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# Metal organic vapour-phase epitaxy (MOVPE) growth of InP and InGaAs using tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) in N<sub>2</sub> ambient

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## Abstract

We have investigated the growth of InP and InGaAs/InP using TBA and TBP in N<sub>2</sub> ambient. This process eliminates both the explosive H<sub>2</sub> and the toxic hydrides as precursors. General growth aspects are reported and the process window for defect free growth is determined to be  $T_{\text{growth}} > 660^\circ$  and a minimal V/III ratio  $\leq 20$  at 100 mbar. The uniformity improves and the electrical characteristics are comparable or better than those of the standard MOVPE process. Broad area bulk (Q(1.57  $\mu\text{m}$ )) lasers reveal current densities below 2 kA/cm<sup>2</sup>. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In general, the metal organic vapour-phase epitaxy (MOVPE) process uses the toxic hydrides PH<sub>3</sub> and AsH<sub>3</sub> as group V-precursors. For safety reasons therefore many alternative, less toxic group V-sources have been investigated. Devices made from structures grown with the alternative group V-sources tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) exhibit state of the art performance see e.g., Ref. [1]. Also other alternative group V-precursors like diethyltertiarybutylarsine

(DEtBA) and ditertiarybutylphosphine (DitBuPH) reveal the ability to grow state of the art devices [2]. The compositional uniformity of quaternary material is significantly enhanced using TBA/TBP in vertical as well as horizontal reactors with H<sub>2</sub> as carrier gas [3].

Up to now point of use purified H<sub>2</sub> is the generally accepted carrier gas for MOVPE. For some years now efficient N<sub>2</sub> purifiers are also available. The electrical and optical characteristics of MOVPE-layers grown in N<sub>2</sub> ambient have been investigated and they show improvements in material quality [4,5]. Furthermore, a better wafer uniformity was obtained [6].

The combination of inert N<sub>2</sub> and TBA/TBP was used by Hsu et al. [7] to grow GaAs-based HBT structures, which show maximum oscillation

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frequencies ( $f_{\max}$ ) of up to 120 GHz. Furthermore, Zimmermann et al. [8] compared the use of  $H_2$  or  $N_2$  as carrier gas for the selective area growth (SAG) of InP-based structures using TBA and TBP as group-V sources. They performed their experiments on InP(0 0 1) substrates, patterned with  $SiN_x$  and cleaned/etched before growth. Use of  $N_2$  as carrier gas means an increase in safety and gives an additional parameter to control the gas-phase diffusion of the SAG process.

In contrast to Zimmermann et al. [8], we will report in the following on the combination of  $N_2$  and TBA/TBP for the planar growth on unpatterned InP in a commercial MOVPE system. This would provide an inherently “safe process” for MOVPE of III–V materials and in addition has the potential for increased wafer uniformity.

## 2. Experimental procedure

The growth of the InP and InGaAs layers was carried out in an AIXTRON 200/4 ( $3 \times 2''$ ) low-pressure MOVPE horizontal reactor. The carrier gas was SAES Getter purified nitrogen. The precursors were TBA, TBP, TMIn, and TMGa.  $H_2$  was always used for the MO-source lines. Thus the actual nitrogen content in the reactor was about 90%. The partial pressures were calculated with literature data [9] and the assumption of a linear dependence between the partial pressure and the source flow rate. The gas velocity was kept constant at 0.5 m/s and the growth parameters were  $P_{\text{tot}} = 50$  mbar and  $Q_{\text{tot}} = 8$  slm total flow or  $P_{\text{tot}} = 100$  mbar and  $Q_{\text{tot}} = 15$  slm. The growth temperature and the V/III ratio were varied in the range of 580–700°C and 5–75, respectively.

The growth rate was determined by weighing the typically 300 nm thick InGaAs- and InP-layers, with an estimated relative measurement error of  $\pm 4\%$ . InGaAs was grown at approximately 0.18 nm/s, whereas for InP approximately 0.2 nm/s was applied, except for the 2  $\mu\text{m}$  thick bulk layer for Hall measurement where 0.3 nm/s was used for InP. The composition was measured by high-resolution X-ray diffraction (HRXRD). The majority of the samples were grown on epi-ready InP:S substrates, which were nominally oriented in (0 0 1)

