

Received by OSTI

SEP 25 1992

Center for Advanced Materials

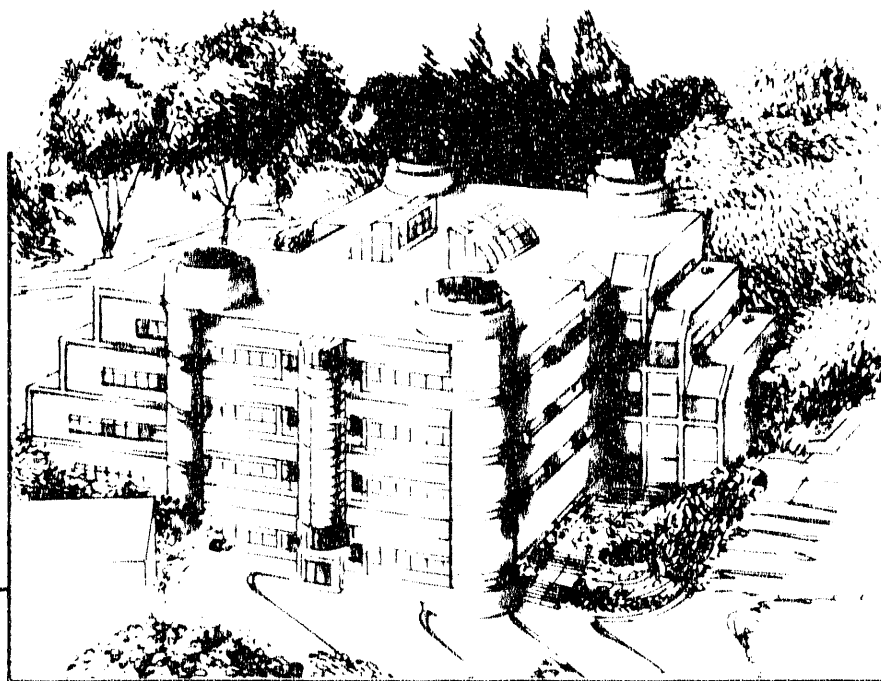
CAM

To be presented at the Materials Research Society
Spring Meeting 1992, San Francisco, CA,
April 27-May 11, 1992, and to be published
in the Proceedings

**TEM Structure Investigations of Low-Temperature
MBE Grown InAlAs Layers on InP<001> Substrate**

P. Werner, Z. Liliental-Weber, K.M. Yu, E.R. Weber,
Z. Rek, and R. Metzger

April 1992



Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4785

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. 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 liability or 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 and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

This report has been reproduced directly from the
best available copy.

TEM STRUCTURE INVESTIGATIONS OF LOW-TEMPERATURE MBE GROWN INALAS LAYERS ON INP<001> SUBSTRATE

P. WERNER*, Z. LILIENTAL-WEBER*, K.M. YU*, E.R. WEBER*,
Z. REK**, R. METZGER***

*Materials Sciences Div., Lawrence Berkeley Laboratory, LBL--32470
Univ. California, Berkeley, CA 94720

**Stanford Synchrotron Radiation Laboratory, Stanford DE92 041199
University, CA 94309

***Hughes Research Laboratories, Malibu, CA 90265

ABSTRACT

The real crystal structure of $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ layers grown on $\text{InP}<001>$ substrate as a function of the growth temperature (between 150°C and 450°C) was investigated. Following structural /electrical analysis were applied to the samples: transmission electron microscopy (TEM), x-ray diffraction and particle induced x-ray emission (PIXE). In the temperature range between 200°C and 450°C good epitaxial growth of InAlAs layers can be achieved with a low density of dislocations and stacking faults. Ordering of group-III elements on $\{111\}$ planes was observed for these layers. Structure models of such ordered domains are discussed. At growth temperatures below 200°C additional As ($\approx 2\%$) is incorporated in the lattice. Growth at temperatures below 200°C leads to the formation of pyramidal defects with As grains in their cores. As-grown as well as annealed InAlAs layers show a nearly constant, high electrical resistance (10^6 - $10^7 \Omega\text{cm}$) in the whole temperature range.

