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An X-ray diffraction study of the solid phase equilibria in some M–In–P systems (M≡Ni, Pd, Pt)

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Abstract

The solid phase equilibria between the Group X transition metals, indium and phosphorus were investigated by X-ray diffraction techniques. Interest was focused mainly on the equilibria including the semiconductor material indium phosphide. The elements and compounds forming equilibria with InP at 600 °C are summarized as follows: Ni–In–P system: In, Ni_2P, Ni_5P_4, NiP_2 and P; Pd–In–P system: In, Pd_2In_3, PdIn, PdP_2 and P; Pt–In–P system: In, Pt_3In_7, PtP_2 and P.

1. Introduction

Recent developments in semiconductor technology have revealed the potential of indium phosphide as a promising material for optoelectronic applications and hyperspeed circuits. The integration between emitter–detector systems and conventional transistors to provide increased data capacity and speed is of special interest. The continuous scaling of microelectronic devices to submicrometre dimensions increases the need for high performance ohmic and rectifying contacts. Much effort has been spent in attempts to find suitable contact materials chemically and morphologically stable at temperatures as high as 800 °C.

Elemental metals are often used for metallization, but unfortunately most of them are not stable towards the semiconductor. A chemical reaction takes place at the interface and new binary or ternary compounds, stable or metastable, are formed. The new compounds change the contact properties and may even cause failure.

It is desirable to find suitable contact materials which do not react with the semiconductor. One possibility is to use a compound which is thermodynamically stable with indium phosphide over the temperature interval of interest. This technique was first demonstrated by Lince *et al.* [1] and Guivarc'h *et al.* [2]. They deposited stable contacts of RhGa on GaAs and $AuGa_2$ on GaSb. It has also been used on InP by Appelbaum *et al.* [3] who deposited stable contacts of Ni_2P with good ohmic properties.

Information on compounds and/or compositions which are thermodynamically stable towards the semiconductor can be obtained from a phase diagram. Knowledge of the solid phase equilibria is therefore a good starting point when looking for suitable contact materials and, eventually, for developing contacts.

This work was undertaken to determine the solid phase equilibria between the transition metals nickel, palladium and platinum with indium and phosphorus. Interest was focused on those parts of the systems involving equilibria with indium phosphide.

When determining ternary phase equilibria, accurate information on the binary boundary systems is of great importance and several researchers have studied these phase diagrams extensively. The binary Ni,Pd,Pt–In systems and the binary Ni,Pd,Pt–P systems are fairly rich in binary phases. However, the binary In–P system is different. It contains only one intermediate compound, indium monophosphide, which has a very narrow homogeneity range. It belongs to the ZnS structure type and is a III–V semiconductor. The phase diagrams are described in refs. 4–12, and the assessed versions are compiled in ref. 13. Crystallographic data on the constituent elements and intermediate phases are reported in ref. 14 where further references are given.

In contrast with the numerous publications dealing with the binary phase equilibria, the literature on the ternary transition metal–indium–phosphorus systems is meagre. The solid phase equilibria in the Ni–In–P system have previously been reported in ref. 15. The results are consistent with a thin film study by Appelbaum *et al.* [3] who suggested that Ni_2P forms a thermodynamically stable equilibrium with InP. Furthermore, Sands *et al.* [16] have studied thin film reactions between nickel and InP at relatively low

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temperatures. They reported the initial formation of an amorphous phase with the approximate composition $Ni_{2.7}InP$ at temperatures below 200 °C. At 300 °C it crystallizes into a hexagonal phase with the same composition. At higher temperatures a third, monoclinic phase is formed, with the composition Ni_2InP.

Thin film reactions in the Pd–In–P system have been investigated by Ivey and Jian [17]. They reported the formation of the ternary phase Pd_2InP at temperatures between 200 and 400 °C. The phase is cubic ($AuCu_3$ structure type) with the cell dimension $a = 4.15$ Å as determined by transmission electron microscopy (TEM). No information on the ternary Pt–In–P system was found in the literature.

