

Lawrence Berkeley National Laboratory

Recent Work

Title

INFLUENCE OF THE InAs-GaAs MISCIBILITY GAP ON THE In/GaAs REACTION

Permalink

<https://escholarship.org/uc/item/4zq7s1jd>

Author

Ding, J.

Publication Date

1986-08-01

c.2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

Materials & Molecular Research Division

NOV 18 1986

LIBRARY AND
DOCUMENTS SECTION

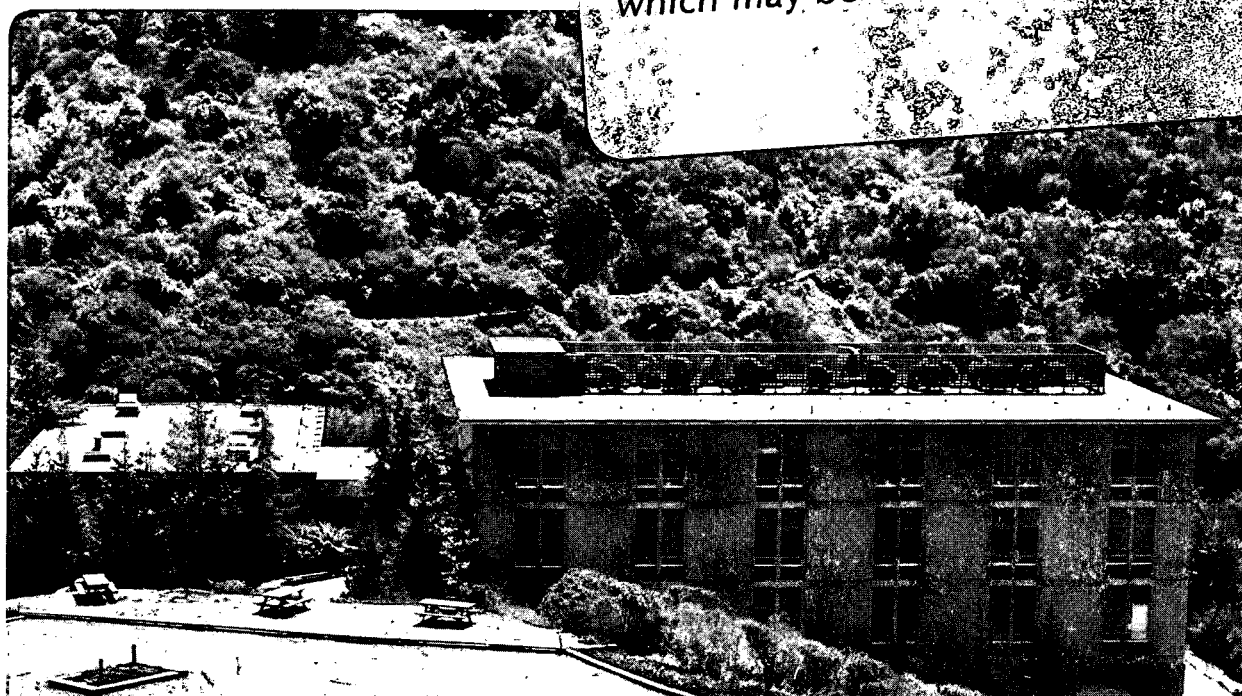
Presented at the 13th International Symposium on
Gallium Arsenide and Related Compounds,
Las Vegas, NV, September 28, 1986

INFLUENCE OF THE InAs-GaAs MISCIBILITY
GAP ON THE In/GaAs REACTION

J. Ding, J. Washburn, T. Sands,
and V.G. Keramidas

August 1986

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks



LBL-22082
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

INFLUENCE OF THE InAs-GaAs MISCIBILITY
GAP ON THE In/GaAs REACTION

J. Ding and J. Washburn

Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

T. Sands and V.G. Keramidas

Bell Communications Research, Inc.
600 Mountain Ave., Murray Hill, NJ 07974

This work was supported by the Director, Office of Energy Research,
Office of Basic Energy Sciences, Materials Science Division of the
U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

INFLUENCE OF THE InAs-GaAs MISCIBILITY GAP ON THE In/GaAs REACTION

J. Ding, J. Washburn, T. Sands* and V.G. Keramidas*

Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

*Bell Communications Research, Inc., 331 Newman Springs Road, Red Bank, NJ 07701

Abstract. The In/GaAs reaction in the temperature range 350–650°C has been studied by analytical and high resolution electron microscopy and electron and x-ray diffraction. Histograms of the compositions of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ precipitates formed during annealing confirm the existence of a miscibility gap in the InAs-GaAs pseudo-binary system. Implications of these results for the fabrication of graded layer $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{n-GaAs}$ ohmic contacts by thermal reaction are discussed.

