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

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Surface chemical modification is used to eliminate the problem of high surface recombination velocity and control surface band bending on InAs(100). Alkanethiols, RSH; $R=CH_3(CH_2)_n$, both neat and in ethanolic solutions, are used to passivate this surface against oxidation, as characterized by Raman scattering and x-ray photoelectron spectroscopy of the adsorbate-covered and bare surfaces. The magnitude of the interfacial band bending is obtained by analysis of Raman scattering from the unscreened longitudinal optical phonon, which arises from the near-surface charge accumulation region. Removing the native oxide with a Br_2:CH_3OH chemomechanical etch reduces the surface band bending, but atmospheric oxidation increases band bending to its original level over several hours. In contrast, alkanethiol passivation of InAs(100) prevents band bending for periods of up to several weeks. © *1999 American Institute of Physics.* [S0003-6951(99)03644-X]

InAs-based devices have recently become important as materials for use in infrared 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 two-dimensional (2D) electron gas contained in a surface-confined charge accumulation region.[2,3] In contrast, the majority of other III–V materials exhibit a depletion region, leading to Schottky barrier formation. Although the lack of a Schottky barrier on InAs(100) may allow ohmic conduction control of the surface is still important.[4–6] The near-surface electronic properties are governed by a high density of surface states and not by metallic overlayer contact potentials.[7] These properties make InAs(100) ideal for applications where interfacial carrier transport is crucial, e.g., studies of the superconducting proximity effect in Nb:InAs structures.[8–10]

While progress has been made in developing passivation schemes for surfaces of GaAs,[11–16] InP,[17,18] and their alloys, little work has addressed InAs.[19] On the other hand, molecular assemblies of alkanethiols RSH; $R=CH_3(CH_2)_n$, have been extensively studied, being used previously to modify GaAs surfaces.[20,21] Raman spectroscopy is used here principally to probe the near-surface electronic properties[7,22–27] that are so important for device applications, and in particular, to determine how passivation affects the charge accumulation region (CAR). X-ray photoelectron spectroscopy (XPS) is used in tandem to examine the chemical nature of the interaction between thiols and InAs.

Bulk grown ($n^+=1.2\times10^{19}\ \mathrm{cm}^{-3}$) InAs obtained from OMK (Slovakia), and molecular-beam epitaxy (MBE)-grown material ($n^+=1\times10^{19}$, 1.2×10^{19}, and $2.0\times10^{19}\ \mathrm{cm}^{-3}$) consisting of 200 nm of n^+-InAs (Si doped) on undoped GaAs with an intervening undoped InAs buffer layer were used. The Raman spectra were obtained with a Coherent 90–6 Ar^+ laser and a Spex 500M single monochromator equipped with a Photometric Series 210 charge coupled device and collected in the $x(y,z)\bar{x}$ configuration, where the longitudinal optical (LO) phonon and coupled phonon-plasmon modes are allowed, while the transverse optical (TO) mode is disallowed.[23] XPS spectra were obtained on a Physical Electronics (PHI 5400) instrument using a Mg K_α source. Samples were etched in a 1% Br_2:CH_3OH (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 indicates the etch rate is 27±4 Å/s. Passivations were carried out in both neat alkanethiol and 1 mM solutions of alkanethiol in deaerated ethanol.

The unprocessed InAs exhibits two Raman modes (Fig. 1), a low-frequency coupled phonon-plasmon, L_-, near 225 cm^{-1}, which originates in the bulk of the n^+-InAs; and an unscreened LO phonon observed at 239 cm^{-1}, which originates in the CAR as a result of wave vector nonconservation. The narrow width of the CAR is associated with uncertainty in the scattering wave vector which allows observation of scattering away from the Brillouin zone center ($q\sim0$). The unscreened LO phonon arises from regions of k space larger than the Fermi–Thomas screening wave vector (k_{FT}).[7] In a series of similarly prepared and processed samples the LO mode intensity can be taken to reflect the spatial extent of the

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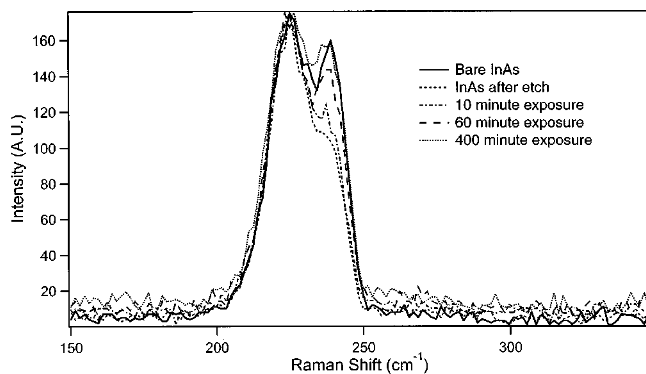

FIG. 1. Bulk InAs ($n=1.2\times10^{19}$ cm^{-3}) spectra taken before and after etching in 1% Br:MeOH. Spectra are for samples exposed to atmospheric O_2 for varying times. Spectra were excited at 457.9 nm.