INTRODUCTION

During the recent few years semi-insulating GaAs could be successfully produced by MBE growth at low temperatures (LT) [1]. Following this effort the growth of ternary compounds such as InAlAs with similar properties has been attempted. The goal of this is to grow crystal layers with a good crystalline quality, high electrical resistivity and fast optical response. Such layers are useful for high-speed electronic and optical devices

$\text{In}_x\text{Al}_{1-x}\text{As}$ MBE layers grown on InP substrates show a good lattice match for $x=0.52$. In the growth temperature (T_g) region between 250°C and 450°C such InAlAs layers are characterized by a high electrical resistivity in the order of $10^7 \Omega\text{cm}$ [2]. This value is relatively constant over this temperature range for as-grown as well as thermally annealed samples. In the case of annealed LT-GaAs, the semi-insulating behavior has been assigned by some workers as due to the overlapping of depletion regions produced by As precipitates [3,4,5]. However, the mechanism which produce high electrical resistivity and short recombination times (several ps) in the case of InAlAs is presently not well understood. There have been up to now no hints in the literature that precipitates of metallic behavior can be generated in ternary semiconductor compounds by thermal annealing, which would be necessary for this concept [3]. Other structural defects such as dislocations or point defects have to be taken into consideration for the explanation of the semi-

insulating behavior of the InAlAs layers. In addition to the high resistivity this temperature range between 450°C and 250°C is also of technological interest since it also avoids an out-diffusion of dopants of neighbored structures or layers.

GaAs layers as well as InAlAs layers grown at temperatures below 200°C leads to the formation of pyramidal defects with As grains in their cores [6]. Such defects, which can act as recombination centers (recombination times ≈ 400 fs [9]) were found for the first time in LT-GaAs MBE layers (see e.g. [7,8]). Lattice strain in these layers due to the incorporation of an excess of As is most possibly responsible for the formation of these defects.

The low temperature is used for a stable growth of InAlAs layers. However, in the case of ternary compounds the situation seems to be more complicated. First, slight changes in the In/Al ratio during the MBE growth cause variations of the lattice constant. Second, the incorporation of additional As below T_g of 250°C leads to a further lattice strain. Lattice strain and mismatch between the InAlAs layer and the InP substrate are responsible for the occurrence of misfit dislocations or stacking faults [6]. A further study of these layers showed that the defect density can reach an amount of 10^8cm^{-2} [10]. However, these former investigations did not allow a clear distinction between these factors and their influence on the real structure of the layer.

It is the aim of this paper to study the dependence of the crystal structure of LT-InAlAs/InP on the growth temperature T_g , the In/Al ratio and the excess of As.

EXPERIMENTAL

A series of 1 μm thick $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ was grown by MBE on a semi-insulating $\langle 001 \rangle$ InP substrate with a growth rate of about 1 $\mu\text{m/h}$ and under an As_4 over pressure. The substrate temperature was varied between 150°C and 450°C. To compare the as-grown structure of the MBE layers with those after thermal annealing a part of the samples were heated at 500°C for 10min after the growth under As overpressure.

The In/Al ratio of 0.52/0.48 should allow a ideal lattice match between the LT-layer and the substrate (lattice constant $a=0.587\text{nm}$). The lattice match was checked during the MBE growth by x-ray rocking curves of the $\{004\}$ reflection. Since Al and As atoms have similar ion-radii in this sphalerite structure a