1. Introduction

Graded $\text{In}_{1-x}\text{Ga}_x\text{As}$ layers on GaAs grown by molecular beam epitaxy (MBE) have been shown to make low-resistance ohmic contacts to n-GaAs (Woodall et al. 1981). Woodall et al. argue that the grading is necessary to smooth out the conduction band discontinuity so that ohmic conduction can occur. Previous Auger electron spectroscopy studies by Lakhani (1984a, 1984b) suggest that a graded $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ heterojunction ($0 \leq x \leq 1$) can also be formed by heat treating thermally-evaporated indium films on GaAs substrates at 350°C. Recently, the interface structures and morphologies of In on GaAs after annealing at 350°C were investigated by Ding et al. (1986) using transmission electron microscopy techniques. The result of this study demonstrated the abrupt nature of the interface between the GaAs substrate and the $\text{In}_{1-x}\text{Ga}_x\text{As}$ islands. Contrary to the results of Lakhani (1984a, 1984b), the $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ interfaces were not graded. Furthermore, only islands with $x \leq 0.2$ or $x \geq 0.8$ were observed. Ding et al. (1986) proposed that the absence of precipitates with $0.2 < x < 0.8$ is direct evidence for a miscibility gap in the InAs-GaAs pseudo-binary system at 350°C. This interpretation is consistent with the calculations of de Cremoux et al. (1981) which suggest the existence of a miscibility gap with a critical temperature between 500°C and 700°C in the InAs-GaAs system. Other theoretical analyses with similar conclusions were reported by Stringfellow (1982) and Onabe (1982). Quillec et al. (1982) grew a series of InGaAsP thin films from the liquid phase on both (100) GaP and (100) InP substrates at relatively high temperatures (610°C ~ 670°C). The experimental results from electron microprobe analyses indicated the existence of a miscibility gap in the $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system, supporting the previous theoretical results. The miscibility gap originates from an enthalpy of mixing (ΔH_{mix}) which is greater than the absolute temperature multiplied by the entropy of mixing ($T\Delta S_{\text{mix}}$) at temperatures below some critical temperature, T_c . Atomistically, immiscibility in a system such as InAs-GaAs

implies that In and Ga atoms repel so that a random distribution of Ga and In on the cation sites of the zincblende structure is not energetically favorable.

In this paper, we extend our previous study of the In/GaAs reaction to include the temperature range 350°C-650°C. Data obtained by electron diffraction, energy dispersive x-ray analysis (EDS) and x-ray diffraction (XRD) clearly demonstrate the extent of the InAs-GaAs immiscibility and suggest a critical temperature between 575°C and 650°C.

2. Experiment and Data Analysis Procedure

Liquid encapsulated Czochralski (LEC) semi-insulating wafers were prepared for In deposition by an ultra-high vacuum (UHV) technique that was described in detail by Ding *et al.* (1986). Following this UHV cleaning procedure, In was deposited onto the rotating substrate (8RPM) to a thickness of 57 nm (~5.7 nm/min.) at 25°C. In order to investigate the miscibility gap in the pseudo-binary InAs-GaAs system, the samples were divided into four groups and annealed for 10 minutes at 350°C, 500°C, 575°C and 650°C respectively in an atmosphere of flowing forming gas (95% Argon, 5% Hydrogen). Both cross-sectional and plan-view TEM samples were prepared by standard techniques (Sands 1986). Observations of each sample were made in a scanning electron microscope (SEM), a Philips 301 TEM and a JEOL 200CX TEM. Energy dispersive x-ray spectrometry (EDS) was performed in a Philips 400ST TEM/STEM, and x-ray diffraction in a Siemens D500 x-ray diffractometer. The $\text{In}_{1-x}\text{Ga}_x\text{As}$ phases formed at the In/GaAs interface after annealing at the various temperatures were identified by electron diffraction analysis and energy dispersive x-ray spectra. Since the ternary $\text{In}_{1-x}\text{Ga}_x\text{As}$ phases exhibit a linear dependence of lattice spacing with composition (Woolley *et al.* 1958), i.e., they obey Vegard's law, the compositions of the precipitates studied can be determined by electron diffraction analysis, especially for In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ precipitates. Due to the overlap of diffraction spots from GaAs and Ga-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$, the estimation of composition by electron diffraction was not straightforward for $x \sim 1$. Instead, the compositions of these Ga-rich precipitates were estimated by applying the EDS technique to cross-sectional samples. The EDS spectra were quantitatively analyzed by determining the proportionality factors K_x/y which relate the height ratios H_x/H_y of the x-ray peaks (proportional to the total counts or intensities) to the concentration ratios $[X]/[Y]$ of the elements X,Y. The relationship between the concentration ratio and the peak height ratio is expressed as:

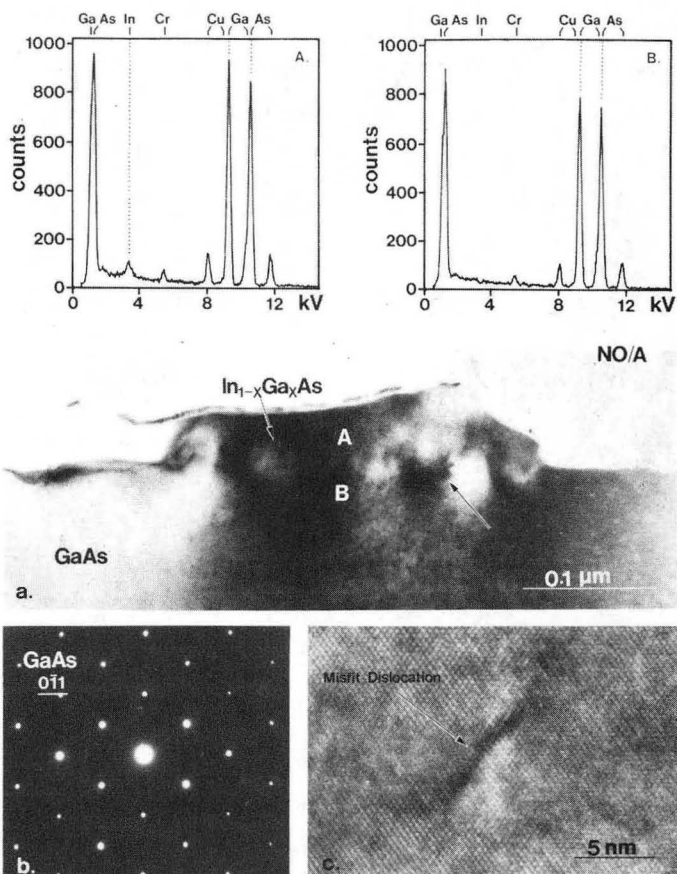
$$[X]/[Y] = K_x/y \cdot H_x/H_y$$

where the proportionality factor $K_{\text{Ga/As}}$ relates the heights of the Ga and As $K\alpha$ peaks in spectra taken from the adjacent GaAs substrate. The value of x in the $\text{In}_{1-x}\text{Ga}_x\text{As}$ is then given by the ratio $[X]/[Y]$ determined from spectra taken from the $\text{In}_{1-x}\text{Ga}_x\text{As}$ precipitate.

3. Results

The interface morphology of the In/GaAs sample after annealing at 350°C for 10 minutes is depicted in Fig. 1. The two beam bright field TEM image is shown in Fig. 1a. A thin film of indium oxide can be seen to cover the reacted island. This precipitated phase has been identified structurally by electron diffraction analysis and compositionally by energy dispersive spectrometry. The EDS spectra from the island A and the substrate B

