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LPE-GROWTH OF HIGH PURITY Ga_{0.47}In_{0.53}As- AND Ga_{0.31}In_{0.69}As_{0.69}P_{0.31}- LAYERS LATTICE MATCHED TO InP

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LPE-GROWTH OF HIGH PURITY $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ AND $\text{Ga}_{0.31}\text{In}_{0.69}\text{As}_{0.69}\text{P}_{0.31}$ LAYERS LATTICE MATCHED TO InP

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Résumé. - Nous avons déposé à 685 °C des couches minces de $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y = 0,75$ et $0,69$) sur InP avec des surfaces brillantes par la méthode de l'épitaxie en phase liquide. Pour les longueurs d'onde entre 1370 nm et 1420 nm il était possible de déposer des couches jusqu'à une épaisseur de 5 μm . La saturation des solutions par l'aide d'un substrat rendait possible de contrôler la composition jusqu'à une précision de $\pm 0,6$ at% As et $\pm 0,3$ at% Ga. Ces pourcentages correspondent à une longueur d'onde de ± 5 nm. GaInAsP a été purifié avec une densité d'électron de $1,5 \cdot 10^{15} \text{ cm}^{-3}$ et avec une mobilité de 13 000 cm^2/Vs à 77 K. Nous avons étudié de quelle manière la pureté de GaInAsP et de GaInAs dépend de la qualité de l'indium, de la préparation des matériaux et du traitement des solutions à température haute. Il était possible de déposer des couches de l'InP sur GaInAsP aux températures au dessous de 570 °C. Les dislocations dans InP dépendent de la température de croissance, de la supersaturation et de la vitesse de refroidissement. La corrélation entre le désaccord du paramètre de réseaux et la composition de l'InP a été mesurée.

Abstract. - $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ layers ($y = 0.75$ and 0.69) for photodetector devices have been deposited lattice matched to InP with mirror smooth surfaces at 685 °C by liquid phase epitaxy. Layers thicker than 5 μm could be grown for both compositions corresponding to photoluminescence peak wavelengths of 1420 nm and 1370 nm. Applying a presubstrate for the saturation of the quaternary solutions enables composition control within ± 0.6 at% As and 0.3 at% Ga. This corresponds to an accuracy in wavelength of ± 5 nm. Net electron concentrations of $1.5 \cdot 10^{15} \text{ cm}^{-3}$ and 77 K mobilities of 13 000 cm^2/Vs have been obtained. The purity of GaInAsP and GaInAs layers depends on the quality of In ingots, the careful preparation of starting materials and on melt baking. The occurrence of cross hatch pattern has been related to growth temperature, supersaturation and cooling rate. We have measured the relationship between composition and lattice mismatch in InP cap layers.

1. **Introduction.** - Fibre optics communication has become of more and more interest during the last years. Due to loss minima of the fibre 1330 nm and 1550 nm are favorable transmission wavelengths. $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ is the mostly used detector material in such systems. For 1300 nm however detectors made from GaInAsP having a larger band-gap are superior in terms of a low dark current [1]. Moreover photodetectors with separate absorption and multiplication region are easier to fabricate with quaternary absorbing material, because the subsequent deposition of InP is easier than on GaInAs. On the other hand a double heterostructure enables the fabrication of planar diodes for light entering from the top.

In this paper we present the LPE growth procedure for thick high purity $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ alloys ($y = 0.69$ and 0.75) and the deposition technique for InP on these alloys.

Results published so far indicate that the growth of these compositions is difficult /2/. Takahei /2/ reported a strong reduction in growth rate at 590 °C and 640 °C for layers containing As between 66 % and 72 %. Only 1.5 μm thin layers with rough surfaces could be obtained. Takahei /2/ quoted from his experiments a miscibility gap in the phase diagram, which was predicted from phase diagram calculations by de Cremoux /3/ and the latest work of Onabe /4/. In this work we have tried temperatures of 685 °C to obtain thick layers and smooth surfaces.

The deposition of InP onto GaInAsP has been tried by several authors /5-8/. Thermodynamic inequilibrium is established when a binary solution of P and In contact the quaternary layer, which will be dissolved immediately. The dissolution depth depends on diffusion of Ga and As atoms and the time when a supersaturated quaternary interface is build up. Ladany /5/ reported that pull over of quaternary solution increases dissolution. Takahashi /6/ found that dissolution becomes more and more severe when the As content in the layers is increased. Applying high supersaturation and high cooling rates Nakajima /7/ could avoid strong dissolution even for GaInAs layers. Low growth temperatures favored the deposition of InP on GaInAsP layers /2, 7, 8/.