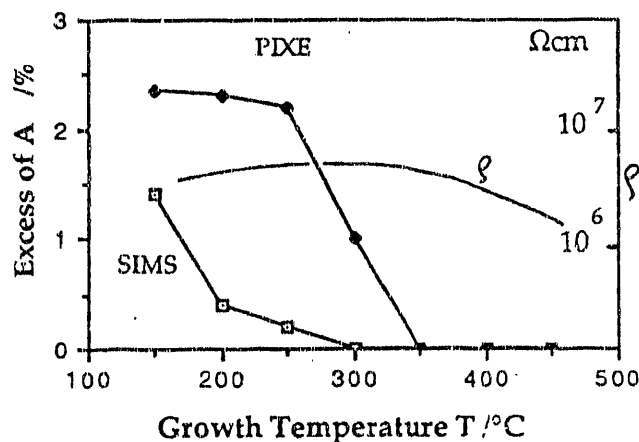


Fig.1 Concentration of excess As in annealed layers as a function of the growth temperature T_g . PIXE and SIMS data are normalized for a sample grown at 450°C. The resistivity of annealed layers is included.

difference in the change of the lattice parameter between the substrate and the layer will mainly be caused by changes of the In content. Particle induced x-ray emission (PIXE) experiments as well as SIMS measurements [2] were used to determine the content of the additional incorporation of As as a function of the growth temperature.

Transmission electron microscopical (TEM) and high-resolution transmission electron microscopical (HREM) observations were done on plane-view samples as well as on cross-section specimens. These experiments were carried out on a JEOL JEM 200CX microscope and on the Atomic Resolution Microscope (ARM) at the Lawrence Berkeley Laboratory.

RESULTS AND DISCUSSION

The starting point of the structure investigation is the determination of the stoichiometry of the InAlAs layers. The results for excess As are given in Fig.1. It shows that additional As is incorporated in the LT-InAlAs layers grown at temperatures below 300°C and reaches a value of about 1.4% at 150°C (SIMS). Taking into account the specific nature of the PIXE measurements and the problem of their calibration we believe that the SIMS values are more accurate. In this diagram the amount of excess of As is normalized to a reference sample grown at 450°C, where no excess of As was expected. Furthermore, this diagram of Fig.1 includes also the resistivity of the layers as a function of T_g . These measurements show resistivity in the range 10^6 - $10^7 \Omega\text{cm}$ for as-grown as well as for annealed samples. There is no obvious relationship between the resistivity values and the As content.

The MBE grown InAlAs layers can contain lattice strain, which is caused by different mechanisms. First, for the layers grown below 300°C incorporation of As leads to a compression of the lattice parameter of the layer, which was confirmed by x-ray diffraction [2]. Second, the In/Al ratio determines the lattice match to the InP<001> substrate. Changes of the In content cause strain fields due to the lattice mismatch. In our series of MBE samples the In/Al ratio of 0.52/0.48 could be kept constant (variation $\times < 1\%$). This ratio gives an exact lattice match between the layer and the substrate, which was proved by x-ray

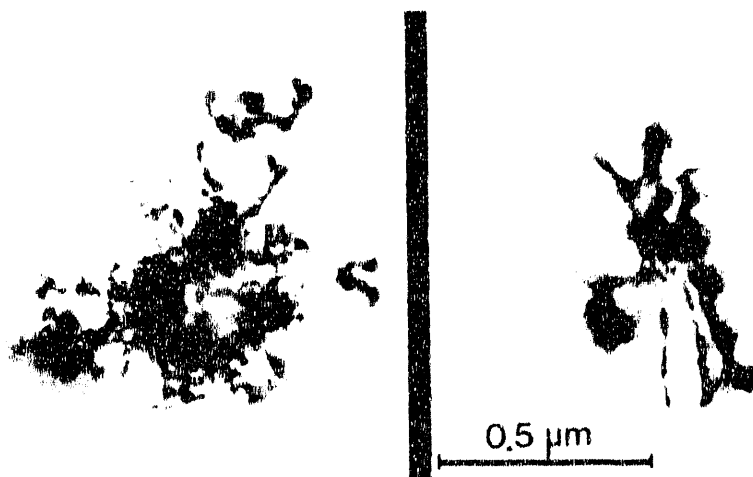


Fig2. TEM micrographs of different stages of pyramidal defects in LT-InAlAs layers. a) Sample grown at 150°C, b) at 200°C.

rocking curves of the corresponding {400} reflections.