with an error of less than  $\pm 0.1^\circ$ . Before growth, the wafers were annealed in  $PH_3$  for 5 min at growth temperature, but at least at 610°C. Under these conditions, a defect-free surface for InP is obtained grown with  $PH_3$  in  $N_2$  at 610°C. An approximately 150 nm thick InP buffer layer, utilising  $PH_3$  in  $N_2$ , was grown at 610°C or higher temperatures for the InGaAs layers. No extended attempt to optimise the wafer treatment procedure before growth, e.g. through high-temperature annealing steps, was done. The surface characteristics were evaluated by Nomarski phase-contrast optical microscopy. The carrier concentration and mobility of the nominally undoped 2  $\mu\text{m}$  thick layers deposited on InP:Fe substrates, which were oriented in (0 0 1)  $\pm 0.3^\circ$ , was obtained from Hall measurements with van de Pauw geometry and a magnetic field of 4 kG.

## 3. Results and discussion

The growth rate depends, as expected, on the partial pressure of the MO's, the gas velocity and the total pressure [10]. However, it is independent on the V/III ratio within the measurement error of  $\pm 4\%$  (e.g. InP, 610°C, V/III = 5–75). This is an indication of very low parasitic gas-phase reactions in contrast to the  $PH_3$ /TMIn case in  $H_2$  [11]. Furthermore, Chui et al. [12] have reported a 30% growth rate decrease by changing the V/III ratio from 5 to 72 for GaAs using TBA in  $H_2$ . They explained this effect with the surface blocking by the TBA species. The influence of the growth temperature on the growth rate is shown for InP in Fig. 1. From 580 to 700°C the growth rate increases by 10%, which is typical for the diffusion limited growth.

The surface morphology for InP and InGaAs is shown in Figs. 2 and 3, respectively. The defect type and density varies primarily with growth temperature but also with V/III ratio. The different defect types are defined in the Appendix. Fig. 2 demonstrates that InP can be grown defect free only for temperatures higher than 660°C and appropriate V/III ratios (for  $P_{\text{tot}} = 50$  mbar at least around 40). Similarly, the defect-free growth of InGaAs is established for growth temperatures higher than

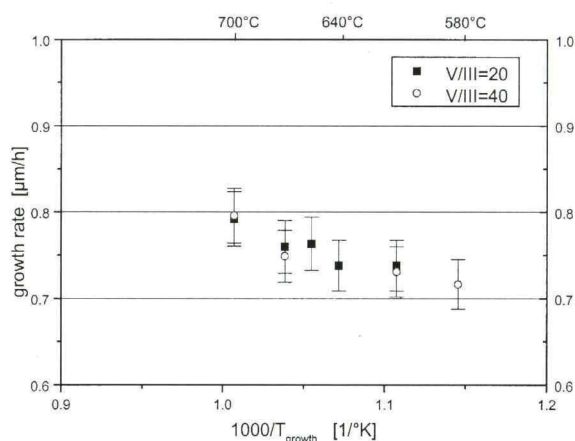


Fig. 1. Growth rate as a function of the inverse growth temperature for InP at different V/III ratios; with  $\text{TMIIn} = 9 \times 10^{-5} \text{ mol/min}$ ,  $P_{\text{tot}} = 50 \text{ mbar}$ ,  $Q_{\text{tot}} = 8 \text{ slm}$ . The growth rate is 10% higher at 700°C compared to 600°C but is independent on the V/III ratio.

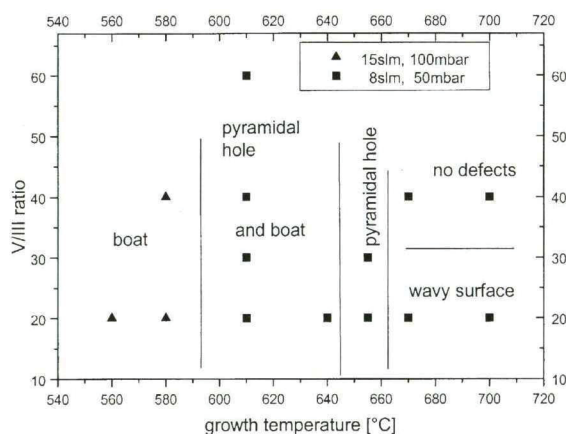


Fig. 2. Defect type distribution for InP grown at different growth temperatures and V/III ratios; with  $\text{TMIIn} = 9 \times 10^{-5} \text{ mol/min}$ ,  $P_{\text{tot}} = 50 \text{ mbar}$ ,  $Q_{\text{tot}} = 8 \text{ slm}$ . Defect free growth is obtained only for growth temperatures higher than 660°C with a V/III ratio  $\geq 40$ .

