

V. GOTTSCHALCH, G. KNOBLOCH, E. BUTTER

Sektion Chemie der Universität Leipzig

Saturation Behaviour of In–Ga–As Melts and Growth of In_{0.53}Ga_{0.47}As Lattice-matched to (001) InP Substrates

This paper presents the saturation behaviour of In–Ga–As melts with monocrystalline GaAs. The coulometric As-analysis confirmed that the source-seed-technique produces In–Ga–As melts of defined compositions. The growth results of the step cooling technique applying both the source-seed technique and the single phase melts are compared.

In dieser Arbeit wird das Sättigungsverhalten von In–Ga–As Schmelzen mit einkristallinem GaAs beschrieben. Die Coulometrische As Analyse der Schmelzen zeigt, daß die Sättigungstechnik Schmelzen definierter Zusammensetzung liefert. Der step cooling Prozeß ergab sowohl für die Nutzung der Sättigungstechnik als auch für den Einsatz einphasiger Schmelzen gleiche Wachstumsergebnisse.

1. Introduction

The ternary mixed crystal In_{0.53}Ga_{0.47}As, lattice matched to (001) InP is an attractive material in the manufacture of emitters or detectors not only for fiber-optic communication but discrete electronic components as well.

In recent years the liquid phase epitaxy (LPE) was demonstrated as being an appropriate tool for depositing solid InGaAs solutions on InP with precise control of the compositional and layer thickness homogeneity, good surface morphology, minimum density of lattice defects and low charge carrier concentration.

Several methods, for instance step cooling (COOK et al.), supercooling (SAKAI et al.; PEARSALL et al. [1978]), equilibrium cooling (TABATABAIE-ALAVI et al.; PEARSALL et al. [1979]) and the two-phase solution technique (POLLACK et al.; ARAI et al.; HYDER et al.), have been extensively employed to grow such epitaxial layers. COOK et al. (1981), TABATABAIE-ALAVI et al., HSIEH and KUPHAL determined the required liquidus data by direct observation, where as NAKAJIMA et al. deduced the values from seed – solution experiments. The latter brought In–Ga–As melts and InP single crystal wafers into contact at varied temperatures. They considered the saturation temperature to be reached when no further melt attack to the solid appeared.

However, a current review of the application of the saturation technique shows only limited correspondence between the attained results. BENCHIMOL and QUILLEC produced supersaturated In melts by using differently oriented GaAs substrates as source materials. These ternary alloys revealed a remarkable capacity for growing thin InGaAs layers lattice matched to (001) InP at a constant temperature of 500 °C. ANTYPAS' experiments, employing a monocrystalline InAs supply, yielded comparable data.

In contradiction, NAKAJIMA et al. (1979) failed to produce a final saturation of the liquid phase with the same solute components. Similarly KUPHAL confirmed this effect, employing a GaAs source.

This work reports the experimental investigation of the GaAs solubility in ternary melts, consisting of In, Ga, and As. The saturation rates of a liquid In—Ga—As alloy, exposed to GaAs single crystals have been measured for their dependence on orientation, contact time and crystal area at a fixed temperature. The melts prepared in this way, were subsequently used to grow solid ternary solutions on (001) InP. These results, based upon the saturation technique were compared to those of the step cooling method with the exact charged constituent weights.

2. Experimental

The saturation experiments of In—Ga—As melts with GaAs followed by the growth of InGaAs layers on (001) InP have been carried out, applying a conventional linear graphite slider system. This equipment enables to use the advantages of the seed-solution-technique: both the accuracy of adjustment to contact time and the separation of single phase solutions. Figure 1 represents a schematic cross section of the growth vessel and illustrates the functions of its elements.

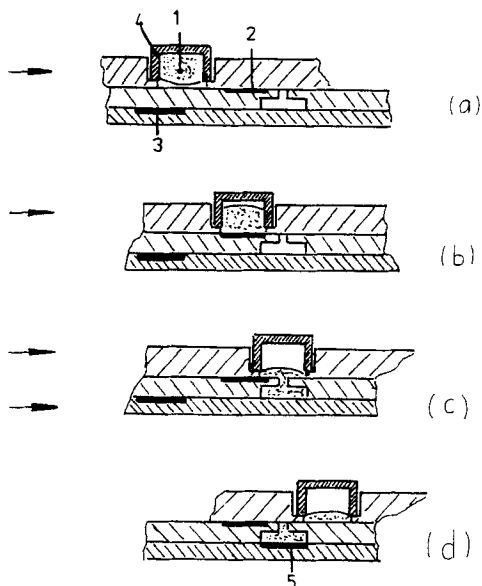


Fig. 1. Scheme of the employed sliding graphite boat during several phases of growth. a) homogenizing undersaturated In—Ga—As melts; b) the saturation with GaAs; c) the separation of the saturated melts; d) isothermal thin layer deposition following a supersaturation by lowering the temperature. (1) undersaturated In—Ga—As melt, (2) GaAs seed, (3) (001) InP substrate, (4) graphite container, (5) vessel containing a prepared growth melt

