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Ding, J.

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

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In/GaAs Reaction: Effect of an Intervening Oxide Layer

J. Ding and J. Washburn

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

T. Sands[a] and V. G. Keramidas

Bell Communications Research, Inc.,
Murray Hill, NJ 07974

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ABSTRACT

The effects of a thin (~ 1.3 nm) intervening native GaAs oxide interface layer on the In/GaAs reaction have been investigated by comparing the reactions of In on GaAs substrates with the native oxide present or desorbed. Transmission electron microscopy of cross-sectional samples reveals that the thin native oxide layer, when present, disrupts the In/GaAs orientation relationship in as-deposited samples and prevents an extensive reaction between In and GaAs at 350°C. These data also show that the In/GaAs reaction at 350°C proceeds by dissolution of the GaAs substrate into the molten In followed by the subsequent nucleation and growth of epitaxial $In_{1-x}Ga_xAs$ particles with $x \leq 0.2$ or $x \geq 0.8$ only, indicating immiscibility. The $In_{1-x}Ga_xAs$/GaAs interfaces are found to be structurally and compositionally abrupt to within ~ 3 nm. The effects of the interfacial native oxide on the In/GaAs reaction and the observation of an InAs-GaAs miscibility gap have implications for the fabrication of In/GaAs ohmic contacts by thermal reaction.

The conventional method for fabricating ohmic contacts to n-GaAs involves the dissolution of GaAs by a Au-Ge eutectic layer and the subsequent epitaxial regrowth of Ge-doped GaAs. Presumably, Ge acts as a donor, thereby producing an n^+-GaAs layer which can be easily penetrated by tunneling electrons.[1] Concerns for lateral uniformity, reproducibility and stability, however, have motivated recent investigations of alternative ohmic contact schemes. One of the approaches involves the formation of a graded $In_{1-x}Ga_xAs$ heterojunction. Such a heterojunction, grown by molecular beam epitaxy (MBE), has been shown to produce a low-resistance ohmic contact to n-GaAs[2] since the Fermi-level is pinned in the conduction band of InAs. The grading of the heterojunction smooths out the conduction band discontinunity, thereby facilitating electron flow. Recent attempts by Lakhani[3,4] to form a similar graded $In_{1-x}Ga_xAs$ heterojunction by thermal reaction of In on GaAs have been less successful due to the localized nature of the reaction. However, Lakhani has suggested that an ion-exchange reaction does produce a graded heterojunction in the isolated reacted regions. As part of our ongoing studies of metal/GaAs interactions we have been examining the role of native oxides in determining the lateral uniformity of the reacted layers.[5,6] In this study, we report on the effects of a thin (~ 1-2 nm) native oxide-hydrocarbon layer on the lateral uniformity of the In/GaAs reaction. High-resolution imaging and analytical microscopy of cross-sectional transmission electron microscope (TEM) specimens reveal that the $In_{1-x}Ga_xAs/GaAs$ heterojunctions formed by heating In/GaAs at 350°C are abrupt.

Undoped (100) GaAs wafers were prepared for In deposition by boiling in organic solvents, swabbing the surface with H_2SO_4, rinsing in deionized water and drying with nitrogen gas. The thickness of the resulting native oxide was determined by high-resolution cross-sectional TEM to be 1.3 ± 0.3 nm. One wafer treated as above was inserted into an MBE chamber. Indium was deposited to a thickness of 57 nm (~ 5.7 nm/min) at 25°C while the substrate was rotated (8 RPM). The system background pressure during deposition was 3.2×10^{-9} torr. A second wafer had In deposited onto it under identical conditions except that, prior to deposition, the native oxide was desorbed. Desorption was accomplished by heating to 600°C in the absence of an As flux until the reflection high energy electron diffraction pattern revealed an arsenic stabilized surface. The sample was then allowed to cool to 25°C (~ 30 min.). Cross-sectional TEM images of these In/GaAs samples revealed no trace of native oxide and a high degree of epitaxy. These samples are thus referred to as "oxide-free" in subsequent sections although the presence of submonolayer coverages of contaminants cannot be excluded.

Portions of both samples were annealed at 350°C for 10 minutes in flowing forming gas (95% N_2, 5% H_2). This annealing temperature was chosen since Lakhani reported a minimum value of the specific contact resistance (1.2×10^{-5} Ωcm^2) after annealing at 350°C. Both plan-view and cross-sectional TEM samples were prepared by standard techniques[7] which involve heating of the samples to a maximum of ~ 80°C for 5 minutes. Specimens were observed 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.

