# Electrochemical Capacitance Voltage Profiling of the Narrow Band Gap Semiconductor InAs

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InAs is a narrow band gap compound semiconductor with potential applications in infra-red detectors and high speed transistors. In order to facilitate device design using this material, it is essential that carrier concentration profiles be accurately known. Capacitance-voltage (CV) profiling is often employed for this purpose. Due to surface Fermi level pinning, it is difficult to form metal Schottky contacts to InAs layers, making conventional CV profiling difficult. Electrochemical CV (ECV) measurements have been successfully performed on InAs epilayers grown by molecular beam epitaxy on GaP. A solution of 0.2 M EDTA with 0.2M NaOH and 10–20% by volume of ethylenediamine acts both as an etchant and as a Schottky contact to InAs. The profiles obtained for undoped InAs layers were compared to Hall effect data, and showed good agreement. ECV profiling of thick layers with p- and n-type doped regions is also demonstrated.

**Key words:** InAs, CV profiling, ECV profiling

## INTRODUCTION

The design of compound semiconductor based devices increasingly requires the integration of materials of differing band gaps. This is achieved by depositing layers of different semiconductors epitaxially on a substrate. Techniques such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) can be used to precisely control the thickness and chemical composition of heteroepitaxial layers, as well as to introduce dopant species in-situ. The electrical properties of some heterostructure systems, such as GaAs/AlGaAs, have been studied extensively, but those of materials such as InAs are not well known. InAs is a narrow band gap semiconductor whose potential applications include infra-red detectors, high speed transistors and magnetic field sensing devices. Lattice mismatches of 7% and 11%, respectively, with GaAs and GaP result in high threading dislocation densities, which are spatially inhomogeneous, when InAs is grown on these substrates.[1,2] This is seen in Fig. 1 for an InAs/GaP heterostructure. The decrease in dislocation density with distance away from the heterointerface leads to a corresponding drop in carrier concentration in nominally undoped material.[2] The lattice defects also in-

teract with chemical impurities, and doping of InAs has not been well investigated. Consequently, a reliable method to study the variation of carrier concentration with depth in InAs needs to be developed. The major techniques available for this are differential Hall effect profiling and capacitance-voltage (CV) profiling.[3] In the Hall method, a controlled amount of material is etched, and the measurement is repeated after each etch step to obtain the carrier distributions. However, in a non-uniform layer, Hall effect data only yield weighted averages of the carrier density and mobility, the interpretation of which can be complicated.[2] Another complication, specifically with regard to InAs, is that the Fermi level is pinned above the conduction band edge at the free surface, leading to surface carrier accumulation.[4] This accumulation layer dominates the conductivity and leads to errors in interpreting the Hall effect data. Due to these reasons, CV profiling is the more attractive alternative to characterize InAs layers. Unfortunately, due to surface Fermi level pinning, it is easy to make good ohmic contacts to InAs, but it is difficult to achieve a reliable metal/InAs rectifying contact, which is necessary for conventional CV measurements. In this paper, the use of the electrochemical CV (ECV) profiling technique to obtain the depth dependence of carrier concentration in InAs epilayers grown on GaP substrates by MBE is reported for the first time.
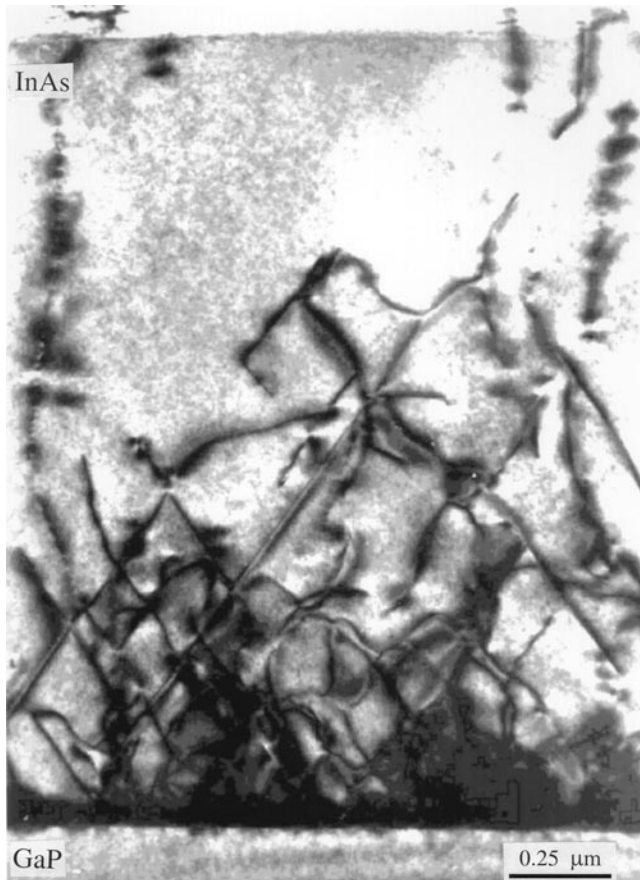
Fig. 1. Cross-section TEM micrograph showing threading dislocations in a 2 μm thick InAs layer grown on GaP.

