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GROWTH AND CHARACTERIZATION OF $In_{0.2}Ga_{0.8}Sb$ DEVICE STRUCTURES USING METALORGANIC VAPOR PHASE EPITAXY

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G. Charache, H. Ehsani, et. al.

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Growth and Characterization of $In_{0.2}Ga_{0.8}Sb$ Device Structures Using Metalorganic Vapor Phase Epitaxy

H. Ehsani, I. Bhat, C. Hitchcock and R. Gutmann
Department of Electrical, Computer and Systems Engineering
Center for Integrated Electronics and Electronics Manufacturing
Rensselaer Polytechnic Institute, Troy, NY 12180-3590
and
G. Charache and M. Freeman
Lockheed Martin Inc., Schenectady, New York 12301-1072

Abstract: $In_{0.2}Ga_{0.8}Sb$ epitaxial layers and thermophotovoltaic (TPV) device structures have been grown on GaSb and GaAs substrates by metalorganic vapor phase epitaxy (MOVPE). Control of the n-type doping up to $1 \times 10^{18} cm^{-3}$ was achieved using diethyltellurium (DETe) as the dopant source. A Hall mobility of greater than 8000 cm^2/Vs at 77K was obtained for a $3 \times 10^{17} cm^{-3}$ doped $In_{0.2}Ga_{0.8}Sb$ layer grown on high-resistivity GaSb substrate. The $In_{0.2}Ga_{0.8}Sb$ epilayers directly grown on GaSb substrates were tilted with respect to the substrates, with the amount of tilt increasing with the layer thickness. Transmission electron microscopy (TEM) studies of the layers showed the presence of dislocation networks across the epilayers parallel to the interface at different distances from the interface, but the layers above this dislocation network were virtually free of dislocations. A strong correlation between epilayer tilt and TPV device properties was found, with layers having more tilt providing better devices. The results suggest that the dislocations moving parallel to the interface cause lattice tilt, and control of this layer tilt may enable the fabrication of better quality device structures.

INTRODUCTION

$In_xGa_{1-x}Sb$ material system is attractive for application in TPV cells since the energy bandgap can be varied from 0.17 eV to 0.72 eV by varying the composition (1). By adding arsenic into the system, lattice-matched $In_xGa_{1-x}As_ySb_{1-y}$ structures can be grown on GaSb substrates. Even though antimonides may have some advantages compared to an $In_xGa_{1-x}As$ system for TPV applications, the growth technology for $In_xGa_{1-x}Sb$ is not as advanced. MOVPE growth of antimonides has emphasized lattice-matched $In_xGa_{1-x}As_ySb_{1-y}$ or the binary compounds GaSb and InSb. Doping studies and dislocation reduction techniques for lattice-mismatched epitaxy have not been investigated in detail for $In_xGa_{1-x}Sb$ layers grown on GaSb substrates (2). Studies on doping characteristics and on methods to reduce dislocation densities in the active layers are required for better antimonide devices.

Preliminary results on the growth and doping of $In_{0.2}Ga_{0.8}Sb$ by MOVPE (3) and p-type doping using Si have been presented before (4). In this paper, recent results on the n-type doping of $In_{0.2}Ga_{0.8}Sb$ by Te and structural characterization of $In_{0.2}Ga_{0.8}Sb$ layers are presented. These epilayers are tilted with respect to the substrates, with the amount of tilt increasing with layer thickness. This result has important implications for the design of step grading techniques for epitaxial growth of device quality $In_{0.2}Ga_{0.8}Sb$.

EXPERIMENTAL PROCEDURES

The ternary epilayers were grown on (100) oriented GaSb and semi-insulating (100) GaAs substrates in a low pressure, rf heated, horizontal MOVPE reactor. Trimethylgallium, trimethylindium, trimethylantimony and diethyltellurium (DETe) were used as the Ga, In, Sb and Te sources, respectively. After degreasing the wafers in organic solvents, the GaAs substrates were etched in Caro's etch (solution containing H_2SO_4:H_2O_2:H_2O, 5:1:1 by volume) for two minutes and the GaSb wafers were etched in 1% bromine-methanol solution for 30 seconds. The GaSb substrates were of low resistivity p-type at room temperature, but were of high resistivity at 77K (sheet resistance of 600 Ω per square) so that Hall measurements could be made on these at 77K.

