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MOLECULAR BEAM EPITAXIAL GROWTH AND CHARACTERIZATION OF In$_{0.53}$Ga$_{0.47}$As AND InP SUBSTRATE

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Abstract. Epitaxial layers of In$_{1-x}$Ga$_x$As lattice matched to InP substrates have been grown by molecular beam epitaxy. By accurate flux measurements epitaxial layers are obtained with lattice mismatch lower than $10^{-3}$. The use of separated cells for indium, gallium and arsenic as well as rotating substrate holder permits to obtain good composition uniformity. Influence of the substrate temperature on the epitaxial layers composition is shown. Arsenic pressure needed for stoichiometric growth in a function of substrate temperature. Results on non-intentional doping and beryllium doping are presented.

1. Introduction

In$_{0.53}$Ga$_{0.47}$As lattice matched to InP is a very promising material for high speed electronic and optoelectronic devices. MBE growth of such material to InP substrate is intensely studied in many laboratories and many results are published in this field. However, such growth offers many difficulties due to: surface preparation and stabilization during growth, precise control of the ternary composition which depends of an accurate measurement of the two group III elements flux, growth at high temperature on arsenic stabilized surface which is a condition to obtain layers with good crystalline and electronic characteristics.

In this paper, we present some results concerning these points. With separate cells technique for indium and gallium, we demonstrate that it is possible to control accurately and in a reproducible way, the solid ternary alloys composition by using a precise measurement of the pressure inside the different molecular beams. The critical ratio between arsenic pressure and metallic elements pressure separating the two surface conditions will be determined as a function of substrate temperature $T_S$. The measurement of the transition time between these two surface structure versus substrate temperature will give the value of the arsenic desorption energy with InGaAs. With a proper choice of growth parameters, $P_{AS}/P_{III}, T_S, P_{In}/P_{In} + P_{Ga}$, we show that InGaAs layers, showing good electrical characteristics and precisely matched to InP, can be obtained with good uniformity.
2. Experimental set up

Our MBE equipment has three different chambers. The first one is a preparation chamber where the molybdenum substrate holder is prebaked under residual pressure of $10^{-8}$ Torr, in order to minimize contamination of the growth chamber. Several substrates can be introduced simultaneously and stored in a wagon permitting the sample transference between the first and the second chamber. This system permits to reduce the loadings and to enable to make comparative experiments on several substrates having received the same preparation conditions.

The second one is an intermediate chamber between the preparation and growth chamber. This arrangement permits a substrate loading or unloading of the growth chamber during a baking out in the preparation chamber.

The third part is the growth chamber. Eight effusion cells can be mounted, of which the molecular flux converge to a rotating substrate holder. The inside of the growth chamber is enclosed by a liquid-nitrogen cooled shroud. Vacuum is obtained by ionic pumps, helped by titanium sublimation wells and helium bath cryopump. Residual gas analysis is performed with a quadrupole mass spectrometer. The epitaxial layers are investigated crystallographically by 10 keV R.H.E.E.D.

3. Substrate preparation

Sputtering ion cleaning of InP substrate [1] gives severe degradation on electronic and luminescent properties, this has been shown by previous MBE experiments. The thermal annealing successful in GaAs MBE experiments is inapplicable to InP substrate due to its low non congruent evaporation at 365°C, while the corresponding temperature for GaAs is 657°C. On the other hand, native oxides on InP are more stable than GaAs oxides, furthermore, on account of its low non congruent temperature, surface contaminants such as oxygen and carbon cannot be satisfactorily removed from InP by heating treatments.

Our substrate preparation consists essentially in a surface passivation in 18 MΩ DI water [1, 2], before substrate's loading and after the following operations:
- chemical polishing with 5 % Br₂ - CH₃OH on large substrates to get good flat surface,
- cleaning in pure agitated H₂SO₄ during 15 min,
- etching in H₂SO₄ : H₂O₂ : H₂O = 5 : 1 : 1 solution,
- etching with 0.3 % Br₂ - CH₃OH solution.