Studies of the surface morphology by SEM reveal that the indium forms isolated islands on both the chemically cleaned (i.e. native oxide present) and the oxide-free GaAs substrates. The island morphology does not change during annealing. However, as Fig. 1 demonstrates, the presence of the native oxide does influence island morphology; In islands on the oxide-free substrate are rectangular with edges parallel to <110> GaAs. Indium islands on the substrate with the native oxide appear to be random in orientation. Electron diffraction and TEM of cross-sectional samples show that each island is a single crystal of In with facets on the {110} and {011} planes. These planes are close-packed planes of body-centered tetragonal indium. In the oxide-free sample, the {011} close-packed planes of In were found to be approximately parallel to the {111} close-packed planes of GaAs, yielding the orientation relationship $[0\bar{1}1]_{GaAs}//[1\bar{1}\bar{1}]_{In}$, $(100)_{GaAs}//(110)_{In}$. In terms of the distorted pseudo-cubic representation of the In structure,[8] this orientation relationship dictates that planes and directions with the same indicies in In and GaAs are approximately parallel. This simple orientation relationship combined with faceting on close-packed In planes explains the morphology in Fig. 1b. Note that, although the In islands on the surface with the native oxide are faceted, the thin oxide layer is sufficient to completely disrupt the In/GaAs orientation relationship resulting in randomly oriented islands.

Annealing the oxide-free sample at 350°C results in the formation of epitaxial $In_{1-x}Ga_xAs$ patches within each In island. One such patch is shown in Fig. 2. Sharp diffraction spots and misfit dislocations separated by 3-4 nm in a narrow band show that the interface is structurally abrupt to within ~ 3 nm. The abrupt nature of the interface is also evidenced by the moiré fringes with well-defined spacing. Using Vegard's law, the composition of the epitaxial patch is estimated to be ~ $In_{0.9}Ga_{0.1}As$. The EDS data are consistent with this result considering that the spectrum from region A (Fig. 2) also contains counts from the surrounding GaAs substrate. Abrupt interfaces were observed in all patches formed on the oxide-free substrate. In other words, graded $In_{1-x}Ga_xAs$ layers were not observed.

Annealing of the sample with the native oxide resulted in a substantially different morphology. Figure 3 shows that most of the indium remains unreacted. Small patches of $In_{1-x}Ga_xAs$ ($x \leq 0.2$) did form locally at pores or thin regions in the native oxide layer. These $In_{1-x}Ga_xAs$ interfaces were again found to be structurally and compositionally abrupt as indicated by the sharp diffraction spots in electron diffraction patterns. Figure 4 is an enlarged view of the $In_{0.8}Ga_{0.2}As$ patch in Fig. 3. It is apparent that accommodation of oxide particles present at the interface results in the formation of stacking faults. In contrast, no such faults were observed after annealing the oxide-free samples (see Fig. 2). These results clearly demonstrate the adverse effects of a thin native oxide layer on the In/GaAs reaction.

Although the intervening oxide determines the extent of the reaction and the defect density in the epitaxial $In_{1-x}Ga_xAs$ islands, the reaction mechanism is essentially the same in both the sample with the native oxide and the sample free of native oxide. We believe that the In/GaAs reaction as observed in these samples does not involve significant solid-state interdiffusion (cation exchange). Such an exchange reaction as observed, for example, in the CuCl(aq)/CdS system[9] requires high cation mobility in the reacted layer at the reaction temperature. Instead the results above are consistent with the interpretation that above the melting point of In (156°C), Ga and As dissolve into the molten In. As the composition of the melt enters the two-phase region of the equilibrium phase diagram between In-Ga(ℓ) and $In_{1-x}Ga_xAs$, the driving force for the nucleation of $In_{1-x}Ga_xAs$ increases. The composition of the epitaxial $In_{1-x}Ga_xAs$ patch is determined by the degree of Ga and As supersaturation in the melt at the time of nucleation. Since nucleation can occur either during annealing or during cooling, a wide range of compositions is possible. In this study, however, we have found $In_{1-x}Ga_xAs$ patches with $x \leq 0.2$ or $x \geq 0.8$. The absence of epitaxial patches with $0.2 < x < 0.8$ suggests that the enthalpy of mixing is sufficiently high so as to create a miscibility gap in the InAs-GaAs system at 350°C. This result is consistent with the calculations of de Cremoux _et al._[10] which suggest the presence of a miscibility gap with a critical temperature between 500°C and 700°C in this system. Such a miscibility gap should make it difficult if not impossible to grow a graded layer from GaAs to InAs by the thermal reaction of In with GaAs below the critical temperature.

