JOURNAL OF MATERIALS SCIENCE 4 (1969) 773–778

The Cd_3As_2-NiAs Pseudobinary Eutectic

S. E. R. HISCOCKS
Department of Physics, Royal Radar Establishment, Great Malvern, Worcestershire, UK

Received 12 January 1969, and in revised form 14 May

Criteria to be followed in predicting new eutectic systems of particular types are discussed briefly, and demonstrated in the discovery of the Cd_3As_2–NiAs eutectic. The eutectic region of the Cd_3As_2–NiAs pseudobinary phase diagram has been determined by thermal and microscopic analysis. Cd_3As_2–NiAs eutectic ingots have been directionally grown by a new process, the liquid encapsulated Stockbarger technique, and shown to exhibit a typical rod-type morphology.

1. Introduction

Eutectic systems involving semiconductors have been receiving an increasing amount of attention over the past few years as their interesting electrical, magnetic, and optical properties have become more apparent [1]. A number of systems based on the III-V compounds have been reported by Weiss and his co-workers [2–4] the most important of which has been InSb–NiSb. This eutectic is of the rod type and consists of rods of metallic NiSb embedded in a matrix of InSb. If the eutectic material is grown directionally so that the rods grow parallel to one another, the resulting composite may be used as an infra-red polariser and also exhibits the most marked magnetoresistive effect observed to date, $\rho_H/\rho_0 = 17$ at room temperature for $H = 10$ kG.

Magnetoresistive elements are cut such that the metallic NiSb rods are perpendicular to both the field and current directions and thus effectively short out the Hall effect voltage which otherwise limits the magnitude of the magnetoresistive effect. In practice it is found that devices based on pure InSb–NiSb are too temperature-sensitive for many uses and to reduce this sensitivity the InSb matrix is suitably doped, resulting in lowered mobilities and magnetoresistive effects.

Cadmium arsenide, Cd_3As_2, is a semiconductor melting at 716° C and exhibiting a phase change at 615° C as a result of which it has not been possible to produce single crystals from the melt. The energy gap has been variously reported as 0.048 eV [5], 0.13 to 0.14 eV [6–9], and 0.4 to 0.6 eV [6, 9, 10] and is thus in some doubt; carrier concentrations in material grown from the vapour below 615° C so as to obtain single crystals [5, 11], or zone-refined with 35 zone passes [12], have not been below 1×10^{18} cm^{-3} (*n*-type). This would appear to be due to non-stoichiometry or to vacancy effects. The reason why this apparently unpromising material has received sporadic attention over a number of years is that despite its high carrier concentration it exhibits very high mobilities, of the order of 15 000 cm^2 V^{-1} sec^{-1} at room temperature, and up to 100 000 cm^2 V^{-1} sec^{-1} at 4° K [8, 13]. Furthermore, the mobility remains close to its peak value down to 4° K unlike that of InSb which drops at temperatures below 77° K. In view of the above it might be hoped that Cd_3As_2 containing metallic rods would provide devices comparable with those of InSb–NiSb, especially at very low temperatures, and it was for this reason that a programme of research into possible eutectic systems of Cd_3As_2 was initiated. The present paper considers the choice of potential eutectic systems and describes the preparation, growth, morphology, and constitution of the Cd_3As_2–NiAs system. The electrical properties of the Cd_3As_2–NiAs eutectic are described elsewhere [14].

2. Prediction of Eutectics

In searching for a eutectic system involving a particular material in a suitable form, in this case Cd_3As_2 as the matrix of a rod-type eutectic, there are certain empirical rules, the application of which will often narrow the choice from several hundred to only two or three. These are briefly outlined and discussed below.

1. In order that a eutectic may be formed it is necessary that the constituents should be (*a*) miscible, at least at the eutectic composition, in the melt, and (*b*) immiscible, again at least at the eutectic composition, in the solid. Condition 1(*a*) requires that the constituents should not be too dissimilar in general bonding type. For example metallic and ionic salt melts are generally immiscible, whereas oxide melts appear to mix more readily with ionic materials than with covalent. Condition 1(*b*) is simpler. Materials having the same crystal structure and of similar type, e.g. the III-V compounds, will in general be miscible in the solid in all proportions, and will not form eutectics. Materials, similar in other respects, but having different crystal structures will never be completely miscible.

2. Two materials will not form a eutectic if they can form a compound. For example Ag_2S and Ga_2S_3 satisfy conditions 1(*a*) and (*b*) but form a compound $AgGaS_2$, the eutectics being formed between this compound and both of the original materials.

