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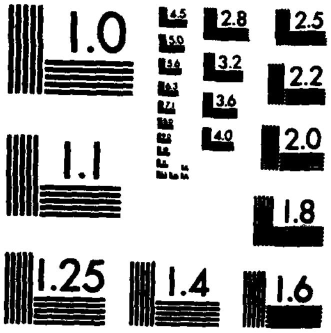

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February 1984

PREPARATION OF HIGH PURITY $Ga_xIn_{1-x}As$ BY THE VPE-HYDRIDE METHOD WITH A GALLIUM/INDIUM ALLOY SOURCE

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The preparation of epitaxial layers of the ternary, $Ga_xIn_{1-x}As$, by the VPE-Hydride technique using a Ga-In alloy source is described. The alloy composition necessary to produce $Ga_{0.47}In_{0.53}As$ was found to be 12.2 mole percent Ga-87.8 mole percent In at source, mixing, and deposition temperatures of 800, 850, and 700°C, respectively. Maximum growth rates of the order of 0.1 μm/min were observed when the source HCl had a flow rate of

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2.3 cc/min. The In content increases slightly with the number of runs using the same alloy. An increase in deposition temperature from 700 to 750°C exhibited no effect on the composition of the $Ga_xIn_{1-x}As$ layer. The electrical properties of the epitaxial layers obtained compare favorably with other growth methods, $n = 2.8 \times 10^{15}$ cm^{-3} (300K) and $\mu = 8852$ cm^2/V-sec (300K). The study illustrates that the use of an alloy in the VPE-Hydride technique using a single-barrel reactor is a viable method to grow epitaxial layers of $Ga_{0.47}In_{0.53}As$.

Preface

The authors gratefully acknowledge the help provided by Jane A. Horrigan in performing x-ray analyses of these samples. Van der Pauw measurements were performed by Joseph P. Lorenzo and Kenneth J. Soda. Single crystal InP substrates were grown and polished by Brian S. Ahern. The authors also wish to *acknowledge the help and advice obtained from William D. Potter and John* K. Kennedy through discussions with them. Finally, the authors wish to thank the team of A. K. Chatterjee, M. M. Faktor, M. H. Lyons, and R. H. Moss and the team of P. Kordos, P. Schumbera, M. Heyen, and P. Balk, both teams were kind enough to send us preprints of their work on growth of InGaAs from an alloy source.

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Preparation of High Purity $Ga_xIn_{1-x}As$ by the VPE-Hydride Method With a Gallium-Indium Alloy Source

I. INTRODUCTION

The ternary system, $Ga_{0.47}In_{0.53}As$, has found wide applications in the fields of optoelectronic and microwave devices. This wide applicability of $Ga_{0.47}In_{0.53}As$ is the result of its electrical characteristics and its having the same lattice constant as InP. Currently, extensive research[1, 2] is being conducted for the development of high quality GaInAs photodetectors for use in optical communications. These detectors are sensitive to the long wavelengths (1.0 to 1.7 µm), where silica fibers exhibit their lowest attenuation. The $Ga_{0.47}In_{0.53}As$ ternary also offers several advantages for use in high-microwave frequency FETs: high low-field electron mobility, high peak electron drift velocity, etc.[3] Superlattice structures of $Ga_{0.47}In_{0.53}As$/InP have recently been reported.[4, 5]

(Received for publication 9 February 1984)

1. Olsen, G.H. (1981) IEEE Device Letters EDL-2:217.
2. Ando, H., Yamauchi, Y., Nakagome, H., Susa, N., and Kanbe, H. (1981) IEEE J. Quantum Electron. QE-17:250.
3. Narayan, S.Y., Paczkowski, T.P., Jolly, S.T., Bertin, E.P., and Martin, R.T. (1981) RCA Rev. 42:491.
4. Razeghi, M., Poisson, M.A., Larivain, J.P., de Cremoux, B., and Duchemin, J.P. (1982) Electron. Lett. 18:339.
5. Usui, A., Matsumoto, Y., Inoshita, T., Mizutani, T., and Watanabe, H. (1981) in Proc. Int. Symp. GaAs and Related Compounds, T. Sugano, Ed., The Institute of Physics (Bristol), Japan, No. 63, p. 137.

The epitaxial layers of $Ga_{0.47}In_{0.53}As$ can be grown by the following four techniques: liquid phase epitaxy (LPE),[6] vapor phase epitaxy (VPE),[7] molecular beam epitaxy (MBE),[8] and metal-organic chemical vapor deposition (MOCVD).[9] All these methods have produced $Ga_xIn_{1-x}As$ layers that possess room temperature mobilities in the 10,000 cm^2 V-sec range, with a high of 13,800 cm^2 V-sec for LPE.[3,8,10,11] The VPE technique can either use $AsCl_3$ (chloride method) or AsH_3 (hydride method) as the source for As. Higher mobilities have usually been achieved with the chloride method,[12,13] but the hydride method has many operating advantages that the chloride method lacks, for example, ease of control, group V reactants are gaseous, etc. Olsen and Zamerowski[14] have published an excellent review paper on the VPE-Hydride method. In previous work on the VPE-Hydride preparation of $Ga_{0.47}In_{0.53}As$, the metallic sources of Ga and In were contained in different barrels of a double-barrel reactor. This paper is a study of the preparation of $Ga_xIn_{1-x}As$ ternaries by the VPE-Hydride technique using an alloy of Ga and In as the metallic source.

