into GaAs at 900° C. They were able to explain their results by reference to the Ga/As/Zn phase diagram for that temperature. In order to carry out a similar analysis for the InP results, it is necessary to know the form of the In/P/Zn phase diagram at 700° C.

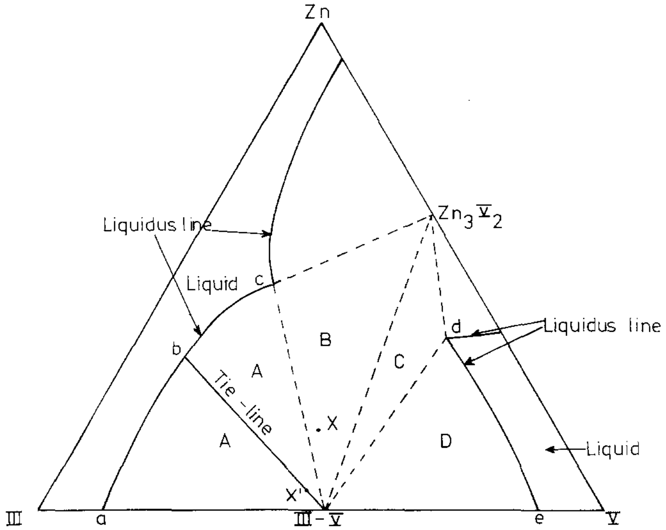


Figure 9 Isothermal section of ternary phase diagram for a III/V/Zn system.

This diagram has not yet been determined experimentally, but two others are known which would be expected to show similar features. These are the diagrams for the Ga/As/Zn system mentioned above [8], and the Ga/P/Zn system [9]. The latter two diagrams are very similar to each other, and it seems worthwhile considering the results of the present work on the assumption that the In/P/Zn system shows the same qualitative features. A phase diagram for a III/V/Zn system is shown in Fig. 9. A diagram of this sort is followed by Ga/As/Zn over the temperature range 700 to 950° C and by Ga/P/Zn in the range 700 to 1040° C.

To be precise, Fig. 9 is a cross-section of the ternary phase diagram, taken for the temperature of diffusion. It gives the various condensed phases that can co-exist for the various possible compositions of the ternary system. Two solids are allowed at the temperature shown; III–V and Zn_3V_2. They are shown as points on the diagram, but strictly each of the solid phases occupies a finite area, bounded by a solidus line. These areas are so small, however, that they cannot be shown on a diagram such as Fig. 9.

The regions likely to be important in this work are labelled A, B, C, D on the diagram. If the system can be described by a point inside region A, then it consists of solid III–V, and a liquid corresponding to a point on the liquidus ac and given by the appropriate tie-line. There is also a vapour composed of zinc, group III and group V vapours. There are thus three components (III, V, Zn) and three phases (solid, liquid, vapour), and the phase rule gives two degrees of freedom. One of these was employed in setting the diffusion temperature. The other is available and can be used by the experimenter to vary the conditions inside the diffusion ampoule. The zinc vapour pressure can, therefore, be varied and, since the solubility of zinc in the semiconductor is primarily fixed by the ambient zinc pressure, this means that the surface concentration of zinc can be varied. Region D is very similar to A, except that the liquid is now given by a point on the liquidus line de.

In region B, four phases co-exist; solid III–V, solid Zn_3V_2, a liquid given by the point c, and the vapour. The phase rule predicts only one degree of freedom under these circumstances and this is used up in setting the temperature. All points in region B therefore have the same phases: moving about within the region merely alters the relative amounts. All points in the region have the same vapour pressures, so all diffusions carried out within the region have the same surface concentration of zinc. Region C resembles B except that the liquid phase is now given by the point d. The various phases that can co-exist are summarized in Fig. 10.

Shih *et al.* [7], in their GaAs work, observed sharp changes in zinc diffusion profiles for small changes in experimental conditions. They suggested that this effect was due to the system crossing a line on the phase diagram and going from one region to another. Assuming a phase diagram such as Fig. 9, a similar explanation can be used to account for the present results on InP.