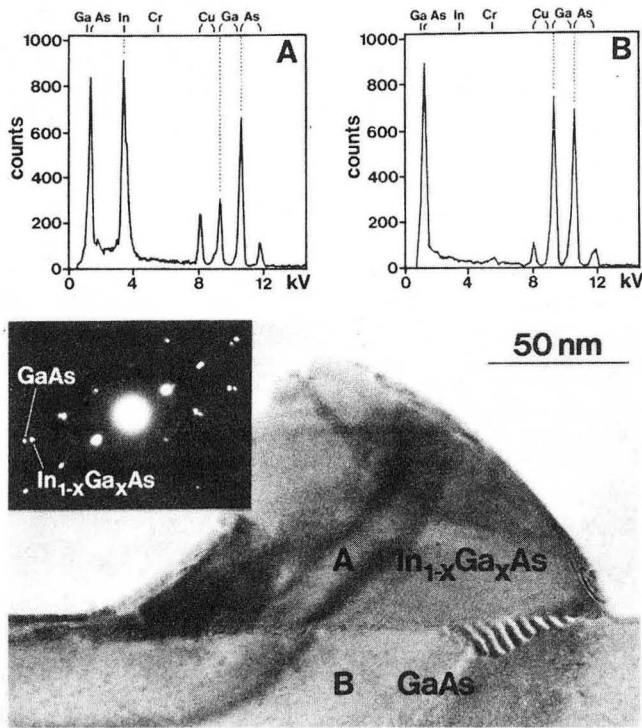
Fig. 1. (a) HRTEM image of the annealed oxide-free sample. The misfit dislocations can be seen at the interface. The indium oxide shell appears on the surface of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ phase. Quantitative microanalysis of the energy dispersive x-ray spectrum A indicates the patch A to have the composition of $\text{In}_{0.02}\text{Ga}_{0.98}\text{As}$. (b) Diffraction pattern taken from the island A and the substrate B shows only the reflections from the GaAs [011] zone axis orientation. (c) Lattice image of a misfit dislocation (arrowed in (a)) at the interface.



XBB 862-1253

(shown above the image) yield a composition of $\text{In}_{0.02}\text{Ga}_{0.98}\text{As}$ for the Ga-rich ternary phase with the zincblende structure. The diffraction pattern from the interface region shown in Fig. 1b indicates that it is almost impossible to distinguish the diffraction spots of this ternary phase from those of the GaAs substrate because of the small concentration of indium in this epitaxial island. The high resolution lattice image in Fig. 1c reveals the detailed interface morphology. A misfit dislocation can be seen at the interface due to the mismatch (0.16%) between the Ga-rich ternary phase $\text{In}_{0.02}\text{Ga}_{0.98}\text{As}$ and the GaAs substrate. Another example of a precipitate from the same sample is shown in the cross-sectional high resolution micrograph in Fig. 2. The misfit dislocations and moiré fringes appear at the interface, where they result from the two distinct lattice parameters of the epitaxial island and the GaAs substrate. This indicates that the interface is abrupt, i.e., no graded $\text{In}_{1-x}\text{Ga}_x\text{As}$ layer exists at the interface. Based on Vegard's law, the epitaxial island was identified from the diffraction analysis to be the In-rich ternary phase $\text{In}_{0.9}\text{Ga}_{0.1}\text{As}$. The EDS data also confirm that the island is In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$. Precipitates with compositions ($0.2 < x < 0.8$) were not observed.

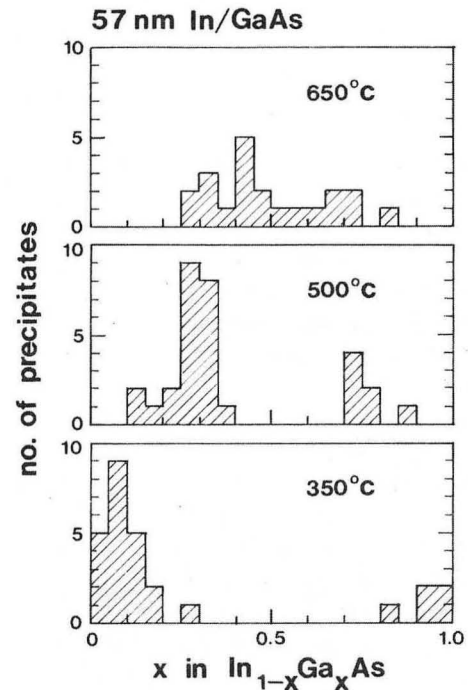
According to the theoretical calculations of de Cremoux *et al.* (1981), a miscibility gap exists in the InAs-GaAs pseudo-binary system with a critical temperature between 500°C and 700°C. To investigate the effect of immiscibility on the In/GaAs reaction, a statistical study was performed by annealing the In/GaAs samples at 350°C, 500°C, 575°C and 650°C. Several cross-sectional specimens from each sample were investigated by TEM and STEM. The distributions of precipitate compositions were determined by electron diffraction and EDS analyses. As can be seen in Fig. 3, three histograms from three different annealing temperatures reveal the extent of immiscibility in this system. It is also clear from the histograms