Not only the chemical treatment of the InP substrates and the source materials but also the preparation of the In—Ga—As batch melts are described elsewhere (GOTTSCHALCH et al.). The batch melts were composed to enable the growth of the InGaAs layers, lattice matched to (001) InP after being saturated by employment of the source-seed-technique. The fabricated single phase melt (Fig. 1 c, d (5)) either served the deposition of solid InGaAs solutions or the analysis of the As fractions. The determination of the As content in the seed-saturated alloys was accomplished both by the coulometric titration of the dissolved melts (KNOBLOCH, GOTTSCHALCH) and the measuring of the mass loss of the cleansed GaAs source materials.

3. Growth of (InGa)As lattice matched to InP

Additional preinvestigations have been made at fixed temperature in the same reactor, aimed at confirming evaluation of the starting conditions and growth results. The melt constitutions for various growth temperatures of $\text{In}_{.53}\text{Ga}_{.43}\text{As}$ layers were calculated using the following experimentally based equations (GOTTSCHALCH et al.), which correlate well with functions found by KUPHAL:

$$X_{\text{As}}(1 - X_{\text{As}}) = 151e^{-7276/T},$$

$$X_{\text{Ga}}(1 - X_{\text{Ga}}) = 1.25e^{-3655/T}.$$

Figure 2 reveals the influence of the liquidus composition on the lattice matched growth of InGaAs on InP at various temperatures.

The growth experiments were carried out at several deposition temperatures and varied Ga fractions in the melt. This procedure made it possible to record the exact solid-liquid

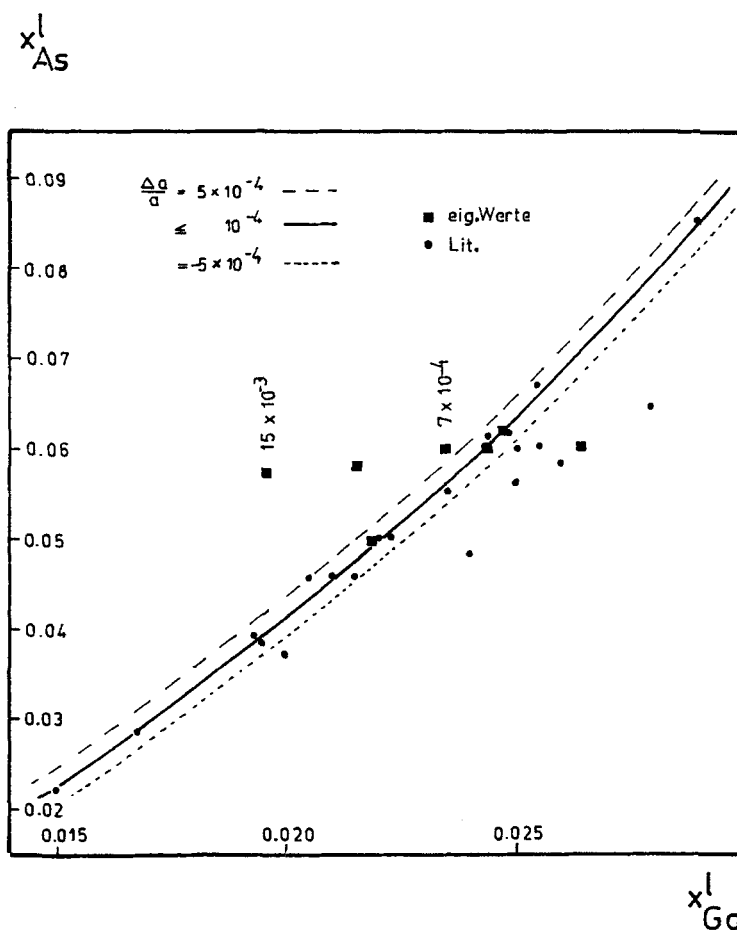


Fig. 2. The InGaAs lattice mismatch of InP in dependence on the As- and Ga fractions of the liquid phase

