MATERIALS AND DETECTORS BASED ON GaInAs GROWN BY HYDRIDE VPE TECHNIQUE UTILIZING A Ga/In ALLOY SOURCE

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ABSTRACT

$Ga_xIn_{1-x}As$ epitaxial layers were grown by a simplified hydride vapor phase epitaxy(VPE) method based on the utilization of Ga/In alloy as the source metal. The effects of a wide range of experimental variables (i.e., inlet mole fraction of HCl, deposition temperature, Ga/In alloy composition) on the ternary composition and growth rate were investigated. Layers of $Ga_{0.47}In_{0.53}As$ lattice matched to InP were successfully grown from alloys containing 5 to 8 at.% Ga. These layers were used to produce state-of-the-art *p-i-n* photodetectors having the following characteristics : dark current, $I_d(-5V)$ = 10-20 nA; responsivity, R = 0.84-0.86 A/W; capacitance, C = 0.88-0.92 pF; breakdown voltage, V_b > 40 V. This study demonstrated for the first time that a simplified hydride VPE process with a Ga/In alloy source is capable of producing device quality epitaxial layers.

INTRODUCTION

$Ga_xIn_{1-x}As$ epitaxial layers have been widely used for optoelectronic and microwave devices. These epitaxial layers have been grown by a variety of techniques including hydride VPE (Vapor Phase Epitaxy). For many applications, the control of composition of ternary $Ga_{0.47}In_{0.53}As$ alloys is very important, because optimally performing devices require epitaxial layers lattice matched to InP substrate as closely as possible.

Recently VPE growth of $Ga_xIn_{1-x}As$ ternary alloys using a Ga/In alloy as the metal source has been studied by several workers [1,2,3]. This approach eliminates the need for the separate control of HCl or $AsCl_3$ flows over source materials and further insures excellent mixing of source zone reaction product, thus providing better uniformity of the composition of deposited epitaxial layers and better reproducibility of the process. Thermodynamic analyses and experimental investigations [2,4,5] indicate that the most critical parameter for determining the epitaxial layer composition is the composition of the Ga/In alloy. Reported

experimental values of the source alloy composition required to produce lattice matched $Ga_{0.47}In_{0.53}As$ epitaxial layers, however, show some discrepancies [4,5,6].

This study reports the influence of alloy source composition and other parameters (e.g., inlet mole fraction of HCl, deposition temperature) on the film composition and growth rate. An interesting observation by Quinlan and Erstfeld [3] is the growth of a limiting $Ga_{0.87}In_{0.13}As$ film composititon by the addition of excess HCl downstream of the source zone. Similar experiments are reported for two different source alloy composition and the results are reported. Finally, state-of-the-art *p-i-n* photodetectors were fabricated in order to demonstrate that an alloy source is capable of producing device quality epitaxial films.

EXPERIMENTAL

The hydride VPE reactor used in this study was the double-barrel reactor design and described else where [7,8]. Instead of using separate Ga and In source boats, a single alloy boat containing Ga and In was inserted into one of the In source barrels. Alloy compositions of 5.35, 8.69 and 15.10 at.% Ga were studied. Excess HCl could be introduced into the mixing zone via a dopont line.

Volatile metal chlorides were generated and transported by a stream of HCl (100%) in H_2 carrier gas. AsH_3 or PH_3 (which was used to stabilize the InP surface prior to deposition and to grow InP cap and buffer layers) was introduced as 10% mixture of AsH_3 or PH_3 in H_2. Substrates grown by LEC method were S or Fe doped InP, cut 2° off the (100) toward the nearest (110).

The layer thickness was measured by optical microscopy on cleaved and stained samples. The composition of $Ga_xIn_{1-x}As$ epitaxial layers was determined from Vegard's law using lattice constants measured with a Siemens single-crystal X-ray diffractometer. The initial and final compositions of the Ga/In source alloy were determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Parametric Studies

The growth rate of $Ga_xIn_{1-x}As$ was studied as a function of deposition temperature in the range 674 to 719 ℃. An Arrehenius plot of growth rate is shown in Fig. 1. The growth rate shows two distinct segments with temperature: a strongly temperature-dependent growth rate at low temperatures and a weakly temperature-dependent growth rate at higher temperatures. At the lower temperatures, the apparent activation energy determined for the deposition of $Ga_xIn_{1-x}As$ from a source alloy of 8.69 at.% Ga was 188 kJ/mol. This value is in close agreement with the values of 184 kJ/mol and 180 kJ/mol reported by Hyder et al [9] and Erstfeld and Quinlan [4], both on (100) InP substrates. Since the growth rate is nearly independent of deposition temperature at higher temperatures,

the deposition is apparently limited by mass transfer. Fig. 1 shows that the growth is primarily limited by chemical reaction at the deposition temperature of 700 ℃.