Double crystal x-ray diffraction was used to determine layer tilt with respect to the substrate, crystalline quality of the layers, composition of the layers, and lattice relaxation. Variation of the peak separation between the epilayers and the substrates as a function of rotational angle (azimuth) was used to determine the lattice mismatch and the epilayer tilt. The residual strain in some films was measured by x-ray diffraction spectra of non-symmetric planes such as (115) and symmetric plans such as (004). Details of the measurement technique can be found elsewhere (5).

RESULTS AND DISCUSSIONS

Earlier work (3) reported n-type doping of $In_{0.2}Ga_{0.8}Sb$ with Te for DETe mole fractions higher than 1×10^{-6}, where the carrier concentration actually decreased as the DETe mole fraction was increased. This decrease was attributed to the formation of Te precipitates or Ga-Te and Sb-Te reactions at the growth surface. These reactions probably resulted in inclusions of undesired precipitates in the layer, causing degradation of crystal quality. Secondary ion mass spectrometry (SIMS) measurements showed that only 2 - 3% of the incorporated Te was active when the total Te concentration was about 2×10^{19} cm^{-3}. The mobility of the layers also decreased as the DETe mole fraction was increased.

In this work, this study was extended to lower concentrations of Te, by modifying the reactor with the addition of a "double dilution" scheme to deliver DETe. In this method, hydrogen through an additional line is used to dilute the DETe/H_2 gas mixtures. Only a small portion of the DETe/H_2 is delivered to the reactor, and the rest is passed through the exhaust lines. The mole fraction of DETe in the reactor can be controlled over a wide range (10^{-8} to 10^{-5}) using this method.

Figure 1 shows the measured carrier concentration at 77K as a function of the DETe mole fraction for layers grown on GaAs and GaSb substrates. The carrier concentration increases linearly with the DETe flow initially, but beyond 10^{18} cm^{-3} the carrier concentration actually decreases with the DETe flow. The continuous line in the graph corresponds to n α (DETe)$^{1.0}$ suggesting a high degree of Te activation at doping concentrations as high as $1 \times 10^{18} cm^{-3}$. TEM of lightly Te-doped $In_{0.2}Ga_{0.8}Sb$ ($< 1 \times 10^{18}$ cm^{-3}) does not show presence of any precipitates.

Figure 2 shows the Hall mobility at 77K versus DETe mole fraction for layers grown on GaAs and GaSb substrates. It was consistently found that the mobility of layers grown on GaSb were higher than those grown on GaAs substrates. For DETe mole fraction less than 5×10^{-9}, p-type layer with low mobility was obtained. The Hall mobility was found to increase with the doping concentration as shown in figure 3, which is opposite to the usually observed behavior in other III-V compounds. Similar behavior (i.e., increase of Hall mobility with the doping concentration) was observed by others as well in both molecular beam epitaxially (MBE) grown GaSb (6) and MOVPE grown GaSb (7) doped with Te. Similar behavior was also observed in bulk grown InSb material (8). Turner et al. (6) and Zitter et al. (8) attributed this to a reduced screening effect of the charged native acceptors by the donors as the donor concentration is reduced. Pascal et al.(7) believed that this is due to an inhomogeneous distribution of Te in the layer and the limiting case of this homogeneity being the presence of p and n regions in the same layers. The physical reason behind this phenomenon is not clear at present. However, our experimental results are consistent with the results reported by other groups.

After doping studies, several TPV device structures were grown in $In_{0.2}Ga_{0.8}Sb$ with various types of step-graded buffer layers. Figure 4 shows two device structures grown in this study. Figure 4(a) shows the technique commonly used, in which several step layers are grown with equal distribution of thickness and composition between the active layer and the substrate. This technique has been found to be successful in GaInAs/InP TPV structures (9). This method is particularly useful when the lattice mismatch between the active layer and the substrate is small, and for materials that relax very quickly beyond the critical layer thickness. Figure 4(b) shows another step-grading technique in which a thick layer with a large lattice mismatch is grown as the first step layer, followed by the growth of a few thin step layers that are closely lattice-matched.