When this surface preparation is properly done, one can observe at room temperature, contrarily to GaAs substrates, a clear R.H.E.E.D. pattern very close to the InP one; This shows that the native oxide obtained by immersing the substrate in H₂O is very thin.

This observation depends on the passivation time and is only possible for a very short duration passivation. To prevent thermal damages during the oxides dissociation at temperature above congruent evaporation, and before increasing the substrate temperature, the substrate is exposed under As₄ flux. The arsenic intensity flux is the same as that during the growth. When the substrate temperature is increasing under these conditions, the R.H.E.E.D. streaks intensity increases, no point appears on the R.H.E.E.D. pattern. The growth starts after the apparition of the one-quarter-order reconstruction pattern, under (1 1 0) azimuth, as described by CHENG et al. [2].

4. Control of the ternary composition by indium and gallium flux measurements

InGaAs matched to InP has indium and gallium composition near 50 %.

In this case, this composition gives a maximum variation for a given relative fluctuation of either group III elements. Therefore it is very important to be able to control and calibrate precisely indium and gallium flux, in order to obtain a precise solid composition.
The coaxial oven technique [2, 3] or the premixed indium, gallium common source technique [4, 5] used by several authors have the inconvenience to have a fixed temperature for a given ternary composition which determines only one growth rate. The use of three separated cells permits to adjust the growth rate for a given composition and inversely.

In our technique, indium and gallium cells are close together (3 cm) and are separated far from the substrate (12 cm). The flux intensity is measured by a Bayard-Alpert (B.A.) gauge which can take the place of growth substrate position. For relative pressure measurements, we have to take into account the relative sensibility of the B.A. gauge for different elements. FLAIM et al. [6] have shown that the relative B.A. gauge sensibility was proportional to the electron number per gas-phase molecule. Using this proportionality, we get for indium and gallium the relative sensibility \( \alpha = 1.43 \).

The composition control is made by X ray measurements and electron microprobe analysis. In order to get a large calibration range, we have studied In\(_1-x\)Ga\(_x\)As growth on the ranges \( 1 > x > 0.8 \) on GaAs substrate and \( 0.55 > x > 0.42 \) on InP substrate.

Figure 1 shows indium atomic percentage in ternary layers as a function of pressure rations \( P^*_{In}/P^*_{In} + P_{Ga} \). For \( P_{In} = 6.2 \times 10^{-7} \) Torr and \( P_{Ga} = 3 \times 10^{-7} \) Torr, the measured ratio pressure \( R_p = \frac{P_{In}}{P_{Ga}} \) is equal to 2.066. This gives the best lattice matched epilayers to InP, \( \Delta a/a < 5 \times 10^{-4} \). The corresponding atomic percentage ratio is \( R_S = 1.13 \), and \( P^* \) is the measured indium pressure corrected by the factor \( R_p/R_S = 1.8 \).

Supposing gallium sticking coefficient to be equal to unity, we deduce an indium sticking coefficient \( S_{In} = \alpha \cdot R_S/R_p = 0.79 \). Experimental points on figure 1 correspond to electron microprobe composition measurements. Good linearity is obtained in a large range of indium pressure. The substrate temperature \( T_S \) was equal to 560°C. Arsenic pressure conditions are described in section IV.
Refering to figure 2, X ray measurements are also used for composition control. Lattice mismatch $\Delta a/a$ is measured on X ray rocking curves obtained with a single X ray diffractometer. This figure shows a typical recording of X ray rocking curve. In spite of the second rate performance of this diffractometer, we are able to measure a lattice mismatch as good as $\Delta a/a = 5 \times 10^{-4}$. Such measurements have been performed on ternary layers grown on InP for two different substrates temperatures.