Concerning the investigation of crystal lattice defects we should separate the low-temperature region of 150-200°C from the region of middle low-temperatures of 250-400°C. A characteristic feature for the first LT-region is the generation of so-called pyramidal defects. These defects have a diameter of about 0.5µm consisting of dislocations, micro-twins and stacking faults. This kind of defects is shown in plane-view in Fig.2. Due to the increasing lattice strain in the layers at such lower temperatures dislocations are created locally. An example for a growth temperature of 200°C is given in Fig.2b. At lower temperatures these defects are transformed to a more complicate structure. Inclusions of hexagonal As are observed within the

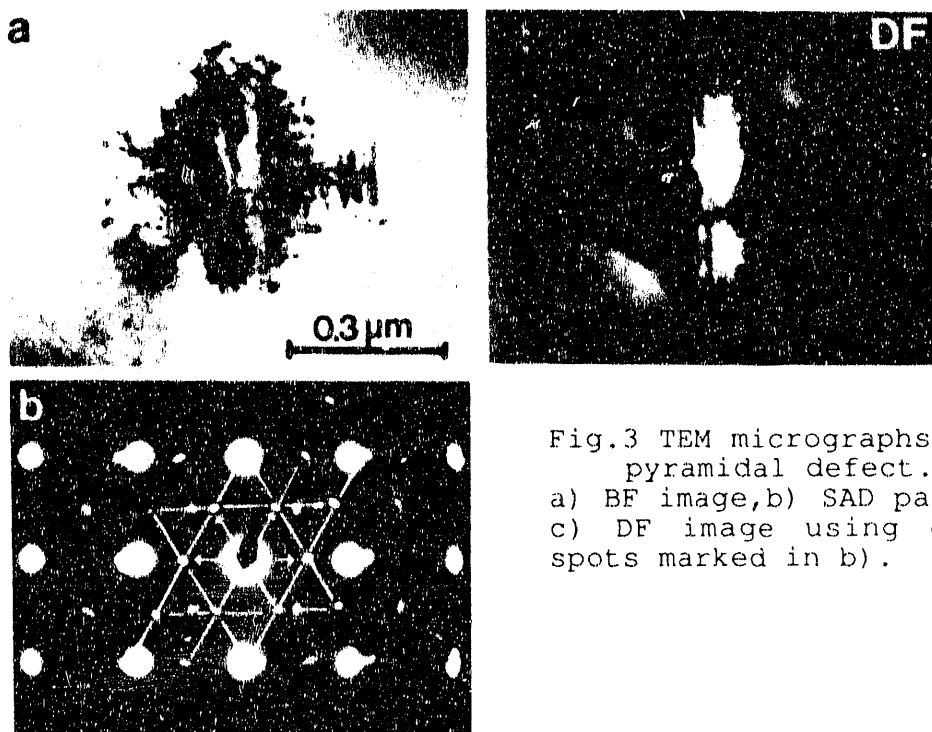


Fig.3 TEM micrographs of a pyramidal defect.
a) BF image, b) SAD pattern, c) DF image using extra spots marked in b).

core of these defects (Fig.2a). TEM dark-field technique (DF) as well as selected area electron diffraction (SAD) were used to identify the nature of such small inclusions. Fig.3a shows a bright-field image of a pyramidal defect seen in $\langle 001 \rangle$ orientation. The additional diffraction spots in the SAD pattern (marked by lines in Fig.3b) are related to the hexagonal phase of As. The DF image (Fig.3c) shows that the As precipitates are small with dimensions of about 20nm. Pyramidal defects were observed in samples grown at 150°C and nearly perfect lattice match with a density of about 10^7cm^{-2} . These pyramidal defects appear at a layer thickness of about 0.5µm.