The ideas behind the second method are as follows: (1) Since there is a large lattice mismatch between the first step layer and the substrate, many dislocations are generated; therefore, the probability of dislocation interaction and annihilation by forming dislocation loops increases. This process can be extremely effective at high threading dislocation densities, but as the defect concentration decreases, the probability of further dislocation interactions decreases. (2) A thicker step layer allows for a complete relaxation of the layer at the growth temperature, which is especially important for materials which relax slowly. (3) The lattice mismatch between the adjacent top step layers is small enough to prevent the nucleation of many more misfit dislocations at individual interfaces. (4) The top step layers will effectively bend the residual threading dislocations that propagate from the initial interface, so that the active layer will be relatively dislocation-free.

Preliminary studies have shown that the device performance of $In_{0.2}Ga_{0.8}Sb$ layers grown by the method as shown in figure 4(b) is better than layers grown by the method shown in figure 4(a). (10) In order to understand the relaxation phenomena in these two structures, x-ray diffraction and TEM measurements were carried out on selected samples. X-ray measurements show that the epitaxial layers are actually tilted with respect to the substrates.

Figure 5 shows the variation of the relative Bragg angle as a function of the azimuth rotation angle for a (004) reflection measured on a 6μm thick $In_{0.2}Ga_{0.8}Sb$ epilayer grown on (100) GaSb substrate. The amplitude of the variation in the Bragg angle for the substrate gives the substrate miscut, and the amplitude of the variation in the Bragg angle for the epilayer gives the substrate miscut plus the relative epilayer tilt with respect to the substrate. As can be seen, the tilt angle between the $In_{0.2}Ga_{0.8}Sb$ epilayer and the GaSb substrate is much higher than the substrate misorientation, which indicates that formation of the epilayer tilt in $In_xGa_{1-x}Sb$/GaSb system is not initiated by the substrate misorientation alone. To determine whether the total tilt angle is formed in the vicinity of the interface (where the density of misfit dislocation is large) or whether it gradually increases, a systematic study was conducted. In this set of experiments, epilayers of different thickness were grown keeping all other parameters constant. Figure 6 shows that the tilt angle increases as the layer thickness increases, indicating that the layer tilt is formed continuously throughout the epilayer.

The full width at half maximum (FWHM) of the layers which is related to the dislocation density was measured and the data are shown in figure 7. Several points should be noted in this figure: (1) The FWHM of the 0.2μm $In_{0.2}Ga_{0.8}Sb$ layer is lower than that of thicker layers, which could be attributed to the layer not being fully relaxed even though the layer is thicker than the critical layer thickness for lattice relaxation. (2) The FWHM increases as the thickness increases until the thickness reaches 0.6μm, since a large population of misfit and threading dislocations form due to the 1.3% lattice mismatch. (3) The FWHM decreases between 0.6μm and 2.5μm, owing to the annihilation of the dislocations. (4) The FWHM of the layers do not decrease significantly beyond 2.5μm. Also, note that the tilt of the epilayer continuously varies with the thickness (see figure 6). This variation of tilt with thickness contributes to the broadening of the x-ray peaks. Hence, it was concluded that the actual FWHM of the layers should be lower than that shown in figure 7.

A long-standing problem in the area of epitaxial growth is the lack of understanding of the relaxation rate of the epitaxial layers and the tilt formation between the layers and the substrates. In lattice-mismatched hetero-epitaxy, misfit dislocations are formed at the interface; and in many cases, a crystallographic tilt of the layer with respect to the substrate is obtained. The tilt of the epilayers depends on the substrate tilt as well as on the growth conditions.

Nagai (11) was the first to propose a model to explain the formation of tilt in a GaInAs/GaAs system. This theoretical model shows that the tilt of the epilayer is a function of the lattice mismatch and the substrate misorientation. Based on this model, the amount of tilt is always less than the substrate misorientation, with the tilt increasing with the substrate misorientation and vanishing if the substrate is nominally (100) oriented. An increase in the tilt angle with respect to the substrate misorientation was also observed in many hetero-epitaxy systems such as CdZnTe/GaAs(12), ZnSe/GaAs(13), and ZnSe/Ge(14). Olsen and Smith(15) proposed that tilt is related to the formation of misfit dislocations and that the component of the Burgers vector perpendicular to the growth plane is responsible for the tilt formation. They showed that the tilt angle of epitaxial layers is directly proportional to the misfit strain, except when misfit is relieved by pure edge dislocations. Their model can only predict an upper limit for the magnitude of tilt.