Figure 2
X ray rocking curve from (400) plane of a 3.5 $\mu$m thick $\text{In}_{1-x}\text{Ga}_x\text{As}$ epitaxial layer

Figure 3
Relative lattice mismatch of epitaxial $\text{In}_{1-x}\text{Ga}_x\text{As}$ on InP as a function of indium pressure for two substrate temperatures 510°C (+) and 560°C (O)
Results are reported on figure 3. Two series of epitaxial layers were grown at $T_S = 510°C$ and $T_S = 560°C$. In both cases, lattice mismatch $\Delta a/a$ has a linear variation versus measured pressure ratio $P_{In}/P_{In} + P_{Ga}$. This behavior permits a good molecular flux calibration. After this calibration, we were able to obtain currently ternary layers which had lattice mismatch to InP less than $10^{-3}$. The indium and gallium pressure measurements have to be done during a long stabilization time after cooling to liquid-nitrogen temperature of the inside shrouds. In our point of view, flux pressures are good experimental parameters but not the cell temperatures because of the progressive growth of indium and gallium droplets on the lateral surface inside the crucibles and consequently increase the beam flux.

Independently, from figure 3, a second observation is that, for a given pressure ratio $P_{In}/P_{In} + P_{Ga}$, epitaxial layers grown at $560°C$ have an atomic indium percentage lower than epitaxial layers grown at $510°C$. It is an indium loss equal to 3%. Indium sticking coefficient is a decreasing function of the substrate temperature. This loss of indium due to desorption mechanism is confirmed by the increasing indium signal on quadrupole spectrometer in the same ratio. These results are compared with those obtained by WOOD et al. [7]. They observe by Auger analysis an indium loss equal to 10% between the two substrate temperatures $500°C$ and $560°C$, but during their ternary growth, indium flux is three times larger than ours. This difference in indium loss can be explained by the FOXON and JOYCE [8] experiment, showing that the desorption rate of indium is proportional to the incident intensity flux, in the assumption of low intensity flux.

5. Composition uniformity

The composition uniformity of epitaxial layers is an important problem in the device realisations. By using a rotating substrate holder and by an accurate flux control, we are able to grow ternary layers $In_{1-x}Ga_xAs$ with good composition uniformity, 0.4% inside a circular surface of 30 mm diameter.

These composition measurements were obtained by electron micropole analysis. Rotating substrate holder permits here to eliminate lateral temperature gradient due to the non-uniform heating of the substrate holder.

6. Influence of substrate temperature on surface growth structures and arsenic pressure

Detailed study of surface structures has been done by CHO et al. [9] on GaAs. They showed that it was necessary to maintain an arsenic pressure about five times larger than the gallium pressure to get an arsenic stabilized surface during growth. We have made similar measurements during InGaAs growth. Arsenic pressure was measured by ionization gauge in the beam flux before growth.

On figure 4, the ratio arsenic pressure $P_{As}$ over elements III pressure $P_{III}$ is a function of reciprocal substrate temperature. We compare our results on InGaAs with these on GaAs. Each curve determines two zones, the upper zone corresponds to arsenic stabilized surface and the lower zone to a metal stabilized surface during growth. The upper curve obtained during InGaAs growth shows that in order to maintain the same situation on the ternary layers than on GaAs, arsenic pressure must be eight times higher than the one required for GaAs growth. The determination of the critical ratio $P_{As}/P_{III}$ which separates the two growth zones is made by observing the change of R.R.E.E.D. patterns corresponding to the two growth zones. Primary electron beam is along $(110)$.

The necessity to maintain this high arsenic pressure to get stoichiometric material is probably due to: the formation of the two $InAs$ and $GaAs$ molecules with their proper arsenic loss, the low energy desorption of $As$ [9], the $As_4$ production by using elementary arsenic cell which gives additional loss during $As_4$ and $As_2$ dissociation on the growth surface. The amount of those three mechanisms can explain a very low arsenic sticking coefficient.
In relation to arsenic desorption, we have measured the transition time $\tau$ between arsenic and metal stabilized surface versus substrate temperature. Transition time is a good approximation of atomic arsenic surface lifetime. In the assumption described by CHO [9] we can write $\tau \propto \exp \frac{E_{AS}}{R} \frac{T_S}{T}$, where $T_S$ is the substrate temperature and $E_{AS}$ is the arsenic energy desorption.