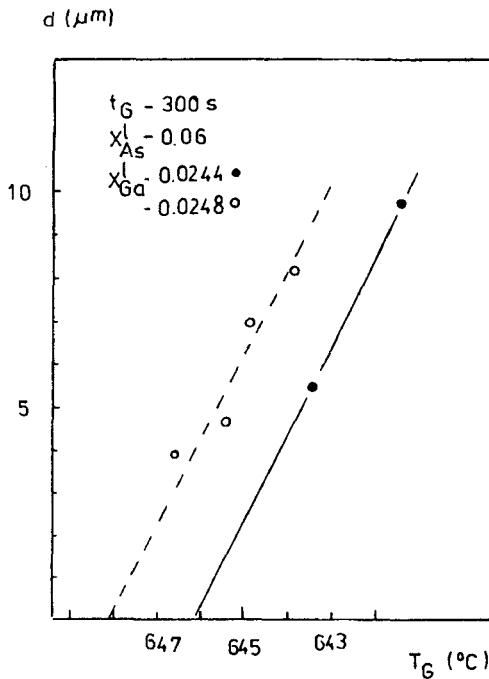


Fig. 3. The determination of the liquidus temperatures by measuring the achieved layer thicknesses in dependence on the supersaturation

(S-L)-equilibrium temperatures between the In–Ga–As melts and the (001) InP substrate whereas the effect of nucleation was neglected. Figure 3 shows the measured layer thicknesses as a function of supersaturation with a constant growth time (300 s) for two differently composed melts. Figure 4 illustrates the connected alteration of the perpendicular lattice mismatch $m = \Delta a/a = (a_{\text{InGaAs}} - a_{\text{InP}})/a_{\text{InP}}$ of the fabricated epilayers.

The listed melt composition values have been obtained from experiments accomplished in the described manner:

$$\begin{aligned} X_{(\text{Ga})} &= 0.0244, & X_{(\text{As})} &= 0.0602, & T^l &= 646.3^\circ\text{C}, \\ X_{(\text{Ga})} &= 0.0221, & X_{(\text{As})} &= 0.04995, & T^l &= 627.8^\circ\text{C}. \end{aligned}$$

These liquidus data supported the successful approach of depositing InGaAs layers of definite thicknesses lattice matched to (001) InP substrates. The observed effects of the experimental conditions can be mathematically expressed by means of calculated functions, valid for a growth temperature of 646 °C:

$$\begin{aligned} \Delta m / \Delta T &= -1.5 \cdot 10^{-4} \text{ K}^{-1}; & \Delta m / \Delta X_{(\text{Ga})}^l &= -1.7; \\ \Delta \lambda^{\text{PL}} / \Delta T &= -3.5 \text{ nm K}^{-1}. \end{aligned}$$

Furthermore, the thickness of the (InGa)As layers follows the diffusion limited growth model:

$$d(\mu\text{m}) = K \cdot \Delta T \cdot t^{0.5}$$

with the constants

$$K_{627.8} = 0.64 \mu\text{m K}^{-1} \text{ min}^{-0.5}, \quad K_{646.3} = 0.87 \mu\text{m K}^{-1} \text{ min}^{-0.5}.$$