In the temperature region between 250°C and 400°C InAlAs layers can be grown with a small defect density ($\approx 10^6 \text{cm}^{-2}$) if a good lattice match to the substrate can be realized ($x=0.52$). In our annealed layers we never could observe precipitation as found in LT-GaAs.

Furthermore, ordering of group-III elements occurs in strained layers in the temperature range between 300°C and 450°C. This phenomenon has already been observed recently in other LT-MBE grown InAlAs layers [7]. The element ordering was

difference in the change of the lattice parameter between the substrate and the layer will mainly be caused by changes of the In content. Particle induced x-ray emission (PIXE) experiments as well as SIMS measurements [2] were used to determine the content of the additional incorporation of As as a function of the growth temperature.

Transmission electron microscopical (TEM) and high-resolution transmission electron microscopical (HREM) observations were done on plane-view samples as well as on cross-section specimens. These experiments were carried out on a JEOL JEM 200CX microscope and on the Atomic Resolution Microscope (ARM) at the Lawrence Berkeley Laboratory.

RESULTS AND DISCUSSION

The starting point of the structure investigation is the determination of the stoichiometry of the InAlAs layers. The results for excess As are given in Fig.1. It shows that additional As is incorporated in the LT-InAlAs layers grown at temperatures below 300°C and reaches a value of about 1.4% at 150°C (SIMS). Taking into account the specific nature of the PIXE measurements and the problem of their calibration we believe that the SIMS values are more accurate. In this diagram the amount of excess of As is normalized to a reference sample grown at 450°C, where no excess of As was expected. Furthermore, this diagram of Fig.1 includes also the resistivity of the layers as a function of T_g . These measurements show resistivity in the range 10^6 - $10^7 \Omega\text{cm}$ for as-grown as well as for annealed samples. There is no obvious relationship between the resistivity values and the As content.

The MBE grown InAlAs layers can contain lattice strain, which is caused by different mechanisms. First, for the layers grown below 300°C incorporation of As leads to a compression of the lattice parameter of the layer, which was confirmed by x-ray diffraction [2]. Second, the In/Al ratio determines the lattice match to the InP<001> substrate. Changes of the In content cause strain fields due to the lattice mismatch. In our series of MBE samples the In/Al ratio of 0.52/0.48 could be kept constant (variation $x < 1\%$). This ratio gives an exact lattice match between the layer and the substrate, which was proved by x-ray

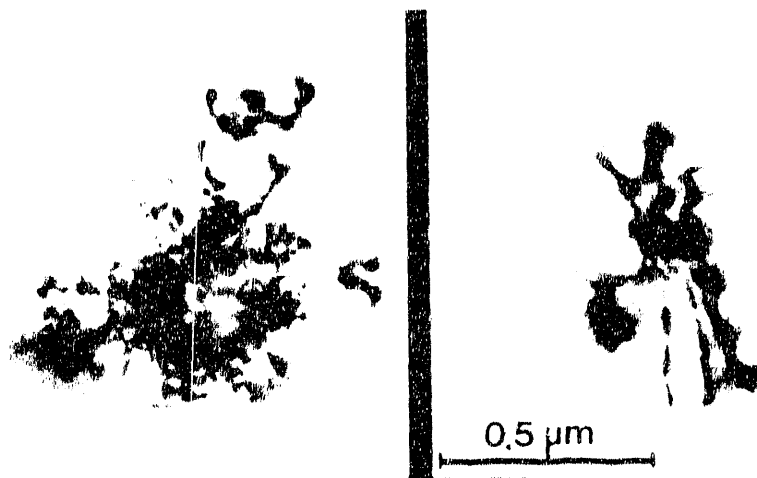


Fig2. TEM micrographs of different stages of pyramidal defects in LT-InAlAs layers. a) Sample grown at 150°C, b) at 200°C.

rocking curves of the corresponding {400} reflections.