2. Experimental details

The starting materials for the alloy preparations were as follows: nickel turnings (Johnson Matthey Chemicals, UK) (99.999%); palladium powder (Johnson Matthey Chemicals, UK) (99.95%); platinum powder (Johnson Matthey Chemicals, UK) (99.95%); indium filings (Puratronic) (less than 5 ppm metal impurities); indium phosphide (Sumitomo, Japan) (semiconductor grade); red phosphorus (99.999%).

A detailed description of the experimental procedures used in the determination of the Ni–In–P phase equilibria is given in ref. 15. Ternary alloys containing palladium and platinum were prepared in evacuated and sealed silica tubes by mixing appropriate amounts of the starting materials. The mixtures were homogenized at 1000 °C for 3 days. The products were then heat treated for about 1 month at 600 °C. After the heat treatment the samples were quenched in ice water and crushed to a powder. A slight attack on the silica tubes was observed for a few samples with high indium content.

Phase analysis and determination of the unit cell dimensions were performed by X-ray powder diffraction using a Guinier–Hägg-type focusing camera with Cu $K\alpha_1$ radiation. Silicon ($a = 5.43106$ Å at 25 °C) was used as internal calibration standard. The peak positions and intensities were determined densitometrically with an automatic film scanner [18]. The local least-squares program UNITCELL was used to refine the cell dimensions. The experimental d values and intensities of the diffraction peaks were compared with calculated values obtained by the program LAZY PULVERIX [19] in order to ensure correct identification of every line in the diffractograms.

3. Results

The solid phase equilibria for the Ni,Pd,Pt–In–P systems are presented as isothermal sections at 600 °C. A common feature of the systems is the large difference in the melting points for the elements. The melting points of the transition metals are of the order of 1500 °C and indium melts at 156 °C. Red phosphorus sublimes at 417 °C but melts under pressure at 590 °C. As a consequence, indium and phosphorus are liquid and gaseous respectively at 600 °C, and the behaviour of phosphorus is strongly influenced by the pressure in the system. The extension of the non-solid areas into the ternaries is excluded from the presentation since it was not experimentally determined. The isothermal sections are constructed solely from the solid phases present in the quenched samples.

3.1. Ni–In–P system

The solid phase equilibria reported for the Ni–In–P system are based on X-ray diffraction data from samples prepared at 800 °C. In addition, the samples were investigated by differential thermal analysis (DTA) in the interval between room temperature and 800 °C. The results form the basis for the solid phase equilibria at 600 °C presented in Fig. 1. The temperature of 600 °C was chosen in order to compare the phase equilibria for all the Group X transition metals at the same temperature. InP forms equilibria with Ni_2P, Ni_5P_4, NiP_2 and phosphorus. The phase relationships at 600 °C in the phosphorus-rich corner of the diagram are not fully clarified. Two phase transitions, at 560 and 600 °C, were observed in sample 4 when examined by DTA. The peak at 560 °C was attributed to the melting of phosphorus. The origin of the peak at 600 °C is doubtful since the thermal behaviour is strongly influenced by the pressure. One possibility is that the peak is caused by the evaporation of phosphorus. It may also originate from a phase transition in NiP_3, whose

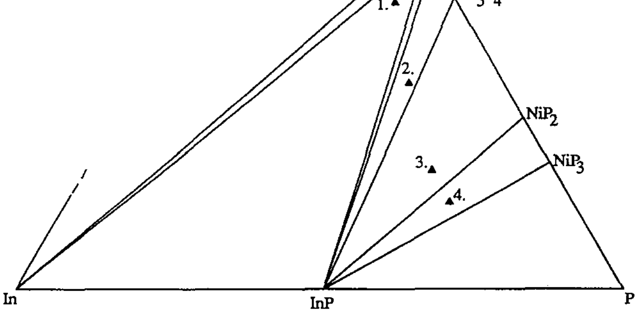

Fig. 1. Sample compositions and ternary phase equilibria in the Ni–In–P system at 600 °C.

thermal behaviour is incompletely known. The sample annealed at 600 °C and the sample used for DTA were investigated by X-ray diffraction, but the existence of NiP_3 was not confirmed. A moderate homogeneity range was found for Ni_2P. Sample compositions, results from the phase analysis and cell dimensions for samples prepared at 800 °C are presented in Table 1.