CAR and, by inference, the magnitude of the surface state density pinning the surface Fermi level.[20]

A comparison of spectra before, and immediately after, etching shows that etching decreases the unscreened LO mode intensity. Without passivation exposure to atmospheric O_2 causes the LO mode, which is quenched by etching, to regenerate within a few hours. Figure 2 demonstrates that when the sample is stored in dry N_2 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 repinning than crystal termination or reconstruction.

To study the passivation of InAs(100), freshly etched samples are 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 are rinsed with ethanol followed by 2-propanol to remove any nonspecifically adsorbed species. Figure 3 shows that passivation gives identical results on either bulk or MBE-grown material. The LO intensity is reduced significantly and the reduced intensity is maintained for one week exposure to atmospheric O_2, indicating that the

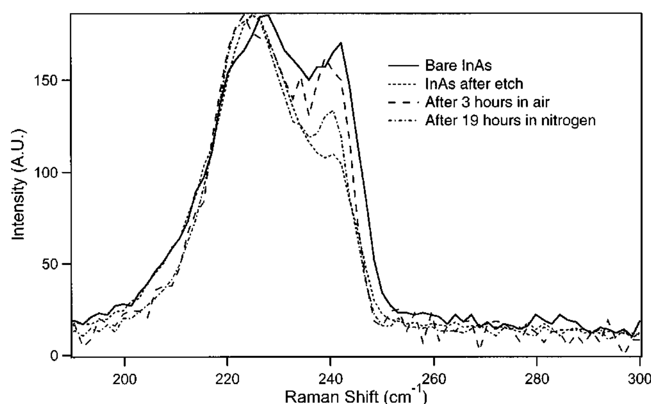

FIG. 2. Bulk InAs spectra taken at intervals after etching in 1% Br:MeOH. Samples were stored in N_2 between measurements with exposure to O_2 in the laboratory ambient during each measurement ≤5 min. Three additional measurements were taken between the etch and the 19 h spectrum, all of which overlay the 19 h spectrum, and are not shown for clarity. A control sample left in the laboratory ambient for 19 h showed a LO mode at the same level as in the original spectrum. $\lambda_{ex}=457.9$ nm.

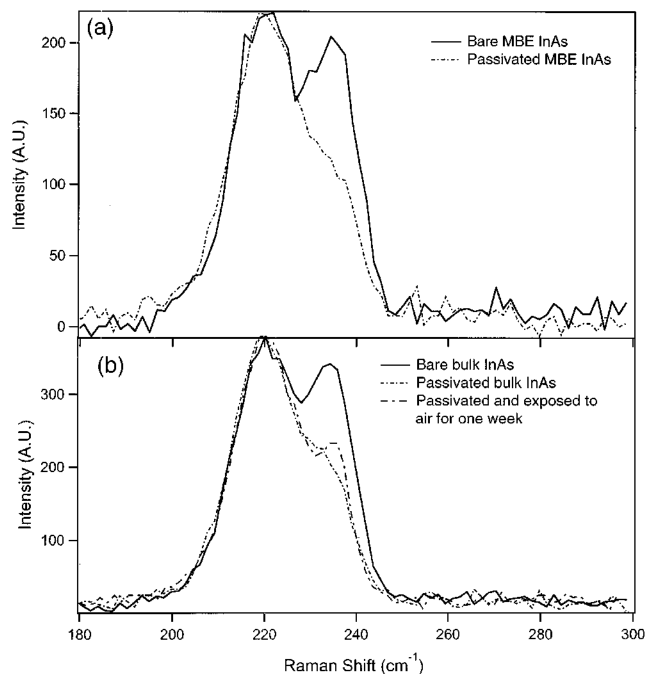

FIG. 3. (a) MBE-grown InAs before and after passivation in 1 mM ethanolic $C_{16}H_{33}SH$ for 18 h. (b) Bulk InAs before passivation, immediately after passivation, and after one week. Passivation was carried out under the same conditions as panel (a). Spectra were excited at 457.9 nm.

Fermi level is unpinned by etching. Exposure of freshly etched InAs(100) surfaces to neat alkanethiol for similar amounts of time does not result in an effective passivating layer, and the LO mode reappears on the same time scale as a freshly etched surface upon exposure to O_2.