3. It is observed that rod eutectics tend to be found where the eutectic composition is below 20 to 25 vol % of one component in the other and lamellar eutectics where the components are in more nearly equal proportions. So far as we know, no attempt has yet been made to correlate eutectic morphologies with the eutectic volume compositions in pseudobinary eutectics and it would be most interesting to see the results of such a survey. Hunt and Chilton [15] have investigated the factors affecting the morphology of eutectics formed between simple metals in six cases and have found that either rod or lamellar types can be obtained in all cases between 17 and 30 vol % while a eutectic at 37 vol % would show no rod-type and one at 9 vol % would show no true lamellar. It was found that there was no dependence of type on rate of growth but considerable dependence on direction of growth. Even more important, it was found that there was a strong dependence on purity of materials, the addition of impurities favouring rod-type eutectics. In summary then, one can predict with some certainty that a two-phase eutectic having less than about 10 vol % of the minor component will show rod morphology while one showing more than say 35 vol % of the minor component will probably show lamellar morphology. Between these limits one might find either or both in a given system depending on interfacial energies, growth direction, and perhaps rate of growth.

4. It is observed that the slopes of the two liquidus curves at the eutectic point tend to be similar and that the slope corresponding to the lower melting of the two constituent phases tends to be the smaller. Both of these follow, in the ideal case, from the van't Hoff equation which reduces to a simple dependence of slope of liquidus on melting point in an ideal dilute solution.

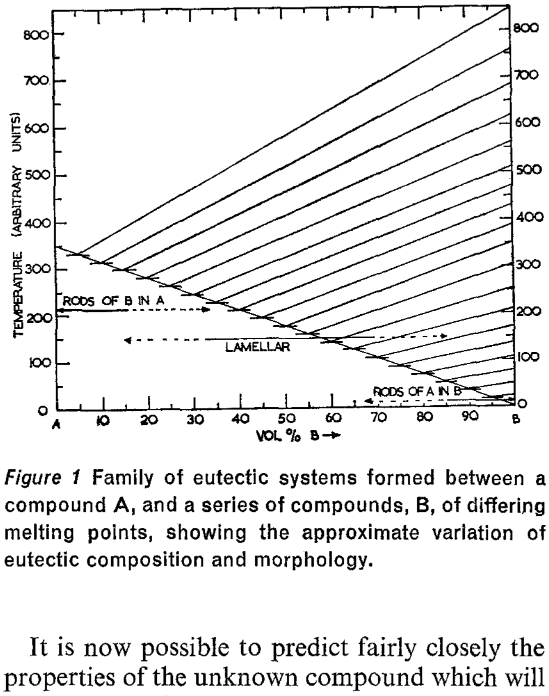

Figure 1 Family of eutectic systems formed between a compound A, and a series of compounds, B, of differing melting points, showing the approximate variation of eutectic composition and morphology.

It is now possible to predict fairly closely the properties of the unknown compound which will form the required type of eutectic with a given compound, The combination of conditions 3 and 4 leads to the sort of relationship shown diagrammatically in fig. 1 and it is possible to make a fairly accurate guess at the melting point of the compound likely to produce a eutectic of a given composition, and therefore type, with the known compound.

One other point should be borne in mind in selecting the unknown compound. If as many elements as possible are common to the two compounds, the chances of producing unwanted intermediate compounds will be considerably reduced and the ease with which high purity materials in the eutectic can be obtained will be greatly increased. The probability of interdoping between the two compounds can be much reduced if the non-common elements can be chosen such that they differ considerably in atomic size.

3. The Cd_3As_2-NiAs Eutectic

The application of the above considerations to the problem of finding a metallic element or compound which will form a eutectic such that rods of a metal are contained in a matrix of Cd_3As_2, MP 716° C, suggested an element or compound melting in the range 900 to 1200° C. Cd has too low a melting point and the compound, $CdAs_2$, to the As-rich side of Cd_3As_2 [16] also has too low a melting point (621° C) and is, in any case, a semiconductor rather than a metal. Known Cd compounds melting in the desired range are few, and are all known to be semiconductors. The choice is thus reduced to high melting point metal arsenides which are metallic. The non-transition metal arsenides, in so far as these are known, are semiconductors, but an examination of the data [16] on transition metal arsenides shows several possibilities, e.g. CoAs (1180° C), Fe_2As (919° C), FeAs (1030° C), Mn_2As (1029° C), MnAs (935° C), Ni_5As_2 (998° C), NiAs (970° C), $PtAs_2$ ($\sim$ 1400° C). All of these for which data are available [17] are listed as semiconductors, but NiAs is reported as having the lowest resistivity $\rho = 2.8 \times 10^{-4}\ \Omega$ cm at 273° K [18]. The NiAs structure is totally different from that of Cd_3As_2 and the Ni atom possesses the greatest size difference with Cd so that Ni–Cd exchange between the phases should not be serious. On this basis, NiAs was selected as the most probable candidate to form a rod-type eutectic of the required type with Cd_3As_2.