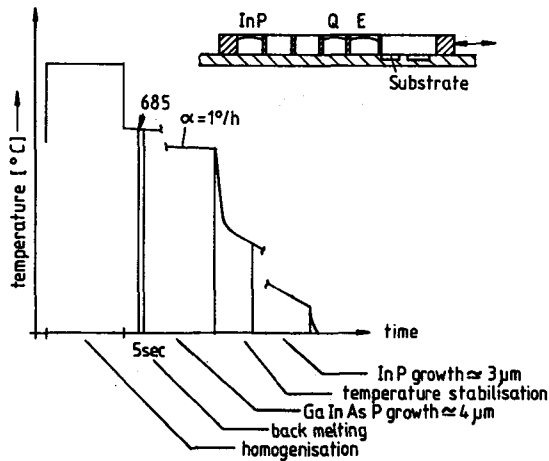


Fig. 1: Growth process of quaternary layers and for InP cap layers

2. Growth process of InP-GaInAsP-InP double heterostructures. - The layers were deposited by liquid phase epitaxy from indium rich solutions. A conventional multibin slider boat made from carbon was used for the growth of detector structures on 100 oriented InP substrates. In Fig. 1 the growth process, which has been proved during our experiments is shown schematically. The solutions were baked first and then saturated at a precisely controlled temperature by use of an InP substrate as a seed. Prior to growth the InP (100) substrates were etched by a 1 % bromine methanol etchant. The solutions were homogenized for several hours some degrees above the saturation temperature. Back melting with pure In of the substrate surface removed the thermal defects on the InP substrate. The growth of the quaternary layer started from 685 °C at a cooling rate of 1 °/h. InP cap layers has been grown at temperatures below 575 °C by a ramp cooling technique. The thicknesses of the layers has been adjusted by selecting the appropriate growth times and supersaturations.

3. Growth of GaInAsP.

3.1 Composition control

The mole fractions of Ga and As have been varied for a saturation temperature of 690 °C to adjust lattice parameter and bandgap. They were controlled by X-Ray and photoluminescence experiments. The phosphorus saturation of the solution has been obtained applying an InP presubstrate as described above. This method gave a composition constancy of $\Delta y = \pm 0.6$ at% and $\Delta x = \pm 0.3$ at%. These percentages has been estimated from the reproducibility of ± 5 nm of photoluminescence peak wavelength. Fig. 2 shows which As mole fraction is necessary for lattice matched $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ layers with $y = 0.75$ ($\lambda = 1420$ nm) and $y = 0.69$ ($\lambda = 1370$ nm). The solid composition has been measured by EDAX. Calculation of the composition from the equations given by Pollak /9/ and from the photoluminescence wavelength are in good agreement (± 3 at%) with the EDAX measurements)

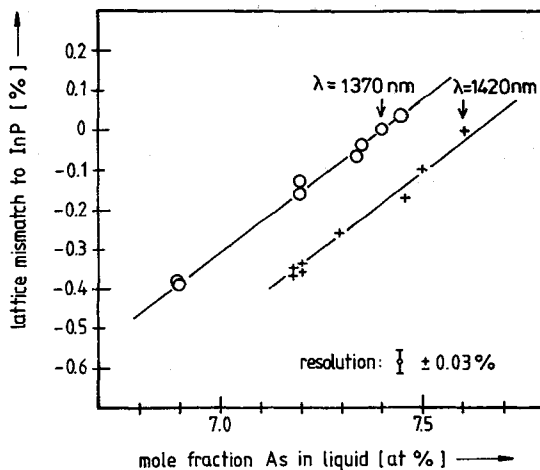


Fig. 2: Relationship between lattice mismatch and As mole fraction of GaInAsP layers with $y = 0.69$ ($\lambda = 1370$ nm) and $y = 0.75$ ($\lambda = 1420$ nm)

3.2 Growth rate of $\text{Ga}_{0.31}\text{In}_{0.69}\text{As}_{0.69}\text{P}_{0.31}$ and $\text{Ga}_{0.34}\text{In}_{0.66}\text{As}_{0.75}\text{P}_{0.25}$ and surface morphology

Smooth surfaces have been obtained for both compositions. No change in surface smoothness and morphology has been observed for all layer thicknesses even up to 5 μm . The typical smooth surface area of a layer containing 0.69 at% As is shown in Fig. 3. No distinct terraced structure just like for InP or GaAs has been found for all quaternary layers.