660°C and V/III ratios of at least 10 for 50 mbar as shown in Fig. 3.

Thus only appropriate V/III ratios (40 for InP and 10 for InGaAs at 50 mbar) and temperatures higher than 660°C result in smooth surfaces. These growth conditions are quite similar to our standard process utilising  $\text{AsH}_3/\text{PH}_3/\text{H}_2$  at 680°C [13].

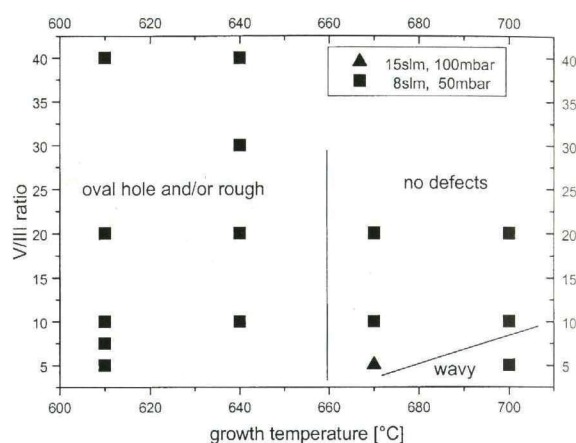


Fig. 3. Defect type distribution at different V/III ratios and growth temperatures for InGaAs; with  $\text{TMIIn} = 4.5 \times 10^{-5} \text{ mol/min}$ ,  $\text{TMGa} = 2.5 \times 10^{-5} \text{ mol/min}$ ,  $P_{\text{tot}} = 50 \text{ mbar}$ ,  $Q_{\text{tot}} = 8 \text{ slm}$ . Defect free growth is obtained only for growth temperatures higher than 660°C with a V/III ratio  $\geq 10$ . By increasing the growth pressure to  $P_{\text{tot}} = 100 \text{ mbar}$  with  $Q_{\text{tot}} = 15 \text{ slm}$ , the V/III ratio can be reduced to 5, to establish a defect free 300 nm thick InGaAs layer. But for a 2  $\mu\text{m}$  thick InGaAs layer the surface gets rough for a V/III ratio of lower than 10.

These relatively high growth temperatures for the alternative group V-sources are in contrast to the growth in  $\text{H}_2$ , where usually temperatures well below 650°C are used [2,14–16]. A possible explanation for this, is suppressed desorption of the butyl groups from the surface in  $\text{N}_2$ . The reduction of the wavy surface by increasing the V/III ratio and thus reducing the surface mobility is in correspondence with previous observations [17]. Furthermore, the wavy surface can be suppressed by a higher total pressure (Fig. 3). This reduces the surface mobility first by the higher pressure itself and second because increasing the pressure from 50 to 100 mbar results in less desorption of the group V-material, thus inducing a higher effective V/III ratio on the surface. This means that at higher total pressures the input V/III ratio can be reduced without degrading the material surface.

In contrast to this observation is the report of Hsu et al. [7]. They reported the growth of GaInP/GaAs in a horizontal MOVPE reactor utilising growth temperatures lower than 660°C using TBA/TBP in  $\text{N}_2$ . The reason for this discrepancy is

unclear but the higher bond strength of the GaAs-based material and thus an other surface chemistry could effect the defect formation. Furthermore, their use of  $\text{CCl}_4$  as carbon precursor results in reactive chlorine which etch the surface during growth and thus can suppress the defect formation. Zimmermann et al. [8] addressed the SAG growth with TBA/TBP/ $\text{N}_2$  at  $T_g = 610^\circ\text{C}$  without observing defects in the unmasked areas. This growth temperature is definitely lower than our observed growth window of  $T_g \geq 660^\circ\text{C}$  and cannot be explained by differences in the temperature measurement.

The electrical characteristics of InP and InGaAs were evaluated on 2  $\mu\text{m}$  thick layers grown without a buffer on InP:Fe substrates at  $680^\circ\text{C}$ ,  $P_{\text{tot}} = 100$  mbar and  $Q_{\text{tot}} = 15$  slm. The InP V/III ratio was 20 and for InGaAs 10. All samples were defect free, as defined in the Appendix. The carrier concentrations and mobilities are shown in Table 1 calculated for the nominal layer thickness. Table 1 shows the results for InP and InGaAs, and for comparison the typical electrical characteristics for our standard process with  $\text{PH}_3/\text{AsH}_3/\text{H}_2$  grown with the same growth parameters.