## THEORY OF ELECTROCHEMICAL CV PROFILING

The ECV technique was developed by Ambridge and co-workers more than 20 years ago.[5] The technique is based on making a liquid electrolyte-semiconductor Schottky contact and measuring the capacitance at a constant reverse bias. A good review is given by Blood.[6] The semiconductor is electrolytically etched between capacitance measurements, leading to depth profiling. Thus, it is a destructive technique, but the depth limitation of conventional CV due to reverse bias breakdown is avoided in ECV measurements. Both the electrolytic dissolution and the etching are performed in the same measurement apparatus, and a small ac signal (<< 1 V), typically at a low frequency of 0.3–3 kHz is superposed on the dc bias during the capacitance measurement step. The carrier concentration at the depletion depth $W_{DEPL}$ is extracted from the slope of the $1/C^2$ vs. V curve at the operating point using the relationship:

$$N(W_{DEPL}) = \frac{2}{q \cdot K_s \cdot \varepsilon_0 \cdot A^2} \cdot \frac{1}{\dfrac{d\left(\frac{1}{C^2}\right)}{dV}} \qquad (1)$$

$$W_{DEPL} = \frac{K_s \cdot \varepsilon_0 \cdot A}{C} \qquad (2)$$

where, q is the electronic charge, $K_s$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of free space and A is the area of the electrolyte-semiconductor junction. Dissolution of the semiconductor depends on the presence of holes. This is easily achieved by forward biasing the Schottky junction for p-doped semiconductors. However, to drive the process in n-type materials, holes are photogenerated by illuminating and reverse biasing the junction. In the case of InAs, the intrinsic carrier concentration at room temperature is very high—$5 \times 10^{14}$ cm$^{-3}$, so that holes are plentiful ($10^{10}$ cm$^{-3}$ or higher) even in n-type samples. As a result, the InAs-electrolyte junction does not have to be illuminated for etching to occur. The depth to which the semiconductor is etched, $W_R$, in a time, t, is determined by Faraday's law of electrolysis:

$$W_R = \frac{M}{z \cdot F \cdot \rho \cdot A} \cdot \int_0^t I_{etch} \cdot dt \qquad (3)$$

where M is the molecular weight of the semiconductor, z is the dissolution valency (z = 6 for InAs and most other III-V semiconductors) which is the number of carriers required for the dissolution of one molecule of the material, F is the Faraday constant (= 96400 C), ρ is the density, and $I_{etch}$ is the dissolution current. As the carrier concentration is measured at the edge of the depletion region, the total depth at which the measurement is made is:

$$x = W_{DEPL} + W_R \qquad (4)$$

## EXPERIMENT

The growth of InAs layers on (001) GaP substrates by MBE has been described elsewhere.[7] Chemical doping was performed in-situ, with Si used as the n-type dopant and Be as the p-dopant. Electrochemical CV measurements were performed using the PN4400 Wide Bandgap Profiler manufactured by Bio-Rad Semiconductor Inc. The main component of the measurement apparatus is an electrochemical cell. The specimen was held tightly against a 3 mm diameter sealing ring, which defines the contact area, by means of spring loaded back contact pins. In the present case, since the InAs is grown on semi-insulating GaP, back contacts could not be utilized. Instead, ohmic contacts were made directly with the epilayer by two front contact pins, tipped with Pb/Sn solder. The electrolyte used was a solution of 0.2 M ethylene-diamine-tetra-acetic-acid (EDTA) with 0.2 M NaOH and 10% ethylenediamine (ED) by volume as additives. The volume fraction of ED is crucial in determining the quality of the measurement. Lower ED content (<5%) leads to a better (i.e., less leaky) Schottky junction, but a constant dissolution current cannot be held. If the ED content is greater than 15%, the etching process tends to become uncontrollable beyond a certain point, leading to extremely rough etch profiles. A volume content of 10% was found to give reproducibly smooth etch craters.

