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Phase equilibria in the In–Rh–As system at 600 °C

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Abstract

Phase equilibria were established in the In–Rh–As system at 600 °C, using X-ray diffraction, electron probe microanalysis, scanning electron microscopy and differential thermal analysis. InAs was demonstrated to be in thermodynamic equilibrium with RhIn₃, Rh₃In₅As₂, RhAs₂ and RhAs₃. The phase Rh₃In₅As₂, which has not been reported previously in the literature, was found to possess the cubic Ir₃Ge₇ (cI40, D8₇) structure, with the lattice parameter $a = 0.9165_{\pm 6}$ nm. A combination of X-ray diffraction and differential thermal analysis experiments indicated that Rh₃In₅As₂ forms peritectically at 829 ± 5 °C, according to the reaction: RhIn + L → Rh₃In₅As₂. A schematic 50 at.% indium In–Rh–As phase diagram isopleth was proposed to illustrate this reaction. RhAs was found to dissolve 8 at.% indium. Rh_{9+x}As₇, RhIn₃ and RhIn also showed some ternary solubility. RhIn exhibited an appreciable range of binary homogeneity, extending from at least 44–49 at.% rhodium at 600 °C. The results of the present investigation suggest that RhIn₃ would be most suitable as a thermodynamically stable, rhodium-based contact to InAs.

Keywords: Phase equilibria; X-ray diffraction; Electron probe microanalysis; Scanning electron microscopy; Differential thermal analysis

1. Introduction

Desirable intrinsic properties, including a small effective electron mass, high low-field electron mobility and a high electron saturation velocity make InAs a promising material for the fabrication of high-speed electronic devices, such as field-effect transistors (FETs) and heterojunction bipolar transistors (HBTs). (For a review of the physical properties of InAs and the current state of InAs device technology, the reader is directed to Ref. [1].)

Metal contacts must often be made directly to InAs in devices such as those described above. The electrical properties of a metal contact to a compound semiconductor depend strongly upon the chemistry of the metal–semiconductor interface. Lin et al. [2] and Beyers et al. [3] have demonstrated the utility of ternary phase diagrams for rationalizing chemical reactions which occur between metal thin films and compound semiconductors and for selecting stable contact materials. Most contacts to compound semiconductors contain at least one transition metal. However, very few In–transition metal–As ternary phase diagrams have

been reported in the literature [4–7]. In the present study, the 600 °C isotherm of the In–Rh–As system has been determined. A schematic 50 at.% indium In–Rh–As phase diagram isopleth has also been proposed.

2. Experimental procedure

Semiconductor-grade InAs and rhodium powder and indium shot of 99.99% purity were intimately mixed and pressed into pellets with total masses of 0.3 g. The pellets were sealed in quartz ampoules which were evacuated to a pressure of 10^{-2} Torr. The ampoules were annealed at 600 °C for 14 days. They were then quenched in ice water, and the samples were ground into powders, and again pressed into pellets, encapsulated in evacuated quartz ampoules and annealed for another 3 months. Subsequently, the ampoules were quenched in ice water, and each sample pellet was cut in half. One half of each sample was crushed and analyzed by X-ray diffraction, using a Scintag automated diffractometer with Cu K α radiation. For selected samples, silicon (National Institute of Standards and Technology specimen, $a = 0.543\,094$ nm) was used as an internal standard, and peak positions and lattice pa-

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rameters were refined using non-linear least-squares computer programs included in the Scintag software package. The other half of each sample was metallographically cross-sectioned and analyzed for composition with an Applied Research Laboratories SEMQ electron microprobe (EPMA), using wavelength-dispersive spectroscopy (WDS) and employing elemental rhodium and a commercially produced InAs wafer as standards. The samples were further examined using an ADEM II scanning electron microscope (SEM) operating in the backscattered electron imaging mode. One sample was analyzed for temperature stability using a Perkin–Elmer Model 1700 Differential Thermal Analysis (DTA) system. To avoid temperature errors due to liquid undercooling, DTA data were taken in the heating mode, at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$. The differential thermal analyzer was calibrated using high-purity lead, zinc, antimony, silver and copper as standards.

