A Methodology for Obtaining Diffusion Coefficients in a three-Phase Ternary Couple : InAs/nickel

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Abstract-- **A methodology was presented for determining the interdiffusion coefficients of phases formed in a ternary diffusion couple using the measured growth rates and the concentration profiles across the couple. Using this methodology the interdiffusion coefficients of theT-Ni_3InAs phase were obtained from several INAs/nickel couples. Assuming the cross-intrinsic diffusion coefficients to be negligible, relationships between intrinsic diffusion coefficients were derived and values were obtained for the three intrinsic diffusion coefficients of the T-phase. The intrinsic diffusivity for nickel was the largest and that for arsenic the smallest. These data rationalized in terms of the structure of the T-phase.**

Index Term-- **Coefficient interdiffusion; Diffusion couples; Intrinsic diffusion; Ni_3InAs.**

1. INTRODUCTION

Two types of composite materials systems have emerged in recent years: layered materials for application in the electronics industry and high-temperature composite materials for applications primarily in the aerospace industry. Both types of materials are multi-component systems and their ultimate performance depends on the stabilities at the interfaces of the layered structural and the structural composites. In this paper, we will focus on interdiffusional phenomena at the interfaces, where Professor J. S. Kirkaldy has made monumental contribution. Since intermediate phases often occur in binary, ternary and high-order systems, a knowledge of the formation and dissolution of these phases during the fabrication, subsequent annealing and eventual service treatment of these composites is essential. A solution to the growth of a two-phase binary system was first proposed by Wagner as given by Yost [1] . This solution was then extended to three-phase binary systems by Castleman [2] and Kidson [3] Heckel and co-workers [4] and Metin, and Inal [5] among others have applied this solution to the growth of multi-phase binary systems.

A general solution for the layer growth of the ternary system was provided by Kirkaldy [6-8]. This solution was applied by Kirkaldy and Brown [9] to study the growth of several two-phase copper-zinc-tin diffusion couples and recently used by Nesbit and Heckel [10] to study several two-phase nickel-chromium-aluminum diffusion couples. It has not been applied to the growth of multi-phase ternary diffusion couples. It is worth noting that Rapp, Ezis and Yurek [11] did calculate the kinetics of displacement reaction $Fe + Cu_2O = 2\ Cu + FeO$. For electronic materials consisting of metal/semiconductor and composite materials consisting of metal/ceramic systems, the phases formed do not normally have large ranges of homogeneity. Determination of the interdiffusion coefficient via the Matano-Boltzmann analysis [12,13] is less feasible since accurate compositional variations within the single-phase regions are intrinsically difficult to measure experimentally. A number of experiment have been carried out to determine the diffusion coefficients involved metal/semiconductor reactions. Jan et. al. [14] has used a method to determine the diffusion coefficient based on ternary diffusion theory. The methodology used to obtain diffusion coefficients from involved an analysis of the layer growth kinetics and the concentration gradients within the single phase regions, if measureable range of homogeneity exists for these phases. This method has been used to obtain satisfactory results from the Ni/GaAs diffusion couples to form Ni_3InAs. The Ni/InAs diffusion couples were expected to behave as the Ni/GaAs diffusion couples did. The phase that formed in a ternary diffusion couple are closely linked to its corresponding ternary phase diagram: the phase diagrams of the Ni-Ga-As system [15] and the Ni-In-As system are quite similar. This would lead one to expect that the Ni/InAs diffusion couples form a reaction layer of a ternary phase. Ni_3InAs just as Ni/GaAs diffusion couples form the ternary phase Ni_3GaAs. Diffusion in Ni_3GaAs is thought to occur by an interstitial mechanisme proposed by Hähnel et. al. [16] It is expected that at a given temperature the growth rate of the Ni_3InAs would be larger that of the Ni_3GaAs. Because indium atoms are larger than gallium atoms, the interstitial space in a Ni3InAs phase would be larger than those in Ni_3GaAs. These two phenomena, the formation of a single Ni_3InAs reaction layer and an increased growth rate, were observed in this experiment.