The etching and measurement are controlled by the

potential across the cell, which is established by passing a current between the semiconductor and a carbon electrode, and measured with reference to a saturated calomel electrode (SCE). The AC signal superimposed on the DC reverse bias is measured with respect to a Pt electrode located near the semiconductor surface. The cell has a window facing the sample surface, both to allow the sample to be illuminated during the etch cycle, and to check the sample-electrolyte junction for the presence of gas bubbles, which can lead to inaccuracies in the contact area. The lamp emits a broad band spectrum spanning both the visible and the ultraviolet. The UV radiation can be blocked by a suitable filter, and the light itself can be cut off by a computer controlled shutter mechanism. A pump which forces a jet of electrolyte onto the sample surface was used periodically to prevent the buildup of reaction byproducts and bubbles near the surface.

Prior to obtaining an ECV profile, the I-V and C-V curves for the sample were obtained. I-V curves provide an indication of the quality of the semiconductor-electrolyte diode, and the bias range over which capacitance measurements can be performed. Anodic (dissolution) current is always displayed as positive and the cathodic (plating) current as negative. Thus,

the I-V curve is used to determine the etching voltage and its polarity. This was chosen to maintain the dissolution current between 0.2 mA and 0.3 mA throughout the measurement. C-V curves are needed to select the measuring voltage, $V_{MEAS}$. Three different models, series, parallel, and 3-term, were used to compute the C-V curve, and $V_{MEAS}$ was chosen in a region where the three models converged and a dissipation factor, D, remained low (<0.4) and flat. The convergence of the three models and the value of D were found to be very sensitive to the ac frequency used to measure the capacitance. Suitably low values of D resulted only for frequencies lower than 1.0 kHz; all of the ECV profiles presented here were measured at 0.5 kHz. The amplitude of the signal was also kept low—0.1 V peak-to-peak. Having determined the etching and measuring bias, the ECV profile was collected, without illumination as explained previously, initially with etch steps of 5 nm. This was reduced to 1 nm as junctions were approached. End-point (i.e., the stage at which the entire InAs layer was etched away) detection was easy since the GaP substrate could not be etched unless the sample was illuminated with UV light. Potential complications could arise due to sidewall contribution and if residual InAs
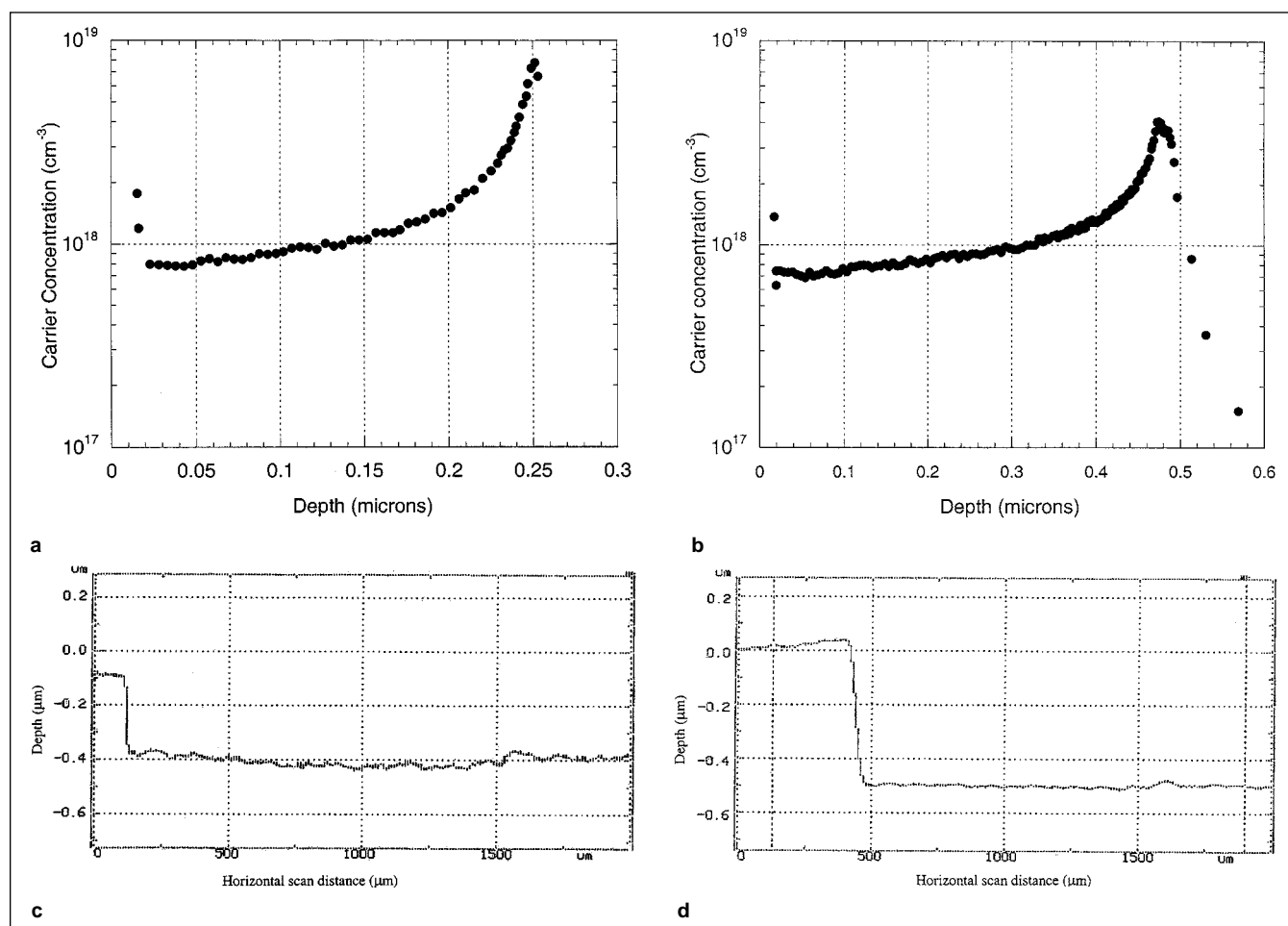