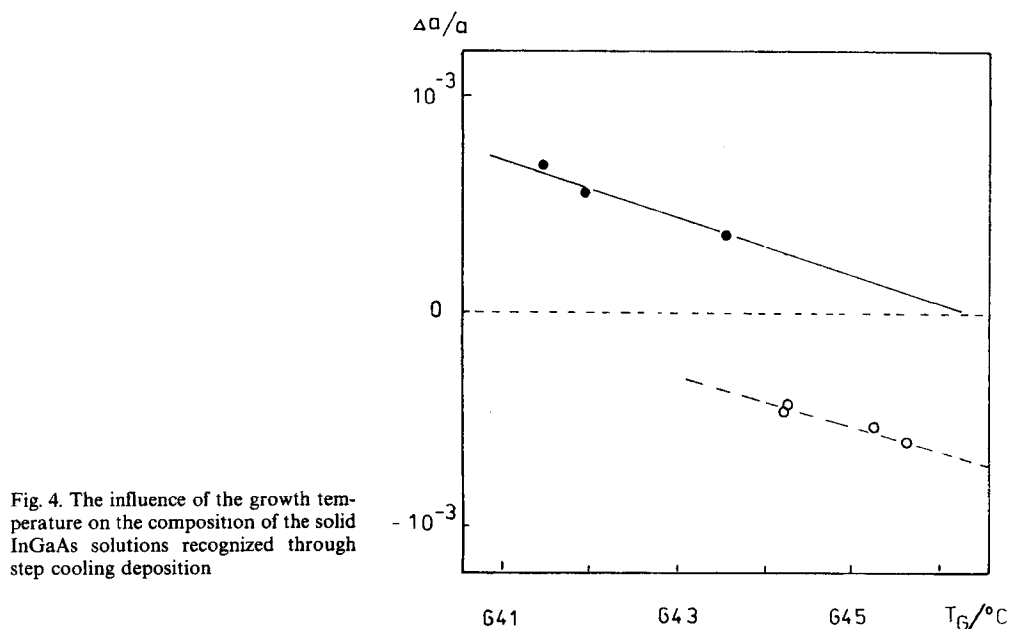


Fig. 4. The influence of the growth temperature on the composition of the solid InGaAs solutions recognized through step cooling deposition

4. Saturation behaviour of In–Ga–As melts with monocrystalline GaAs

Prepared In–Ga–As melts possessing a 70% or 90% saturation level relative to the GaAs content have been used for the investigations of their saturation behaviour under conditions of varied contact time of the melt and the seed, orientation and size of the GaAs source. The examination of the seed-saturated melt compositions was arranged by measuring the mass loss of the GaAs crystals and analysing the As content of the liquid phase (KNOBLOCH, GOTTSCHALCH). The coulometric As determination was preceded the dissolution of the melts by concentrated HNO_3 , its evaporation by H_2SO_4 (96%) and the reduction of As^{5+} to As^{3+} using $\text{N}_2\text{H}_6\text{SO}_4$.

A comparison of both methods is to be achieved by contrasting the As mass fractions (W_{As} = mass of As/mass of melt). Figure 5 features the time dependent saturation behaviour of In–Ga–As melts with differently oriented GaAs single crystals at 628.6 °C.

The following conclusions had been drawn:

- The As mass fractions determined through mass loss measurements exceeded the computed values of the phase diagram and show the dependence on the orientation of the solid state sources: $W_{(\text{As})}(111)\text{A} > W_{(\text{As})}(100) > W_{(\text{As})}(111)\text{B}$.
- On the other hand, the As quantities in the melts delivered through coulometric titration accord well with the theoretically awaited data and fall below the values, found by the other method. In addition no influence of the crystal orientation was experienced in this case.

Figure 6a reveals the dependence of the saturation behaviour on the extent of the S-L interface. Whilst the As values determined by mass loss measurements apparently increase, the coulometrical analysis exhibits constant As fractions in the liquid phase.