The use of a single metallic source in the preparation of $Ga_xIn_{1-x}As$ has two distinct advantages over the preparation using two separate metal sources: (1) the flow of hydrogen chloride over the source that converts Ga and In to their respective chlorides does not have to be as finely controlled as is necessary with separate metallic sources and (2) only a single-barrel reactor is necessary for the growth of ternaries. This second advantage obviously reduces the cost of the operation.

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[6] Chand, N., Syrbu, A.V., and Houston, P.A. (1982) Electron. Lett. 18:613.

[7] Susa, N., Yamauchi, Y., Ando, H., and Kanbe, H. (1979) Japan J. Appl. Phys. 19:L17.

[8] Cheng, K.Y., and Cho, A.Y. (1982) J. Appl. Phys. 53:4411.

[9] Whiteley, J.S., and Ghandhi, S.K. (1982) J. Electrochem. Soc. 129:383.

[10] Oliver, J.D., and Eastman, L.F. (1980) J. Electron. Mat. 9:693.

[11] Razeghi, M., Poisson, M.A., Hirtz, P., de Cremoux, B., and Duchemin, J.P. (1982) Technical Abstracts, Electronic Materials Conference, paper I-2, p. 49, Colorado State University, Fort Collins, Colo., 23-25 June.

[12] Erstfeld, T.E., and Quinlan, K.P. (1982) J. Electron. Mat. 11:647.

[13] Fairhurst, K., Lee, D., Robertson, D.S., Parfitt, H.T., and Wilgross, W.H.E. (1980) A study of the vapor phase epitaxy of indium phosphide, Proc. 1980 NATO Sponsored InP Workshop, June, RADC-TM-80-07, Rome Air Development Center, Hanscom AFB, MA 01731.

[14] Olsen, G.H., and Zamerowski, T.J. (1980) Crystal growth and properties of binary, ternary and quaternary (In, Ga)(As, P) alloys grown by the hydride vapor phase epitaxy technique, Progress in Crystal Growth and Characterization, B. R. Pamplin, Ed., Vol. II, Pergamon Press Ltd., London, pp. 309-375.

The use of an alloy source for the preparation of $Ga_xIn_{1-x}As$ by the VPE technique has been studied by a number of investigators. In 1965, Minden[15] used an alloy source of Ga and In in a modified VPE- Chloride method to prepare epitaxial layers of $Ga_xIn_{1-x}As$. Recently, Chatterjee, Faktor, Lyons, and Moss[16] studied the use of the alloy with the VPE-Chloride technique and presented a thermodynamic model describing the system. They demonstrated that a low-doped, lattice-matched Ga/In arsenide epilayer could be obtained in a reproducible and controlled manner. Kordos, Schumbera, Heyen, and Balk[17] studied the growth of $Ga_xIn_{1-x}As$ with the VPE-Hydride system using a Ga-In alloy. Their results with a two temperature-zoned reactor differ from those reported in this paper for a three temperature-zoned reactor.

A simple thermodynamic model is derived in the present paper. Theoretical values for the alloy compositions (Ga-In) evaluated as a function of the compositions of the epitaxial layers show that the model is consistent with the experimental data. Deviations between the calculated and experimental values reflect the importance of kinetic factors in these deposition reactions.

2. EXPERIMENTAL SECTION

The preparation of the epitaxial layers of the ternaries, $Ga_xIn_{1-x}As$, was studied in the quartz reactor as shown in Figure 1. The quartz reactor has three temperature zones: source, mixing, and deposition, which are heated by "clamshell" resistance heaters. The reactor has three inlet flow systems for AsH_3/H_2, HCl/H_2, and H_2. The flow rates are regulated by Tylan mass flow controllers. The reactant gases are the highest purity products obtainable. Arsine (99.998%) was supplied as a 10 percent mixture in hydrogen (99.999%) from Ideal Gas Products, Edison, N.J. The hydrogen carrier gas, supplied by American Industrial and Medical Products, Auburn, Mass., was 99.999 percent pure. The hydrogen was purified further by a hydrogen purifier (Palladium Diffusion Process-Engelhard). Hydrogen chloride from Precision Gas Products, Inc., Rahway, N.J., was 99.995 percent. Indium (99.9999 percent) was obtained from Metal Specialties, Inc., Fairfield, Conn. Gallium was 99.9999 percent pure and a product of Alusuisse Metals, Inc., Fairlawn, N.J. The alloys were prepared by putting the appropriate

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15. Minden, H.T. (1965) J. Electrochem. Soc. 112:300.