3. Results and discussion

Before discussing the results obtained in the present study, the results of previous investigations of phase equilibria in the In–Rh–As system will be reviewed.

3.1. Review of phase equilibria in the constituent binary systems

The binary In–As system is well known [8]. InAs is the only intermediate phase in this system. Its composition range, crystal structure, lattice parameter, and temperature stability are given in Table 1. According to Hall [25], the maximum solubility of arsenic in liquid indium is about 5 at.% at $600\text{ }^{\circ}\text{C}$.

No Rh–In phase diagram has been reported in the literature. Okamoto [26] has assessed the published data pertaining to this system. Schubert et al. [11] determined that two intermediate phases, RhIn_3 and RhIn , were in thermodynamic equilibrium with each other at temperatures between $200\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$. They also found X-ray diffraction evidence of a possible rhodium-rich phase after annealing a sample at $1100\text{ }^{\circ}\text{C}$ for 1.5 h, but did not identify a new phase.

Crystal structure data are given in Table 1 for the phases RhIn_3 and RhIn . Their ranges of homogeneity, melting temperatures and melting behavior have not been determined. Schubert et al. observed microstructural evidence in an as-cast sample of the eutectic solidification of rhodium and RhIn . They estimated the eutectic temperature to be in excess of $1300\text{ }^{\circ}\text{C}$. In the absence of additional intermediate phases, and assuming that the melting temperature of RhIn is higher than that of RhIn_3 , the existence of the eutectic reaction: $\text{L} \rightarrow \text{Rh} + \text{RhIn}$ implies that RhIn melts congruently. It further implies that the congruent melting temperature

of RhIn is higher than the eutectic temperature, i.e. higher than $1300\text{ }^{\circ}\text{C}$. Verbeek and coworkers [13] prepared RhIn by arc-melting the elements together. They found the alloy to be homogeneous upon solidification, which again suggests the congruent melting of RhIn . RhIn_3 probably melts peritectically, as does the isostructural phase CoGa_3 [11].

The solubility of indium in solid rhodium has not been investigated. Dieva [27] measured the maximum solubility of rhodium in liquid indium as a function of temperature between 327 and $967\text{ }^{\circ}\text{C}$. According to Dieva's measurements, the maximum solubility of rhodium in liquid indium is about 0.6 at.% at $600\text{ }^{\circ}\text{C}$.

The Rh–As phase diagram has not been determined. Most of what is known about the system was established by Heyding and Calvert [14] and Quesnel and Heyding [16], whose work was later modified in the composition region 37–44 at.% arsenic by Pivan and Guérin [21] and Pivan et al. [22]. Six rhodium arsenides have been demonstrated to exist: RhAs_3 , RhAs_2 , RhAs , $\text{Rh}_{9+x}\text{As}_7$ (where $0 \leq x \leq 1.5$), $\text{Rh}_{12}\text{As}_7$ and Rh_2As . Data pertaining to their crystal structures and composition ranges are given in Table 1. According to Quesnel and Heyding [16], Rh_2As exists in two allotropic forms: a low-temperature cubic form and a high-temperature orthorhombic form.

Pivan and Guérin [21] detected superlattice lines in their X-ray diffraction patterns of Rh_9As_7 powder and single crystal $\text{Rh}_{10.5}\text{As}_7$, corresponding to an hexagonal structure in which the a lattice parameter is three times that of the original structure. However, Raub et al. [28] reported the existence of a different type of hexagonal superlattice structure near the rhodium-poor limit of homogeneity of $\text{Rh}_{9+x}\text{As}_7$, in which the c lattice parameter increases by a factor of about 1.5 and the a lattice parameter remains the same as that of the original structure. They interpreted this superlattice as a "stacking disorder" in the original structure.