To date, the experimental results showed that the amount of tilt angle between the epitaxial layers and the substrates with exact (100) orientation (0.1-0.2^{o} off) is less than a few hundred arc-sec. To the authors knolwledge, this is first time that a large amount of tilt was observed for growth on nominally (100) oriented substrates, and also that the epilayer tilt increases with the thickness.

To investigate the propagation behavior of dislocations, TEM microscopy was carried out on several samples. Figures 8(a) and 8(b) show the TEM bright field images for two different layers of nominally 2μm thick $In_xGa_{1-x}Sb$ epilayers grown on GaSb substrate with a 0.3μm thick GaSb buffer layer. The figures clearly show a zone of dislocations buried at a depth of 1.5 - 1.7μm below the surface. On these and other samples that were studied, long dislocations parallel to the misfit networks were observed just above the misfit zone; and in several part of the samples these dislocations seem to bend parallel to the surface at different depths from the surface. Most of the threading dislocations which originate at the misfit networks are deflected parallel to the interface (converted to misfit dislocations) and then terminated. Beyond approximately 1μm thick layers, few dislocations were observed in the area studied by TEM. These dislocations which are parallel to the interface may be responsible for the lattice tilt. Since these dislocations are found to move parallel to the interface at different distances from the interface, the tilt is also a function of the layer thickness.

The inclination angle of the layers grown with the two step grading schemes described before was compared. It was found that when the step graded layer consists of 15 steps with equal thickness and 0.09% lattice mismatch between adjacent layers, the value of tilt angle was very low (about 35 arc-sec). On the other hand, a large tilt angle was observed (about 2100 arc-sec) when a thick initial layer of larger composition and lattice mismatch was grown followed by a few thinner steps. Since the lattice tilt does not intrinsically have any effect on the device performance, the presence of tilt may indicate that the layers are relaxed through dislocation motion along the growth plane so that active layers are dislocation-free. Therefore, layers with larger tilt yielded better quality TPV devices.

CONCLUSIONS

N-type doping studies carried out on $In_{0.2}Ga_{0.8}Sb$ grown on GaAs and GaSb show that the doping concentration increases with the DETe mole fractions as expected, up to $1x10^{18}cm^{-3}$. When the DETe mole fraction is increased further, the doping concentration is actually decreased. TPV device structures using two different step-grading techniques have been grown and characterized. It was found that the epitaxial layers are tilted with respect to the substrates and the amount of tilt increases with layer thickness. The layer tilt and the device quality are found to be correlated. TEM studies of some selected layers show that the dislocations originating at the misfit networks move parallel to the interface at various distances from the interface, which may explain the layer tilt.

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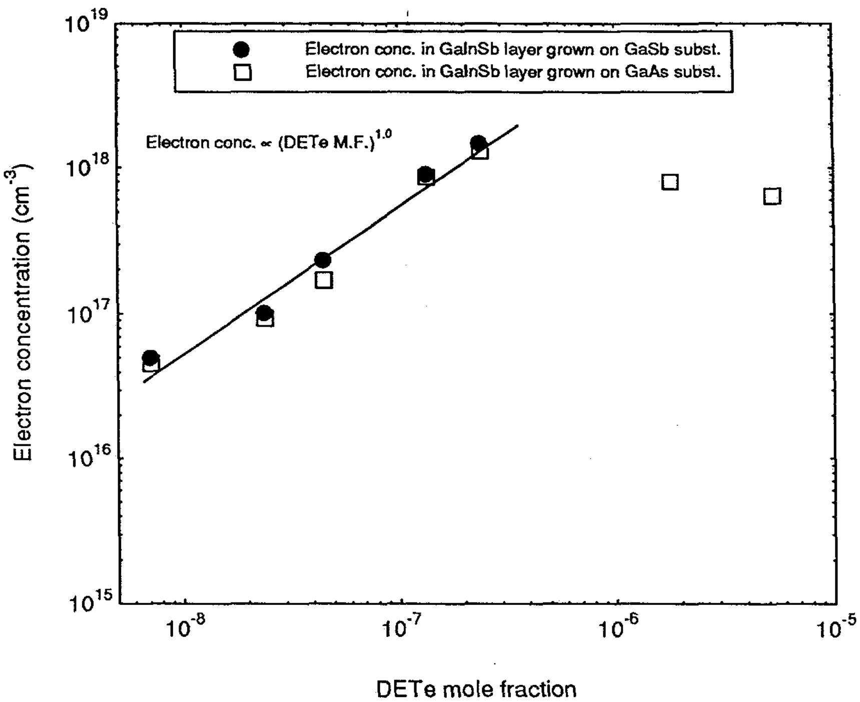


Figure 1 Carrier concentration at 77K versus DETe mole fraction in $In_{0.2}Ga_{0.8}Sb$ grown on GaAs and GaSb substrates.