We have studied the relationship of layer thickness and deposition time for both compositions. Layer thickness data are summarized in Fig. 4. No limitation in layer thickness has been found. Up to 6 μm has been grown in 30 min. In our experiments we didn't find effects that a miscibility gap will be present at 685 °C. The line drawn in Fig. 4 demonstrates a $t^{1/2}$ law which is found in theory for diffusion limited growth. However the growth rate changed drastically when the phosphorus content differed from the equilibrium value. In this case the surfaces became rough and only thin layers were obtained.

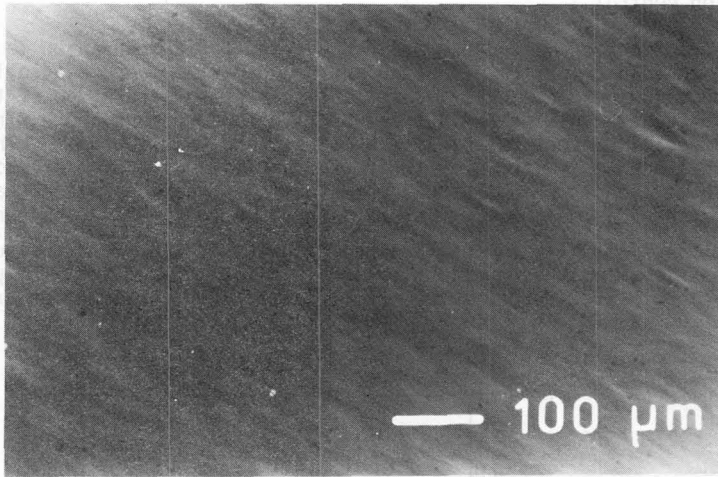


Fig. 3: Nomarsky Interference contrast micrograph (NIC) of a GaInAsP layer ($y = 0.69$)

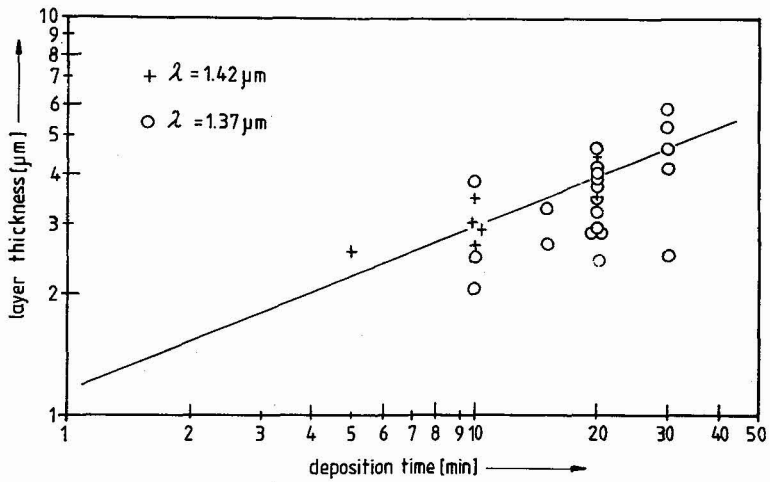


Fig. 4: Time dependence of layer thickness for GaInAsP layers lattice matched to InP. The solid line demonstrates a $t^{1/2}$ law for diffusion limited growth

4. Preparation of high purity GaInAsP layers. - The net carrier concentration of epitaxial layers could be improved by baking the solutions at high temperatures. No procedure has been published so far for layer compositions with $y = 0.69$ and 0.75 . In this work we have tested the baking techniques. Only etched ingots have been used. Table 1 gives some characteristic results of our experiments. Etching the GaAs and InAs ingots like the InP substrates the starting point could be improved by a factor of 2. The results without and with etching are given in column 1 and 2. Heat treatment of the solutions for 10 h at $700\text{ }^\circ\text{C}$ reduced the doping level by half. No significant difference has been found if the ternary solution or the quaternary solution has been baked.

In etched	X	X	X	X		X	X
GaAs, InAs etched	-	X	X	X		X	X
tern. solution baked	-	-	-	10h	↓ the same solution baked	-	-
P saturation of ternary solution	X	-	X	X		X	X
quatern. solution baked	-	-	10h	-	10h	20h	20h
P saturation of quatern. solution	-	-	X	-	X	X	-
$N_D - N_A$ [10^{15} cm^{-3}]	40-60	10-20	8	7	3.9	3.6	1.6
$\mu(77\text{K})$ [cm^2/Vs]			11000	10000	11900	11000	13000
total baking time		0h		10h		20h	

Table 1: Purification method for $\text{Ga}_{0.31}\text{In}_{0.69}\text{As}_{0.69}\text{P}_{0.31}$ layers