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 Fig. 4. The XPS spectra taken at 45° (not shown) and 90° shows no oxide present in the passivated samples. Spectra taken at 15° exhibit a small oxygen signal, suggesting that this 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. The In and As XPS peaks cannot be fit with an elemental contribution alone, but must include additional contributions from As_xS_y and In_xS_y as expected. These results indicate a low oxygen concentration at the alkanethiol-InAs boundary in passivated samples and strongly suggest sulfur bonding at this interface. The decrease in the S/C ratio and increase in the O/C ratio observed at shallow take-off angles is consistent with the sulfur atom residing at the film-InAs interface and only adventitious oxygen at the film-air boundary.

The thickness of the CAR may be determined by measuring the relative intensities of the LO and L_- modes using an abrupt junction model[28]

$$\frac{I_{\mathrm{LO}}}{I_{L_-}}=\frac{R_{\mathrm{LO}}}{R_{L_-}}(e^{2\alpha d}-1), \tag{1}$$

where $\alpha=0.0516$ nm^{-1} is the absorption coefficient of InAs at 457.9 nm, d is the CAR thickness, R_{LO} and R_{L_-} are the

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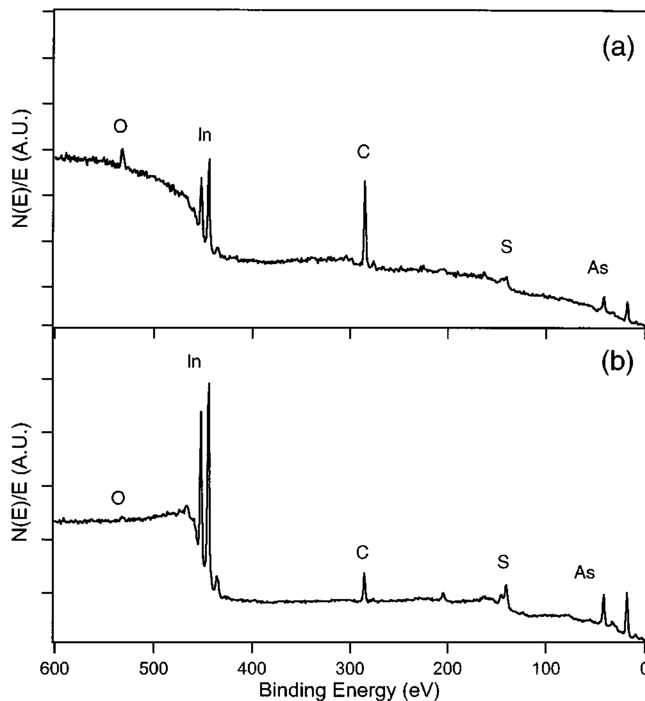

FIG. 4. XPS spectra of a bulk InAs passivated in 1 mM ethanolic $C_{16}H_{33}SH$ for 18 h. Spectra were collected at detector angles of (a) 15° and (b) 90°, relative to the surface.

scattering coefficients, and I_{LO} and $I_{L_}$ are the intensities of the LO and L_- modes, respectively. The ratio $R_{LO}/R_{L_}$ is derived from independent experiments in which the LO and L_- mode intensities are measured on undoped and n^+-InAs materials. For unpassivated samples, the CAR is 35 Å, and $R_{LO}/R_{L_}$ is determined to be 1.88.[29] 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[30]

$$d=\sqrt{\frac{2\epsilon\phi}{en}}, \tag{2}$$

where ϵ is the static dielectric constant ($\epsilon=15\epsilon_0$ for InAs), e is the electron charge, n is the doping density, and ϕ is the band bending ($|E_{c,\mathrm{surf}}-E_{c,\mathrm{bulk}}|$). Prior to etching or passivation ϕ=89±4 meV. After passivation, ϕ=24±3 meV for bulk and 27±3 meV MBE-grown material. The Raman spectra are also analyzed to determine the carrier lifetime by fitting the spectral lineshapes of the LO mode to a Lorentzian line shape and the L_- mode to a hydrodynamic model line shape given by[31]

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

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. Passivation increases the lifetime from 2.8×10^{-14} to 3.7×10^{-14} s in the bulk InAs, and from 2.5×10^{-14} to 3.0×10^{-14} s in MBE-grown InAs. Taken together, the reduction in the band bending and increase in electron lifetimes in the near-surface region argue that alkanethiol adsorption on InAs(100) unpins the surface Fermi level and effectively passivates the InAs surface.

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