Fig. 2. ECV carrier concentration profiles of (a) a 0.25 μm thick undoped InAs layer grown on GaP, and (b) a 0.5 μm undoped InAs layer grown on GaP. Also shown (c,d) are the corresponding profilometer traces of the etch craters.
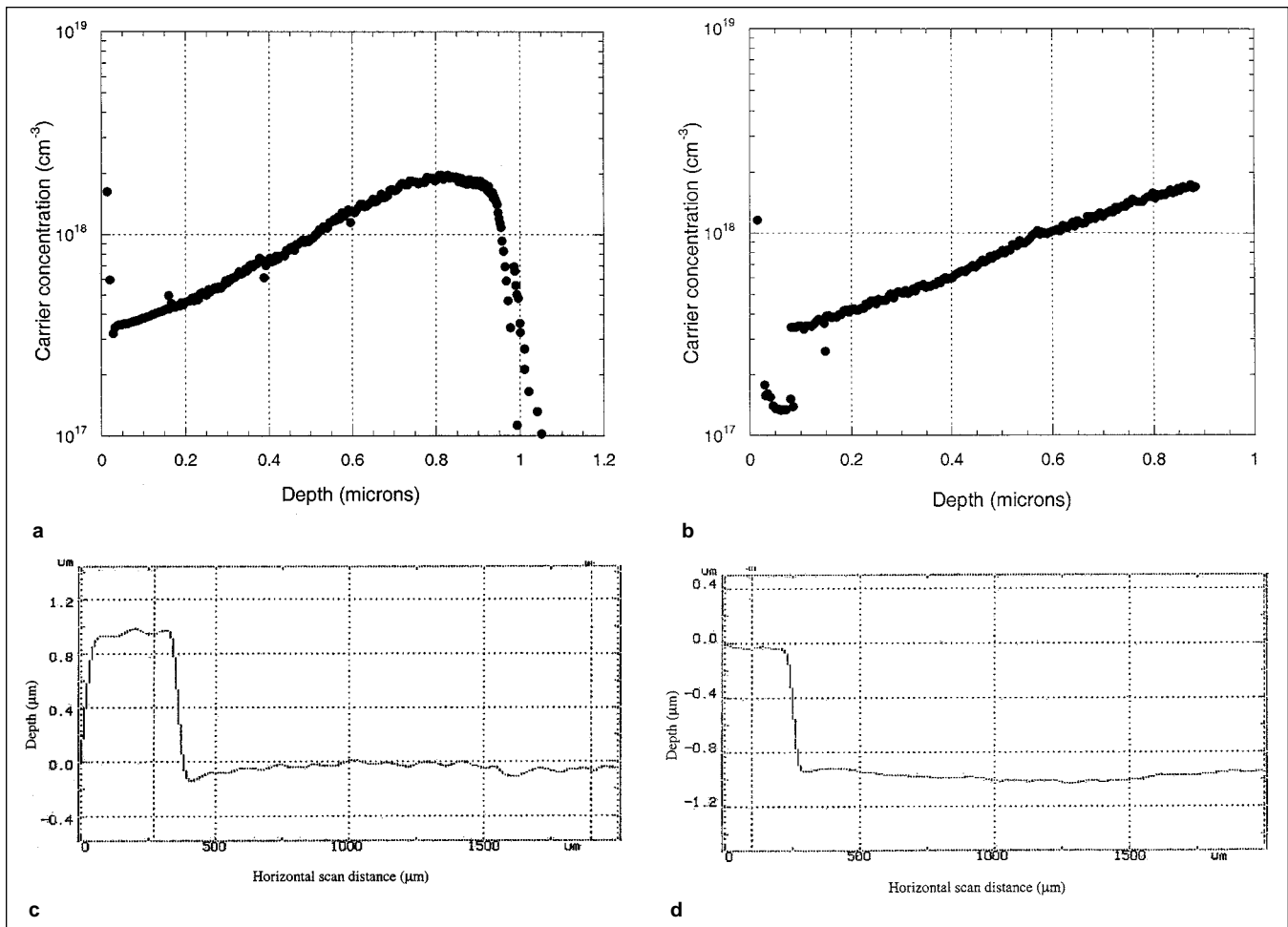
Fig. 3. ECV carrier concentration profiles of (a) a 1 μm thick InAs layer delta-doped near the heterointerface with $6 \times 10^{12}$ cm$^{-2}$ of Be, and (b) a 1 μm layer delta-doped near the heterointerface with $2 \times 10^{13}$ cm$^{-2}$ of Be. Also shown (c,d) are the corresponding profilometer traces of the etch craters.