16. Chatterjee, A.K., Faktor, M.M., Lyons, M.H., and Moss, R.H. (1982) J. Cryst. Growth 56:591.

17. Kordos, P., Schumbera, P., Heyen, M., and Balk, P. (1981) in Proc. Int. GaAs and Related Compounds, T. Sugano, Ed., The Institute of Physics (Bristol), Japan, No. 63, p. 131.

amounts of the metals into a quartz boat. The masses of the alloys used varied between 99 and 107 g. The surface areas of the alloy in the quartz boats were approximately 26 cm^2. The alloys were prebaked for 50 hr in a hydrogen atmosphere before any runs were performed. This procedure as reported by Kordos et al[17] lowers the carrier concentrations in the resulting epitaxial layers.

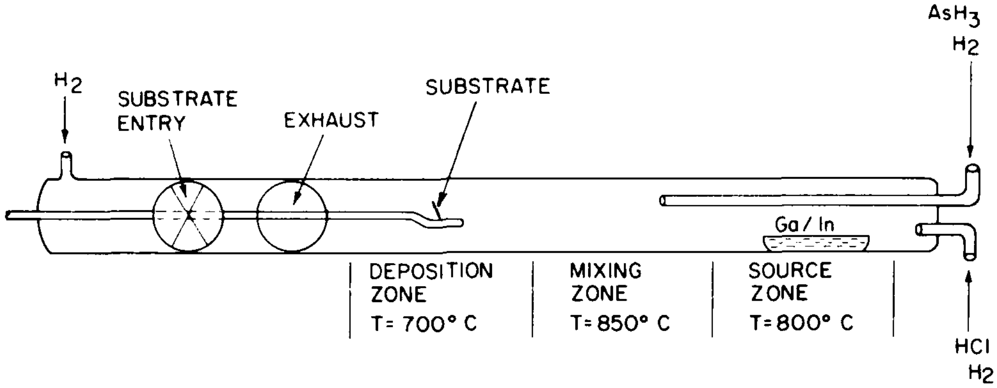

Figure 1. Quartz Reactor for the Preparation of Epitaxial Layers of $Ga_xIn_{1-x}As$

The formations of the epitaxial layers were studied at various alloy compositions, HCl flow rates, and source, mixing, and deposition temperatures. The alloy composition ranged from 3.2 mole percent Ga-96.8 mole percent In to 15.6 mole percent Ga-84.4 mole percent In. The source temperature was varied from 697 to 800°C, while the mixing and deposition temperatures varied from 697 to 850°C and 587 to 750°C, respectively. The HCl flow rate ranged from 1.5 to 6.0 cc/min. The flow rate of arsine was constant in all the experiments at a value of 10 cc/min. The hydrogen carrier gas flow rates were 445 cc/min at both the arsine and HCl inlets; another 90 cc/min of H_2 entered the reactor as part of the arsine mixture. The growth rates were determined from the surface area of the substrate, mass of deposit, density of the ternary, and time duration of growth; the value obtained was halved, for essentially equal amounts of the ternary grew on both sides of the substrate. The time of growth was usually 225 min.

The substrates were prepared from a liquid encapsulated Czochralski (LEC)-grown InP (Fe-doped) Boule. The treatment of the InP substrate before growth is described in Reference 12.

The compositions of the grown ternaries of $Ga_xIn_{1-x}As$ were determined from Vegard's law in which lattice constant is plotted as a function of the composition. Microprobe analyses verified this method of determining the composition. The lattice constants were determined by x-ray diffractometry with CuKα irradiation using InP as an internal standard. Diffraction peak profiles indicated that the layers were of good and uniform composition.

Carrier concentrations (n) and mobilities (μ) were obtained from resistivity and Hall measurements at room temperature by the van der Pauw technique.[18] A permanent magnet provided a field of 3 kG for the Hall measurements.

The residual compositions of the Ga-In alloys were determined by atomis absorption spectroscopy. The alloys for these analyses were remelted and quenched at $0^{o}C$ to prevent formation of Ga-In solid solutions. During the course of a series of runs, the alloy becomes richer in In content.

3. THERMODYNAMIC ANALYSIS

A simple thermodynamic model is derived to determine the mole fraction of Ga and In in the alloy that is necessary to produce a defined composition of $Ga_xIn_{1-x}As$. A simplified model can be helpful in the initial phase of a study to enable one to predict the alloy composition that will give a specified ternary of $Ga_xIn_{1-x}As$. The model can also clarify as to whether thermodynamic or kinetic factors are responsible for the deviations of the experimental results from the calculated equilibrium values.