For InP the background doping was  $5 \times 10^{14}$  ( $3 \times 10^{14}$ )  $\text{cm}^{-3}$  at 300 K (77 K) and the mobility 3400 (66 000)  $\text{V s/cm}^2$ . For InGaAs we determined a carrier-concentration of  $2 \times 10^{14}$  ( $9 \times 10^{13}$ )  $\text{cm}^{-3}$  and a mobility of 9800 (50 000)  $\text{V s/cm}^2$ . Compared to the conventional process with  $\text{PH}_3/\text{AsH}_3$  under  $\text{H}_2$  (V/III ratio  $\approx 100$ ), the background dop-

ing level is reduced by a factor of approximately 5 for InP and 10 for InGaAs. No correction for the depletion layers was included in the Hall data calculation. Estimating the depletion layer widths, the background doping increases and the background doping difference is reduced by about a factor of 2. In conclusion, the use of the TBA/TBP/ $\text{N}_2$  process instead of the  $\text{PH}_3/\text{AsH}_3/\text{H}_2$  leads to an improvement in all electrical data, except for the 77 K mobility of InGaAs which we attribute to a lower conductive layer at the InGaAs/InP:Fe interface following a simple two conducting layer model for Hall measurements [18].

The relaxed mismatch variation of InGaAs over 40 mm of a 50 mm diameter wafer was reduced to less than 80 ppm as measured by HRXRD, as opposed to 150 ppm in the  $\text{H}_2$  case. Furthermore the uniformity for an InGaAs/InP MQW structure with 8 nm thick wells and 8 nm thick barriers also improves [6], and the area within a certain specified wavelength doubles compared to the  $\text{H}_2$  case as shown in Fig. 4. Apart from the improved InGaAs composition uniformity an improved thickness uniformity contributes to this MQW result. Further uniformity aspects have been discussed in more detail in Ref. [19].

To test the utility of this process with TBA/TBP/ $\text{N}_2$ , broad stripe DH-laser diodes with 200 nm thick 1.57  $\mu\text{m}$  quaternary material were processed. The threshold current density for  $900 \times 50 \mu\text{m}^2$  stripe lasers is 1.9  $\text{kA/cm}^2$ , which was comparable to the  $\text{PH}_3/\text{AsH}_3/\text{H}_2$  process [2].

Table 1

Hall-measurement data for InP and InGaAs are calculated without considering a depletion layer. (The growth was carried out at  $680^\circ\text{C}$  and 100 mbar with a V/III ratio of 20 and  $\text{TMin} = 1.3 \times 10^{-4}$  mol/min for InP, utilising TBP/ $\text{N}_2$ , whereas for InGaAs a V/III ratio of 10,  $\text{TMin} = 4.5 \times 10^{-5}$  mol/min and  $\text{TMGa} = 2.6 \times 10^{-5}$  mol/min, was used with TBA/ $\text{N}_2$ . For the  $\text{PH}_3/\text{AsH}_3/\text{H}_2$  process, a V/III  $\approx 100$  was employed. The background doping is reduced for the TBA/TBP/ $\text{N}_2$  process whereas the mobilities are the same for both processes)

| MOVPE-process                         | Temp.<br>(K) | InP                  |                       | InGaAs               |                       |
|---------------------------------------|--------------|----------------------|-----------------------|----------------------|-----------------------|
|                                       |              | ( $\text{cm}^{-3}$ ) | ( $\text{V s/cm}^2$ ) | ( $\text{cm}^{-3}$ ) | ( $\text{V s/cm}^2$ ) |
| TBA/TBP/ $\text{N}_2$                 | 300          | $5.0 \times 10^{14}$ | 3400                  | $2.0 \times 10^{14}$ | 9800                  |
|                                       | 77           | $3.0 \times 10^{14}$ | 66 000                | $9.0 \times 10^{13}$ | 50 000                |
| $\text{AsH}_3/\text{PH}_3/\text{H}_2$ | 300          | $3.0 \times 10^{15}$ | 3000                  | $3.0 \times 10^{15}$ | 9000                  |
|                                       | 77           | $1.0 \times 10^{15}$ | 60 000                | $1.0 \times 10^{15}$ | 62 000                |