In an initial investigation of the proposed eutectic system stoichiometric quantities of Ni and As powders were added to previously prepared Cd_3As_2 [19] and allowed to react in Cd_3As_2 solution. Weighed quantities were sealed into a silica ampoule, fitted with a thin re-entrant tube to contain a thermocouple, to produce 10 mol % NiAs in Cd_3As. The ampoule, containing a calibrated Pt–Pt 13% Rh thermocouple, was heated to 750° C in a vertical furnace and then cooled slowly while a temperature versus time plot was taken. The resulting ingot was sectioned and polished and, on examination, found to show a completely rod-type morphology at a composition close to the eutectic point.

The actual value of the eutectic composition was investigated in two ways: thermal and microscopic analysis. Thermal analysis was carried out in sealed silica ampoules fitted with narrow bore re-entrant silica tubes so that the thermocouple junction was effectively immersed in the melt. The Pt–Pt 13% Rh thermocouple was calibrated with Al (660.1° C) and Cu/Ag eutectic (779° C). The composition range 0 to 15 mole % NiAs was investigated and showed a eutectic composition of about 9 mole % NiAs (fig. 2). Thermal analysis ingots were finally examined microscopically.

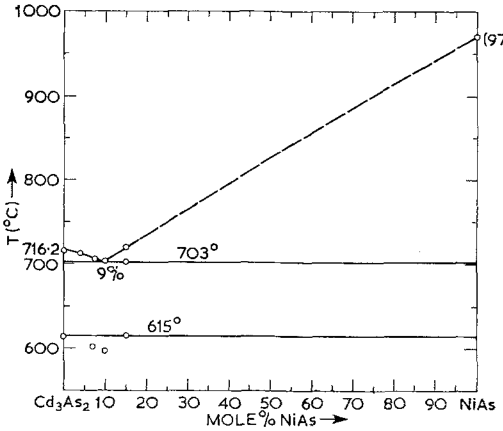

Figure 2 The pseudobinary phase diagram of the Cd_3As_2-NiAs system. Points represent, in most cases, the average of heating and cooling thermal arrests.

An area containing a perfectly regular array of rods was sectioned perpendicular to the rods, photographed at low magnification and the rods in this known area counted. Using a magnification of × 2650 the diameters of 75 of these essentially circular cross-sections were measured. The average rod diameter was 2.64 μm with a standard deviation of less than 0.12 μm. The averaged separation of the rods, found from a smaller sample, was 14.3 μm. From the number of rods and their average area, an area percentage and hence the volume percentage of NiAs was calculated to be 2.2. From the known densities and molecular weights of Cd_3As_2 and NiAs the eutectic composition was calculated to be 2.664 wt % NiAs or 9.07 mole %, which is in good agreement with thermal analysis results.

4. Directional Growth of Cd_3As_2-NiAs

Eutectic crystals were grown by a new technique, the liquid encapsulated Stockbarger technique, which is essentially similar to that developed for the initial preparation of the Cd_3As_2 [19]. The experimental arrangement is shown in fig. 3. An RRE type crystal puller and induction heater were used as a controlled pressure, hot-zone furnace. The crucible, of high density, high purity graphite, was suspended from the pull rod so that it could be lowered or raised at controlled speeds through the induction heating coil.

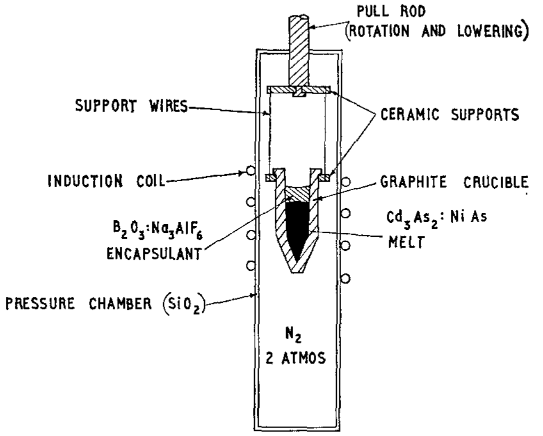

Figure 3 Schematic representation of the liquid encapsulated Stockbarger technique.