The influence of the source alloy composition on the film composition and growth rate is shown in Fig. 2. The plot shows that an alloy composition of 5.8 at.% Ga is necessary for the composition of $Ga_{0.47}In_{0.53}As$ at the given operating condition. The Ga mole fraction in the epitaxial layer is considerably higher than the mole fraction of Ga in the alloy source. This behavior is expected on the basis of thermodynamics since the Gibbs energy of formation of InAs at the growth temperature from the monochloride is approximately 25 kJ/mol more positive than the value for GaAs [10]. Positive deviations from ideal-solution behavior in the In-rich alloy solution [11] further contribute to a distribution coefficient greater than one. Fig. 2 shows the results of several other investigators using an alloy source. The general trends are similar but the alloy composition required for lattice-matched growth varies between 3.2 to 12.2 at.% Ga. These results suggest that the composition of the film is influenced by the operating parameters and reactor design. In this study, for example, lattice-matched $Ga_{0.47}In_{0.53}As$ epitaxial layers could be grown with both 5.35 and 8.69 at.% Ga alloys by adjustment of the process parameters. Fig. 2 also shows that the growth rate decreases with increasing Ga mole fraction in the alloy source. This decrease is consistent with the growth rates reported for the separate binary compounds [12-14].

The dependence of film composition on the inlet HCl mole fraction is shown in Fig. 3, where the results for three different alloys, 15.10, 8.69, and 5.35 at.% Ga, are reported. The Ga content of the deposited layers increases with x°_{HCl} and exhibits a limiting value when x°_{HCl} is greater than $6x10^{-3}$ atm. The limiting film compositions of $Ga_xIn_{1-x}As$ prepared from different alloy sources are 0.85, 0.74 and 0.43 for the alloy compositions 15.10, 8.69, and 5.35 at.% Ga, respectively. A thermodynamic analysis predicts an increase of Ga in the deposited epitaxial layer with increasing x°_{HCl} or equivalently Cl/H molar ratio. InCl is more stable than GaCl [15] and tends to remain in the vapor phase which increases the Ga content of $Ga_xIn_{1-x}As$.

The growth rates of $Ga_xIn_{1-x}As$ as a function of inlet HCl mole fraction are shown in Fig. 4. The growth-rate data exhibit a maximum for each of the three alloy compositions studied. The maxima occur at a Ⅲ/Ⅴ ratio of approximately one, corresponding to the stoichiometry of the film. The increase in growth rate at low values of inlet HCl mole fraction is the result of simply supplying more metal chlorides to the system. This is the region where the GaAs mole fraction is increasing in the film (Fig. 3). At high values of inlet HCl mole fraction, the growth rate decreases as the Ⅲ/Ⅴ ratio increases, apparently first order in x°_{HCl}. This result is consistent with the explanation by Shaw [16] that the deposition rate of GaAs in the kinetically limited regime is controlled by competitive adsorption between metal chlorides, HCl, and arsenic species at As growth sites.

The effect of adding excess HCl to the mixing zone on the film composition and growth rate is shown in Fig. 5. Injection of HCl to the mixing zone has been used to reduce Si background doping, reduce the growth rate, and

eliminate wall deposition. The Ga content in the deposited layers increases slightly with increasing added HCl and eventually reaches a constant value. The gallium increase is more pronounced for films prepared from the source containing the smaller amount of Ga (5.35 at.% Ga). The decrease in growth rate with added HCl was first order. This decrease in growth rate was also observed by other investigators [3,17] when a threshold amount of HCl was exceeded. The present study showed that a limiting composition of $Ga_{0.88}In_{0.12}As$ was obtained with the 15.10 at.% Ga source alloy. This result agrees with the limiting value of $Ga_{0.87}In_{0.13}As$ reported by Quinlan and Erstfeld [3] with the use of a 11.8 at.% Ga source alloy.

Photodetectors fabricated with the VPE hydride-alloy technique

Planar *p-i-n* photodetectors were fabricated with 3.5 ㎛ active layers of $Ga_{0.47}In_{0.53}As$ grown from a 6.61 at.% Ga alloy source and shown in Fig. 6. The active layers were grown between a 3.25 ㎛ InP buffer layer and a 1.00 ㎛ InP cap layer on a (100) S-doped InP substrate. The photodetectors with 75 ㎛ active diameters were fabricated using standard planar technology. The fabrication procedure has been adequately described by Forrest et al. [18].