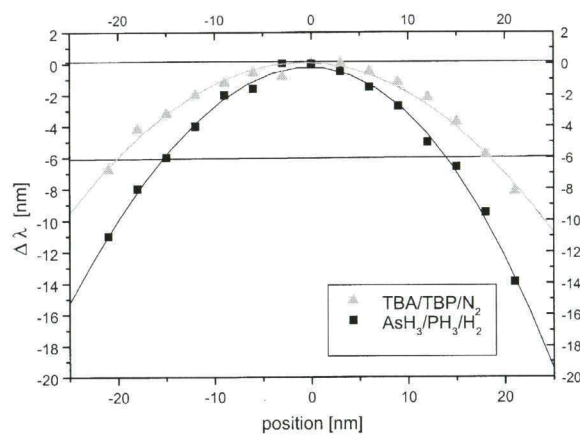


Fig. 4. The absolute wavelength deviation ( $\Delta\lambda$ ) of  $PL_{\max}$  for a MQW structure is shown for 40 mm of a 2" wafer grown with TBA/TBP/ $N_2$  and  $AsH_3/PH_3/H_2$ . The MQW consists of  $20 \times 8$  nm thick InGaAs wells and 8 nm thick InP barriers. The two lines at  $-6$  and  $0$  nm indicate a hypothetical useful wafer area within a tolerance of  $\pm 3$  nm. Thus, the useful wafer area doubles for the TBA/TBP/ $N_2$  process.

#### 4. Conclusions

It is shown that the defect-free deposition of InP and InGaAs/InP via MOVPE is possible using TBP and TBA in  $N_2$  ambient. The growth window for this process is evaluated and the growth temperature for defect-free deposition is higher than  $660^\circ\text{C}$  and the V/III ratio is roughly 10–20% of the standard MOVPE process. The electrical properties are comparable or better than with the standard process ( $PH_3$ ,  $AsH_3$  in  $H_2$ ). With the new process it is possible to grow good quality DH-lasers. The uniformity across the wafer improves significantly with respect to composition as well as thickness.

#### Acknowledgements

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#### Appendix A. Defect types

The different kinds of defects, which were observed during this investigation, are defined in the

following. Figs. 5a–c show optical microscope pictures of some defects. The defect dimensions can be obtained from these pictures and were cross checked by AFM investigations.

An *oval hole defect* (Fig. 5a) has an oval shape in the dimension of up to  $8\ \mu\text{m}$  long and  $3\ \mu\text{m}$  wide. The plateau in the middle of the defect is about 30 nm lower than the wafer surface and has steep borders. In the middle of these plateaus usually a small swelling is situated with a height of 3 nm relative to the plateau-ground. The longer dimension of the ovals lies in the  $[0\ \bar{1}\ 1]$  direction. The dimensions of the defects on a wafer vary. This kind of defect seems to be the same as the type IV defect in Ref. [20].

A *boat defect* (Fig. 5b) has also an oval shape with the dimensions of up to  $25\ \mu\text{m}$  long and  $6\ \mu\text{m}$  wide. The top of the defects is about 100 nm higher than the wafer surface and the side planes show crystallographic planes. The orientation of the long direction is in  $[0\ 1\ 1]$  and thus perpendicular to the oval hole defect. The defect sizes differ on the wafer.

A *pyramidal hole defect* (Fig. 5c) has the shape of an inverted pyramid with the dimensions of  $13 \times 13\ \mu\text{m}^2$ . The "top" of these defects is about 35 nm lower than the wafer surface and the sides are oriented in  $\langle 0\ 1\ 1 \rangle$ . The sizes of the defects are the same on a wafer. Furthermore, this type is usually not statistically distributed over the wafer but lined up, especially in the  $[0\ \bar{1}\ 1]$  direction close to the big flat.

A *wave defect* shows a regular, wave like surface modulation with an amplitude of 2.5 nm and a "period" of  $3\ \mu\text{m}$ . It can be reduced with higher V/III ratio or lower growth temperature [17].

The surface is called *rough*, if the amount of defects is so large that no separate defect type can be detected with respect to the upper definitions. Thus, the amount of defects is so large that they interfere/collide with each other.

A wafer is called *defect free* if the wafer has no wave-defects, is not rough and has less defects than  $15/\text{cm}^2$  of the above or other types.