Figure 4
Limit pressure ratio As/In + Ga separating arsenic and metal stabilized surface structure, as a function of reciprocal substrate temperature. Full circles: this work on InGaAs. Open circles: CHO. A.Y. [9] on GaAs.

Figure 5
Transition time $\tau$ (sec) between arsenic and metal stabilized surface structure, versus reciprocal substrate temperature.
We show on figure 5 results of $\tau$ measurements as a function of substrate temperature. $\tau$ measurements were made with a chronometer, which gives enough accuracy in this time range. From the $\tau$ evolution with substrate temperature, we get $E_{d_{\text{As}}} = 1.4 \pm 0.2$ eV. This value is almost equal to indium energy desorption $E_{d_{\text{In}}} = 1.5$ eV measured by FOXON [8]. Those very close values of $E_{d_{\text{As}}}$ and $E_{d_{\text{In}}}$ suggest a congruence desorption of InAs.

7. Electrical properties and p type doping

a) Undoped epitaxial layers: Undoped InGaAs epitaxial layers were grown on semi-insulating InP substrates, Fe doped and EPD = 3 x $10^4$ cm$^{-2}$. Growth direction is along (0 0 1). Purity of source materials is 6 N. The growth temperature is equal to 510°C and the arsenic pressure inside the flux is kept above 10$^{-5}$ Torr.

Our median results are $N_D - N_A = 3 \times 10^{15}$ cm$^{-3}$ with the corresponding electron mobility $\mu_e = 8000$ cm$^2$/V.sec at room temperature and $\mu_e = 25000$ cm$^2$/V.sec at liquid nitrogen temperature. Our best results are actually $N_D - N_A = 2 \times 10^{15}$ cm$^{-3}$ with $\mu_e (300) = 11.000$ cm$^2$/V.sec and $\mu_e (77) = 43.000$ cm$^2$/V.sec. The thickness of the layers is typically 4 $\mu$m.

b) Beryllium doping: We report here some results on beryllium doping experiments of InGaAs epitaxial layers.

Figure 6

Hole concentration in beryllium doped InGaAs layers, as a function beryllium source temperature

Figure 6 shows the hole concentration versus reciprocal beryllium cell temperature. The aperture of the beryllium curve is 3 cm$^2$ and the growth rate is 1.8 um/h. The surface morphologies are comparable to those obtained on undoped layers except for the highest experimental point corresponding to $3.3 \times 10^{19}$ cm$^{-3}$ doping level. It seems that $2 \times 10^{19}$ cm$^{-3}$ is the maximum doping level which does not bring about a change on the surface morphology observed by R.H.E.E.D. pattern.
Conclusions

By an accurate flux measurement we obtain reproducible ternary In$_{1-x}$Ga$_x$As composition with lattice mismatch to InP $\Delta a/a < 10^{-3}$. We measure indium sticking coefficient $S_{In} = 0.79$ for a substrate temperature equals to 560°C, indium desorption is observed between the substrate temperatures of 510°C and 560°C. This corresponds to a composition variation of 3%. We show that to get stoichiometric growth, arsenic pressure must be eight times higher than the corresponding arsenic pressure needed for GaAs growth. We determine the arsenic desorption energy $E_{dAs} = 1.4 \pm 0.2$ eV. Good composition homogeneity of epitaxial layers is obtained by using a rotating substrate holder. Undoped layers are obtained with the median values $N_D - N_A = 3 \times 10^{15}$ cm$^{-3}$, $\mu_e (300 \text{ K}) = 8000 \text{ cm}^2/\text{V.s}$, $\mu_e (77 \text{ K}) = 25,000 \text{ cm}^2/\text{V.s}$ and the best one $N_D - N_A = 2 \times 10^{15}$ cm$^{-3}$, $\mu_e (300 \text{ K}) = 11,000 \text{ cm}^2/\text{V.s}$ and $\mu_e (77 \text{ K}) = 43,000 \text{ cm}^2/\text{V.s}$. Finally beryllium doping up to $1.4 \times 10^{19}$ cm$^{-3}$ has been achieved without modification of surface morphology.

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