XBB 862-933

Fig. 2. High resolution image of the annealed cross-sectional oxide-free sample. The misfit dislocations and the moiré fringes indicate an abrupt interface. Inset diffraction pattern was taken from the region including the reacted patch A and the substrate B. The patch A was estimated to be $\text{In}_{0.9}\text{Ga}_{0.1}\text{As}$ by diffraction analysis. The energy dispersive x-ray spectra obtained from the patch A and the substrate B are also shown to identify the patch as $\text{In}_{1-x}\text{Ga}_x\text{As}$.

that the critical temperature (i.e., the temperature above which InAs and GaAs are completely miscible) is between 500°C and 650°C. This miscibility gap in the InAs-GaAs pseudo-binary system was also revealed experimentally by x-ray diffractometry. The x-ray results from this system are shown in Fig. 4. Slow traces of the 400 peaks of the GaAs substrate and $\text{In}_{1-x}\text{Ga}_x\text{As}$ ($0 < x < 1$) precipitates were obtained by employing $\text{CuK}\alpha$ radiation in an x-ray diffractometer. When compared with the spectrum from the as-deposited sample, the spectrum from the sample annealed at 350°C shows an additional peak corresponding to In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ and a shoulder on the GaAs 400 peak corresponding to Ga-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$. This result is in agreement with EDS and electron diffraction data in Fig. 3. As the annealing temperature is increased, the In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ 400 peak shifts toward the direction of increasing Ga content (i.e., increasing x). The diffraction peak from the In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ ternary phase peak merges with the Ga-rich shoulder at 650°C, suggesting that the critical temperature is close to 650°C. Furthermore, it is apparent from the broad Ga-rich shoulder in the x-ray data that significant interdiffusion is taking place at 650°C.



XBL 868-3109

Fig. 3. Histograms of the numbers of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ precipitates with respect to composition x from the three samples annealed at the different temperatures (350°C, 500°C and 650°C).

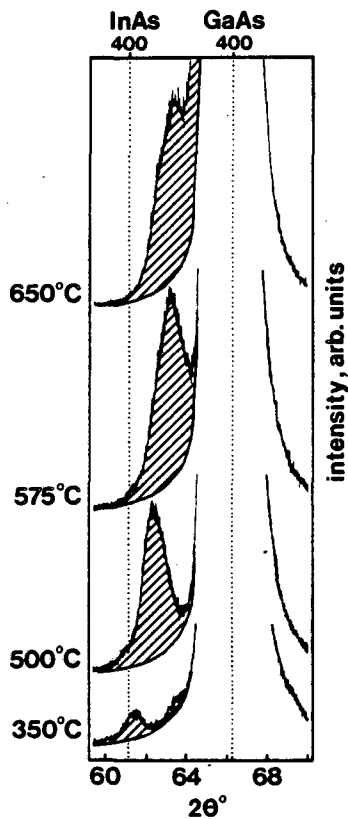
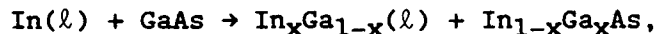


Fig. 4. Slow trace XRD patterns of the 400 reflections of as-deposited In on (100) GaAs, and after annealing for 10 minutes at 350°C, 500°C, 575°C and 650°C, respectively (CuK α radiation). Each trace is compared with the trace from the as-deposited sample (broken line).

4. Discussion

The assumption is that the system rapidly approaches equilibrium. The observation that there is extensive reaction even at temperatures as low as 350°C excludes solid state interdiffusion between In and Ga as the reaction mechanism for temperatures <650°C. This is in agreement with a previous study (Ding *et al.* 1986) where the reaction involving the dissolution of Ga and As into the molten In (melting $T \sim 156^\circ$) and the subsequent precipitation of $\text{In}_{1-x}\text{Ga}_x\text{As}$ was discussed. In the reaction of the form



the presence of a liquid phase ensured that mixing was rapid and that the final states of the system, after annealing is close to equilibrium.