This ternary system is produced according to the two following equations:

$$GaCl(g) + 1/4\ As_4(g) + 1/2\ H_2(g) \rightarrow GaAs(s) + HCl(g) \qquad (1)$$

$$InCl(g) + 1/4\ As_4(g) + 1/2\ H_2(g) \rightarrow InAs(s) + HCl(g) \quad . \qquad (2)$$

The equilibrium constants for these equations are the following:

$$K_{GaAs} = \frac{\gamma_{GaAs}\ N_{GaAs} p_{HCl}}{P_{GaCl}\ P_{A_4}^{1/4}\ P_{H_2}^{1/2}} \qquad (3)$$

$$K_{InAs} = \frac{\gamma_{InAs}\ N_{InAs}\ p_{HCl}}{P_{InCl}\ P_{As_4}^{1/4}\ P_{H_2}^{1/2}} \quad , \qquad (4)$$

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[18] van der Pauw, L.J. (1958) Philips Res. Repts. 13:1.

where γ and N are the activity coefficient and mole fraction, respectively, of the binary arsenides, and p is the partial pressure of the gaseous species. The As_4 species is assumed to be the only species of arsenic to react with the group III-chlorides. Minagawa et al[19] showed in their thermodynamic calculations that As_4 is the major species of arsenic present, with minor amounts of arsenic present as As_2 and unreacted AsH_3. The ratio of the pressures of GaCl to InCl determines the composition of the $Ga_xIn_{1-x}As$ epilayer. This ratio can be evaluated from Eqs. (3) and (4) as shown in the following relationship:

$$\frac{p_{GaCl}}{p_{InCl}} = \frac{\gamma_{GaAs} N_{GaAs} K_{InAs}}{\gamma_{InAs}(1 - N_{GaAs}) K_{GaAs}} , \qquad (5)$$

where $1 - N_{GaAs}$ is the mole fraction of InAs in $Ga_xIn_{1-x}As$. The values of K_{GaAs} and K_{InAs} were calculated from the thermodynamic values reported by Kirwan[20] and Minagawa, Seki, and Eguchi,[19] respectively. The ratio of K_{InAs}/K_{GaAs} was calculated to be 0.135 at 700°C. The activity coefficients are obtained from the following equations are presented by Panish and Ilegems.[21] The interaction

$$\ln \gamma_{GaAs} = \frac{\Omega}{RT} (1 - N_{GaAs})^2 \qquad (6)$$

$$\ln \gamma_{InAs} = \frac{\Omega}{RT} N_{GaAs}^2 \qquad (7)$$

parameter, Ω has a value of 3000 cal $mole^{-1}$ for $Ga_xIn_{1-x}As$.

The value calculated for the pressure ratio of the monochlorides of Ga and In, P_{GaCl}/P_{InCl}, for a specified $Ga_xIn_{1-x}As$ composition can be substituted into the equation describing the reaction of HCl with the alloy to give the proper alloy composition necessary to produce a desired ternary. Hydrogen chloride reacts with Ga and In according to the following equations:

$$Ga(l) + HCl(g) \rightarrow GaCl(g) + 1/2\ H_2(g) \qquad (8)$$

$$In(l) + HCl(g) \rightarrow InCl(g) + 1/2\ H_2(g) \quad . \qquad (9)$$

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[19] Minagawa, S., Seki, H., and Eguchi, H. (1972) Japan J. Appl. Phys. 11:855.

[20] Kirwan, D.J. (1970) J. Electrochem. Soc. 117:1572.

[21] Panish, M.B., and Ilegems, M. (1972) Progress in Solid State Chemistry, Vol. 7, Pergamon Press, New York, pp. 39-83.

The higher order chlorides of the metals have not been taken into consideration since they have been shown to be present in only minor amounts.[22] The equilibrium constants for these equations are as follows:

$$K_{GaCl} = \frac{p_{GaCl}\, p_{H_2}^{1/2}}{\gamma_{Ga}\, N_{Ga}\, p_{HCl}} \tag{10}$$

$$K_{InCl} = \frac{p_{InCl}\, p_{H_2}^{1/2}}{\gamma_{In}\, N_{In}\, p_{HCl}} \quad , \tag{11}$$

where γ, N, and P have their usual meanings. Solving for P_{GaCl}/P_{InCl} gives the following expression:

$$\frac{p_{GaCl}}{p_{InCl}} = \frac{K_{GaCl}\, \gamma_{Ga}\, N_{Ga}}{K_{InCl}\, \gamma_{In} (1 - N_{Ga})} \quad . \tag{12}$$

The value of K_{GaCl}/K_{InCl} is approximately 1.3 at 800°C as reported by Chatterjee et al.[16] The activity coefficient ratio is calculated from the relationshp by Panish and Ilegems,[21] where the interaction parameter is 1066 cal mole^{-1}. A value of 1.5 was used for the ratio, γ_{Ga}/γ_{In}. The $N_{Ga}/1 - N_{Ga}$ is the ratio of the mole fractions of Ga to In in the alloy that will give a definite composition of $Ga_xIn_{1-x}As$. Values of P_{GaCl}/P_{InCl} corresponding to definite compositions of $Ga_xIn_{1-x}As$ as related in Eq. (5) were used to calculate a series of values of N_{Ga} and $1 - N_{Ga}$ in Eq. (12). The theoretical values of the mole fraction of Ga in the ternary vs the mole fraction of Ga in the alloy are depicted in Figure 2. The difference observed between the calculated values and the experimental depicts the non-ideality of the system. This non-ideality, which will be discussed later, is possibly related to kinetic factors.

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[22] Ban, V.S. (1972) J. Cryst. Growth 17:19.

