Near-surface electronic structure on InAs (100) modified with self-assembled monolayers of alkanethiols.

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Abstract

Using surface chemical modification to eliminate the generic problems of high surface recombination velocity and Fermi level pinning is studied on InAs(100). Raman scattering and X-ray photoelectron spectroscopy (XPS) are used to investigate passivation, provided by alkanethiols, RSH; $R = CH_3(CH_2)_n$ both neat and in ethanolic solutions, of this surface against oxidation. The magnitude of the interfacial band-bending is obtained by analysis of Raman scattering from the unscreened LO phonon, which arises from the near –surface charge accumulation region (CAR). Removing the native oxide with a $Br:CH_3OH$ chemomechanical etch reduces the surface band bending, but atmospheric oxidation increases band bending to its original level over several hours. Chemical passivation prevents band-bending for periods up to several weeks.

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InAs-based devices have become important recently as materials for use in IR photodetectors and high speed transistors[1]. InAs is unusual among III-V materials in that the surface Fermi level is pinned above the conduction band on the (100) and (111) surfaces, giving rise to a 2-D electron gas contained in a surface-confined charge accumulation region[2,3] In contrast, the majority of important low-index surfaces of other III-V materials exhibit a depletion region, caused by surface Fermi level pinning near the valence band, which leads to Schottky barrier formation. Although the lack of a Schottky barrier on InAs(100) solves many transport problems, control of the surface is still important. For example, the inverted surface band bending in InAs is accompanied by motionally bound states which detrimentally affect electron transport through the CAR[4-6]. In addition the high density of surface states in InAs pins the surface Fermi level and limits the effectiveness of common strategies, e.g., depositing metals with different work functions,[7] for controlling the near-surface electronic properties.

While significant progress has been made in developing effective passivation schemes for surfaces of other III-V materials such as GaAs,[8-19] InP,[20,21] and the ternary and quaternary alloys derived from them, little prior work exists addressing InAs; the one available study demonstrating that Se applied to MBE-grown InAs produces anomalously high band bending[22]. On the other hand molecular assemblies of alkanethiols, RSH; R = $CH_3(CH_2)_n$, have been extensively studied, and they have previously been used to modify GaAs surfaces.[23,24] Thus, the current work represents a natural extension of the GaAs efforts in an effort to control the near-surface electronic properties of InAs. Raman spectroscopy is used principally here to probe the near-surface electronic properties[7,25-30]

that are so important for device applications, and in particular to determine how passivation affects the CAR. XPS is used in tandem to examine the chemical nature of the interaction between thiols and InAs.

Bulk grown ($n^+ = 1.2 \times 10^{19}\,\text{cm}^{-3}$) InAs was obtained from OMK (Slovakia), and MBE-grown material ($n^+ = 1 \times 10^{19}\,\text{cm}^{-3}$, $1.2 \times 10^{19}\,\text{cm}^{-3}$, $2.0 \times 10^{19}\,\text{cm}^{-3}$) consisting of 200 nm of n^+-InAs (Si doped) on undoped GaAs with an intervening undoped InAs buffer layer. The Raman spectra were obtained with a Coherent 90-6 Ar$^+$ laser and a Spex 500M single monochromator equipped with a Photometrics Series 210 CCD and were collected in the x(y,z)$\bar{\text{x}}$ configuration where x, y, and z represent the (100), (010) and (001) lattice directions, respectively. In this configuration, the LO phonon and coupled phonon-plasmon modes are allowed, while the TO mode is disallowed[26]. XPS spectra were obtained on a Physical Electronics (PHI 5400) instrument using a Mg K$_\alpha$ source. The lines used to evaluate the relative concentrations of elements at the surface of the wafer are: O(1s), binding energy (B.E.) ≈ 531 eV, As($3d_{5/2}$, $3d_{3/2}$), B.E. $\approx 42, 43$ eV, In($3d_{5/2}$, $3d_{3/2}$), B.E. $\approx 444, 452$, S($2p_{3/2}$, $2p_{1/2}$), B.E. ≈ 163 eV and C(1s), B.E. ≈ 285 eV. Samples were etched in a 1% Br$_2$:CH$_3$OH (Br:MeOH) solution for 30 s and kept in N$_2$ to prevent oxide growth between the etch and passivation steps. Profilometry on step-profiles determined the etch rate to be 27 ± 4 Å/s . Passivations were carried out in both neat alkanethiol and 1 mM solutions of alkanethiol in deaerated ethanol.