Based on the above results, it is evident that it is the native oxide layer that is responsible for the limited reaction of In on chemically prepared GaAs substrates (i.e. with the oxide present) as observed by Lakhani.[3,4] Because of the presence of the miscibility gap in the InAs-GaAs system, the resulting preferred compositions of $In_{1-x}Ga_xAs$, and the observed abruptness of the $In_{1-x}Ga_xAs$/GaAs interfaces, "ohmic" conduction cannot be attributed solely to conduction through a graded layer. Additional effects such as thermionic-field emission through enhanced electric field regions near sharp corners in the abrupt $In_{1-x}Ga_xAs$/GaAs interface must be significant and should be considered in any model of "ohmic" conduction in this system.

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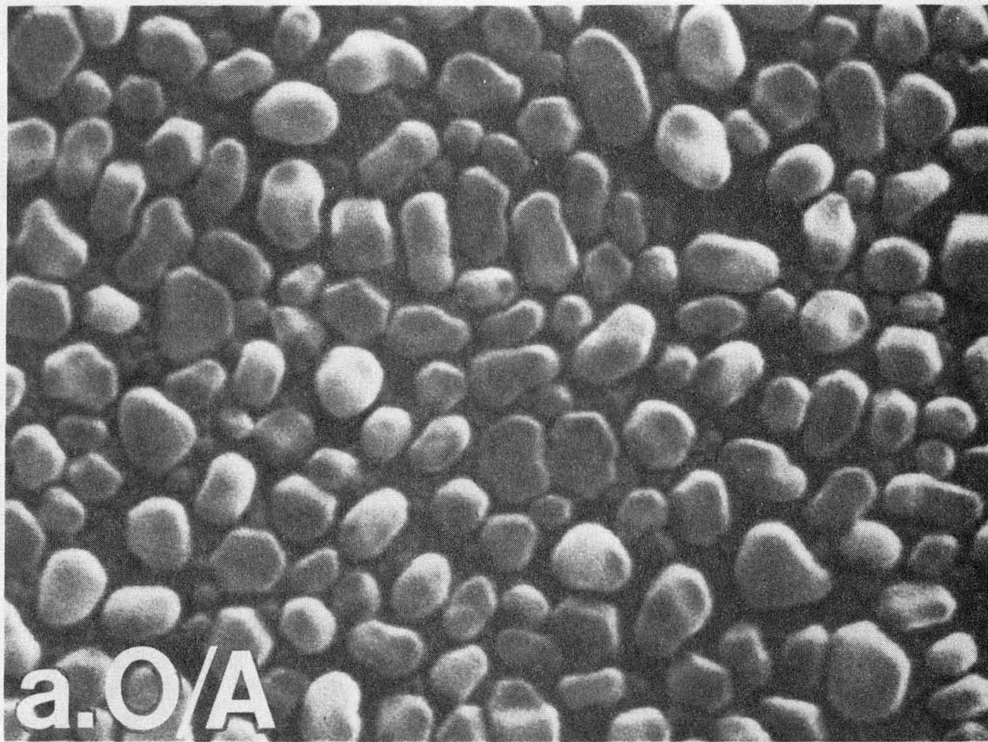
Figure Captions

Fig. 1. High magnification SEM images of the annealed samples (a) with and (b) without the intervening native oxide.

Fig. 2. High resolution cross-sectional image of an $In_{1-x}Ga_xAs$ island formed during annealing of the oxide-free In/GaAs 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 $In_{0.9}Ga_{0.1}As$ 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 $In_{1-x}Ga_xAs$.

Fig. 3. TEM micrograph of an annealed (011) cross-sectional sample of In/GaAs with the intervening native oxide. The native oxide appears as a white line at the interface. Two reacted patches are visible within the largely unreacted indium island. The composition of the patches was estimated to be $In_{0.8}Ga_{0.2}As$ by diffraction analysis. Diffraction pattern gives the reflections from the $In_{0.8}Ga_{0.2}As$, two indium grains and the GaAs substrate.

Fig. 4. Lattice image of the $In_{0.8}Ga_{0.2}As$ patch shown in Fig. 12. The patch is faceted on the {111} and {100} close-packed planes. The microtwins and stacking faults formed to accommodate the oxide particles at the interface during the growth of $In_{0.8}Ga_{0.2}As$.