Both procedures given in column 3 and 4 of Table 1 resulted in doping levels of $7.5 \times 10^{15}\text{ cm}^{-3}$. Baking the solutions twice for 10 hours or once for 20 hours carrier concentrations of $3.7 \times 10^{15}\text{ cm}^{-3}$ and 77 K mobilities of $11\,900\text{ cm}^2/\text{Vs}$ have been obtained. These results are shown in the columns 5 and 6 of Table 1. The experiment in column 7 of Table 1 demonstrates that without additional saturation of the solution after baking a further improvement is achieved. A net electron density of $1.6 \times 10^{15}\text{ cm}^{-3}$ and a 77 K mobility of $13\,000\text{ cm}^2/\text{Vs}$ has been obtained. However in this case the layers were mismatched due to the evaporation loss of P. On the other hand difficulties arise for surface morphology and layer thickness. From our experiments an exponential decay with a time constant of 6 - 8 h was calculated. Until recently a procedure for high purity GaInAsP layers with $y = 0.7$ was published by Kuphal /10/. In prebaking for 100 h at $750\text{ }^\circ\text{C}$ and a baking time of 5 h at $660\text{ }^\circ\text{C}$ for the solutions gave doping levels compared to ours for 20 hours solutions baking. We believe that the layers of Table 1 are purer because of the higher mobility compared to the reported of $9\,800\text{ cm}^2/\text{Vs}$.

In addition to the preparation techniques the good selection of ingot materials seemed to limit the lowest doping level for a given process. We have tested several batches from different supplies for depositing high purity GaInAs layers. A standard heat treatment resulted in layers of net electron concentrations between $2\text{-}8 \times 10^{15}\text{ cm}^{-3}$. For a serie of layers the doping level scattered by a factor of 2 within one batch. As a consequence the quality of different batches is dis-

cernable. On the other hand it has been difficult to decide from the elemental analysis which batch will lead to purer layers. The most favored residual impurities are Si, O and S which might deteriorate the purity could not explain our results. Therefore we believe the best way to select an In batch is to grow several layers and then to decide if the purity is sufficient or not.

5. Growth of InP cap layers. - The deposition of InP onto quaternary layers has been reported at low growth temperatures /3, 8, 9/. However too low temperatures will limit the layer thickness. Therefore we have used 10 °C supersaturated solutions at 575 °C and a cooling rate of 0.4 °C per minute. The layer showed cross hatch pattern, which reflects that parts of the quaternary layers have been dissolved. The surface of such a layer is shown in Fig. 5a. At 560 °C the cross hatch pattern diminishes as shown in Fig. 5b. We found in agreement with Nakajima /7/ that at higher cooling rates and at high supersaturation the dissolution is reduced. In Fig. 6 an InP layer, which has been deposited at 560 °C with good surface morphology is shown. In this case we used a 18 °C supersaturated solution at a cooling rate of 8 °C per minute. The fact that no cross hatch pattern is observable might indicate that the dissolution of the quaternary layer has been suppressed. From lattice parameter, photoluminescence and EDAX measurements we found that layers with a lattice mismatch of $\pm 0.05\%$ contains about 1.5 at% As and the same amount of Ga.

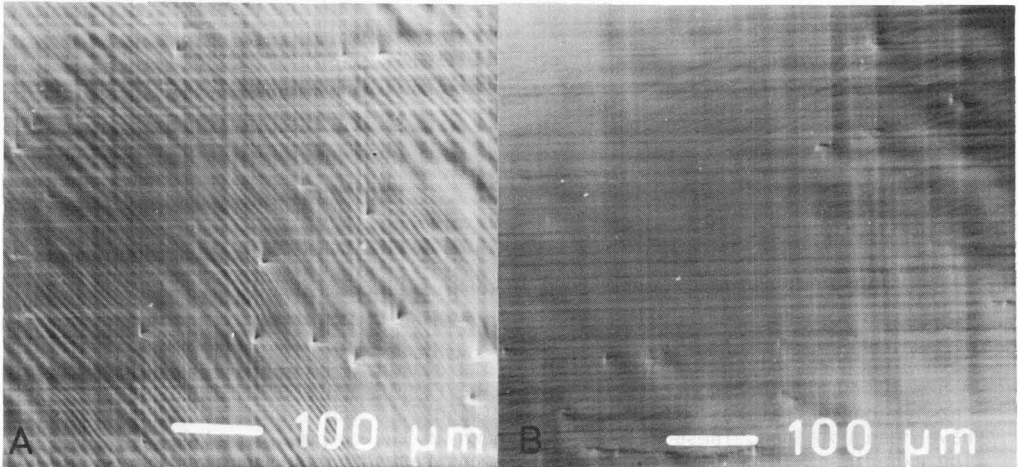


Fig. 5: InP layers grown on GaInAsP ($y = 0.69$)
 a) Growth temperature: 575 °C (NIC)
 b) Growth temperature: 560 °C (NIC)

In Fig. 7 a chemically etched cleavage plane of a double heterostructure is shown, which demonstrates the good quality of both interfaces.