were left over due to non-uniform etching. Upon completion of the measurement, the smoothness of etch was obtained by scanning the crater using a Tencor Instruments Alpha-Step 200 profilometer. This was also used to verify the depth etched.

## RESULTS AND DISCUSSION

Electrochemical CV profiling was carried out on undoped InAs layers ranging in thickness from 0.25 μm to 2.0 μm; 1.0 μm thick layers delta doped near the InAs/GaP heterointerface with Be; and doped layers that contained both n- and p-type regions. The results obtained from each of these categories of samples are discussed below.

### Undoped InAs Layers

Due to the large lattice mismatch between InAs and GaP, a two-dimensional periodic array of misfit dislocations (mostly edge type) results at the interface between these two materials.[8] Hall effect measurements performed on thin InAs layers yielded a sheet electron concentration of $10^{13}$ cm$^{-2}$, which was invariant with layer thickness. It was suggested that an extended defect structure at the intersection of 90° misfit dislocations, which would appear with a den-

sity of $\sim 10^{13}$ cm$^{-2}$, was responsible for the generation of electrons at the heterointerface.[8] Associated with the misfit dislocation network are threading dislocations that propagate from the interface to the free surface. The threading dislocation density is highest near the interface and diminishes away from the interface as seen in Fig. 1. This microstructural inhomogeneity leads to variation of the carrier concentration with depth. Consequently, a multilayer analysis was used to interpret Hall effect data, details of which can be found in Ref. 2. The carrier density was found to decrease monotonically with the dislocation density, with the highest value near the interface, consistent with the model of misfit dislocation-related carrier accumulation. ECV profiling presented a convenient method of confirming these predictions. Figure 2a and b are ECV profiles of 0.25 μm and 0.5 μm InAs layers respectively. Profilometer traces of the crater are included for each of the samples to demonstrate the flatness of the etch profile. It is clear that the carrier density does indeed vary as predicted, with carrier accumulation at the heterointerface evident. An interesting feature is that initially a high carrier concentration is measured near the surface, but this settles down to a lower value beyond the first few data

points. Simultaneously, the value of the dissipation factor also dropped, and the convergence of the 3 models improved. This phenomenon is reproducible, though the exact cause is unknown. It is possible that the presence of surface states give rise to a larger carrier concentration when the first data point is collected after etching away the thin capping layer (5–10 nm in thickness), but reducing the first etch step depth to 1 nm did not make a difference. A few etch steps are required to establish a stable Schottky barrier between the electrolyte and the semiconductor.

## InAs/GaP Doped at the Interface with Beryllium

ECV profiling was performed on 1.0 μm thick InAs samples that were doped in a narrow region near the heterointerface with a p-type dopant—Be. The carrier concentration was highest near the heavily dislocated interface, hence compensating the electronic charge with Be could result in greater electrical uniformity throughout the layer. The effects of such a delta-doped layer cannot be measured by the Hall effect, since it yields a carrier density averaged over the entire layer. The occurrence of charge compensation was clearly seen in the ECV profiles. Two samples were grown, one with a Be sheet concentration of $6 \times 10^{12}$ cm$^{-2}$ and the other with $2 \times 10^{13}$ cm$^{-2}$, and the ECV profiles obtained are shown in Fig. 3a and b, respectively. As a result of the Be doping, the carrier accumulation at the interface (see Fig. 2) disappears. In the case of the sample with the lower doping, the etching continued through the interface until the GaP substrate was reached, which was verified by illuminating the sample with UV light to obtain an etch current. However, the higher Be doping resulted in an etch block, and the dissolution current fell to a negligibly low value before the substrate was reached.