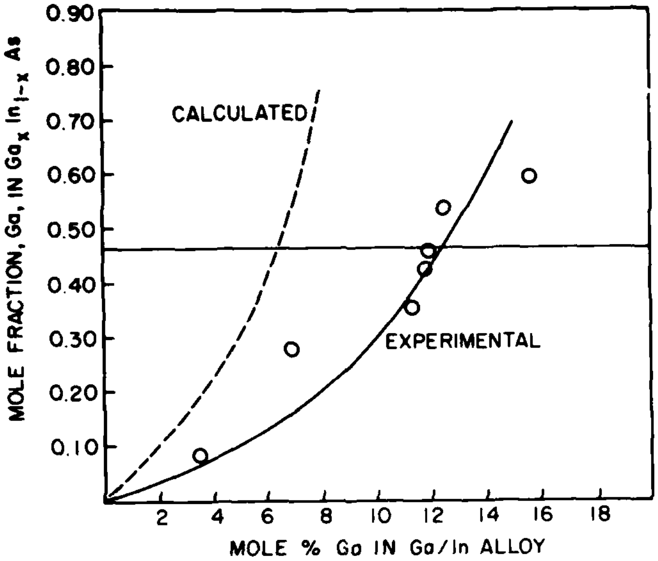

Figure 2. Compositions of the Ternaries, $Ga_xIn_{1-x}As$, Prepared From Various Alloy (Ga-In) Mixtures. --- (Theory) and o—o (Experimental). AsH_3 = 10 cc/min, HCl = 2.3 cc/min, and H_2 = 980 cc/min. Substrate temp = 700°C, mixing temp = 850°C, and source temp = 800°C

4. RESULTS

Various parameters were studied initially to determine that parameter values produce epitaxial layers of high quality with consistent growth rates. Superior quality epitaxial layers of the ternary, $Ga_xIn_{1-x}As$, were obtained when the source, mixing, and deposition temperatures were 800, 850, and 700°C, respectively. The flow rates of HCl in these preliminary experiments were in the vicinity of 2.3 cc/min. The flow rate of AsH_3 was 10 cc/min while that of the hydrogen carrier gas was 980 cc/min. The flow rates of AsH_3 and H_2 were maintained at these values throughout the study. The x-ray diffractometry studies used for the determination of the lattice constants showed that the layers were normally of good quality and uniform composition. After these preliminary results were obtained, the determination of the alloy composition required to give a specific ternary composition of $Ga_xIn_{1-x}As$ was undertaken. Growth rates of the ternary systems were determined as functions of HCl flow rate and deposition temperature. Activation energies of the formation of the epitaxial layers were obtained from Arrhenius plots of growth rates vs reciprocal of the deposition temperatures.

Figure 2 shows the composition of the ternary, $Ga_xIn_{1-x}As$, obtained as a function of the alloy composition used. The values exhibited are for a deposition temperature of 700°C and a HCl flow rate of 2.3 cc/min. The plot of the experimental data intersecting the $Ga_{0.47}In_{0.53}As$ composition line gives a value of 12.2 mole percent Ga-87.8 mole percent In as the alloy necessary to prepare $Ga_{0.47}In_{0.53}As$. Epitaxial layers with a value of $|\Delta a/a| < 10^{-3}$ are considered to be lattice-matched[10] to InP. These values of $\Delta a/a$ correspond to $Ga_xIn_{1-x}As$ layers that range in composition from $Ga_{0.49}In_{0.51}As$ to $Ga_{0.45}In_{0.55}As$. Inspection of Figure 2 indicates that alloy compositions with a Ga content between 11.9 and 12.9 mole percent are capable of producing $Ga_xIn_{1-x}As$ epitaxial layers that are lattice-matched to InP. A series of runs with an alloy composition of 11.9 mole percent Ga produced epitaxial films that were lattice-matched to InP one-third of the time. Kordos et al.[17] reported that 7 mole percent Ga in the alloy produced the $Ga_{0.47}In_{0.53}As$ ternary. This large discrepancy between 7 mole percent to that found in the present work (12.2 mole percent Ga) may possibly be due to the difference between their two temperature-zoned reactor and our three-zoned reactor.

The compositions of the ternary were studied as a function of the number of runs performed with an alloy. The plots obtained are shown in Figure 3 and are typical of the ternary compositions found for various alloy compositions. Figure 3 shows the ternary compositions obtained from two initial alloy compositions: 11.5 mole percent Ga and 11.9 mole percent Ga. The data show that the average composition of the ternaries exhibits a slight increase in In content as more runs are performed. An increase in the In content of the ternary was expected since an analysis of an alloy after 30 hr of reaction time showed that the mole fraction of In had increased by 4 percent. This is in agreement with the extrapolated value of 2 percent from data of Chatterjee et al.[16] Figure 3 shows an important aspect of this type of work, in which a certain amount of scatter is observed in the composition of the epitaxial layers from one run to the next. This scatter may be attributed to the free radical nature of these reactions. Various workers[23] have shown that changes in the surfaces of a reactor greatly influence the course of free radical reactions. The surfaces of the reactors used for epitaxial growth undergo constant change when the different parameters of the systems are varied. This scatter may account for the lack of observation of the increase in In content for the ternaries obtained in the series of 25 runs reported by Kordos et al.[17]

The growth rates of the ternary, $Ga_xIn_{1-x}As$, were determined as functions of the source HCl flow rate and deposition temperature. Hydrogen chloride reacts with the Ga and In in the alloy to form GaCl(g) and InCl(g) [see Eqs. (8) and (9)].