The melting behavior and melting temperatures of the Rh–As phases are unknown. Quesnel and Heyding [16] reported that they did not observe any liquid phases in the metal-rich portion of the system at temperatures up to $1000\text{ }^{\circ}\text{C}$, nor did they find evidence of melting in the arsenic-rich region of the system at temperatures up to $900\text{ }^{\circ}\text{C}$. In agreement with these observations, Guérin et al. [17], who determined the Ga–Rh–As phase diagram at $1000\text{ }^{\circ}\text{C}$, found all of the Rh–As phases except for RhAs_3 to exist at that temperature. Pivan and Guérin [21] have also reported that $\text{Rh}_{12}\text{As}_7$ and $\text{Rh}_{9+x}\text{As}_7$ are stable up to at least $1200\text{ }^{\circ}\text{C}$.

The solubility of arsenic in solid rhodium has not been determined. However, Schulz et al. [29], when investigating phase equilibria in the Ga–Rh–As system at $800\text{ }^{\circ}\text{C}$, found arsenic to be insoluble in rhodium by EPMA.

Table 1

Compositional stabilities, crystal structures, lattice parameters and temperature stabilities of constituent binary phases in the In–Rh–As system

Phase	Composition (at.% In or As)	Structure	Lattice parameters (nm)	Temperature (°C)
InAs	50.0 [8]	cubic, ZnS, cF8, B3 [8]	$a = 0.6058$ [9]	942 (c) [8] ^a
RhIn ₃	25.0 [10]	tetragonal, CoGa ₃ , tP16 [10]	$a = 0.701$ [10] $c = 0.715$	unknown (p) ^b
RhIn	50.0 [12]–56.0 ^c	cubic, CsCl, cP2, B2 [12]	$a = 0.3190$ [13]	unknown, but > 1300 (c) [11]
RhAs ₃	75.0 [14]	cubic, CoAs ₃ , cI32, D0 ₂ [14]	$a = 0.84507$ [15]	unknown, but < 1000 [16,17]
RhAs ₂	66.7 [18]	monoclinic, CoSb ₂ , mP12 [16]	$a = 0.60629$ [19] $b = 0.60816$ $c = 0.61498$ $\beta = 114.707^\circ$	unknown, but > 1000 [16,17]
RhAs	50.0 [14]	orthorhombic, MnP, oP8, B31 [14]	$a = 0.5645$ [20] $b = 0.3595$ $c = 0.6061$	unknown, but > 1000 [16,17]
Rh _{9+x} As ₇	40.0–43.8 [21]	hexagonal, Cr ₁₂ P ₇ , hP26 [21]	$a = 0.9219$ [21] $c = 0.3532$ ($x = 1.5$)	unknown, but > 1200 [21]
Rh ₁₂ As ₇	36.8 [16]	hexagonal, Rh ₁₂ As ₇ , hP22 [22]	$a = 0.9297$ [22] $c = 0.3657$	unknown, but > 1200 [21]
Rh ₂ As(α)	33.3 [14]	cubic, anti-CaF ₂ , cF12, C1 [14]	$a = 0.56753$ [23]	$T \leq 683$ [24]
Rh ₂ As(β)	33.3 [16]	orthorhombic, Co ₂ Si, oP12, C23 [16]	$a = 0.5904$ [23] $b = 0.3918$ $c = 0.7352$	683 [24] $\leq T <$ unknown, but > 1000 [16,17]

^aThe letters “c” and “p” denote congruent and peritectic melting respectively.

^bMelting behavior of RhIn₃ is tentatively assigned based upon the melting behavior of the isotypic phase CoGa₃ [11].

^cDetermined in the present study.

3.2. Review of phase equilibria in the In–Rh–As system

No experimental investigation of phase equilibria in the In–Rh–As system has been reported in the literature. Klingbeil and Schmid-Fetzer [30] have calculated a room temperature phase diagram isotherm of the In–Rh–As system, using experimental thermodynamic data for InAs [31] and estimated thermodynamic data for the binary Rh–In and Rh–As phases [32]. Their calculations predicted that RhIn₃, RhAs₃, RhAs₂ and RhAs would be in thermodynamic equilibrium with InAs. However, as was discussed by Klingbeil and Schmid-Fetzer, such calculated diagrams, while often qualitatively correct, must be confirmed experimentally. For example, if an uncertainty of ± 8 kJ g-atom⁻¹ was assumed for the estimated thermodynamic data, the authors found nine alternative tie-lines to be possible in the In–Rh–As system. Furthermore, the occurrence of ternary phases, which may drastically alter the topologies of such calculated diagrams, cannot be predicted a priori.