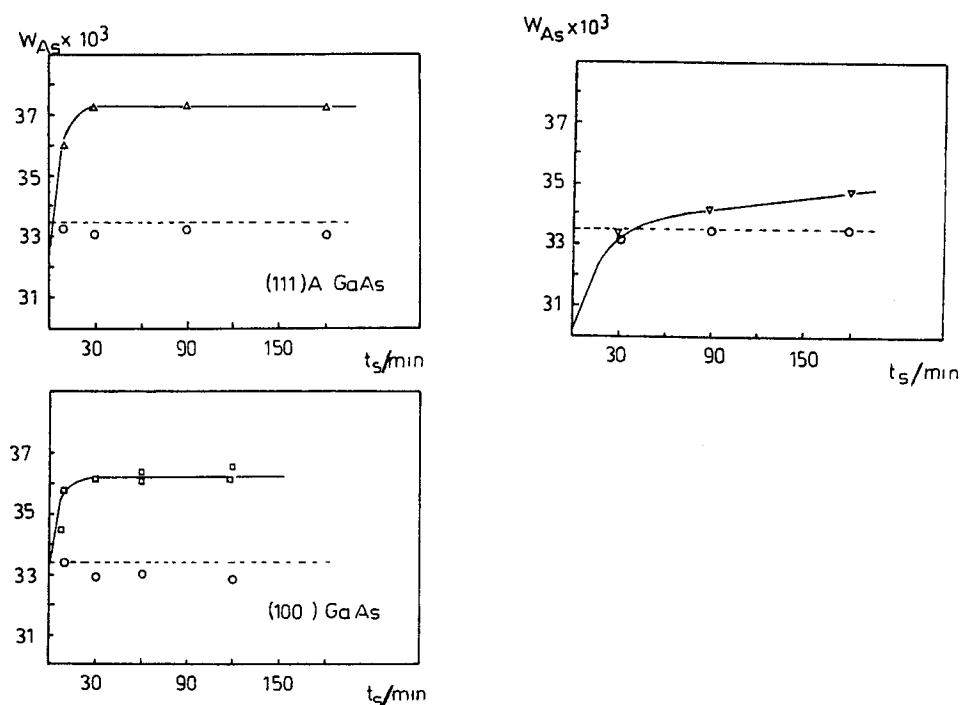


Fig. 5. Saturation behaviour of In–Ga–As melts employing differently oriented source materials. (a) (111)A-GaAs (b) (100)-GaAs (c) (111)B-GaAs. Δ , ∇ mass-loss-technique, \circ coulometric titration

However, polycrystalline (InGa)As depositions on the GaAs-source materials have also been indicated by X-ray- and ESCA investigations. Resulting from the experimental findings, the following saturation mechanism of In–Ga–As melts with GaAs can be assumed:

In the moment when the contact is brought about the ternary liquid phase and the binary crystals have to be considered to represent a non-equilibrium state. Therefore the system strives to achieve an equilibrium by formation of a ternary layer on the GaAs seeds. Recent research has demonstrated that (InGa)As of the given liquidus composition does not produce compact monocrystalline layers on (001) GaAs (BOLHOVIYANOW, VAULIN). Consequently a melt equilibrated polycrystalline (InGa)As deposition must protect the GaAs source from the liquid phase attacks. In contradiction to InP (its exposition to a liquid In–Ga–As phase yields a thin monocrystalline quaternary layer according to OE and SUGIYAMA) the processes at work on the GaAs surface strongly influence the melt composition and contribute to the deviations of the coulometrically found values from the As fractions, determined through mass loss measurements. Precise liquidus data were numerically computed, through both the employment of the values received by the use of the noted methods of examination and the analysis of the crystalline phase deposited on the $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ source. Figure 6b clearly shows that the Ga content in the melt alters according to the amount of deposited mixed crystals on GaAs even when the same As atomic fractions are applied and only the extent of the S-L interface varies. Subsequent growth experiments and compositional analysis of the formed (InGa)As epilayers have proved this phenomenon to be true. The same influence as described in paragraph 3 was detected.