Such a reaction can be qualitatively understood by reference to a hypothetical isothermal section of the In-Ga-As phase diagram for $T < T_c$ (Fig. 5). From this schematic diagram, it is apparent that when a limited amount of GaAs is involved in the reaction, as many as three phases, namely In-Ga(ℓ), In-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ and Ga-rich $\text{In}_{1-x}\text{Ga}_x\text{As}$ can result. We propose that in the initial stages of the reaction, Ga and As are dissolved into the molten In so that the average composition of the system remains on the vertical line connecting In and GaAs. As more Ga and As are incorporated

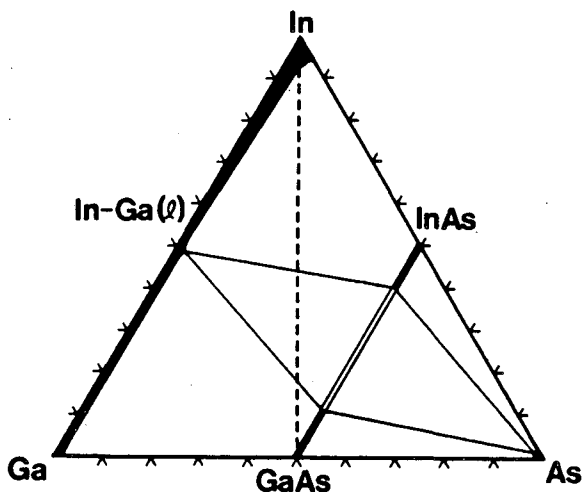


Fig. 5. Schematic isothermal sections of In-Ga-As phase diagram at a temperature below T_c . Assuming no loss of arsenic during annealing, the average composition of the system remains on the vertical dashed line.

into the molten material, i.e., as the molten In-Ga-As becomes supersaturated in Ga and As, the driving force for nucleation increases. Nucleation of $\text{In}_{1-x}\text{Ga}_x\text{As}$ occurs at some time during the annealing treatment, most likely during cooling. The compositions of the phases formed depend on the degree of supersaturation at the time of nucleation. Misfit dislocations were observed only at the $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ interface and no diffraction spot streaking (indicative of compositional grading) was detected. These observations suggest that once a precipitate is nucleated, it continues to grow at the same composition. The strain energy or dislocation energy associated with spatial variations in composition will inhibit compositional grading.

5. Conclusion

The experimental results described in this paper provide direct evidence for the existence of a miscibility gap in the InAs-GaAs pseudo-binary system. It follows that the formation of graded $\text{In}_{1-x}\text{Ga}_x\text{As}$ ($0 < x < 1$) layers by thermal reaction of In on GaAs is not possible under furnace annealing conditions (slow heating and cooling) unless the annealing temperature is above the critical temperature, estimated in this study to be between 575°C and 650°C . If a graded layer is indeed necessary to form a low-resistance In-base ohmic contact to n-GaAs (i.e. to smooth out the InAs-GaAs conduction band discontinuity), our results suggest that fabrication of graded $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ ohmic contacts by thermal reaction must involve annealing at temperatures above the critical temperature. Observation of ohmic conduction in In/GaAs samples annealed at temperatures significantly below T_c (Lakhani 1984a, 1984b) can only be attributed to other mechanisms such as thermionic-field emission at small diameter protrusions in the $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ interface (see Fig. 2).

Acknowledgments

It is a pleasure to acknowledge the expert technical assistance of Tom Brennan of Bell Communication Research, Inc. for the thin film deposition. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

- Cremoux, B. de, Hirtz, P. and Ricciardi, J., 1981 Inst. Phys. Conf. Ser. 56 115.
 Ding, J., Washburn, J., Sands, T. and Keramidis, V.G., 1986 Appl. Phys. Lett. 49 818.
 Lakhani, A.A., 1984a J. Appl. Phys. 56 1888.
 Lakhani, A.A. 1984b Materials Lett. 2 508.
 Onabe, K., 1982 Japan J. Appl. Phys. 21 L323.
 Quillec, M., Daguet, C., Benchimol, J.L. and Launois, H., 1982 Appl. Phys. Lett. 40 325.
 Sands, T., 1986 Mat. Res. Soc. Symp. Proc. 62 in press.
 Stringfellow, G.B., 1982 J. Crystal Growth 58 194.
 Woodall, J.M., Freeouf, J.L., Pettit, G.D., Jackson, T. and Kirchner, P., 1981 J. Vac. Sci. Technol. 19 626.
 Woolley, J.C. and Smith, B.A., 1958 Proc. Phys. Soc. Lond. 72 214.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*