3.3. Phase equilibria in the In–Rh–As system at 600 °C

The experimentally determined In–Rh–As 600 °C phase diagram isotherm is shown in Fig. 1. A three-phase region of thermodynamic equilibrium was found to exist between InAs, RhAs₂, and Rh₃In₅As₂, a ternary phase which has not been reported previously in the literature. RhIn₃ was also shown to be in thermodynamic

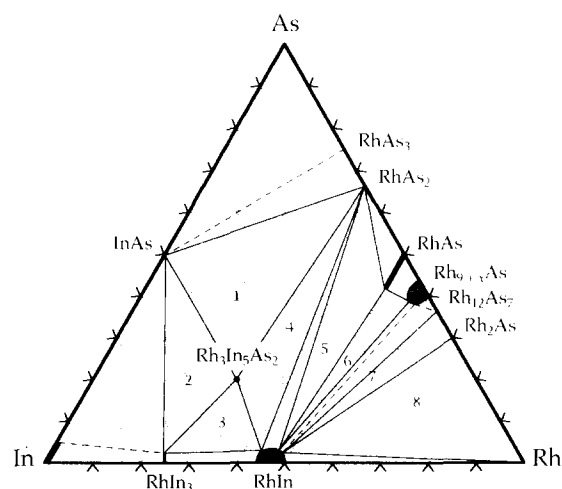


Fig. 1. Phase equilibria in the In–Rh–As system at 600 °C. The numerals within the diagram represent the gross sample compositions and sample numbers used in the present investigation. The phases identified in each sample by X-ray diffraction and the compositions of these phases as determined by EPMA are given in Table 2.

equilibrium with InAs. According to the Gibbs phase rule, RhAs₃ must be in thermodynamic equilibrium with InAs as well, based upon the other tie-lines determined in the present investigation. However, the RhAs₃–InAs tie-line was not confirmed experimentally. A backscattered SEM micrograph of sample 2, depicting the coexistence of RhIn₃, Rh₃In₅As₂ and InAs, is given in Fig. 2.

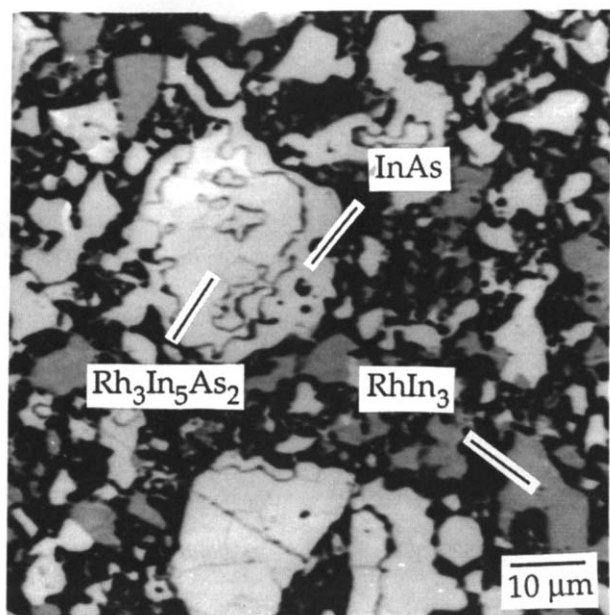


Fig. 2. A backscattered SEM micrograph of sample 2, depicting the coexistence of the phases InAs, RhIn₃ and Rh₃In₅As₂.