The Raman spectrum of InAs exposed to various processing steps is given in Figure 1. The spectrum of the unprocessed sample shows two modes: a low-frequency coupled phonon-plasmon mode, L., observed near 225 cm^{-1}, originating in the bulk of the n^+-InAs, and an unscreened LO mode observed at 239 cm^{-1} originating from the CAR as

a result of wavevector non-conservation. The narrow width of the CAR is associated with uncertainty in the scattering wavevector: scattering from regions of k-space corresponding to wavelengths smaller than the Thomas-Fermi screening length is observed[7]. In a series of similarly prepared and processed samples the LO mode intensity can be taken to reflect the spatial extent of the CAR and, by inference, the magnitude of the surface state density pinning the surface Fermi level.[23]

Comparing the spectra before and immediately after etching shows a decrease in the unscreened LO mode intensity. Also shown in Fig. 1 is the result of exposing the freshly etched sample to atmospheric O_2 for varying times. Without passivation the LO mode, quenched by etching, is observed to regenerate within a few hours. Figure 2 shows the effect of storing the sample in dry N_2, removing the sample only periodically for Raman measurements. A small increase in LO intensity is observed after the first measurement, which subsequently stabilizes. We infer from these observations that exposure to O_2 repins the Fermi level above the conduction band. Apparently, surface oxidation plays a more significant role in Fermi level re-pinning than crystal termination and reconstruction.

To study the passivation of InAs(100) freshly etched samples were treated with 1 mM ethanolic solutions of alkanethiol: octadecanethiol, $n = 17$, hexadecanethiol, $n = 15$, and dodecanethiol, $n = 11$. After exposure to the passivating agent, samples were rinsed with ethanol followed by 2-propanol to remove any non-specifically adsorbed species. Each solution and both materials sources, *i.e.*, bulk and MBE-grown, give substantially the same results, as shown in Figure 3. The LO intensity is reduced significantly relative to unetched material, indicating that the Fermi level is unpinned by etching.

Furthermore, this reduced LO mode intensity is maintained for over a week of exposure to atmospheric O_2 on both sample types. Similar exposure of freshly-etched InAs (100) surfaces to neat alkanethiol for similar amounts of time does not result in an effective passivating layer, as determined by the temporal behavior of the Raman spectra after exposure to O_2.

In order to determine the chemical composition of the near-surface region of passivated surfaces, XPS spectra of alkanethiol films on InAs(100) were taken at 15° and 90° take-off angles (measured from surface), as exhibited in Figure 4. The XPS spectra taken at 45° (not shown) and 90° show no oxide present in the passivated samples. Spectra taken at 15° show a small oxygen signal in the spectrum, suggesting that the oxygen signal originates from the top surface of the film. The S/C intensity ratio increases from 0.048 to 0.075 for spectra taken at 15° and 90°, respectively, indicating that the sulfur signal originates below the carbon in the thiol. Also, the In and As XPS peaks cannot be fit with an elemental contribution alone, but must include an additional contribution in the region that As_xS_y and In_xS_y should appear. These results indicate oxygen is present sparingly at the alkanethiol-InAs boundary in passivated samples and strongly suggests sulfur bonding at this interface. The decrease in the S/C intensity ratio and increase in the O/C intensity ratio observed at shallow take-off angles is consistent with the interpretation that the sulfur atom resides at the film:InAs interface and any oxygen signal is adventitious at the film-air boundary.