It must first be pointed out that Fig. 9 refers only to the condensed phases so that any material in the vapour is not included. Now group V elements are more volatile than group III, so if a pure

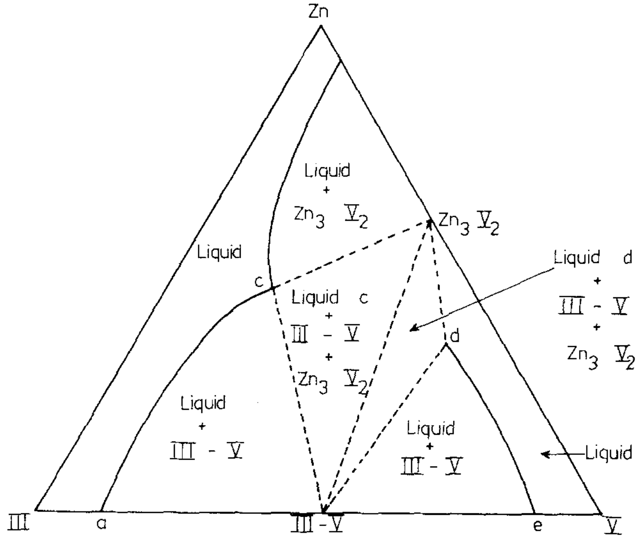


Figure 10 As Fig. 9, showing various phases that can co-exist.

piece of InP is heated, the system of Fig. 9 moves to the indium side of InP on the base-line, because more phosphorus than indium has entered the vapour phase. In this case the system consists of solid InP in equilibrium with liquid a. If a piece of zinc is added, the system is therefore described by a point just above InP on the diagram, and a little to the left. If the amount of zinc is sufficient, this puts the system in region B: such a point is marked X on the diagram. The weight of zinc used in these experiments is very small compared to the weight of InP, so the point X must be very close to InP. As long as the system stays within region B, changing the experimental conditions does not change the vapour pressures inside the diffusion ampoule. As noted above, this means that all such diffusions will have the same surface concentration. It seems likely that the relatively constant surface concentrations of the class 1 diffusions correspond to experiments in which the system stays within region B.

Reducing the amount of zinc below a certain critical level will cause the system to cross into region A. The system is then described by a point such as X. The liquid in the ampoule will change rather sharply from composition c to b. Liquid b is less rich in zinc that is liquid c, so it is reasonable to expect that the zinc pressure over b would be less than that over c. Hence a reduction in surface concentration would be expected. This behaviour is, in fact, shown in Fig. 2, giving rise to the much lower surface concentrations characteristic of class 2 diffusions. Further reduction in zinc weight brings b nearer to point a, and reduces the surface concentration even more.

A similar explanation can be employed to account for the fact that an increase in the amount of phosphorus in the system brings about a sharp change in surface concentration. In this case, the phosphorus causes the system to move from the monovariant region B to region D, passing through C. Again, crossing lines on the phase diagram causes a sudden change in the vapour pressures inside the diffusion ampoule, bringing about a large change in diffusion results for a small variation in experimental conditions (Fig. 3).

4.2. Surface features

Surface features were observed only in class 1 diffusions which, according to the argument given above, correspond to region B of the phase diagram. It is interesting to consider why diffusions taking place in regions A and D of the diagram do not give features. Surface features are the remnants of solid and liquid phases that formed on the semiconductor surface during the diffusion. If none are seen, there are three possible reasons:

(1) the condensed phases formed somewhere other than the semiconductor surface;

(2) they formed in such small quantities that they were not observable;

(3) no condensed phases formed during the diffusion.

Reason 1 cannot be rejected for class 2 diffusions on the present evidence. However, it is difficult to see why condensed phases should decide to form at least partly on the semiconductor surface if the diffusion takes place in region B, but not if it takes place in regions A or D. The lack of features in diffusions taking place in region A is probably due to reason 2. In order to calculate the amounts of condensed phase, it is necessary to have detailed information on the In/P/Zn phase diagram which is not available at present. It is worth noting, however, that this information is available for the Ga/As/Zn system [10] and that calculations of amount of condensed phase can be done fairly easily. It is found that on the gallium side of the phase diagram, equivalent to regionA of Fig. 9, the amounts of condensed phase are very small for a wide range of experimental conditions.