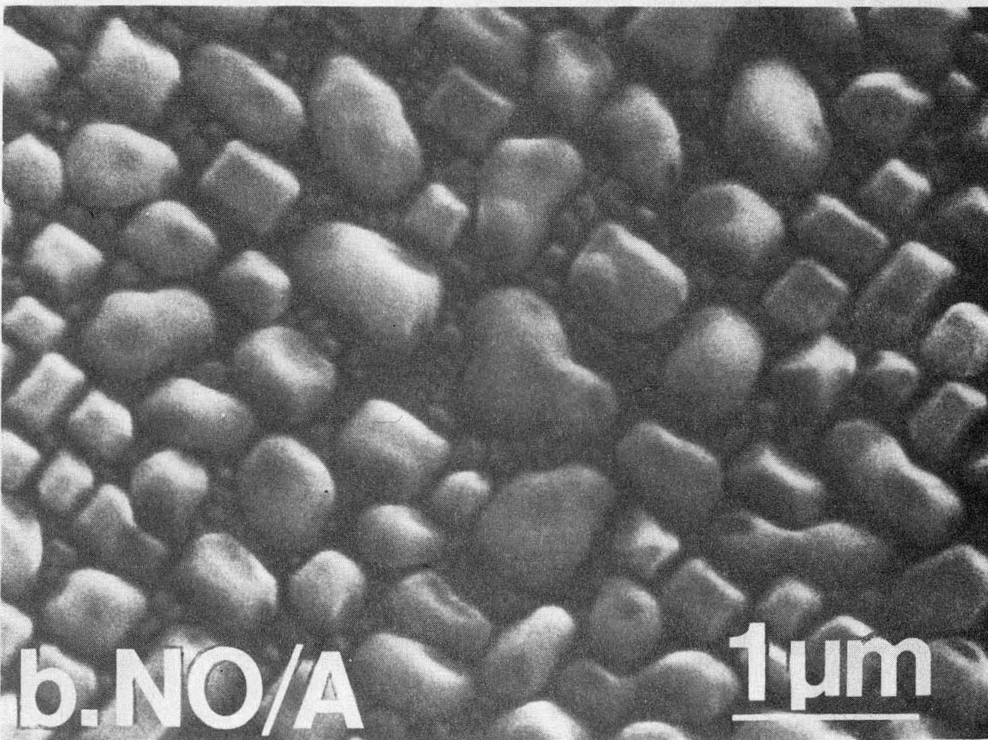


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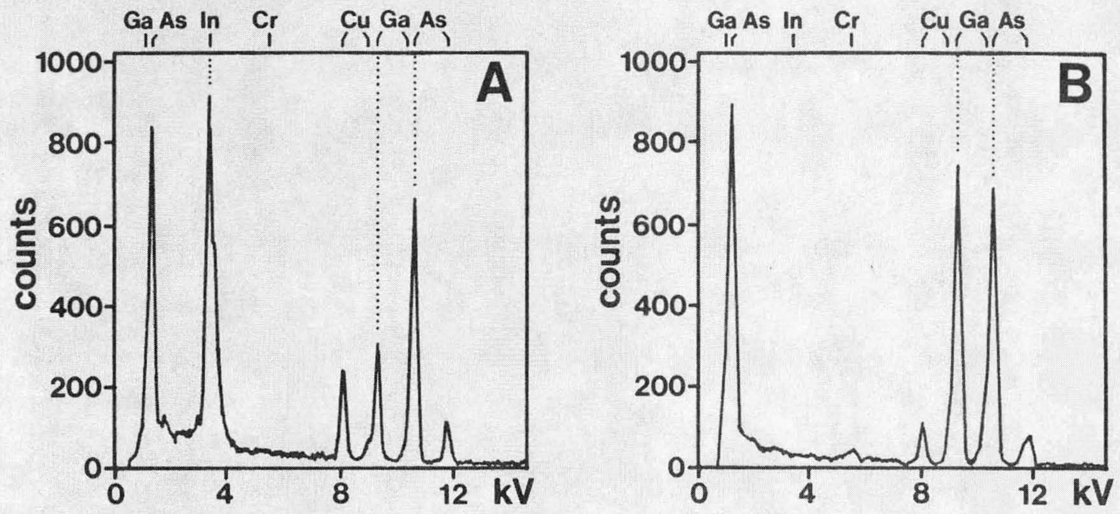
Fig. 1