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23. Trotman-Dickenson, A.F. (1955) Gas Kinetics, Academic Press, New York, p. 152.

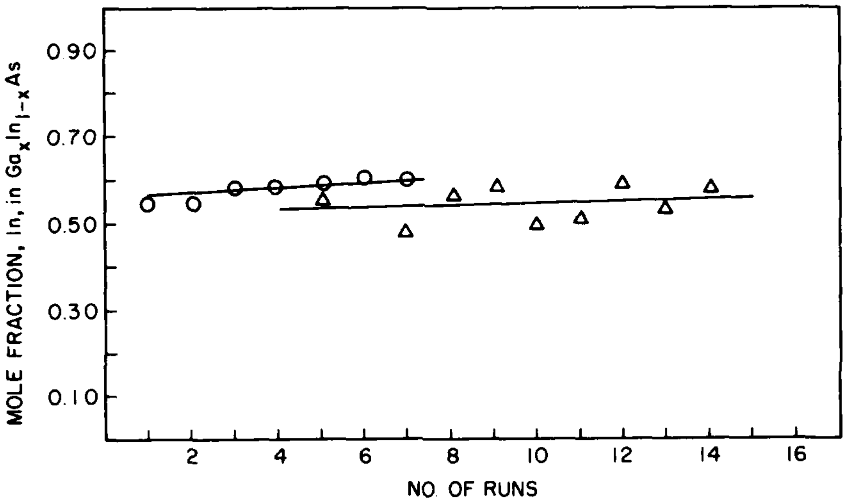

Figure 3. Mole Fraction of Indium in $Ga_xIn_{1-x}As$ as a Function of the Number of Runs. o——o, Alloy composition = 11.5 mole percent Ga and 88.5 mole percent In. △——△ Alloy composition = 11.9 mole percent Ga and 88.1 mole percent In. AsH_3 = 10 cc/min, HCl = 2.3 cc/min, and H_2 = 980 cc/min. Substrate temp = 700°C, mixing temp = 850°C, and source temp = 800°C

The metal chlorides react with the As_4 at the InP-substrate surface in the deposition zone to form the $Ga_xIn_{1-x}As$. The growth rates for the epitaxial layers grown from an alloy composition of 11.9 mole percent Ga-88.1 mole percent In are shown in Figure 4. These results were obtained at a source temperature of 800°C, a mixing temperature of 850°C, and deposition temperatures of 700 and 725°C.

The maximum growth rates for the ternary were obtained when the HCl flow rate was approximately 2.3 cc/min. The curves shown in Figure 4 are typical of the data obtained for all the systems studied in the present investigation where the maximum growth rates occurred in the vicinity of a HCl flow rate of 2.3 cc/min. The maximum growth rates for the various alloy compositions investigated are presented in Table 1. The growth rate of the ternary at 700°C increases with increasing In concentration in the alloy. Indium arsenide[24] has been shown to have a higher growth rate than GaAs[25] in their homoepitaxial growth by the VPE-Chloride technique. Growth rates as low as 0.015 μm/min were obtained at

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[24] Mizuno, O., Watanabe, H., and Shinoda, D. (1975) Japan J. Appl. Phys. 14:184.

[25] Makagawa, M., and Ikoma, H. (1971) Japan J. Appl. Phys. 10:1345.

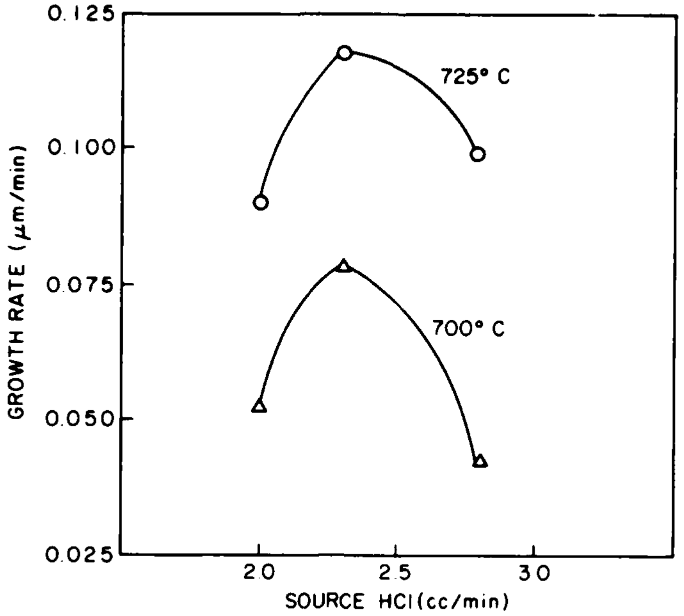

Figure 4. Growth Rate of Epitaxial Layers of $Ga_xIn_{1-x}As$ as a Function of Source HCl Flow Rate. o — o, Deposition temp = 725°C. Δ — Δ, deposition temp = 700°C. Alloy composition = 11.9 mole percent Ga and 88.1 mole percent In. AsH_3 = 10 cc/min and H_2 = 980 cc/min. Source temp = 800°C and mixing temp = 850°C