Several constituent binary phases exhibited ternary solubility. These included RhAs, which dissolved about 8 at.% indium, Rh_{9+x}As₇, which dissolved about 4 at.% indium, RhIn₃, which dissolved about 2 at.% arsenic, and RhIn, which dissolved approximately 3 at.% arsenic. RhIn was found to have a significant range of binary homogeneity as well. Based upon the samples of the present investigation, RhIn exists from at least 44 to 49 at.% rhodium at 600 °C. Indium and arsenic seemed to be virtually insoluble in rhodium. However, the temperature employed in the present investigation was quite low compared with the melting point of rhodium, and therefore substitutional diffusion of indium and arsenic in rhodium may have been too slow for equilibrium conditions to be achieved.

The phase Rh₂As was found to have the low-temperature cubic structure at 600 °C, in accordance with the experimental work of Quesnel and Heyding and Secoué et al. [24]. The lattice parameters of the four phases exhibiting ternary solubility were not appreciably different from those of the pure binary phases.

The phase Rh_{9+x}As₇ in sample 6 appeared to exhibit a superlattice structure at 600 °C. However, there was significant overlap between the X-ray diffraction peaks of the phases RhIn, RhAs and Rh_{9+x}As₇ in this sample, which made the accurate determination of many of the peak positions somewhat difficult. It is interesting to note that the strongest superlattice peaks observed in the present investigation could be indexed using either the superlattice structure proposed by Raub et al. [28] or the superlattice structure reported by Pivan and Guérin [21]. This suggests that both Raub and coworkers and Pivan and Guérin observed the same superlattice

peaks, but adopted different lattice parameters to index them. Owing to the fact that Pivan and Guérin observed the tripling of the *a* parameter in Weissenberg photographs of a single crystal specimen, their proposed superlattice structure must be presumed to be the correct one.

The ternary phase Rh₃In₅As₂ was found by X-ray diffraction analysis to possess the Ir₃Ge₇ (cI40, D8_f) crystal structure, a complicated, γ -brass-like structure with four formula units (40 atoms) per unit cell [33]. Rh₃In₅As₂ has a body-centered cubic Bravais lattice, with the lattice parameter $a = 0.9165_{\pm 6}$ nm. According to EPMA, Rh₃In₅As₂ has a narrow range of homogeneity.

3.4. The 50 at.% indium In–Rh–As phase diagram isopleth

The temperature stability of Rh₃In₅As₂ was determined using a combination of DTA and X-ray diffraction analysis of two additional samples. Their gross compositions were In-30at.%Rh-20at.%As, corresponding to the stoichiometry Rh₃In₅As₂, (sample 9) and In-27at.%Rh-23at.%As (sample 10). The samples were prepared and annealed according to the experimental procedure outlined in Section 2. Subsequently, samples 9 and 10 were confirmed by X-ray diffraction analysis to consist of single-phase Rh₃In₅As₂ and a mixture of InAs and Rh₃In₅As₂ respectively.

A portion of sample 9 was subjected to DTA. The DTA heating curve exhibited a sharp, pronounced thermal arrest at 829 ± 5 °C, and a broad, very shallow arrest between 829 °C and about 900 °C. The exact temperature range of this latter arrest was difficult to ascertain, owing to its shallowness.

One may assume that the pronounced thermal arrest at 829 °C in the DTA curve corresponds to the reaction which leads to the decomposition of Rh₃In₅As₂. However, the presence of a second, shallow arrest indicates that complete melting of the sample does not occur until approximately 900 °C.

In order to determine the types of reactions which occurred over this temperature range, the remainder of sample 9 and sample 10 were pressed into pellets, encapsulated in evacuated quartz ampoules, annealed at 900 °C for 10 min, and quenched in ice water. From the morphologies of the pellets, it was clear that both samples had melted during this heat treatment. Subsequent X-ray diffraction analysis of the samples showed sample 9 had transformed into InAs, Rh₃In₅As₂ and RhIn upon solidification. Sample 10, however, transformed upon solidification into the same two phases, InAs and Rh₃In₅As₂, as were present at 600 °C.