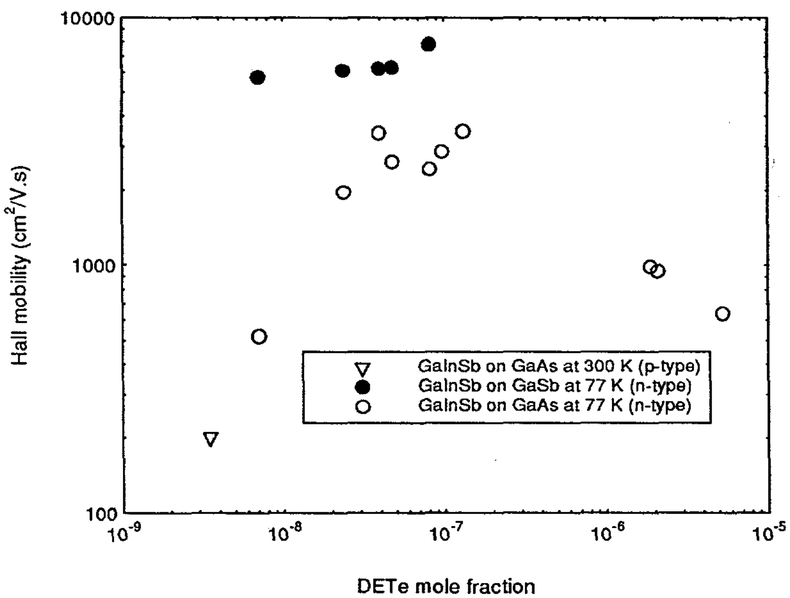


Figure 2 Hall mobility versus DETe mole fraction for $In_{0.2}Ga_{0.8}Sb$ layers grown on GaAs and GaSb substrates.

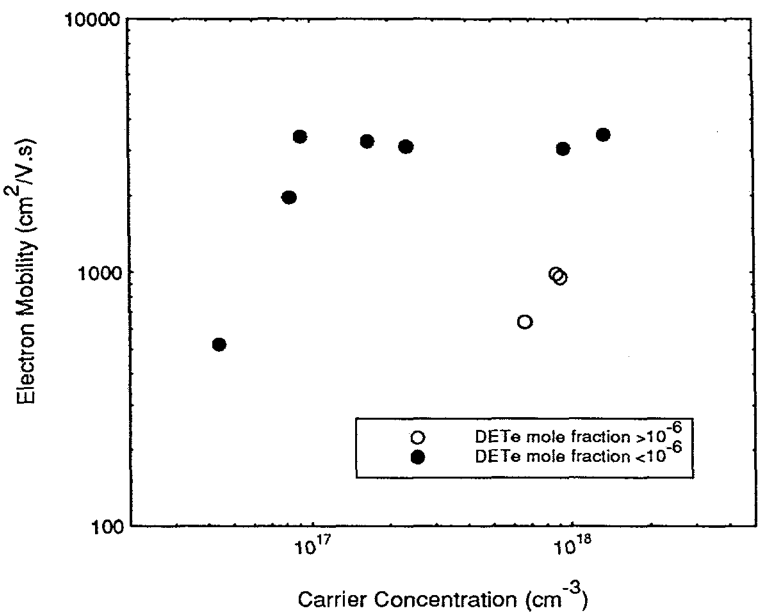
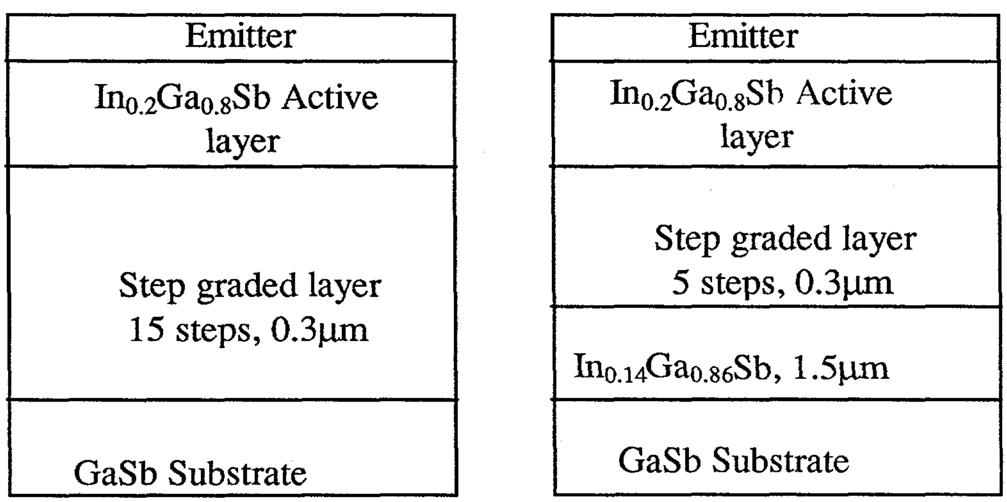