Whether a defect is caused by the substrate or by the growth conditions is difficult to say, because both these effects cannot be separated. But if the size of the observed defects is the same over

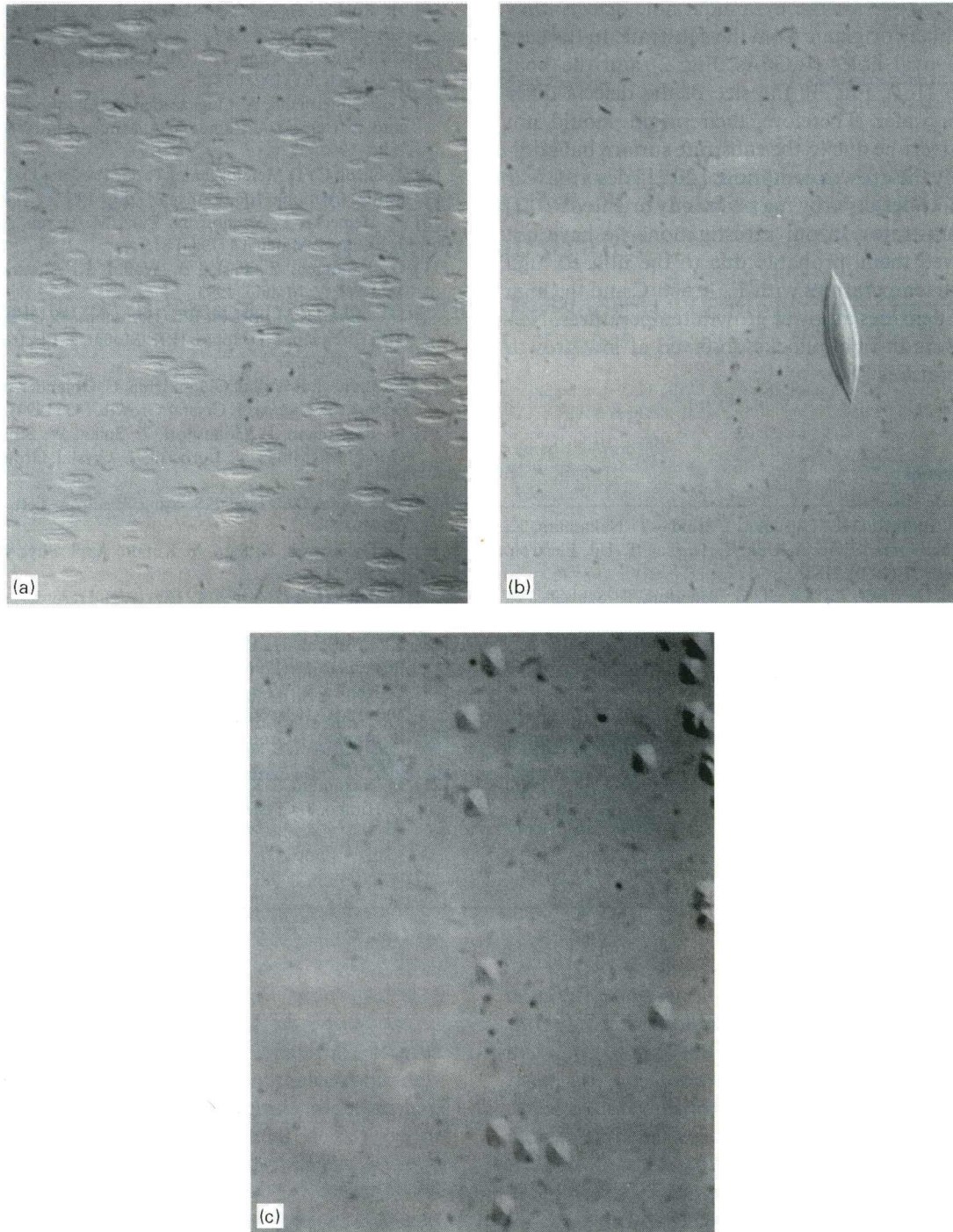


Fig. 5. Optical microscope photo of: (a) oval hole defects with a magnification of  $1000\times$ ; (b) a boat defect with a magnification of  $1000\times$ ; (c) pyramid hole defects with a magnification of  $400\times$ .

the wafer, e.g. for the pyramidal hole defects, they more likely originate from the substrate. In the case of the oval holes (InGaAs, Fig. 2) and the boat defects (InP, Fig. 3), the size of the defects differ over a wafer. Therefore, their origin should not exclusively be due to the substrate surface but additionally the growth conditions [20,21] describe tear drop like defects growing on exactly oriented (0 0 1) InP substrates. In our investigations we have not observed them, probably due to the utilised high growth temperatures with  $T_g \geq 660^\circ\text{C}$  and the high defect densities at lower growth temperatures. Neither were in-rich hillocks observed at low growth temperatures [14].

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