Conclusions. - At a temperature of 685 °C it is possible to deposit up to 6 μm thick GaInAsP layers with $y = 0.69$ and 0.75 lattice matched to InP with mirror smooth surfaces. It has been found that the growth is diffusion limited. No difference in growth rate has been obtained for both compositions. The use of a presubstrate to saturate the quaternary solution gives reproducible composition control within ± 0.6 at% As and 0.3 at% Ga. This corresponds to an accuracy of ± 5 nm of photoluminescence peak wavelength. GaInAsP layers of $1.5 \times 10^{15} \text{ cm}^{-3}$ and $13000 \text{ cm}^2/\text{Vs}$ can be achieved applying careful ingot pre-

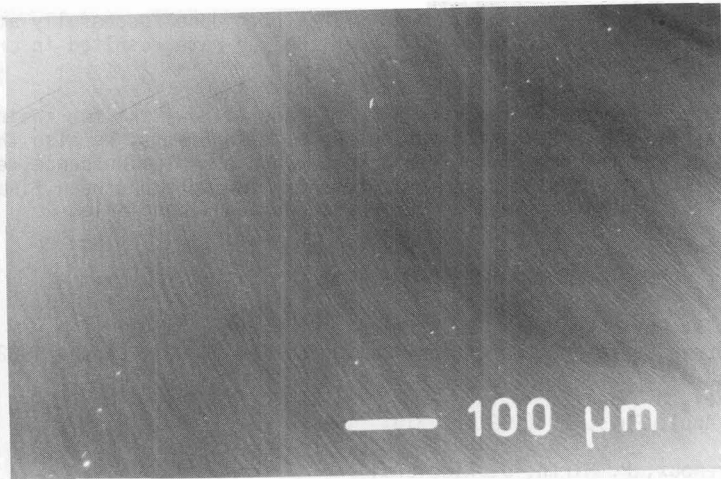


Fig. 6: InP layer grown on GaInAsP ($y = 0.69$)
 growth temperature 560 °C, cooling rate =
 8 °/min, supersaturation 18 °C (NIC)

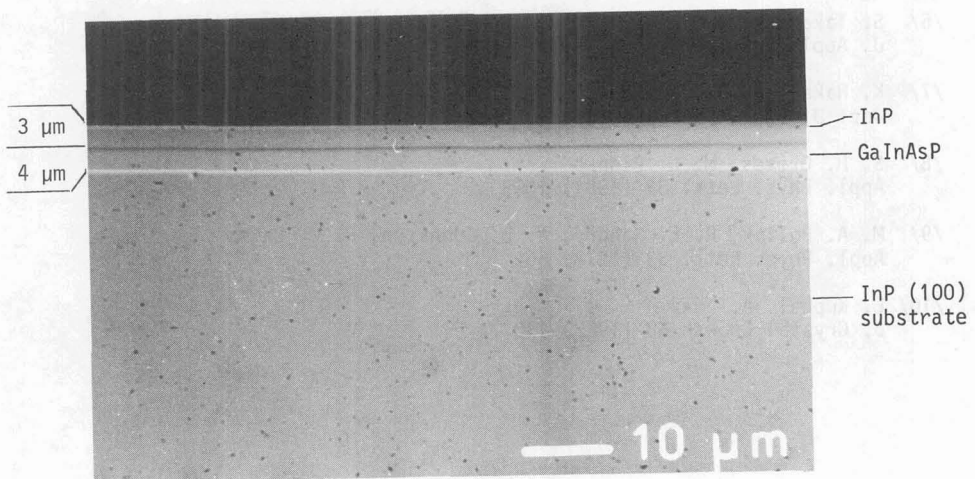


Fig. 7: Cleavage plane chemically etched of a double
 heterostructure demonstrating the good quality
 of both interfaces (NIC)

paration and baking of the solutions for 20 h at 700 °C. The careful choice of In is essential to improve the doping level of these layers at moderate baking times. First experiments of InP growth onto GaInAsP has been done successfully at low temperatures. High supersaturation and a high cooling rate resulted in cross hatch pattern free InP capping layers.

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