## $Al_xIn_{1-x}As$/GaP Heterostructures

$Al_xIn_{1-x}As$/InAs heterostructures grown on a GaP substrate can be used to build heterojunction bipolar transistors (HBTs). ECV profiling can be used to study the electrical properties of $Al_xIn_{1-x}As$ layers. Two samples were grown, one with a 0.2 μm layer of $Al_{0.1}In_{0.9}As$ directly on GaP, and the other with a 0.4 μm layer of $Al_{0.2}In_{0.8}As$, followed by 10 nm of InAs on GaP. The addition of Al to InAs increases the band gap of the semiconductor. Hall effect measurements showed that the sheet carrier density decreased as the Al content in the $Al_xIn_{1-x}As$ increased. From this it can be inferred that the magnitude of the carrier accumulation at the heterointerface is reduced. A thicker layer of $Al_{0.2}In_{0.8}As$ had to be grown since a 0.2 μm thick layer would be completely depleted even for small reverse biases. ECV profiles from these samples are shown in Fig. 4a and b, respectively. Figure 4 complements the information obtained from Hall effect measurements. Not only was the interfacial carrier accumulation reduced, but the background carrier concentration also dropped with increasing Al content. The lattice mismatch between $Al_xIn_{1-x}As$ (x = 0.1 or
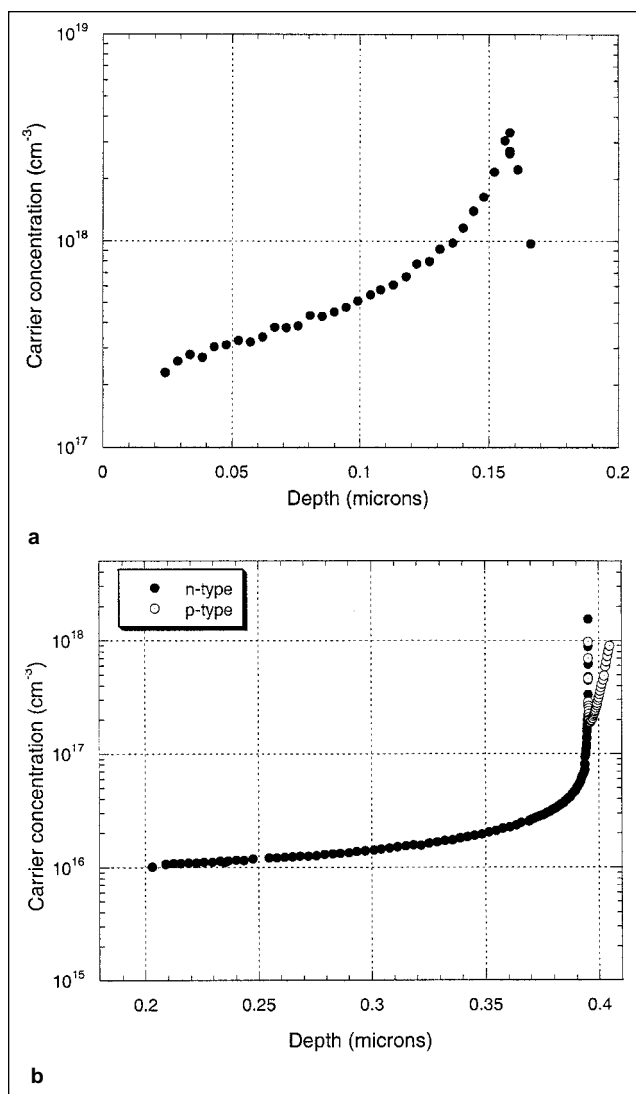


Fig. 4. ECV carrier concentration profiles of (a) a 0.2 μm thick undoped $Al_{0.1}In_{0.9}As$ layer grown on GaP, and (b) a 0.4 μm undoped layer of $Al_{0.1}In_{0.9}As$ on a 12.5 nm layer of InAs grown on $10^{18}$ cm$^{-3}$ p-doped GaP.