The preparation of the Cd_3As_2 has been described elsewhere [19]. Cadmium metal was of "6 nines" quoted purity (Koch Light Laboratories Ltd); arsenic was obtained in the β (non-oxidising) form and quoted as 99.999% (Hoboken); nickel was quoted as "spectroscopically pure" (Johnson Matthey Ltd), and the B_2O_3 encapsulant was pre-dried (British Drug Houses Ltd). The encapsulant was further baked out at 1000° C under vacuum with the addition of 1 wt % Na_3AlF_6 to lower the viscosity [20] as in the preparation of Cd_3As_2.

The growth procedure was as follows. The charge, consisting of the required quantities of NiAs (or Ni and As), Cd_3As_2, and the B_2O_3/$NaAlF_6$ was placed in the crucible with NiAs at the bottom and the encapsulant on top. The system was evacuated, flushed with N_2 three times, and pressurised at 1.5 to 2 atmospheres of N_2. The heater was switched on with the crucible below the level of the coil and then the crucible raised so that the encapsulant on the top melted first and sealed in the reactants. As the crucible was raised further the Cd_3As_2 melted and dissolved the NiAs. After equilibrium was achieved, the crucible was lowered at 1 to 2 cm/h through the coil so that crytallisation took place from the point at the bottom, in the usual Stockbarger manner. The crucible was rotated at 10 rpm throughout, to maintain thermal symmetry, and temperatures were measured with an optical pyrometer. It was important to ensure that the temperature at the hottest point did not rise above about 750° C, or else the equilibrium pressure of the melt – $\sim$ 0.80 atm at 716° C [21] – tended to exceed the pressure of the ambient with consequent loss of material.

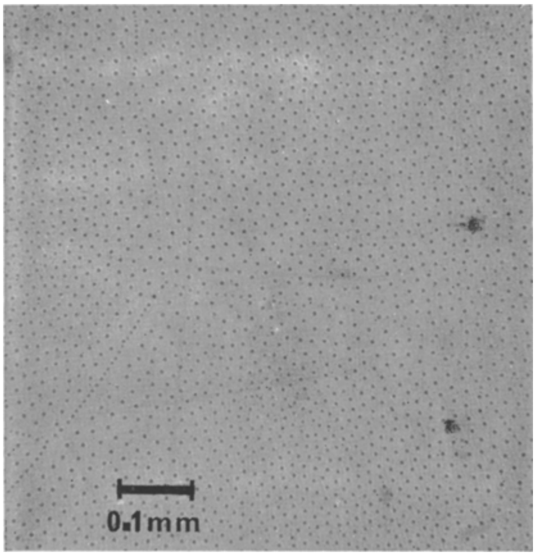

Figure 4 Cd_3As_2-NiAs eutectic directionally grown. Section at right angles to growth direction. Rods are of NiAs in a matrix of Cd_3As_2 and have been slightly defocused for contrast in this photograph.

Samples prepared by the above process showed continuous eutectic along almost their entire length (3 to 4 cm) with none of the eutectic banding normally associated with fluctuations in either temperature or lowering rate. There was, however, evidence of a convex solid/melt interface in that the rods tended to splay out towards the outside of the ingot. Figs. 4 and 5 show sections of eutectic ingots, slightly defocused for contrast, cut perpendicular and parallel to the rod direction. It can be seen that these show a polycrystalline matrix with smaller rods in the grain-boundaries. Both figs. 4 and 5 were selected to show grain-boundaries, although most of the material had a larger grain size than might be suggested by fig. 4, and in no case was a single crystal matrix obtained. It may be seen

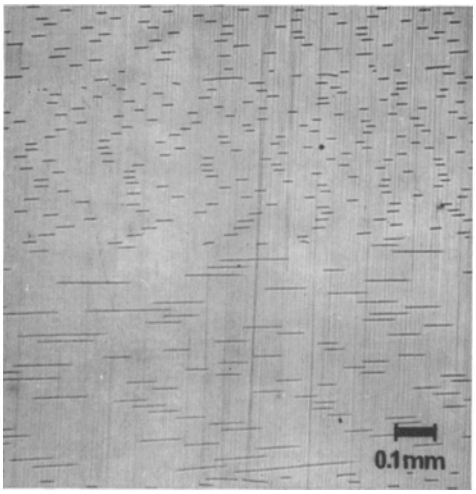

Figure 5 As for fig. 4 but sectioned parallel to the growth direction. A difference in rod orientation, relative to the matrix, between the upper and lower halves of the picture shows a slight dependence of rod direction on the matrix orientation in the two grains.

from fig. 5, where two grains meet at a boundary parallel to the growth direction about half up the figure, that there is clear evidence of a relationship between the rod direction and the crystal orientation of the matrix which modifies the tendency for the rods to grow parallel to the growth direction. No attempt has been made to study this dependence.