Concerning the investigation of crystal lattice defects we should separate the low-temperature region of 150-200°C from the region of middle low-temperatures of 250-400°C. A characteristic feature for the first LT-region is the generation of so-called pyramidal defects. These defects have a diameter of about 0.5 μm consisting of dislocations, micro-twins and stacking faults. This kind of defects is shown in plane-view in Fig.2. Due to the increasing lattice strain in the layers at such lower temperatures dislocations are created locally. An example for a growth temperature of 200°C is given in Fig.2b. At lower temperatures these defects are transformed to a more complicate structure. Inclusions of hexagonal As are observed within the

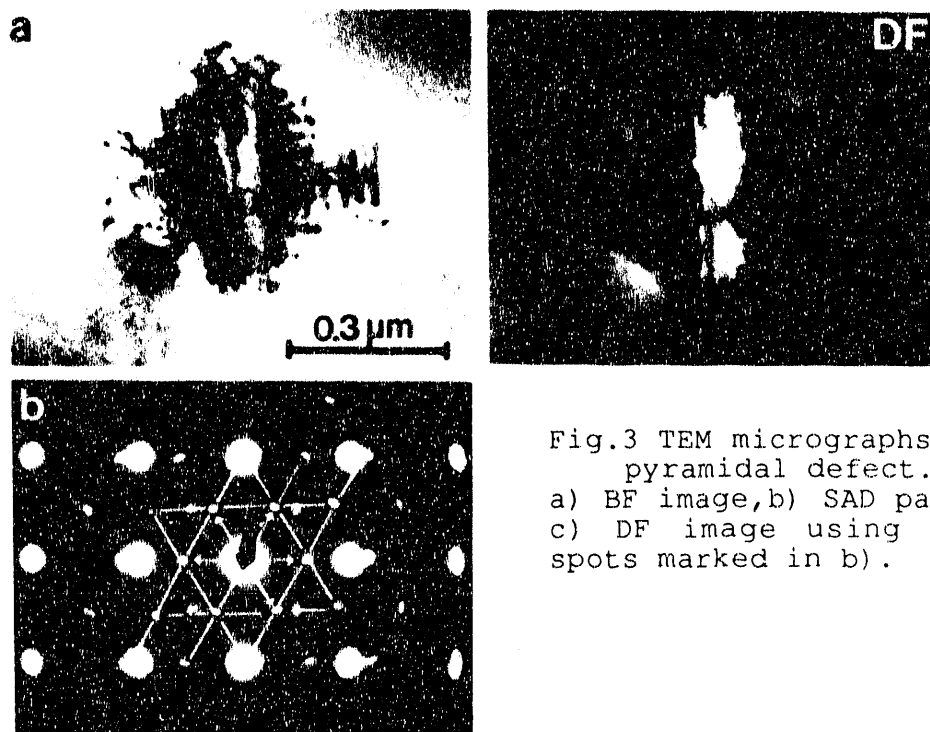


Fig.3 TEM micrographs of a pyramidal defect.
a) BF image, b) SAD pattern, c) DF image using extra spots marked in b).

core of these defects (Fig.2a). TEM dark-field technique (DF) as well as selected area electron diffraction (SAD) were used to identify the nature of such small inclusions. Fig.3a shows a bright-field image of a pyramidal defect seen in $\langle 001 \rangle$ orientation. The additional diffraction spots in the SAD pattern (marked by lines in Fig.3b) are related to the hexagonal phase of As. The DF image (Fig.3c) shows that the As precipitates are small with dimensions of about 20nm. Pyramidal defects were observed in samples grown at 150°C and nearly perfect lattice match with a density of about 10^7cm^{-2} . These pyramidal defects appear at a layer thickness of about 0.5 μm .

In the temperature region between 250°C and 400°C InAlAs layers can be grown with a small defect density ($\approx 10^6 \text{cm}^{-2}$) if a good lattice match to the substrate can be realized ($x=0.52$). In our annealed layers we never could observe precipitation as found in LT-GaAs.