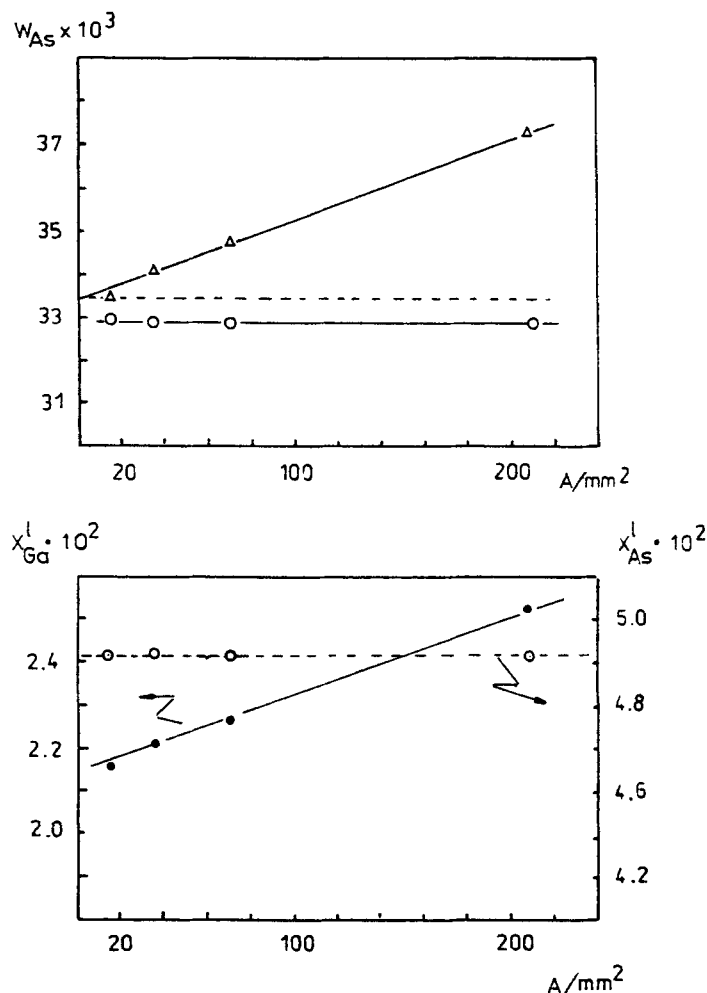


Fig. 6. Effects of the S-L interface size on the saturation behaviour: (a) the relationship between the As-fraction and the liquid phase wet GaAs surface; (b) the computed liquidus data as a function of the melt covered crystal surface

5. Summary

Using coulometrical As analysis it was confirmed that GaAs-saturated melts of definite compositions can be produced from In – Ga – As liquid phases employing the source-seed-technique. The extent of the S-L interface determines the amount of the deposited polycrystalline (InGa)As on the source materials and thus the melt composition. The mass and the mixing proportions of this polycrystalline material were shown to depend on the orientation of the seeds. (InGa)As layers, lattice matched to (001) oriented InP substrates have been successfully grown, applying liquid phases in both reported manners. The way in which melt preparation affected the deposition of the layers was not found to be of any significance.

The authors greatly indebted to Mr. Becher for technical assistance.

References

- ANTYPAS, G. A.: J. Electrochem. Soc. **117** (1970) 1393
ARAI, S., SUEMATSU, Y., ITAYA, Y.: IEEE, J. Quantum Electronics QE-**16** (1980) 197
BENCHIMOL, J. L., QUILLEC, M.: J. Physique **43** (1982) C5
BOLHOVITYANOV, Yu. B., VAULIN, Yu. D.: Thin solid films **98** (1982) 41
COOK, L. W., TASHIMA, M. M., TABATABAIE, N., LOW, T. S., STILLMAN, G. E.: J. Cryst. Growth **56** (1982) 475
COOK, L. W., TASHIMA, M. M., STILLMAN, G. E.: J. Electron. Mater. **10** (1981) 119
GOTTSCHALCH, V., RHEINLÄNDER, B., OELGART, G., GRÜHL, H.-G., BAYER, G., SCHWARZ, G., VOGEL, K.: Cryst. Res. Technol. **25** (1990) 637
HYDER, S. B., ANTYPAS, G. A., ESCHER, J. S., GREGORY, P. E.: Appl. Phys. Lett. **31** (1977) 551
HSIEH, J. J.: IEEE, J. Quantum Electronics QE-**17** (1981) 118
KNOBLOCH, G., GOTTSCHALCH, V.: Cryst. Res. Technol. **20** (1985) 1205
KUPHAL, E.: J. Cryst. Growth **67** (1984) 441
NAKAJIMA, K., KUSUNOKI, T., AKITA, K.: FUJITSU Scientific and Technical J. **16** (1980) 59
NAKAJIMA, K., TANAHASHI, T., AKITA, K., YAMAOKA, T.: J. Appl. Physics **50** (1979) 4975
OE, K., SUGIYAMA, K.: Appl. Phys. Letters **33** (1978) 449
PEARSALL, T. P., HOPSON, R. W., Jr.: J. Appl. Physics **48** (1977) 4407
PEARSALL, T. P., BISARO, R., ANSEL, R., MERENDA, P.: Appl. Phys. Lett. **32** (1978) 497
PEARSALL, T. P., QUILLEC, M., POLLACK, M. A.: Appl. Phys. Lett. **35** (1979) 342
POLLACK, M. A., NAHORY, R. E., DE WINTER, J. C., BALLMAN, A. A.: Appl. Phys. Lett. **33** (1978) 314
SAKAI, K., MATSUSHIMA, Y., AKIBA, S., YAMAMOTO, T.: Jap. J. Appl. Physics **18** (1979) 1009
TABATABAIE-ALAVI, K., PEREA, E. H., FONSTAD, C. G.: J. Electron. Mater. **10** (1981) 591

(Received, accepted January 9, 1991)

Authors' address:

Dr. V. GOTTSCHALCH, Dr. G. KNOBLOCH, Prof. Dr. sc. E. BUTTER
Sektion Chemie der Universität Leipzig
Linnéstr. 3
O-7010 Leipzig/FRG