2. TERNARY DIFFUSION THEORY

Figure 1 shows the concentration profiles for the growth of a β-phase from a ternary α/γ diffusion couple and the corresponding ternary isothermal section at constant pressure. The width of the β-phase layer as a function of time is [4-9]

$$w^{\beta} = \left[\xi^{\beta,\gamma} - \xi^{\alpha,\gamma}\right] = Z^{\beta,\gamma}\sqrt{t} - Z^{\alpha,\beta}\sqrt{t} = w^{\beta}\sqrt{t} \quad (1)$$

Where w^{β} is Thickness of a β-phase growing from a α/γ couple , $\xi^{\alpha,\beta}$ is position of the α/β interface $z^{\alpha,\beta}$ is A parameter relating $\xi^{\alpha,\beta}$ and $\sqrt{t}$, t is time , $Z^{\beta,\alpha}$ is parameter relating $\xi^{\beta,\gamma}$ and $\sqrt{t}$, and W^{β} is a parameter relating w^{β} and $\sqrt{t} = \left[z^{\beta,\gamma} - z^{\alpha,\beta}\right]$.

The above results can easily be adapted to the growth of an η-phase ternary system [4-9]. It is evident from Eq. (1) that the growth of a phase β in a semi-infinite ternary diffusion couple depends on the interdiffusion coefficients of β and those of α and γ as well as the concentrations at the two interfaces and the range of homogeneity for these phases. It has often been found empirically that the growth of a phase from a diffusion couple is parabolic with time and that the temperature dependence of the parabolic rate constant follows Arrhenius behavior. However, there is no clear physical interpretation for the parabolic rate constants and activation energies obtained since they depend on the properties not only of the phase involved but also those of its neighboring phases.

Having the value of $\check{D}_{i1}$'s and $\check{D}_{i2}$'s for all the pertinent phases with i = 1,2, the composition at the various interface and the ranges of homogeneity from accurate phase diagram data, Eq. (1) allow us to calculate the growth of phases in a semi-infinite ternary diffusion couple. However, as has been mentioned, for many systems of current technological interest such Indium-Metal-Arsenic for electronic materials or for multi-component structural materials, values of $\check{D}_{i1}$'s and $\check{D}_{i2}$'s are not known. As stated in the introduction, we wish to obtain the interdiffusion coefficients using Eq. (1), the growth rates of intermediate phases and the concentration profile obtained experimentally from semi-infinite ternary InAs/Nickel diffusion couples.

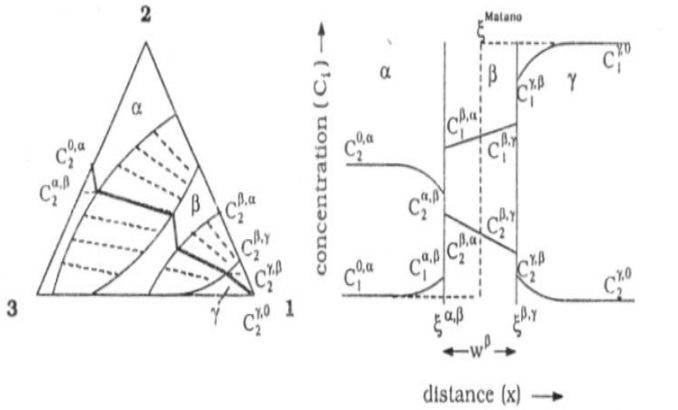

Fig. 1. The relationship between the diffusion zone interface concentrations for a three-phase Ternary diffusion couple at constant temperature snd pressure and the isothermal phase Diagram for this ternary system

3. EXPERIMENTAL PROCEDURE

Semiconductor grade, (100)-oriented n-type InAs wafers of 400 to 1200 μm thickness and 99,99 % purity nickel rod 6 mm in diameter were used for diffusion couples. Wafer was cut into 4.5 x 4.5 mm pieces and the rod was cut out into 2.5 mm thick disks. The contact surface of Ni, first ground with silicon carbide papers # 320, 400, 600, 1000, then polished with alumina 1μm, 0.3 μm and 0.05 μm. Ni and InAs pieces were rinsed twice in acetone, cleaned ultrasonically in hot trichloroethylene for 10 minutes, rinsed again in acetone and then cleaned ultrasonically in de-ionized water for 5 minutes. The cleaned pieces were etched in HCl : H_2O (1:1) solution, Ni pieces for 1 minute and InAs pieces for 4 minutes. Immediately after etching, Ni and InAs pieces were pressed together with two 6 mm in diameter quartz rods and sealed in 7 mm inside diameter quartz tubing under pressure of 10^{-3} torr.