0.2) and GaP is not significantly different from that between InAs and GaP, so the dislocation microstructure remained similar. This was confirmed by TEM investigations of the $Al_xIn_{1-x}As$/GaP samples. The decrease in carrier density is an indication that the dislocation/point defect related energy levels responsible for carrier generation in InAs remained fixed with respect to the vacuum level while the conduction and valence band edges moved apart due to Al addition.

## p- and n-type Doped InAs

The most important use for ECV profiling is in the investigation of doped layers. It is critical to optimize the doping concentration, and the location of junctions (p-n or isotype) in order to design devices. The interaction of chemical dopants with heavily dislocated InAs is not well characterized. Be delta doping was shown to compensate the interfacial charge, but the conductivity remained n-type. In order to dope InAs p-type, very high concentrations of Be are needed.
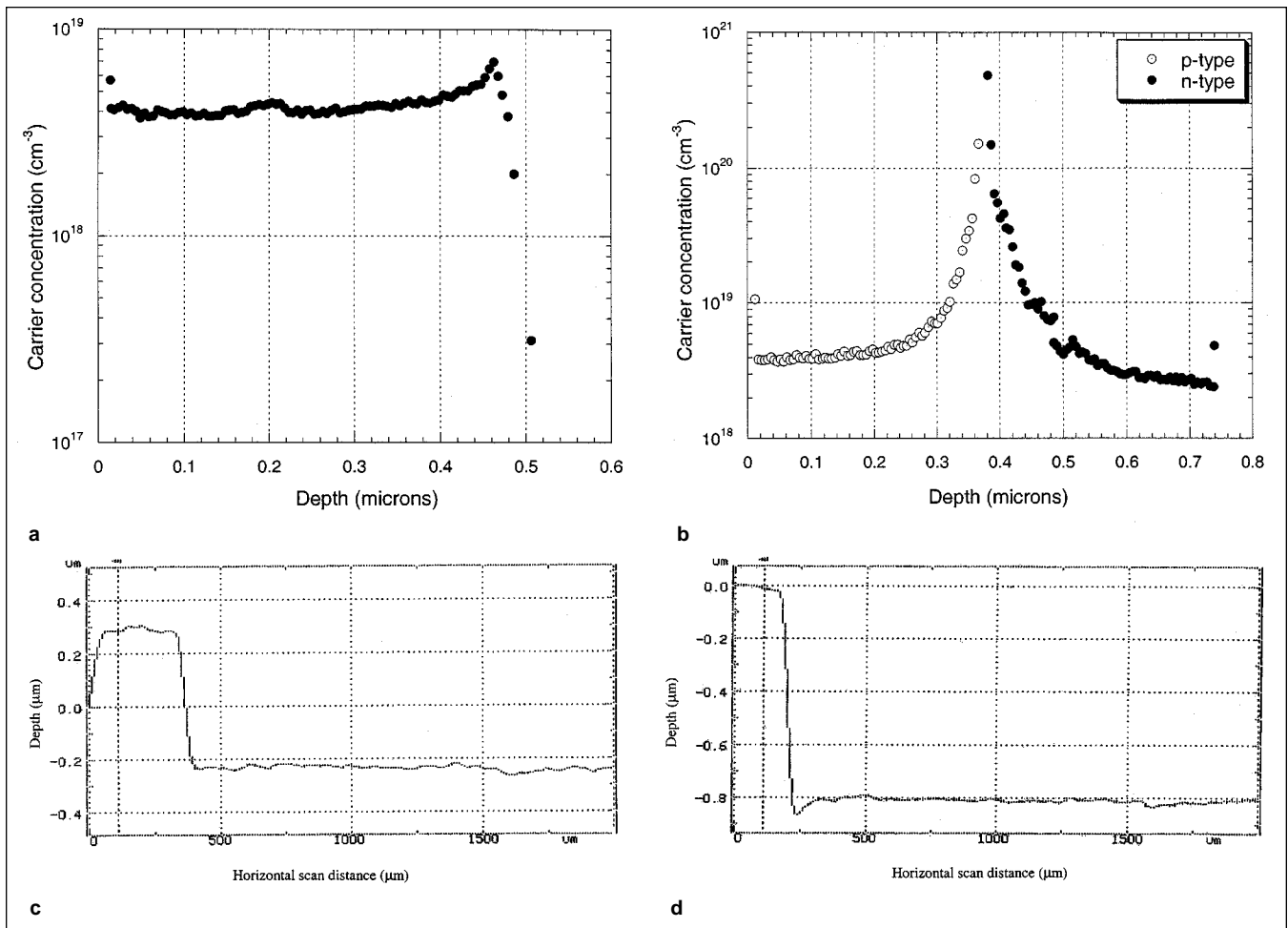
Fig. 5. ECV carrier concentration profiles of (a) a 0.5 µm thick InAs layer nominally doped with $2 \times 10^{18}$ cm$^{-3}$ of n-dopant Si, and (b) a 1 µm layer of InAs nominally doped with $5 \times 10^{18}$ cm$^{-3}$ of p-dopant Be. Also shown (c,d) are the corresponding profilometer traces of the etch craters.
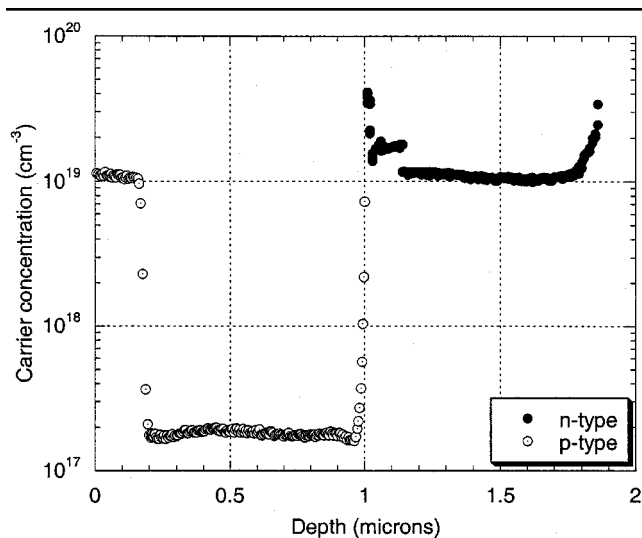