The characteristics of the devices fabricated with the present technique compares favorably with InGaAs *p-i-n* photodetectors reported in the literature [19]. The fabricated photodetectors exhibited the following properties: dark current, 10 to 20 nA at -5 V; capacitance, 0.88 to 0.92 pF; responsivity, 0.84 to 0.86 A/W; and breakdown voltage, > 40 V. The data demonstrates that epitaxial layers of $Ga_{0.47}In_{0.53}As$ grown from Ga/In alloys are suitable for the production of state-of-the-art *p-i-n* photodetectors for fiber optic applications.

SUMMARY

The VPE-hydride process using a Ga/In alloy source has been studied in detail for the preparation of epitaxial layers of $Ga_xIn_{1-x}As$. The compositions and growth rates were measured as a function of process parameters. The results revealed that reaction kinetics and mass transfer play important roles, particularly in determining the growth-rate behavior. An equilibrium analysis, nevertheless, could explain the film compositional behavior for most process parameter changes. Lattice-matched $Ga_{0.47}In_{0.53}As$ epitaxial layers could be grown on InP substrates with alloys containing 5 to 8 at.% Ga.

The study demonstrated that the VPE-hydride method with an alloy source can be successfully used to fabricate high quality *p-i-n* photodetectors.

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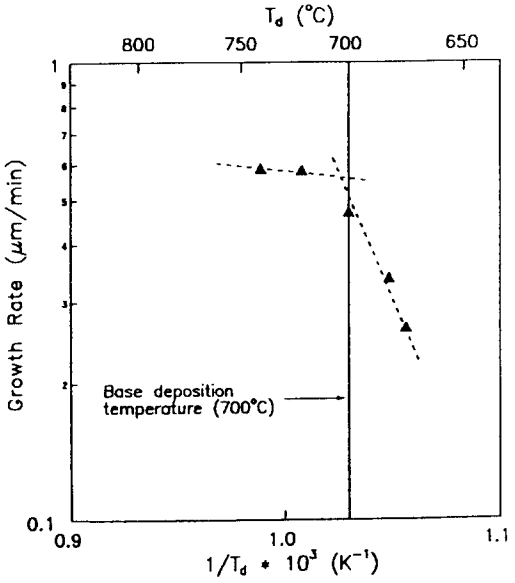

Figure 1 : Arrhenius plot of growth rate of $Ga_xIn_{1-x}As$ at x_{Ga} (l) = 0.0869, x^*_{HCl} = 0.0024, $x^*_{AsH_3}$ = 0.0034, and total flow rate = 4200 sccm. The low temperature apparent activation energy is 188 kJ/mol.

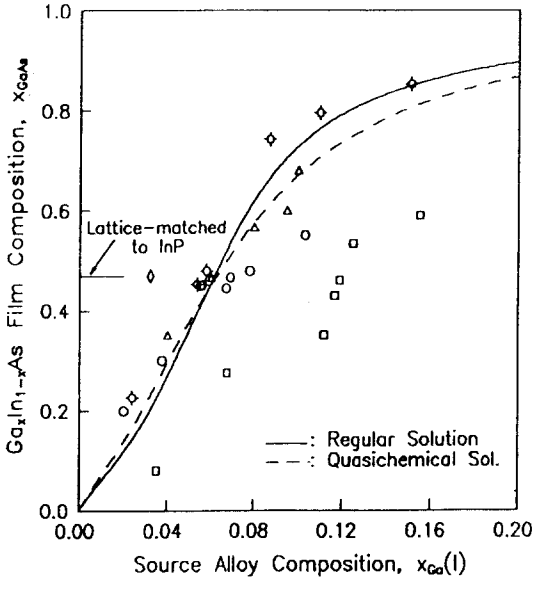

Figure 2 : The film composition of $Ga_xIn_{1-x}As$ as a function of the Ga mole fraction in the source alloy at T_d = 700 °C, x^*_{HCl} = 0.0072, and $x^*_{AsH_3}$ = 0.0034. ◇, this study; △, Jacobs *et al.*[5]; ○, Kordos *et al.*[6]; □, Erstfeld and Quinlan[4]; ◇, Chatterjee *et al.*[2].