Figure 3 Hall mobility at 77K versus carrier concentration for $In_{0.2}Ga_{0.8}Sb$ layers grown on GaAs substrate. Data for high flow of DETe (mole fraction > 10^{-6}) are also plotted.



(a) (b)

Figure 4 Two types of step grading methods used in this study

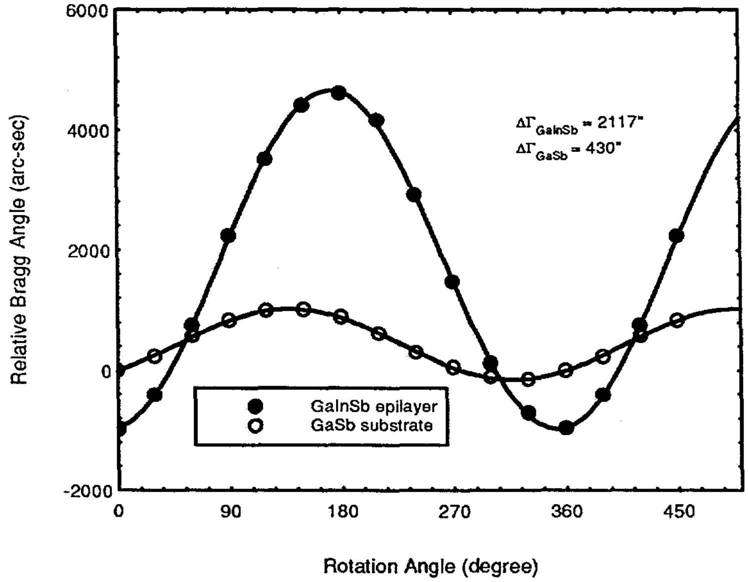


Figure 5 Relative Bragg angle versus azimuth rotation angle. The amplitude difference between the epi and the substrate indicates the layer tilt with respect to the substrate.

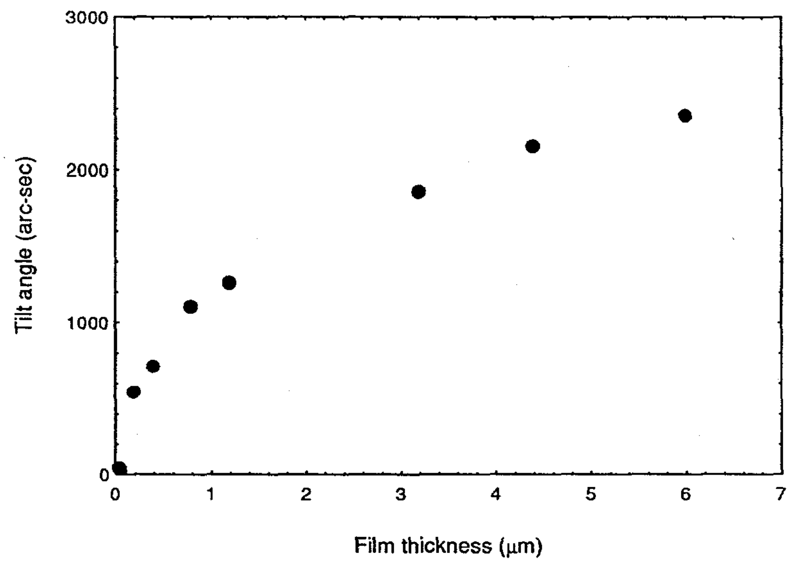


Figure 6 Epilayer tilt with respect to the substrate for different values of layer thickness.