Given the presence of distinct inelastic light scattering signatures from the CAR and the bulk, the thickness of the CAR can be determined from the Raman spectra by

measuring the relative intensities of the LO and L. modes using an abrupt junction model according to [31]:

$$\frac{I_{LO}}{I_{L-}} = \frac{R_{LO}}{R_{L-}}(e^{2\alpha d} - 1)$$ (1)

where $\alpha = 0.0516$ nm^{-1} is the absorption coefficient of InAs at the excitation wavelength of 457.9 nm, d is the CAR thickness, R_{LO} and R_{L-} are the scattering coefficients, and I_{LO} and I_{L-} are the Raman intensities of the LO and L. modes, respectively. The ratio R_{LO}/R_{L-} is determined by finding d for an unetched sample independently, by comparing the intensity of the LO mode on n^+-samples to the LO mode on an undoped sample[32]. For unpassivated samples, the CAR is 35 Å,[32] and R_{LO}/R_{L-} is determined to be 1.88. After passivation, the width narrows to 17 ± 1 Å for the bulk sample (-52%) and 16 ± 1 Å for the MBE sample (-55%).

From the CAR thickness the reduction in band bending can be determined from,[33]

$$d = \sqrt{\frac{2\varepsilon\phi}{en}}$$ (2)

where ε is the static dielectric constant ($\varepsilon = 15\varepsilon_0$ for InAs), e is the electron charge, n is the doping density and ϕ is the band bending ($|E_{c,surf} - E_{c,bulk}|$). Prior to etching or passivation ϕ is 89 ± 4 meV. After passivation, ϕ is determined to be 24 ± 3 meV for bulk samples and 27 ± 3 meV for MBE samples. The Raman spectra are also analyzed to determine the carrier lifetime by fitting the spectral lineshapes of the LO mode to a Lorentzian lineshape, and the L. mode to a lineshape derived from a hydrodynamic model of electron response given by,[34]

$$\left(\frac{d^2R}{d\omega d\Omega}\right) \propto \frac{\Gamma\left(\omega_0^2 - \omega^2\right)^2}{\left[\omega^2\left(\omega_l^2 - \omega^2\right) - \omega_p^2\left(\omega_l^2 - \omega^2\right)\right]^2 + \Gamma^2\omega^2\left(\omega_l^2 - \omega^2\right)^2} \qquad (3)$$

where $1/\Gamma$ is the phenomenological electron lifetime and ω_p, ω_t and ω_l are the frequencies of the plasmon, TO phonon and LO phonon, respectively. For the bulk samples, the lifetime increased from 2.8×10^{-14} s to 3.7×10^{-14} s, while in the MBE samples it increased from 2.5×10^{-14} s to 3.0×10^{-14} s. Taken together, the reduction in the band bending and increase in electron scattering lifetimes in the near-surface region argue that alkanethiol adsorption on InAs(100) largely unpins the surface Fermi level and effectively passivates the InAs surface.

In summary, treatment of freshly-etched InAs (100) surfaces with ethanolic alkanethiol solutions produces surfaces layers which passivate the InAs surface. The passivation, stable for more than one week in atmospheric O_2, is characterized by reduced band bending and a concomitant increase in the electron scattering time on both bulk and MBE-grown material, as measured by the reduction in CAR width. Treatment with neat alkanethiol does not passivate the InAs surface as effectively. Exposure of the InAs surface to the atmosphere between etching and passivation inhibits the formation of the passivation layer. Etching InAs surfaces in a Br:MeOH solution also reduces the surface band bending and CAR width, but without passivation exposure to atmospheric O_2 repins the surface Fermi level in a few hours.

Illinois at Urbana-Champaign also supported by DOE Grant DE FG02 91 ER45439. TAT

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Figure Captions

Figure 1.   Bulk InAs ($n = 1.2 \times 10^{19}$ cm^{-3}) spectra taken before and after etching in 1% Br:

MeOH. Spectra are for samples exposed to atmospheric O_2 for varying times.

Spectra were excited at 457.9 nm.

Figure 2.   Bulk InAs spectra taken at intervals after etching in 1% Br:MeOH. Samples

were stored in N_2 between measurements with exposure to O_2 in the

laboratory ambient during each measurement ≤ 5 min. Three additional

measurements were taken between the etch and the 19 h spectrum, all of

which overlay the 19 h spectrum, and are not shown for clarity. A control

sample left in the laboratory ambient for 19 h showed an LO mode at the same

level as in the original spectrum. $\lambda_{ex} = 457.9$ nm.