All of the phases which appeared in the samples upon solidification (InAs, Rh₃In₅As₂ and, nominally, RhIn) contain 50 at.% indium. It is therefore useful

Table 2

Gross sample compositions, phases identified by X-ray diffraction and compositions of phases determined by electron probe microanalysis (EPMA)

Sample number	Sample composition (at.%)			Phases by X-ray diffraction	Composition of phases by EPMA		
	In	Rh	As		In	Rh	As
1	40	20	40	InAs	50.3	0.0	49.7
				Rh ₃ In ₅ As ₂	51.1	28.6	20.3
				RhAs ₂	0.4	33.7	65.9
2	60	20	20	InAs	50.2	0.0	49.8
				Rh ₃ In ₅ As ₂	51.7	29.0	19.3
				RhIn ₃	73.6	24.1	2.3
3	58	32	10	Rh ₃ In ₅ As ₂	52.4	29.4	18.2
				RhIn ₃	73.5	23.9	2.6
				RhIn	53.7	44.3	2.0
4	32.5	35	32.5	Rh ₃ In ₅ As ₂	50.1	28.4	21.5
				RhIn	52.7	44.0	3.3
				RhAs ₂	0.4	33.7	65.9
5	27.5	45	27.5	RhIn	50.3	46.9	2.8
				RhAs ₂	0.2	35.0	64.8
				RhAs	7.8	50.3	41.9
6	24.5	51	24.5	RhIn	48.4	47.4	4.2
				RhAs	7.6	50.2	42.2
				Rh ₉₊₁ As ₇	4.4	57.1	38.5
7	21	58	21	RhIn	48.0	49.1	2.9
				Rh ₁₂ As ₇	0.2	63.6	36.2
				Rh ₂ As	3.2	65.2	31.6
8	15	70	15	Rh	0.0	98.6	1.4
				RhIn	47.5	49.1	3.4
				Rh ₂ As	0.7	66.8	32.5

to construct a 50 at.% indium In–Rh–As phase diagram isopleth to illustrate the melting behavior of Rh₃In₅As₂. A schematic 50 at.% indium In–Rh–As phase diagram isopleth has been proposed in Fig. 3. The reasoning which led to its construction is given below.

First, in order to explain the coexistence upon solidification of InAs, Rh₃In₅As₂ and RhIn in sample 9, one may assume that the isopleth is pseudobinary in the vicinity of 829 °C. This conclusion is based on the following argument. As was mentioned previously, the gross sample composition of sample 9 was 50 at.% indium (In-30at.%Rh-20at.%As, or Rh₃In₅As₂). Both InAs and Rh₃In₅As₂ comprise 50 at.% indium and have very narrow ranges of homogeneity. If the solidified sample consisted solely of InAs, Rh₃In₅As₂ and RhIn, the RhIn phase would also have to contain 50 at.% indium, or there would be no mass balance between the gross sample composition and the phases formed upon solidification. (The RhIn phase may contain dissolved arsenic, however.) Furthermore, if all of the phases in sample 9 contained 50 at.% indium upon solidification, the solidification path, i.e. the path on the liquidus surface followed by the liquid composition during the course of solidification, would have to proceed

in the direction of 50 at.% indium content as well. In a ternary phase diagram, it is very unlikely that the solidification path would proceed entirely in a direction of constant composition unless that composition represented a pseudobinary isopleth.

Second, if the 50 at.% indium isopleth were indeed pseudobinary in the vicinity of 829 °C, the reaction which leads to the melting of Rh₃In₅As₂ would have to involve three phases, two of which obviously would be the liquid and Rh₃In₅As₂. However, sample 9 contained three phases upon solidification, meaning that either InAs or RhIn appears as the result of a second reaction. This second reaction may be identified by considering sample 10, which contained a mixture of InAs and Rh₃In₅As₂ both before and after solidification. The solidification behavior of this sample may only be explained by the existence of the eutectic reaction: L → InAs + Rh₃In₅As₂. By definition, this reaction must occur at a temperature which is lower than the melting temperatures of InAs and Rh₃In₅As₂, and therefore must occur at a temperature lower than 829 °C.