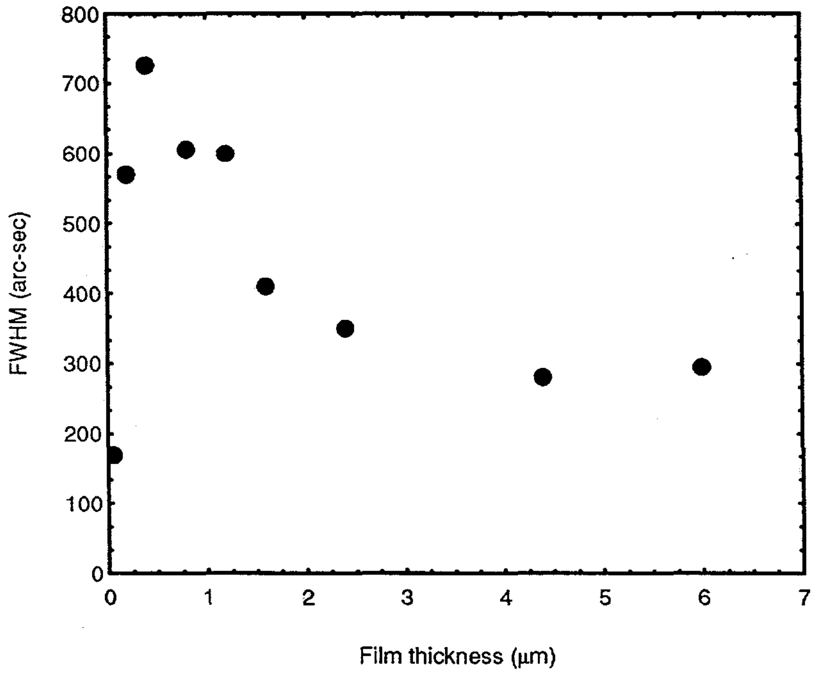


Figure 7 The FWHM of InGaSb layers grown on GaSb substrates as a function of layer thickness.

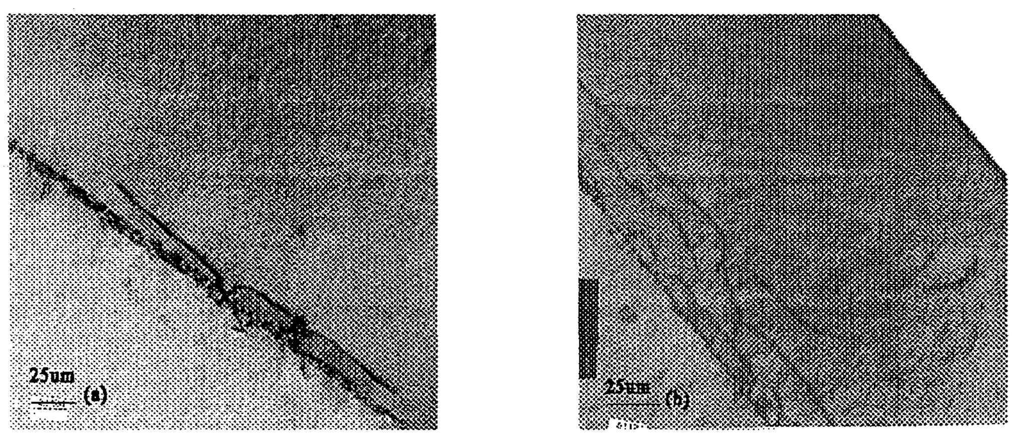


Figure 8 Bright field TEM micrographs of a Si doped (a) and Te doped (b) $In_{0.2}Ga_{1-x}Sb$ layer grown on GaSb with a 0.3μm thick buffer layer. Note the deflection of dislocations parallel to the interface, and at different distances from the interface.