Figure 3   (a) MBE-grown InAs before and after passivation in 1 mM ethanolic

$C_{16}H_{33}SH$ for 18 hours. (b) Bulk InAs before and after passivation under the

same conditions. Spectra were excited at 457.9 nm.

Figure 4.   XPS spectra of a bulk InAs passivated in 1mM ethanolic $C_{16}H_{33}SH$ for 18

hours. Spectra were collected at detector angles of (a) 15° and (b) 90°, relative

to the surface.

Figure 1

Intensity (A.U.)
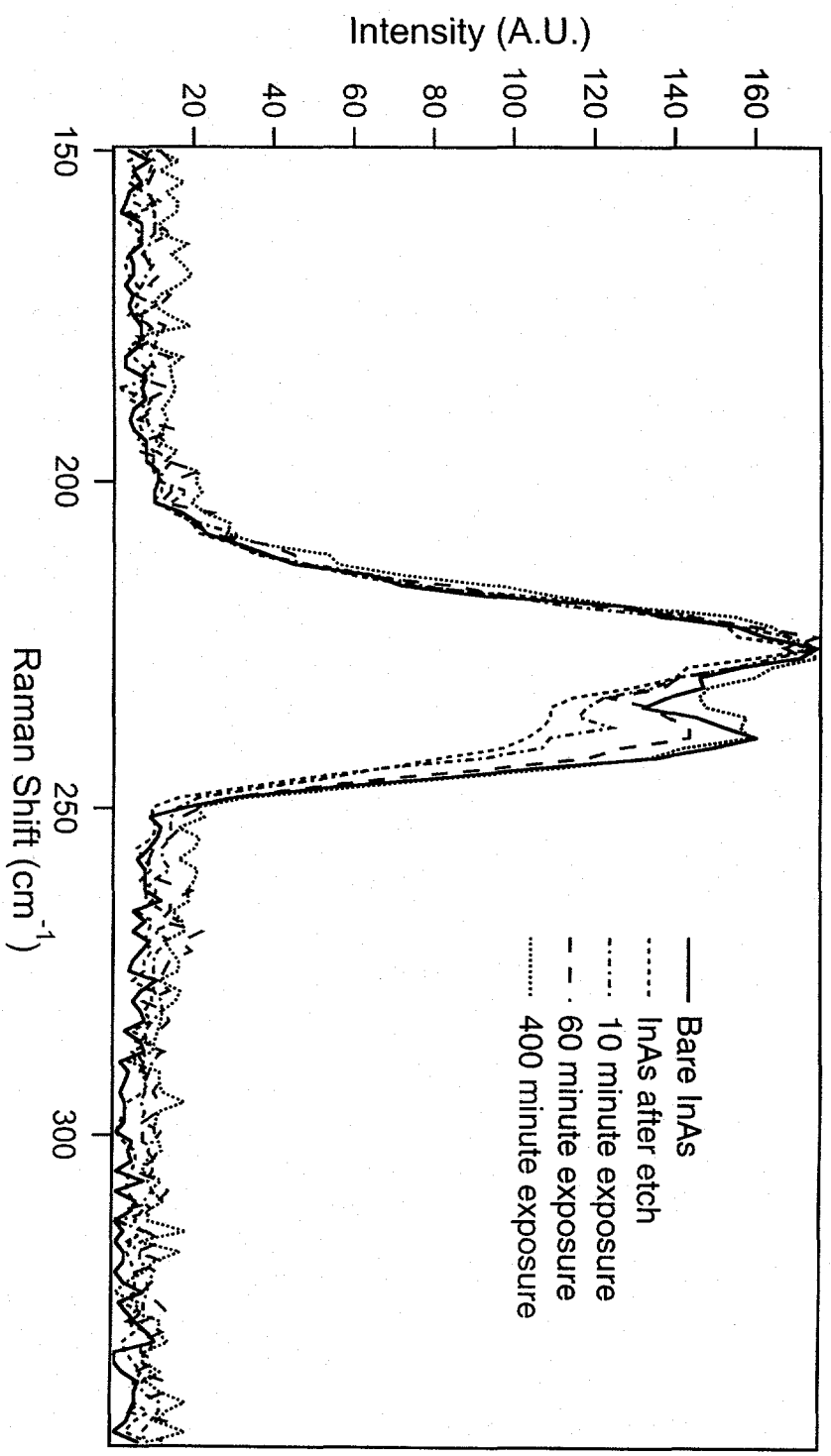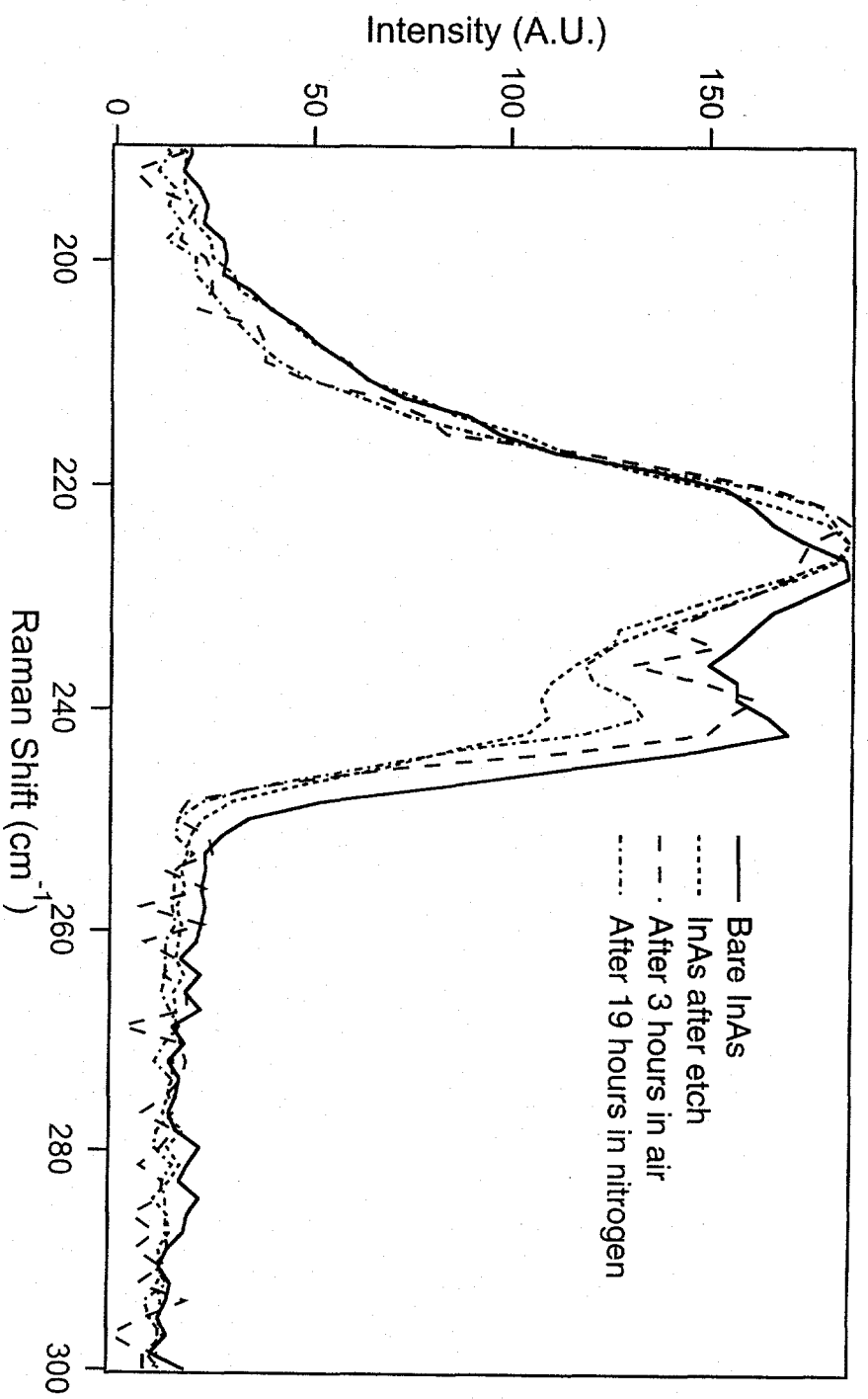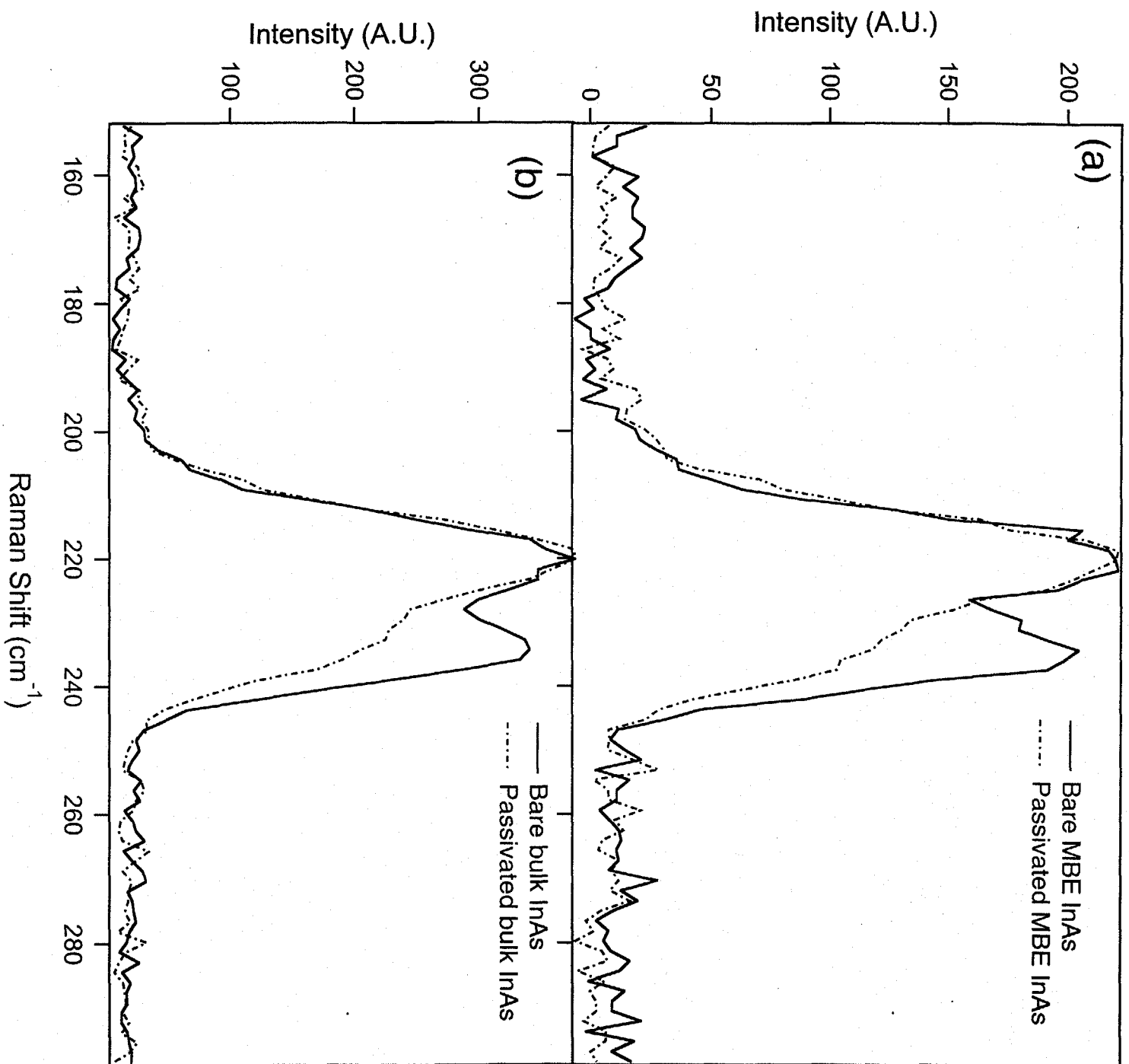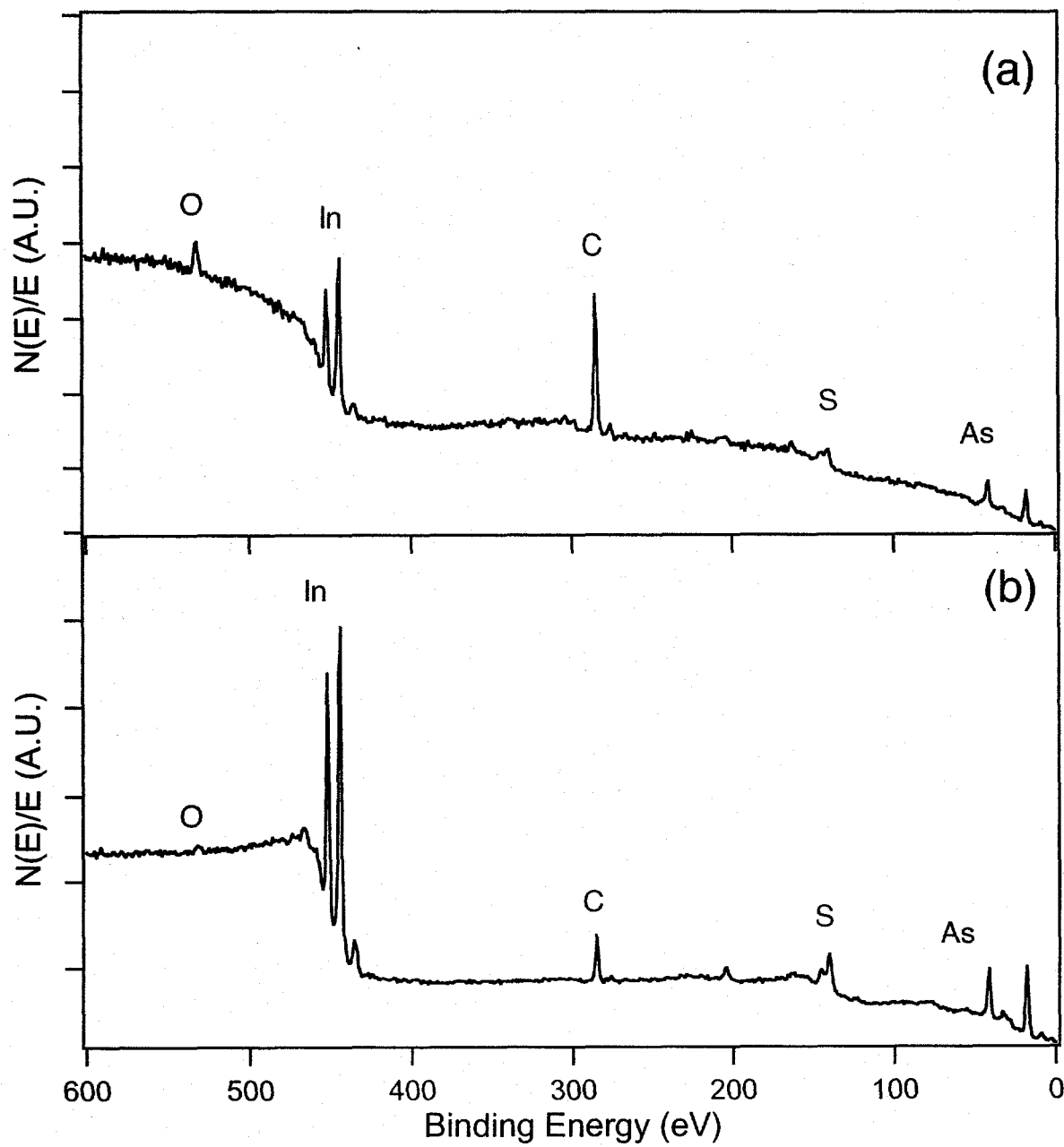
Raman Shift (cm⁻¹)

Bare InAs
InAs after etch
10 minute exposure
60 minute exposure
400 minute exposure

Figure 2

Intensity (A.U.)

Raman Shift (cm⁻¹)

Bare InAs
InAs after etch
After 3 hours in air
After 19 hours in nitrogen

Figure 3

Figure 4