The differences in *apparent* lengths of rods seen in fig. 5 are due to very slight differences in the angles which they make with the surface and are not related to actual lengths except in so far as they show the minimum lengths. No attempt has been made to determine actual lengths, but in the surface single rods as long as 1 mm have been found. Ideal growth conditions should, in principle, allow all rods to be continuous over the entire length of the crystal.

Finally it is interesting to note that, while Cd_3As_2–NiAs eutectic ingots were, due to the phase change, polycrystalline, they showed far fewer cracks than does pure melt grown Cd_3As_2, so that cracks could be avoided entirely in the $2 \times 2 \times 5$ mm^3 specimens cut from the ingots for electrical evaluation. The reason for this difference is not clear. It may be the lower temperature gradients involved in the Stockbarger growth or it may simply be an example of "fibre reinforcement" of the Cd_3As_2 matrix by the NiAs rods.

5. Summary

It has been shown that the systematic application of certain criteria make it possible to predict new eutectic systems and their probable morphologies. The new system Cd_3As_2–NiAs was predicted on this basis and has been shown to be a typical rod-type eutectic with metallic rods of NiAs embedded in a Cd_3As_2 matrix. The phase diagram of the pseudobinary Cd_3As_2–NiAs system in the eutectic region has been investigated by thermal analysis and microscopy. Directionally solidified ingots have been grown by a new process, the liquid encapsulated Stockbarger technique.

Acknowledgement

The author wishes to thank Mr P. D. West for his experimental assistance throughout this work, Mr G. Pearson for assistance in the thermal analysis, and his colleagues at RRE, especially Dr D. T. J. Hurle and Dr J. B. Mullin, for their interest and advice.

Published by permission of the Director of the Royal Radar Establishment, copyright by the Controller, Her Majesty's Stationery Office.

References

1. F. S. GALASSO, *J. Metals* **19** (1967) 17.
2. H. WEISS and M. WILHELM, *Z. Physik* **176** (1963) 399.
3. H. WEISS, *Electron News* (12 October 1964) 42.
4. B. PAUL, H. WEISS, and M. WILHELM, *Solid State Electronics* **7** (1964) 835.
5. E. D. HAIDEMENAKIS *et al*, *Solid State Comm.* **4** (1966) 65.
6. T. S. MOSS, *Proc. Phys. Soc.* **B63** (1950) 167.
7. W. J. TURNER *et al*, *Phys. Rev.* **121** (1961) 759.
8. *Idem*, *J. Appl. Phys.* **32** (Supplement) (1961) 2241.
9. W. ZDANOWICZ, *Acta Phys. Polonica* **20** (1961) 647.
10. YA. A. UGAI and T. A. ZYUBINA, *Inorg. Matls.* **1** (1965) 860.
11. B. KOLTIRINE and M. CHAMMEREUIL, *Phys. Stat. Sol.* **13** (1966) K1.
12. E. M. SWIGGARD, *J. Electrochem. Soc.* **114** (1967) 976.
13. E. D. HAIDEMENAKIS *et al*, *J. Phys. Soc. Japan* **21** (Supplement) (1966) 189.
14. C. T. ELLIOTT and S. E. R. HISCOCKS, *J. Phys. D* (*Brit. J. Appl. Phys.*) Series 2, **2** (1969) 1.
15. J. D. HUNT and J. P. CHILTON, *J. Inst. Metals* **91** (1963) 338.
16. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
17. "Electronic Properties of Materials", Part I, edited by H. Thayne Johnson (Plenum Press, New York, 1965).

18. W. MEISSUER *et al*, *Ann. der Phys.* **17** (1963) 593.
19. S. E. R. HISCOCKS and C. T. ELLIOTT, *J. Materials Sci.* **4** (1969) 784.
20. S. E. R. HISCOCKS in preparation.
21. *Idem*, *J. Phys. E.* (*J. Sci. Instr.*) Series 2, **2** (1969) 417.