For diffusions taking place in region D, reason 3 is the most likely cause. The liquids predicted by the phase diagram are rich in phosphorus. Such a liquid must be associated with a very high vapour pressure of phosphorus. If the amounts of zinc and phosphorus in the diffusion ampoule are small, then there is insufficient material to sustain a very high vapour pressure, and the liquid boils away. The number of phases is reduced to two and all of the added zinc and phosphorus go into the vapour phase. Since no liquid forms, the high-quality surface of the specimen is maintained throughout the diffusion. As before, the argument cannot be put in a quantitative manner because of the lack of information on the In/P/Zn system. The well-investigated Ga/As/Zn system can again be used, however, to provide some insight into the situation. If zinc is diffused into GaAs with arsenic in the ampoule, the same effect is usually observed, i.e. the initial high-quality surface of the semiconductor is maintained, with no surface features appearing. Calculations using the available data show that this is because no liquid can form unless substantial quantities of arsenic are used in the ampoule [11].

Let us return to the features that were observed for class 1 diffusions. During such a diffusion, three phases should co-exist; solid InP, solid Zn_3P_2 and a liquid phase given by point c on the liquidus. It seems reasonable to identify the Zn + P phase which predominates in the square and maltese cross features with Zn_3P_2. Similarly the indium-rich phase of Fig. 7 and Fig. 8 can be associated with the liquid c. At the temperature of the diffusions, Zn_3P_2 is a solid. It must grow on the indium phosphide by some process of epitaxy, and the shape would therefore be expected to reflect the crystallography of the substrate. The indium phosphide slices were of (1 0 0) orientation, so it is not surprising that the features were rectangular. The indium-rich phase, on the other hand, is a liquid at 700° C, and would therefore be expected to be approximately hemispherically shaped.

It remains to be explained why the rectangular figures predominated for short diffusion times and the hemispherical ones were the only features observed after diffusions of several hours. This observation shows that there was some time-varying factor at work in the various phases present in the ampoule. In general, such a possibility is not considered in diffusion work. The system within the ampoule is usually considered as being made up of two sub-systems, one inside the semiconductor slice, and the other outside. Call these the internal and external systems respectively. The internal system is not at equilibrium: diffusion is taking place inside the semiconductor, and this is essentially a non-equilibrium process. The external system is generally assumed to be at equilibrium, however, and this is the justification for using the equilibrium phase diagram to account for the phases that occur. The link between the two systems is the surface concentration of zinc, C_s. As far as the internal system is concerned, C_s is the surface value of the diffusion profile. In the external system, it is the solubility of zinc in indium phosphide under the conditions of the experiment (see for example, [12]).

The assumption that the external system is at equilibrium throughout the experiment is never strictly correct. This is because it is continually losing zinc to the internal system, i.e. zinc is continually entering the semicconductor slice. This is a relatively slow process, however, and the phase diagram can still be of use, provided care is taken. During a class 1 diffusion, the external system is in region B. Suppose that after a few minutes it is at the point X. The relative amounts of phase c and Zn_3P_2 are determined by the relative lengths of the tie-lines between X and the two points representing the phases. (The reader is reminded that no claim for accuracy is made for Fig. 9: it is merely a guess based on the known phase diagrams of two other systems.) As the diffusion proceeds, zinc is lost to the internal system, so the point X moves further away from the zinc vertex on the diagram. The lengths of the tie-lines therefore change, so the relative amounts of the two phases also change. In fact, as Fig. 9 is drawn, the effect would be to increase the amount of indium-rich phase relative to Zn_3P_2, as is observed in the experiments.

5. Conclusions

This work has shown that under certain conditions very high surface concentrations can be obtained when zinc is diffused into indium phosphide. Associated with these high concentrations are surface features which can be divided into two main types according to shape and composition. For short diffusion times, a zinc-rich phase predominates but for longer times an indium-rich one is seen. It is possible to explain these results in terms of a proposed phase diagram.

Acknowledgements

We should like to thank Thorn Lighting Ltd for financial support of the work, and also R. Hall and K. Brown of Thorn for a number of valuable discussions.

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Received 28 April and accepted 8 September 1975.