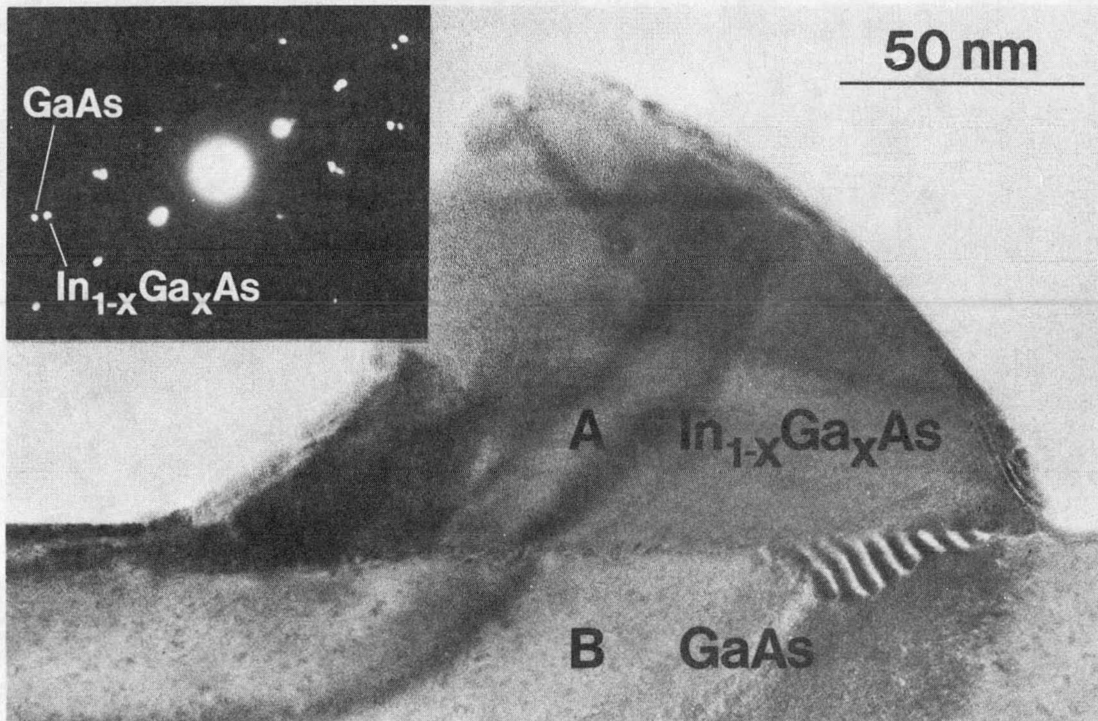


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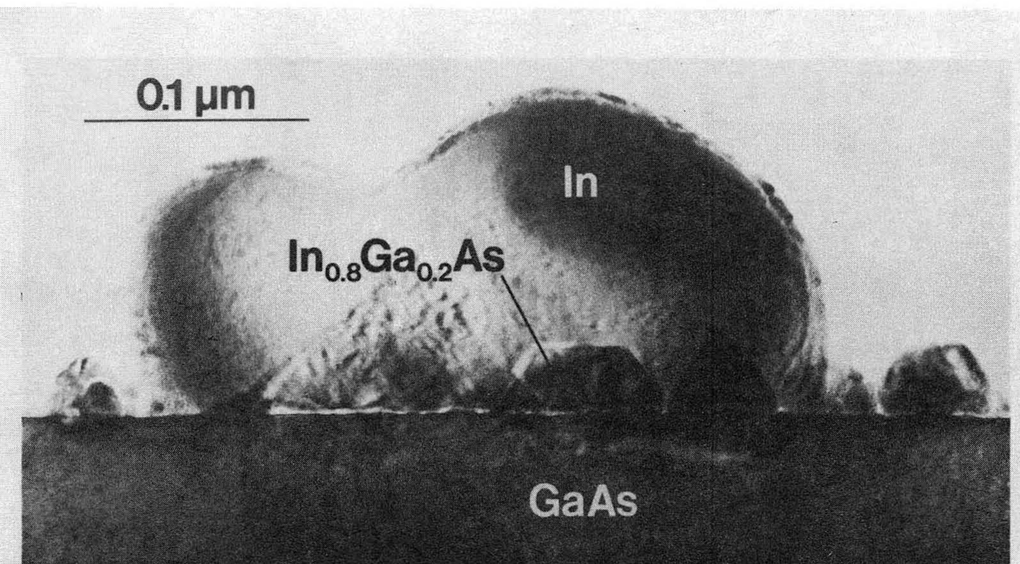
Fig. 2