Fig. 6. ECV carrier concentration profile of a 2 µm thick InAs sample that contained n$^+$, n, and p$^+$ doped regions.

Figure 5a is an ECV profile of a 1.0 µm InAs sample nominally doped uniformly with $5 \times 10^{18}$ cm$^{-3}$ of Be. The hole concentration remains at the expected level of $5 \times 10^{18}$ cm$^{-3}$ until a depth of about 0.3 mm from the surface. This corresponds to a region of low dislocation density, where the background electron density is below $10^{18}$ cm$^{-3}$. However, as the dislocation density increased, a p-n junction was reached and beyond 0.4 µm, the majority carriers were electrons. The electron density did not increase as the interface was approached, indicating that the presence of Be had a compensating effect in this region. Since the intrinsic carrier density, $n_i$, is $8 \times 10^{14}$ cm$^{-3}$ for InAs at room temperature, an electron density, n, of $2 \times 10^{18}$ cm$^{-3}$ implies that

$$p = \frac{n_i^2}{n} \approx 3 \times 10^{11} \text{cm}^{-3} \qquad (5)$$

which is 7 orders of magnitude lower than the nominal Be concentration. So, the specific mechanism of compensation due to Be is unclear, but it can be speculated that the Be atoms interact with the structural defects responsible for electron generation (threading dislocation kink sites or associated point defects) and deactivate some of these. It is necessary to perform secondary ion mass spectrometry (SIMS) measurements on these samples to obtain the Be profile. This would yield information on whether the Be atoms are gettered by dislocations or segregate

away from the dislocated regions. On the other hand, the background electron density due to the dislocations enhances chemical n-type doping. Figure 5b is an ECV profile of a 0.5 µm InAs sample doped uniformly with $2 \times 10^{18}$ cm$^{-3}$ of Si. The measured carrier concentration was $4 \times 10^{18}$ cm$^{-3}$, which remained constant with depth, rising only near the heterointerface as expected.

If the doping levels are greater than $10^{19}$ cm$^{-3}$, uniform p- and n-type regions result. Figure 6 is an ECV profile from a sample that contains n$^+$, n, and p$^+$ regions. The initial 0.2 µm was grown doped with $10^{19}$ cm$^{-3}$ of Si. The next 0.8 µm was nominally undoped. Following this was a $10^{19}$ cm$^{-3}$ p-doped region. Apart from some uncertainty near the n-p$^+$ junction, the ECV profile shows that the expected constant carrier concentrations were achieved in the highly doped regions.

## SUMMARY

ECV profiling was shown to be a valuable technique for the electrical characterization of InAs. The importance of optimizing the electrolyte chemistry to obtain both a good Schottky barrier and uniform etching was emphasized. ECV profiling of InAs was demonstrated to be useful both to complement Hall effect measurements for undoped samples, and to characterize doped layers which could not be studied by the Hall effect. A combination of ECV and SIMS measurements can be used to improve the understanding of dopant interactions with heavily dislocated InAs epilayers.

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