3.2. *Pd-In-P system*

The alloys prepared in this system were homogenized at 1000 °C and then heat treated at 600 °C for about 1 month, with one exception. Sample 5 was homogenized at 800 °C and heat treated at 600 °C. This was necessary in order to prevent the formation of PdIn, which was readily formed at 1000 °C. PdIn proved to be tenaciously retained once it had been formed.

The nominal compositions of selected alloys, the phases present and their unit cells are presented in Table 1. As shown in Fig. 2, InP forms equilibria with indium, Pd_2In_3, PdIn, PdP_2 and phosphorus. All attempts to obtain the binary phosphide PdP_3 were unsuccessful. This observation is consistent with those reported by Gullman [8], who studied the Pd–P system extensively. Of the phases formed in the investigated part of the system, PdIn is the only one exhibiting an appreciable homogeneity range. It extends from 48 to 62 at.% Pd.

As regards the cell dimensions, there is a distinct maximum at the composition PdIn. An explanation may be that, when the mole fraction of palladium N_{Pd} is greater than 0.5, palladium and indium atoms are randomly mixed. However, when $N_{Pd} < 0.5$ there are vacancies on the palladium sites. The structure is fully

TABLE 1. Results from the phase analysis (standard deviations in parentheses)

System	Sample	Nominal composition	Phases detected	Cell dimensions			
				a (Å)	*b* (Å)	*c* (Å)	*β* (°)
Ni–In–P	1	$Ni_{55}In_{10}P_{35}$	Ni_2P	5.8642(7)		3.385(2)	
			InP	5.872(5)			
			In	3.253(1)		4.951(2)	
	2	$Ni_{40}In_{15}P_{45}$	Ni_2P	5.8434[a]		3.3988[a]	
			Ni_5P_4	6.7894(4)		10.989(1)	
			InP	5.8699(3)			
	3	$Ni_{25}In_{20}P_{55}$	Ni_5P_4	6.792(1)		10.987(4)	
			NiP_2	6.362(6)	5.617(6)	6.078(6)	126.18(9)
			InP	5.8728(3)			
	4	$Ni_{20}In_{15}P_{65}$	NiP_2	6.3684(4)	5.6171(6)	6.072(1)	126.24(9)
			InP	5.8702(1)			
			P				
Pd–In–P	1	$Pd_{15}In_{70}P_{15}$	$PdIn_3$	9.4362(5)			
			InP	5.8697(4)			
			In	3.2538(3)		4.9483(7)	
	2	$Pd_{20}In_{60}P_{20}$	Pd_2In_3	4.537(2)		5.511(4)	
			$PdIn_3$	9.4347(6)			
			InP	5.8701(2)			
	3	$Pd_{37}In_{52}P_9$	PdIn	3.2296(4)			
			Pd_2In_3	4.5414(4)		5.5243(7)	
			InP	5.8697(3)			
	4	$Pd_{40}In_{35}P_{25}$	PdIn	3.2485(8)			126.428(5)
			PdP_2	6.7793(4)	5.8569(6)	6.2071(5)	
			InP	5.8675(8)			
	5	$Pd_{10}In_{15}P_{75}$	PdP_2	6.7762(6)	5.8573(7)	6.2078(7)	126.418(5)
			InP	5.8699(2)			
			P				
Pt–In–P	1	$Pt_{15}In_{70}P_{15}$	Pt_3In_7	9.443(6)			
			In	3.2523(6)		4.946(1)	
			InP	5.8666(4)			
	2	$Pt_{15}In_{55}P_{25}$	Pt_3In_7	9.4315(4)			
			PtP_2	5.6953(2)			
			InP	5.8691(2)			
	3	$Pt_{15}In_{25}P_{60}$	PtP_2	5.6965(3)			
			InP	5.8700(2)			
			P				

[a] No standard deviation was calculated since too few lines were present.