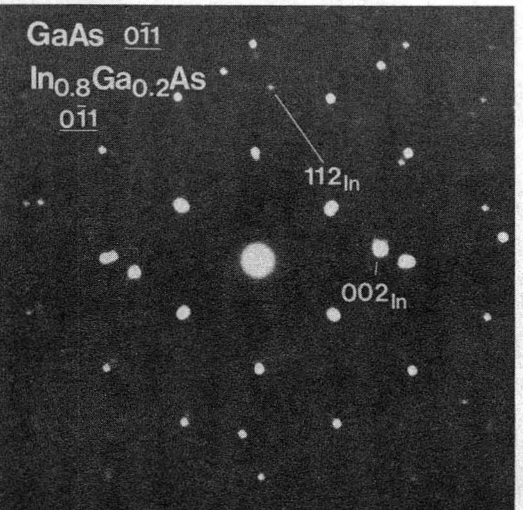


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Fig. 3

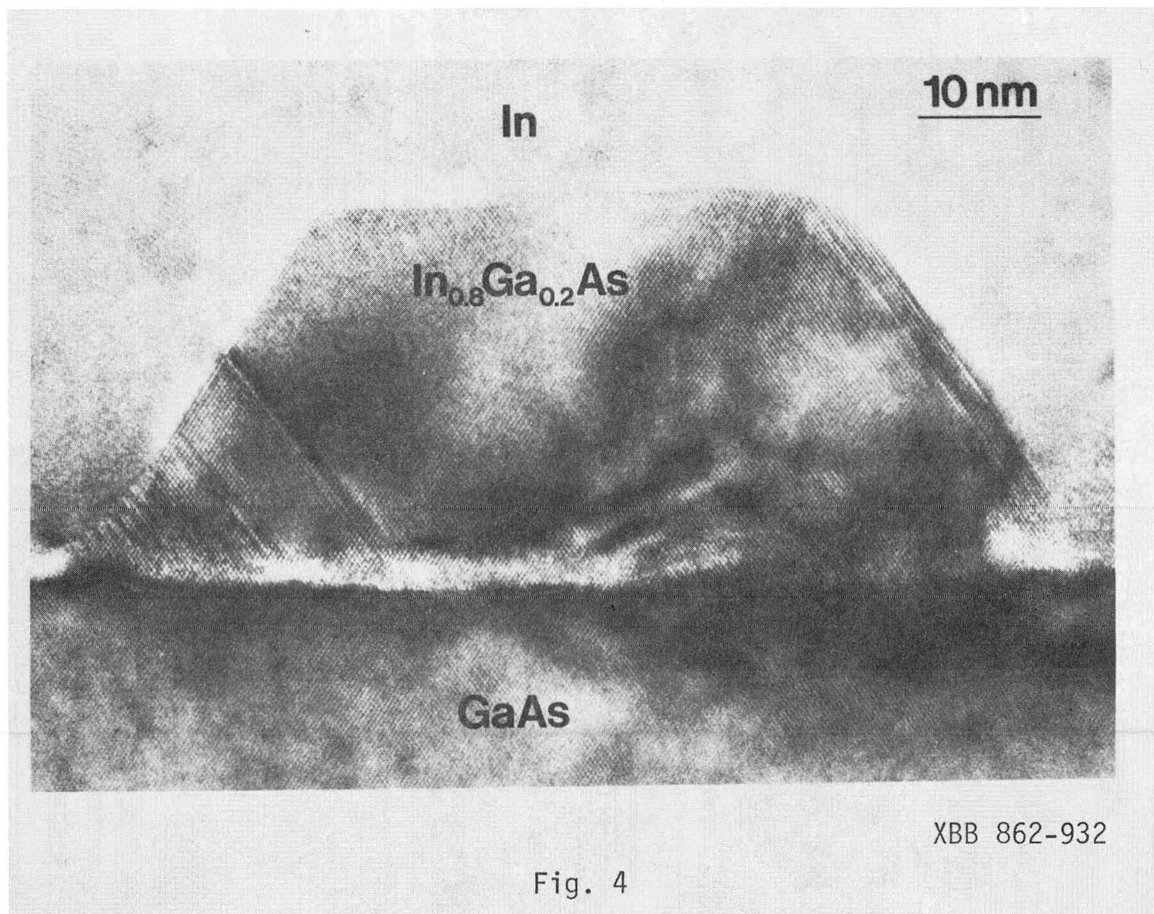

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Fig. 4

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TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720