deposition temperatures of 600°C with an alloy source of 3.2 mole percent Ga-96.8 mole percent In. The source and mixing temperatures were 800 and 850°C, respectively. The composition of the epitaxial layer obtained at this parameters was $Ga_{0.15}In_{0.85}As$.

The average energy of activation for the data presented in Table 1 is 163 kJ/mole. A value of 176 kJ/mole was found for the energy of activation for $Ga_{0.53}In_{0.47}As$ prepared from a 12.3 mole percent Ga alloy. This value is in close agreement with the value of 44 kcal/mole (184 kJ/mole) reported by Hyder et al.[26] These authors used the VPE-Hydride technique with separate metal sources.

The data showed that varying the flow rates of the source HCl had no effect on the composition of the epitaxial layer that is formed. This would be expected

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[26] Hyder, S.B., Saxena, R.R., Chiao, S.H., and Yeats, R. (1979) Appl. Phys. Lett. 35:787.

since the ratio of GaCl(g) to InCl(g) would be independent of HCl flow rates. No definite trend could be found in our work for the effect of deposition temperature on the composition of the epitaxial layer. Experiments were even carried out at 750°C (a mass transport-limited region) with no effect. This was not surprising since the temperature coefficient of the compositional ratio as shown in Eq. (5) is small.[16] Kordos et al,[17] reported a 0.2 percent increase in the Ga content of the ternary per degree increase in temperature.

Table 1. Growth Rates of $Ga_xIn_{1-x}As$ Formed From Various Alloy Compositions at Two Deposition Temperatures. HCl flow rate = 2.3 cc/min, AsH_3 flow rate = 10 cc/min, and H_2 flow rate = 980 cc/min. Source temp = 800°C, mixing temp = 850°C, and deposition temp = 700 and 725°C

Alloy Composition (mole % Ga)	$Ga_xIn_{1-x}As$	Growth Rate at 700°C (μm/min)	Growth Rate at 725°C (μm/min)
15.6	$Ga_{0.58}In_{0.42}As$	0.082	0.133
12.3	$Ga_{0.53}In_{0.47}As$	0.082	0.139
11.9	$Ga_{0.46}In_{0.54}As$	0.078	0.119
11.5	$Ga_{0.43}In_{0.57}As$	0.076	0.108
11.1	$Ga_{0.37}In_{0.63}As$	0.053	0.105
7.0	$Ga_{0.29}In_{0.71}As$	0.109	---
3.2	$Ga_{0.08}In_{0.92}As$	0.188	---

The carrier concentrations (n) and mobilities (μ) were determined for a series of samples and are presented in Table 2. The results represent the average of a number of determinations for many of the ternaries. The carrier concentrations all fall in the vicinity of 4.0×10^{15} cm^{-3} while the mobilities range from 3064 to 7204 cm^2/V-sec. A plot of the mobility vs layer composition, with the exception of the $Ga_{0.44}In_{0.56}As$ result, indicates a smooth curve with a maximum occurring in the region of $Ga_{0.42}In_{0.58}As$ as reported by Kordos et al,[17] and Whitely and Ghandhi.[27] Whitely and Ghandhi[27] observed their highest mobilities with the layer composition of $Ga_{0.42}In_{0.58}As$. This is similar to our work, where the highest mobilities were obtained with the composition of $Ga_{0.41}In_{0.59}As$. These high

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[27] Whiteley, J.S., and Ghandhi, S.K. (1983) J. Electrochem. Soc. 130:1191.

Table 2. Carrier Concentrations (n) and Mobilities (μ) of Various Ternaries at Room Temperature

Ternary	n (cm^{-3})	μ (cm^2/V-sec)
$Ga_{0.56}In_{0.44}As$	2.6×10^{15}	3982
$Ga_{0.52}In_{0.48}As$	4.4×10^{15}	4164
$Ga_{0.51}In_{0.49}As$	2.0×10^{15}	6601
$Ga_{0.45}In_{0.55}As$	2.4×10^{15}	5947
$Ga_{0.44}In_{0.56}As$	5.6×10^{15}	3064
$Ga_{0.41}In_{0.59}As$	3.4×10^{15}	7204
$Ga_{0.40}In_{0.60}As$	5.8×10^{15}	4991
$Ga_{0.39}In_{0.61}As$	8.4×10^{15}	3722