The samples were annealed at temperatures ranging from 450 ^{o}C to 600 ^{o}C, for different lengths of time. After annealed, the diffusion couples were removed from the furnace, quenched in ice water. First cut was made approximately 1 cm from both sides of reacted metal and semiconductor and the samples were mounted in epoxy mold with the cross-section facing down.. Finally, as soon as this epoxy cured, the middle sections of the diffusion couples were cut (those which contained the Ni/InAs section). The standard metallographic grinding and polishing procedures were employed using silicon carbide grinding papers from # 320 to # 1500 and alumina slurries from 1 μm to 0.05 μm, then metallographically cross-section for analysis. Samples were coated with graphite and examined with an Applied Research Laboratories SEMQ electron microprobe (EPMA), using wavelength-dispersive spectroscopy (WDS) and employed elemental nickel and commercially produced InAs wafer as standards.

4. RESULTS AND DISCUSSION

When InAs and nickel are brought into contact, a ternary phase with the nominal composition Ni_3InAs, designed as T, is formed. Ni_3InAs is not a true ternary phase, but a part

of Ni solid solution which extends to Ni_3In_2. Bulk Ni/InAs diffusion couples experiments were carried out at 450 ^oC, 500 ^oC, 550 ^oC and 600 ^oC for different periods of time. The results obtained at 450 ^oC, 500 ^oC, 550 ^oC and 600 ^oC are presented in Fig. 2. In all of these diffusion couples, only the-T-phase formed between the end phase, InAs and nickel. Fig. 3a shows a typical micrograph and Fig. 3b EPMA composition profile, which was taken from Ni/InAs diffusion couple annealed at 600 ^oC for 9 hours. Longer annealed time may cause disappearance of the Ni_3InAs phase. The growth of T in terms of its thickness, x, as a function of $\sqrt{t}$ is given in Fig. 2. Within the scatter of the data, x varies linearly with $t^{1/2}$ for all four temperatures, indicating diffusion-controlled kinetics. The parabolic growth constants obtained from Fig 2 are shown in Fig. 4, which reflects the linear log(growth constant) versus 1000/T relationship.

To obtain the diffusion coefficients of Ni_3InAs from its growth rate and concentration profiles across the diffusion couples we must have the appropriate diffusion equations. In a three phase ternary diffusion couple system made up of component A, B, and C, a typical concentration profile might look like in Fig. 1. The growth of a three-phase ternary diffusion couple involves two interfaces. At each of these interface, there are two independent mass balance, equations as given by equation (2) and (3), was a total of four independent equations.

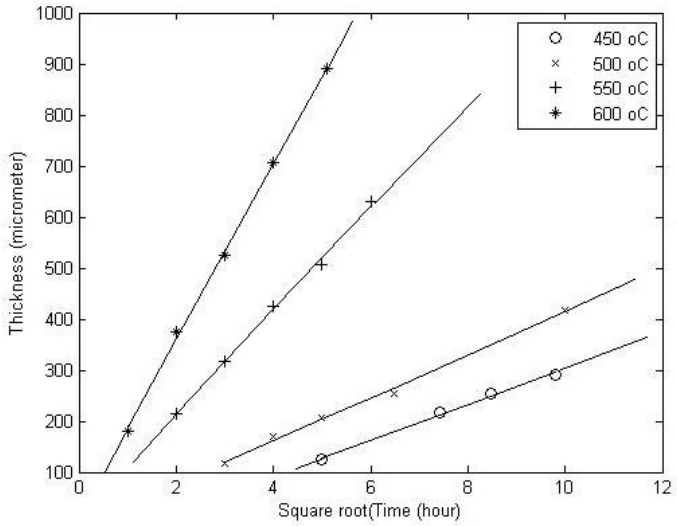

Fig. 2. The growth rates of T-Ni3InAs from Ni/InAs as a function annealing temperture and time.