Furthermore, ordering of group-III elements occurs in strained layers in the temperature range between 300°C and 450°C. This phenomenon has already been observed recently in other LT-MBE grown InAlAs layers [7]. The element ordering was

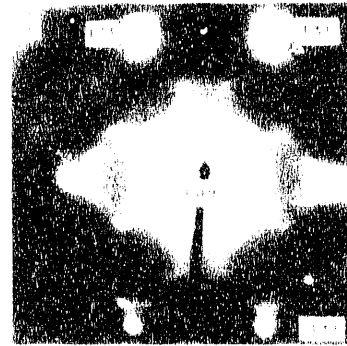
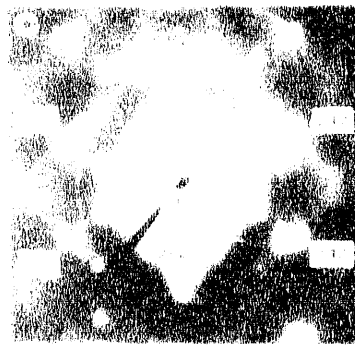
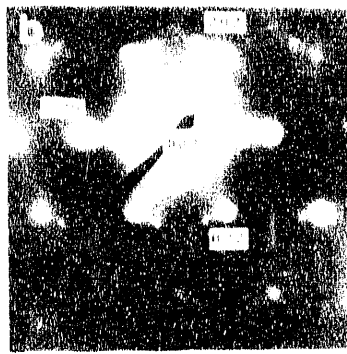
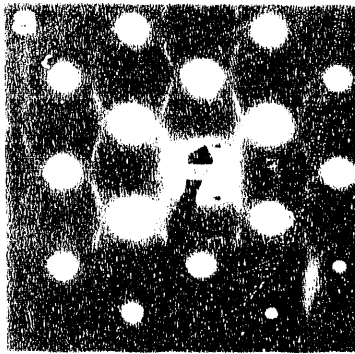


Figure 1. (a) Hexagonal lattice of bright spots. (b) Central bright spot surrounded by six other bright spots in a hexagonal arrangement. (c) Central bright spot surrounded by six other bright spots in a hexagonal arrangement. (d) Central bright spot surrounded by six other bright spots in a hexagonal arrangement.

The figure shows four micrographs (a, b, c, d) of a hexagonal lattice of bright spots. Micrograph (a) shows a hexagonal lattice of bright spots on a dark background. Micrographs (b), (c), and (d) show a central bright spot surrounded by six other bright spots in a hexagonal arrangement. The intensity of the central spot and the surrounding spots varies between the three micrographs.

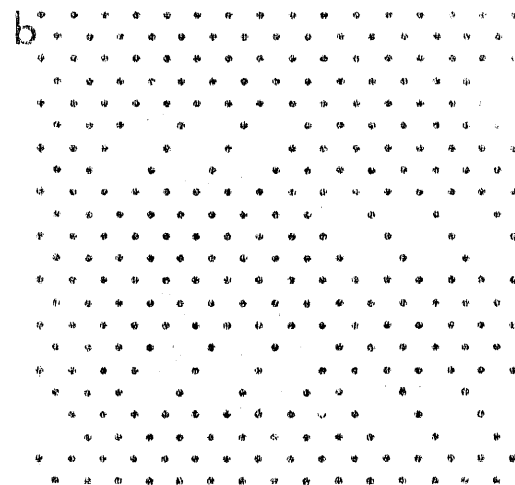
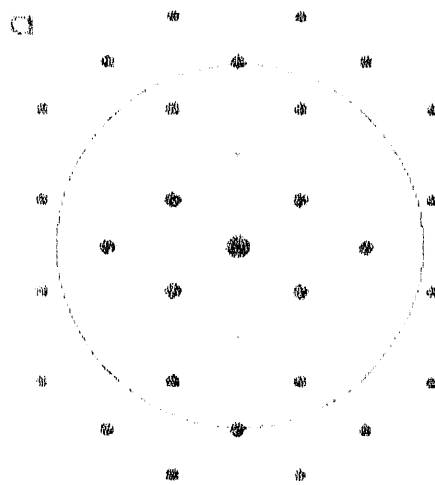


Figure 2. (a) Hexagonal lattice of points with a central point and a circle around it. (b) Hexagonal lattice of points.