One may now conclude that the presence of InAs in sample 9 is due to the eutectic reaction between InAs and Rh₃In₅As₂. Therefore, the melting reaction

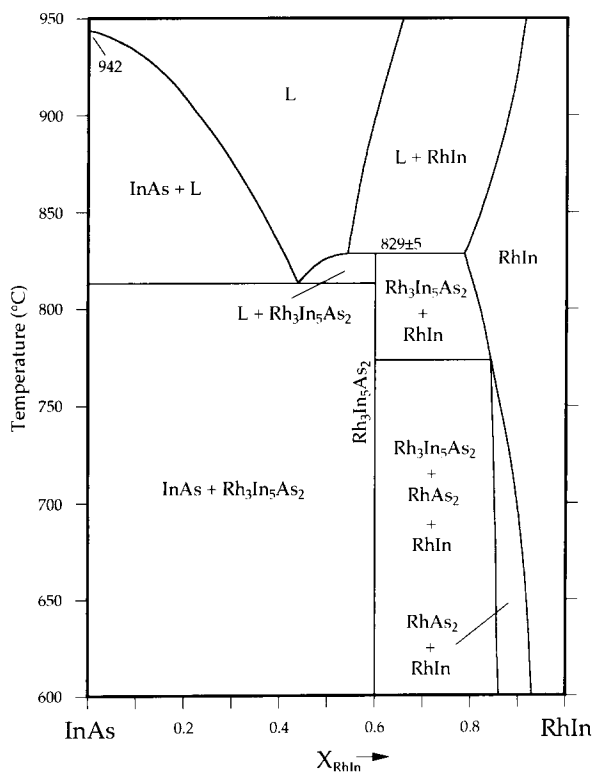


Fig. 3. A schematic 50 at.% indium In–Rh–As phase diagram isopleth, based upon the results of DTA and X-ray diffraction analysis of two solidified samples, and arguments outlined in Section 3.4. of the text.

at 829 °C involves the liquid, $\text{Rh}_3\text{In}_5\text{As}_2$ and RhIn . Because the melting temperature of RhIn is much higher than 829 °C, this reaction must be peritectic, of the form: $\text{L} + \text{RhIn} \rightarrow \text{Rh}_3\text{In}_5\text{As}_2$. The shallow thermal arrest between 829 °C and 900 °C then corresponds to the two-phase region $\text{L} + \text{RhIn}$, and the liquidus surface is located at approximately 900 °C at this composition. InAs , $\text{Rh}_3\text{In}_5\text{As}_2$ and RhIn form during solidification of a sample of the composition $\text{In}_{30}\text{at.}\% \text{Rh}_{20}\text{at.}\% \text{As}$ ($\text{Rh}_3\text{In}_5\text{As}_2$) because global equilibrium is not generally achieved in peritectic solidification processes. During solidification, RhIn is the first phase formed from the melt, and there is insufficient time for the liquid and RhIn to react to form $\text{Rh}_3\text{In}_5\text{As}_2$ before the temperature of the eutectic reaction: $\text{L} \rightarrow \text{InAs} + \text{Rh}_3\text{In}_5\text{As}_2$ is reached.

Finally, the 50 at.% indium phase diagram isopleth must be consistent with the 600 °C ternary isotherm presented in Fig. 1. However, one may see from Fig. 1 that the isotherm is not pseudobinary along the composition 50 at.% indium, because $\text{Rh}_3\text{In}_5\text{As}_2$ is not in thermodynamic equilibrium with RhIn containing 50 at.% indium, but rather is in thermodynamic equilibrium with RhIn containing 53 at.% indium. This allows the three-phase region $\text{RhAs}_2 + \text{Rh}_3\text{In}_5\text{As}_2 + \text{RhIn}$ and the two-phase region $\text{RhAs}_2 + \text{RhIn}$ to cross the line of 50 at.% indium content.