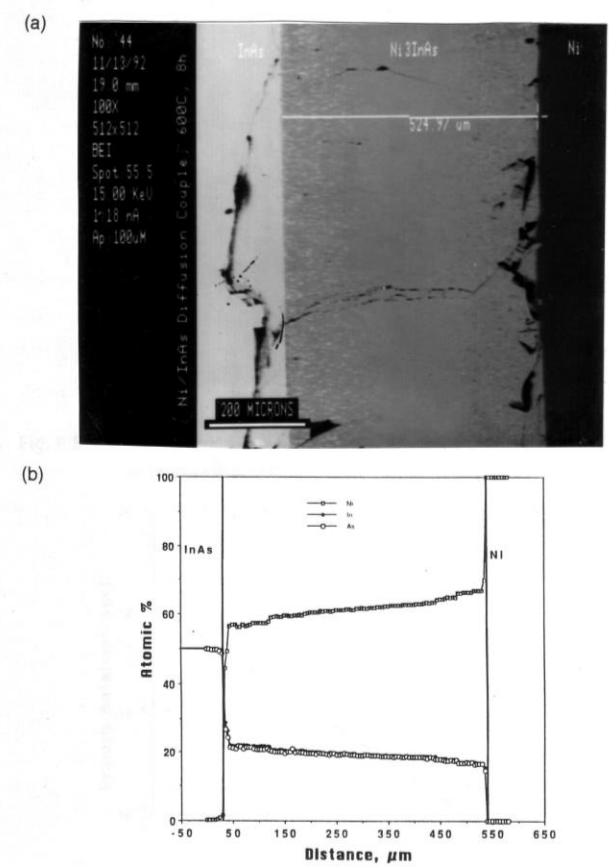

Fig. 3a. Photomicrograph backscattering electron image. b. EPMA compositional profile of Ni/InAs diffusion couple annealed at 600 ^oC for 9 hours showing the formation Ni_3InAs phase.

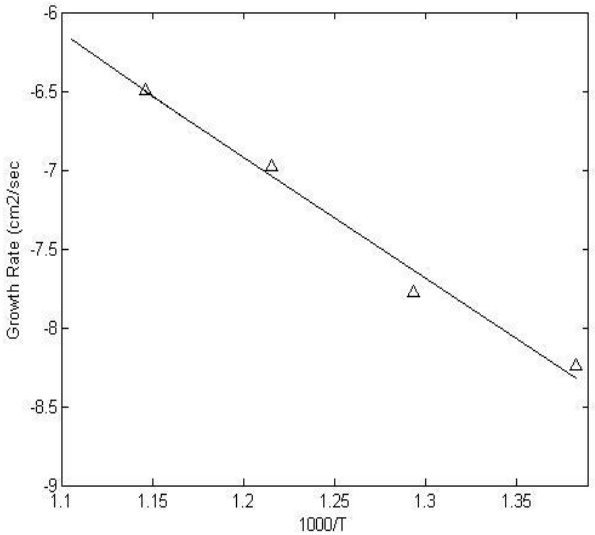

Fig. 4. The growth rates of T-Ni3InAs from Ni/InAs bulk diffusion couples annealed at 450 ^oC, 500 ^oC, 550 ^oC and 600 ^oC.

For the α/β interface:

$$\left(C_i^{\alpha,\beta} - C_i^{\beta,\alpha}\right)\frac{\partial \xi^{\alpha\beta}}{\partial t} = J_i^{\alpha,\beta} - J_i^{\chi,\alpha} \qquad (2)$$

For the β/γ interface :

$$\left(C_i^{\beta,\gamma} - C_i^{\gamma,\beta}\right)\frac{\partial \xi^{\beta,\gamma}}{\partial t} = J_i^{\beta,\gamma} - J_i^{\gamma,\beta} \qquad (3)$$

Thus, the equation at each interface can be integrated with respect to time, assuming constant. Ď's to yield four equations, two at the α/β boundary

$$\xi^{\alpha,\beta} = -\frac{2\left[-D^{\alpha}{}_{i1}\,K_1{}^{\alpha,\beta} - D^{\alpha}{}_{i2}\,K_2{}^{\alpha,\beta} + D_{i1}{}^{\beta}K_1{}^{\beta,\alpha} + D^{\beta}{}_{i2}\,K_2{}^{\beta,\alpha}\right]\sqrt{t}}{\left[C_i{}^{\alpha,\beta} - C_i{}^{\beta,\alpha}\right]} \qquad (4)$$

And two at the β/γ boundary,

$$\xi^{\beta,\gamma} = \frac{2\left[-D^{\beta}{}_{i1}\,K_1{}^{\beta,\gamma} - D^{\beta}{}_{i2}\,K_2{}^{\beta,\gamma} + D_{i1}{}^{\beta}K_1{}^{\beta,\alpha} + D^{\beta}{}_{i2}\,K_2{}^{\beta,\alpha}\right]\sqrt{t}}{\left[C_i{}^{\alpha,\beta} - C_i{}^{\beta,\alpha}\right]} \qquad (5)$$

A fifth equation is given by

$$w = \xi^{\alpha,\beta} - \xi^{\beta,\gamma} = W\sqrt{t} \qquad (6)$$

Where $\xi^{\alpha,\beta}$ and $\xi^{\beta,\gamma}$ are the interface positions, $Ď_{i1}$ is an interdiffusion coefficient, C_1 is an interface concentration, t is annealing time, w is the width of reaction layer, and W is the growth constant. $K_i^{\beta,\alpha}$ is a function of the interdiffusion coefficients, the concentration gradients, the concentration at the surface.