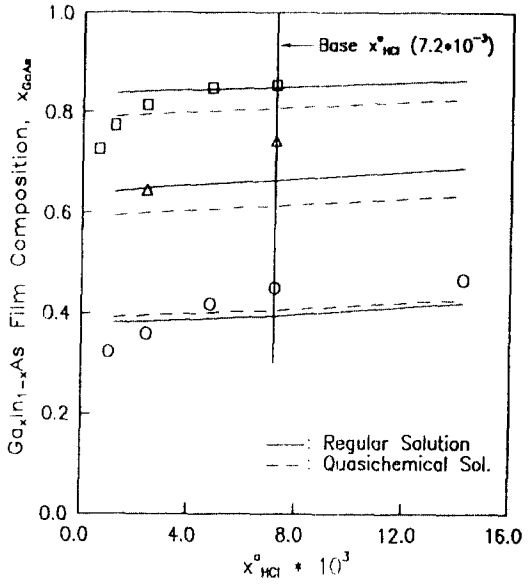

Figure 3 : The film composition of $Ga_xIn_{1-x}As$ as a function of inlet HCl mole fraction at T_d = 700 °C and $x^{\circ}_{AsH_3}$ = 0.0033. Source alloy compositions: □, x_{Ga} (l) = 0.1510; △, x_{Ga} (l) = 0.0869; O, x_{Ga} (l) = 0.0535.

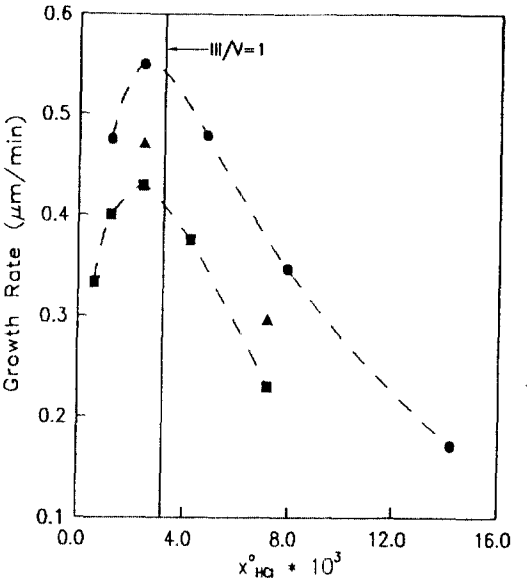

Figure 4 : The growth rate of $Ga_xIn_{1-x}As$ as a function of inlet HCl mole fraction at T_d = 700 °C and $x^{\circ}_{AsH_3}$ = 0.0033. Source alloy compositions: □, x_{Ga} (l) = 0.1510; △, x_{Ga} (l) = 0.0869; O, x_{Ga} (l) = 0.0535.

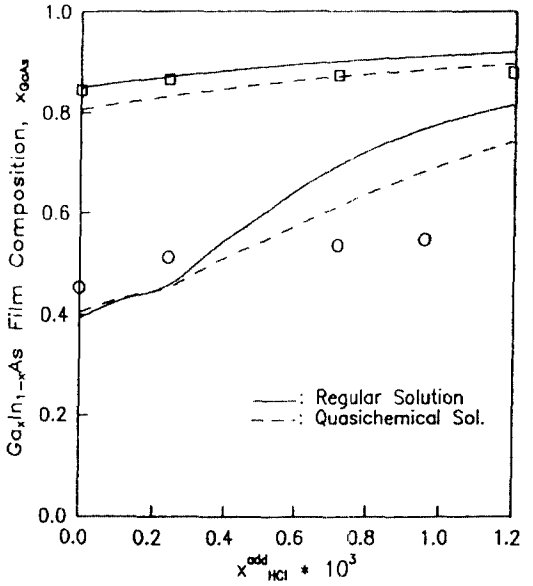

Figure 5 : The film composition of $Ga_xIn_{1-x}As$ as a function of added HCl mole fraction at T_d = 700 °C, x°_{HCl} = 0.0072, and $x^{\circ}_{AsH_3}$ = 0.0033. Source alloy compositions: □, x_{Ga} (l) = 0.1510; O, x_{Ga} (l)= 0.0535.

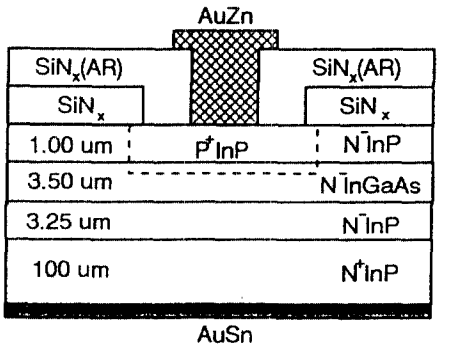

Figure 6 : Schematic of planar InGaAs/InP *p-i-n* photodetector with active layer grown from Ga/In alloy source.