mobilities in the In > 0.53 range have been attributed to less dislocation formation in layers under compressive stress.[28] The best values obtained in the present study for n and μ at room temperature were 2.8×10^{15} cm^{-3} and 8852 cm^2/V-sec, respectively, for a sample whose composition was $Ga_{0.41}In_{0.59}As$. These values compare favorably to the results previously reported: Kordos et al,[17] reported a value of 4000 cm^2/V-sec for the mobility for the same ternary composition. Towe[29, 30] obtained a value of 9400 cm^2/V-sec for the mobility with a carrier concentration of 6.4×10^{15} cm^{-3} at room temperature for the composition $Ga_{0.47}In_{0.53}As$. Towe prepared the ternary with the VPE-Hydride technique using two metal sources. Cheng and Cho[8] prepared $Ga_{0.47}In_{0.53}As$ (Si-doped) by the MBE method and reported values of μ = 8500 cm^2/V-sec and n = 1×10^{16} cm^{-3} at room temperature. A high value of 13,800 cm^2/V-sec for the mobility (with n = 1.9×10^{15} cm^{-3}) at room temperature has been reported by Oliver and Eastman[10] for LPE prepared $Ga_xIn_{1-x}As$. The MOCVD technique for the growth of $Ga_{0.47}In_{0.53}As$ used by Whiteley and Ghandhi[27] gave values of 5800 cm^2/V-sec and mid 10^{16} cm^{-3} for μ and n at room temperature, respectively. Comparison

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[28] Miller, B.I., and McFee, J.H. (1978) J. Electrochem. Soc. 125:1310.

[29] Towe, E. (1982) J. Appl. Phys. 53:5136.

[30] Towe, E. (1981) M.S. Thesis, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Mass.

of the present results with those previously reported shows that the system using the alloy source is well suited to grow high quality $Ga_xIn_{1-x}As$ epitaxial layers.

5. DISCUSSION

The present study shows that the use of an alloy source in the VPE-Hydride method is a viable technique for the epitaxial growth of the ternary, $Ga_xIn_{1-x}As$. This technique has the added advantages of (1) the HCl flow rate does not have to be as finely controlled as in the case with two metal sources, and (2) the use of a single-barrel reactor which is simpler than a double-barrel reactor. The x-ray diffraction and microscopic studies showed that the $Ga_xIn_{1-x}As$ epilayers were of high quality and uniform composition. At least 14 samples can be grown from the same alloy source. The carrier concentrations and mobilities of the samples obtained were in the same range as the best samples prepared by the other techniques, with the exception of those grown by LPE. With continued research, the present method could possibly achieve results comparable to the LPE technique.

The study of the growth rates of $Ga_xIn_{1-x}As$ as a function of source HCl flow rate showed that maximum rates are obtained when the HCl flow rate is in the vicinity of 2.3 cc/min (see Figure 4). The decrease in growth rate below 2.3 cc/min is probably due to the corresponding decrease in concentration of the monochlorides of the group-III metals being formed, and thus able to react at the surface of the substrate. The decrease in the growth rate beyond 2.3 cc/min is probably due to the predominance of unreacted HCl etching both the substrate and the growing ternary layer. The growth rate increased with temperature (700 to 725°C) indicating that growth was occurring in the kinetic limited region. At 750°C, the growth rate slightly decreased characteristic of the mass-transport limited region.

Comparison of the calculated curve (Figure 2), derived from the simplified model, with the experimental results shows a surprisingly close similarity between the two. The sameness of the shape of the two curves implies that the parameters discussed in the simplified model are those which are operating in the deposition of $Ga_xIn_{1-x}As$. The displacement of the experimental curve to the right of the theoretical curve can be shown to result from kinetic factors. The equilibrium constants in Eq. (12), K_{GaCl} and K_{InCl}, are proportional to the forward and reverse rate constants ratio, k_f/k_r, for Eqs. (8) and (9), respectively. When the k_f's for GaCl and InCl formation are decreased by 18 percent and increased by 18 percent, respectively, and the corresponding k_r's are respectively increased and decreased by the same factor, the theoretical curve in Figure 2 becomes coincident with the experimental curve. The 0.18 factor is not an unreasonable deviation of the rate constants for these heterogeneous reactions. This close agreement when these kinetic factors are taken into consideration emphasizes their importance in the modeling of these processes. Although the analyses mixes thermodynamic and kinetic terms, we feel our argument is valid since we are merely describing trends. These simulated changes could as well be applied to the K_{InAs}/K_{GaAs} ratio in Eq. (5). The differences between theory and experiment may not only be due to kinetic factors but may also be due to errors in the literature used in the calculation of thermodynamic values. Faktor and Haigh[31] have shown that errors in the literature can result in derived thermodynamic values that are inaccurate.

Analyses of the different procedures to grow epitaxial layers of the III-V compounds have shown that the roles of VPE and MBE are expected to increase greatly[32] in the future. The present study shows that the VPE-Hydride technique can be simplified by the use of an alloy source. This simplification is accomplished with no loss in the quality of the epitaxial layer. Optoelectronic devices fabricated from these layers are currently under investigation at this laboratory and will be reported at a later date.

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