SUMMARY

This study shows that 1 μ m thick InAlAs films can be grown by MBE on <001> InP substrates with high crystalline quality at low-temperatures down to about 200°C. If an ideal lattice match during MBE growth can be achieved ($x_{In}=0.52$), a defect density in the order of 10⁶cm⁻² was observed. Small changes of the In content can increase the dislocation density by about two orders of magnitude. In the LT-region below 200°C so-called "pyramidal defects" are generated during the MBE growth, which are also observed in the case of LT-GaAs. These defects, which consist of dislocations, stacking faults, twins and hexagonal As, seem to be the result of a lattice stress relieving process.

The element analysis shows that additional As can be incorporated in LT-MBE InAlAs layers. Despite some discrepancies between the results of SIMS and PIXE measurements there is an increasing excess of As below 300°C up to about 2% at 150°C. However, this incorporation of As does not correlate with the semi-insulating behavior of these layers, which is nearly constant between 200°C and 450°C. Since As precipitates were not observed in annealed LT-InAlAs layers the semi-insulating property of such ternary compound cannot be explained by As rich precipitates as it was proposed for the case of LT-GaAs layers. Point defects with trapping properties have to be taken into account for the explanation of these properties.

ACKNOWLEDGMENT

This work was supported by the US AirForce under contract AFOSR-ISSA-90-0009. The use of the facility at the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory was supported by the Department of Energy under Contract No. DE-AC03-76FS00098. Many thanks to M.O'Keefe and R.Kilaas for supporting the computer simulation work. P.W. also wants to thank the Alexander von Humboldt Foundation/ Germany for providing him with financial support during his stay as a visiting scientist at LBL Berkeley.

REFERENCES

1. F.W.Smith, A.R.Calawa, C.L.Chen, M.Manfra, and L.J.Mahoney, IEEE Electron. Device Lett. 9, 77 (1988)
2. R.A.Metzger, A.S.Braun, W.E.Stanchina, M.Lui, R.G.Wilson, T.V. Kargodorian, L.G.McCray, and J.A.Henige, J.Crystal Growth 111, 445 (1991)
3. A.C.Warren, J.M.Woodall, J.L.Freeouf, D.Grischkowsky, D.T. McInturff, M.R.Melloch, N.Otsuka, Appl.Phys.Lett. 57, 1331 (1990)
4. Z.Liliental-Weber, A.Claverie, F.Smith, and A.R.Calawa, Appl. Phys. A53, 141 (1991)
5. Z.Liliental-Weber, G.Cooper, R.Mariella, and C.Kocot, J.Vac.Sci.Technol.B9, 2323 (1991)
6. A.Claverie, K.M.Yu, W.Swider, Z.Liliental-Weber, M.O'Keefe, R.Kilaas, J.Pamulapati, and P.K.Bhattacharya, Appl.Phys.Lett. 60, 989 (1992)
7. M.Kaminska, Z.Liliental-Weber, E.R.Weber, R.Leon, and Z.Rek, J.Vac.Sci.Technol.B7, 710 (1990)
8. Z.Liliental, A.Claverie, P.Werner, W.Schaff, and E.R.Weber, Materials Sci.Forum Vol.83-87, 1045 (1992)
9. S.Gupta, P.K.Bhattacharya, J.Pamulapati, and G.Mourou, Appl. Phys. Lett. 57, 1543 (1990)
10. A.Claverie, Z.Liliental-Weber, P.Werner, W.Swider, P.K.Bhattacharya, S.Gupta, and S.Mourou, MRS Full Meeting, Boston 1991, Sympos.F, in press

END

**DATE
FILMED**

12/18/92