As discussed in section 2 and presented in Fig. 1, the growth of a three-phase ternary diffusion couple involved two interfaces. At each of these interfaces, there are two independent mass balance equations, yielding a total of independent equations. In addition, we have one more equation, i.e. Eq (1) for the growth of a particular phase β. However, for such a system we have a total 12 interdiffusion coefficient, Ď's (four Ď's for each of the three phases), and two interface positions, i.e. $\xi^{InAs,T}$ and $\xi^{T,Ni}$. In order to solve this problem, there is a need to reduce the total number of unknown parameters to be determined. In a Ni/InAs couple, phase A is nickel, phase B is the Ni3InAs reacted layer, and phase C is InAs. Due to the low solubility of Ni in InAs and the low solubility of In and As in nickel, diffusion in pure A and C may neglected. This reduces the number unknowns to six: $\xi^{\alpha,\beta}$, $\xi^{\beta,\gamma}$, $Ď_{11}$, $Ď_{12}$, $Ď_{21}$, $Ď_{22}$. The number of unknowns may be reduce to five using relations between intrinsic diffusion coefficient and interdiffusion coefficients developed by Darken [17] and alternative method proposed by Dayananda et. al. [18, 19] and Garimella et. al. {20]. Assuming the cross-term of the diffusion coefficients to be negligible, the thee intrinsic diffusion coefficients, i.e. D_1, D_2 ,D_3, are sufficient to describe the behavior of a ternary phase. Darken's relationship becomes :

$$Ď_{11} = D_1 + C_1 (D_3 - D_1) \qquad (7)$$

$$Ď_{12} = C_1 (D_3 - D_2) \qquad (8)$$

$$Ď_{21} = C_2 (D_3 - D_1) \qquad (9)$$

$$Ď_{22} = D_2 + C_2 (D_3 - D_2) \qquad (10)$$

Where C_1 and C_2 are concentration of components 1 and 2. In this experiment, C_1 and C_2 are assumed to be average concentration of components 1 and 2 in the Ni_3InAs reaction layer.

Table I
Intrinsik diffusion coefficients, $Ď_{Ni}$, $Ď_{In}$ and $Ď_{As}$

T (oC)	$Ď_{Ni}$ (cm^2/sec)	$Ď_{In}$ (cm^2/sec)	$Ď_{As}$ (cm^2/sec)
450	7.12×10^{-9}	1.37×10^{-9}	1.25×10^{-9}
500	1.07×10^{-8}	1.67×10^{-9}	1.59×10^{-9}
550	6.74×10^{-8}	5.71×10^{-9}	2.65×10^{-9}
600	2.11×10^{-7}	1.45×10^{-8}	5.95×10^{-9}
Q (kJ/mol)	117 ± 8	77 ± 8	47 ±

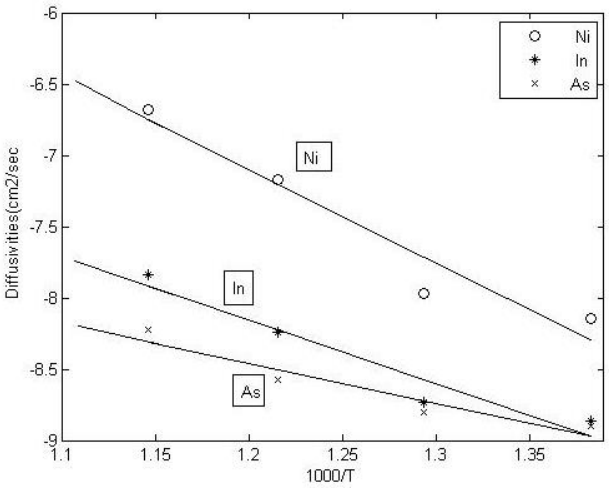

Fig. 5. Arrhenius plot of $Ď_{Ni}$, $Ď_{In}$ and $Ď_{As}$ with activation energies being 117, 77 and 47 kJ/mole respectively.