The pseudobinary nature of the isopleth in the vicinity of 829 °C and the ternary nature of the isopleth at 600 °C must be reconciled with each other. This would be accomplished if the solubility of arsenic in RhIn were to increase from about 3 at.% at 600 °C to about 7 at.% at some temperature between 600 °C and 829 °C. If this were to occur, the composition of RhIn which is in thermodynamic equilibrium with RhAs_2 and InAs would become rhodium-rich to the point where neither the three-phase region $\text{RhAs}_2 + \text{Rh}_3\text{In}_5\text{As}_2 + \text{RhIn}$ nor the two-phase region $\text{RhAs}_2 + \text{RhIn}$ would any longer cross the line of 50 at.% indium content. (This would occur for geometrical reasons, as may be understood by an inspection of Fig. 1.) At the temperature at which this occurred, the isopleth would become pseudobinary, and would be consistent with the isopleth in the vicinity of 829 °C.

3.5. Metallization schemes for InAs based upon the use of rhodium

Based upon the results of the present investigation, rhodium is not suitable as a contact material to InAs , if thermodynamic stability is a concern. If a thin film of rhodium were deposited on an InAs substrate and allowed to reach thermodynamic equilibrium, the final reaction products would be $\text{Rh}_3\text{In}_5\text{As}_2$ and RhAs_2 . The temperature at which chemical reactions occur between rhodium and InAs may be quite low. Indicative of this possibility, Schulz and Chang [34] found rhodium thin films to react with GaAs after annealing at 200 °C for 1 h.

The phases which are in thermodynamic equilibrium with InAs could potentially be used as stable contact materials. However, RhAs_3 and RhAs_2 are semiconductors [35,36], and therefore would not be suitable electrically as contact materials. $\text{Rh}_3\text{In}_5\text{As}_2$ is presumably metallic, and could be used as a thermodynamically stable contact material. Fabrication of an $\text{Rh}_3\text{In}_5\text{As}_2$ thin film may be impractical, however, because it requires the deposition of arsenic. Arsenic deposition may not be compatible with conventional methods of deposition, such as d.c. magnetron sputtering or electron beam evaporation. Therefore, RhIn_3 would probably be the best rhodium-based contact material to InAs , because it could be fabricated more easily than $\text{Rh}_3\text{In}_5\text{As}_2$ and is also in thermodynamic equilibrium with InAs .

4. Conclusions

Phase equilibria were established in the In–Rh–As system at 600 °C. A region of three-phase equilibrium was found to exist between the phases InAs , RhAs_2 and $\text{Rh}_3\text{In}_5\text{As}_2$, a ternary phase discovered in the present investigation. RhIn_3 and RhAs_3 were also shown to be

in thermodynamic equilibrium with InAs at this temperature.

Several constituent binary phases exhibited ternary solubility. These included RhAs, which dissolved about 8 at.% indium, $\text{Rh}_{9+x}\text{As}_7$, which dissolved about 4 at.% indium, RhIn_3 , which dissolved about 2 at.% arsenic and RhIn, which dissolved approximately 3 at.% arsenic. Ternary solubility did not appreciably change the lattice parameters of these phases. RhIn was found to have a significant range of binary solubility as well, extending from at least 44 to 49 at.% rhodium at 600 °C.

The ternary phase $\text{Rh}_3\text{In}_5\text{As}_2$ was found by X-ray diffraction analysis to crystallize in the Ir_3Ge_7 (CI40 , D8_f) structure, a complicated γ -brass-like structure with four formula units (40 atoms) per unit cell. Its Bravais lattice is body-centered cubic, with the lattice parameter $a = 0.9165_{\pm 6}$ nm. $\text{Rh}_3\text{In}_5\text{As}_2$ also exhibited a narrow range of homogeneity. Based on a combination of DTA and X-ray diffraction experiments, the phase was postulated to form peritectically at 829 ± 5 °C according to the reaction: $\text{RhIn} + \text{L} \rightarrow \text{Rh}_3\text{In}_5\text{As}_2$. A schematic 50 at.% indium In–Rh–As phase diagram isopleth was proposed, which illustrates this reaction. The proposed isopleth is pseudobinary at high temperatures.

The results of the present investigation suggest that both $\text{Rh}_3\text{In}_5\text{As}_2$ and RhIn_3 would be suitable as contacts to InAs. However, RhIn_3 would be a better contact material from a practical point of view, because it would probably be easier to fabricate by conventional methods than would the arsenic-containing ternary phase.

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