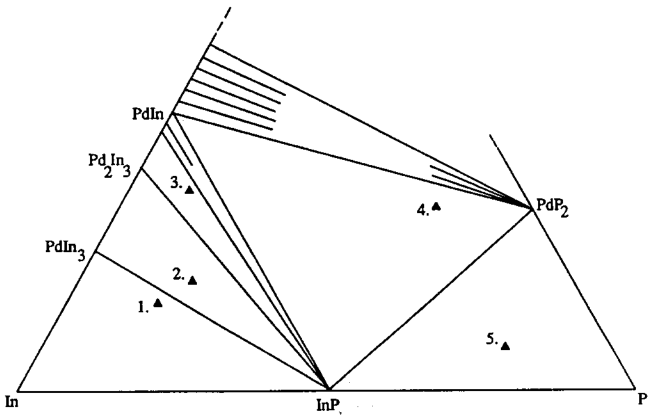

Fig. 2. Sample compositions and ternary phase equilibria in the Pd–In–P system at 600 °C.

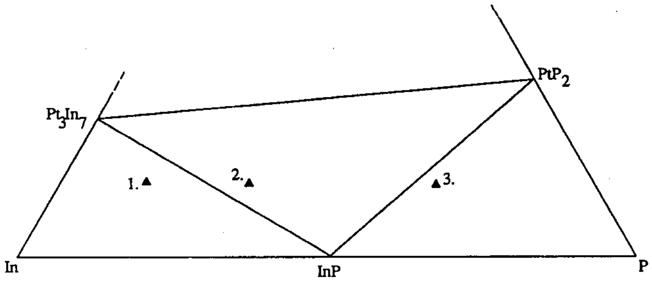

Fig. 3. Sample compositions and ternary phase equilibria in the Pt–In–P system at 600 °C.

ordered at the composition PdIn. The same behaviour has been observed for the PdIn isomorphs CoAl, NiAl, CoGa and NiGa. A comparison between the cell dimensions obtained in this work and the cell dimensions reported by Nover and Schubert [20] indicates that the vertex of the InP–PdIn–PdP_2 three-phase region connected to PdIn is close to the stoichiometric composition PdIn.

The metal-rich part of the Pd–P system is notorious for the formation of metastable states. In spite of this, the formation of equilibria in the investigated part of the system was quite rapid. PdP_2 was found to react with the humidity in the air forming phosphoric acid.

3.3. Pt–In–P system

The preparation routine for the Pt–In–P alloys was exactly the same as described above for the Pd–In–P system. The compositions and results from the phase analysis are presented in Table 1. The system exhibits some resemblance to the Pd–In–P system and, in this case, InP forms equilibria with indium, Pt_3In_7, PtP_2 and phosphorus (Fig. 3). The variations in the cell dimensions are small, thus indicating narrow homogeneity ranges in the system.

4. Discussion

Although the metals belong to the same group in the periodic table and the binary metal–indium and metal–phosphorus systems are fairly rich in compounds, the three ternary sections are quite different. In the nickel system, equilibria are formed only between binary metal phosphides and InP. However, in the Pd–In–P system, equilibria are formed primarily between InP and the binary metal indium compound. However, a common feature is the equilibrium between InP and the metal diphosphide.

As mentioned in Section 1, one purpose of this study was to produce reliable chemical information which may be helpful when choosing suitable contact materials to indium phosphide. From a chemical perspective, a suitable contact material must be stable under the circumstances under which the component is operating, *i.e.* there must be no phase transformations in the temperature interval of interest, in this case between room temperature and 800 °C, and the contact material must not react with anything in the environment.

In the Ni–In–P system, Ni_2P, Ni_5P_4 and NiP_2 are thermally stable and none of them react markedly with air, water or quartz. Of the palladium compounds, only one, PdIn, is a possible contact material. $PdIn_3$ and Pd_2In_3 both melt at fairly low temperatures (664 and 709 °C respectively) and PdP_2 is easily formed but reacts with the humidity in the air and so is unsuitable as a contact. Finally, for the platinum system, both of the binary phases forming equilibria with InP (Pt_3In_7 and PtP_2) can be used as contact materials from a chemical viewpoint.

Acknowledgment

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