Although this methodology can be used to obtained numerical values for the interdiffusional cross-terms, it should be noted that this analysis was performed under the assumption of negligible cross-intrinsic diffusion coefficients, which is reasonable for phases with limited ranges of homogeneity. However, the phase T-Ni3InAs does possess

are appreciable for range of homogeneity, and therefore this assumption may be somewhat simplistic. Furthermore, it should be remembered that in performing these calculations, diffusive fluxes in the nickel and InAs phases were assumed to approach zero.

The result values for intrinsic diffusion coefficients and interdiffusion coefficients of T-Ni_3InAs are given in Table I and II and presented in Fig. 5 and 6, respectively. The results show that nickel is the fastest diffusing species, indium the next fastest and arsenic is the slowest.

Table II
Interdiffusion coefficients, , $Ď_{11}$, $Ď_{12}$, $Ď_{21}$, $Ď_{22}$ with 1 being Ni and 2 As
(Determine from intrinsic diffusion coefficients)

T (^{o}C)	$Ď_{11}$	$Ď_{12}$	$Ď_{21}$	$Ď_{22}$
450	3.58×10^{-9}	7.39×10^{-11}	-1.11×10^{-9}	1.27×10^{-9}
500	5.24×10^{-9}	1.74×10^{-10}	-1.70×10^{-9}	1.64×10^{-9}
550	2.92×10^{-8}	1.90×10^{-9}	-1.18×10^{-9}	2.58×10^{-9}
600	8.91×10^{-8}	5.31×10^{-9}	-3.74×10^{-8}	7.58×10^{-9}
Q(kJ/mol)	121 ± 10	151 ± 9	149 ± 9	90 ± 8

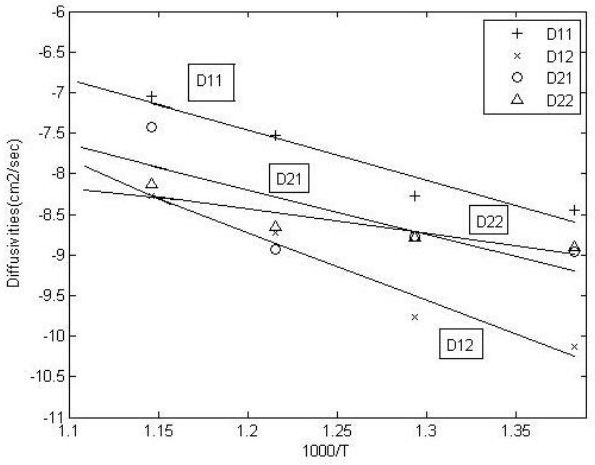

Fig. 6. Arrhenius plot of $Ď_{11}$, $Ď_{12}$, $Ď_{21}$, $Ď_{22}$ with 1 being Ni and 2 As (determined by using intrinsic diffusivities), the activation energies are 121, 151, 149 and 90 kJ/mol respectively.

5. Conclusion

It has been shown that the growth rates of intermediate phases and experimentally determined concentration profiles across the phases may be used to determine their interdiffusion coefficients, which may in turn be utilized to calculate the growth of phases in ternary diffusion couple as function of time at a given temperature. Furthermore, the analysis may be used to find intrinsic diffusion coefficients in each phase, which may be helpful in developing atomic interpretations of diffusion in this phases.

The analysis outlined above was applied the growth of T-Ni_3InAs in semi-infinite, Ni/InAs diffusion couple to determine diffusion coefficients. In performing the calculations, determination of the Interdiffusion coefficients for nickel and InAs was neglected and the cross-term diffusivities for T-Ni_3InAs ($Ď_{12}$ and $Ď_{21}$) were assumed to be vanishing small. By assuming cross-intrinsic diffusional terms to be negligible, relationship between interdiffusion coefficients and intrinsic coefficients were derived and the intrinsic diffusivities of nickel, indium and arsenic in T-Ni_3InAs were determined. The intrinsic coefficients were then substituted into these relationships, yielding values of interdiffusion coefficients and cross-interdiffusional terms. The intrinsic diffusivity of arsenic was found to be two orders of magnitude smaller than that of nickel at 600 ^{o}C.

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