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Surface Preparation of InAs (110) Using Atomic Hydrogen

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تجهيز سطح مادة InAs (110) باستخدام التنظيف الهيدروجيني

تيموثي فيل، كريستوفر مكنفيل و سالم بن حمود الحارثي

خلاصة: يختص هذا البحث بدراسة كيفية إنتاج سطوح نظيفة لمادة InAs (110) خالية من شوائب الجو كالكربون والأكسجين بإستخدام التنظيف الهيدروجيني . النتائج العملية والنظرية توضح أن الأسطح الناتجة من التنظيف الهيدروجيني خالية من أي تاف في خصائصها الإلكترونية والتركيبية.

ABSTRACT: Atomic hydrogen cleaning has been used to produce structurally and electronically damage-free InAs(110) surfaces. X-ray photoelectron spectroscopy (XPS) was used to obtain chemical composition and chemical state information about the surface, before and after the removal of the atmospheric contamination. Low energy electron diffraction (LEED) and high-resolution electron-energy-loss spectroscopy (HREELS) were also used, respectively, to determine the surface reconstruction and degree of surface ordering, and to probe the adsorbed contaminant vibrational modes and the collective excitations of the clean surface. Clean, ordered and stoichiometric InAs(110)-(1×1) surfaces were obtained by exposure to thermally generated atomic hydrogen at a substrate temperature as low as 400ºC. Semi-classical dielectric theory analysis of HREEL spectra of the phonon and plasmon excitations of the clean surface indicate that no electronic damage or dopant passivation were induced by the surface preparation method.

KEYWORDS: InAs(110), Hydrogen Cleaning, Plasmon Excitations, HREEL, XPS

1. Introduction

The preparation of clean, ordered and stoichiometric III-V semiconductor surfaces is generally problematic without the extensive facilities available with molecular beam epitaxy (MBE). Even in an MBE-chamber, the thermal desorption of oxides in the presence of an arsenic partial pressure to prepare the surface of InAs is made difficult by the need for precise control of substrate temperature because the oxide and arsenic desorption temperatures are very close together (Schäfer *et al* 2000). When MBE facilities are unavailable, the standard method of *in situ* cleaning of polar InAs surfaces is cycles of low energy ion bombardment and annealing. However, this has been shown to cause severe structural damage, resulting in the introduction of defects, enhanced carrier concentrations and reduced mobilities within the outermost 1000 Å of the material (Magnée *et al* 1995, Bell *et al* 1996a, Bell *et al* 1996b). Traditionally, the non-polar (110) surfaces of III-V materials have been produced by cleaving in vacuum, as this is the fracture plane of these zinc-blende materials. However, from cleave to cleave large variations in the surface step densities result. These steps have been observed using scanning tunnelling microscopy where (111), (112) and (110)-type steps have all been identified on InAs(110) (Liang *et al* 1993). The consequent modification of the surface, where the reactivity is likely to be dominated by the step density profile, will result in significant non-uniformity in the surface properties with each cleave. This is evident from photoemission studies, where the expected flat-band condition, with no electron accumulation, is rarely achieved for InAs(110). The surface electronic structure is extremely sensitive to the presence of cleave-induced steps, which result in downward band bending and accumulation layer formation (Karlsson *et al* 1998). An alternative surface preparation technique, atomic hydrogen cleaning (AHC), offers an effective way of obtaining clean, undamaged InAs(110) surfaces with uniform step densities. This method has previously been shown to be an efficient, relatively low temperature technique for obtaining clean, ordered and damage-free GaAs(001) and InP(001) surfaces (Kikawa *et al* 1994, Petit and Houzay 1992, Petit and Houzay 1994, Goto *et al* 1995).

AHC of the polar (100) and (111) surfaces of InAs has previously been studied using Auger electron spectroscopy (AES), high-resolution electron-energy-loss spectroscopy (HREELS) and low energy electron diffraction (LEED) (Bell *et al* 1997, Bell *et al* 1998). Whilst the removal of contamination by AHC was confirmed by AES, no chemical state information was available to indicate the reaction mechanisms that occur during AHC. Here, the use of x-ray photoelectron spectroscopy (XPS) before and after AHC, with some complementary use of HREELS as an adsorbate vibrational spectroscopy, permits the investigation of the processes by which AHC of InAs(110) proceeds. LEED was used to monitor the surface ordering before and after the cleaning process. HREELS was used to study the surface vibrational modes of the contaminants on the as-loaded surfaces and collective excitations of the clean surface.

2. Experimental Details

Samples from S-doped InAs(110) wafers ($n \sim 4 \times 10^{18}$ cm^{-3}) were individually loaded into the HREELS spectrometer (base pressure $< 5 \times 10^{-10}$ mbar) without any *ex situ* treatment. Molecular hydrogen was thermally cracked in an atomic hydrogen source (EPI Europe) as it passed over the W-filament held at ~ 2100ºC (as measured by an infrared pyrometer) with an estimated $H_2 \rightarrow H^*$ conversion efficiency of about 6-7% for the conditions used (Sutoh *et al* 1995). Hydrogen doses were measured in terms of molecular hydrogen exposures in kilo-Langmuirs (kL) (1 kL = 10^{-3} torr.s). During AHC, the chamber pressure was typically 3×10^{-5} mbar. The distance between the sample and the atomic hydrogen source was approximately 5 cm. Each sample was degassed for one hour to 360ºC prior to AHC, and annealed to 400ºC during AHC by a combination of the atomic hydrogen source filament and the sample filament mounted behind. HREEL spectra were recorded using a range of incident electron energies between 7 and 100 eV with a resolution of 10 meV full width at half maximum (FWHM). XPS spectra were collected to obtain chemical composition and chemical state information before and after AHC, using unmonochromated Al K_α radiation and a 150º spherical sector analyser, with an overall system resolution of ~1.4 eV for the settings used.

3. Results and Discussion

XPS spectra from the as-loaded InAs(110) surface are shown in Figure 1 (dotted lines). The main contribution to the C 1s XPS spectrum indicates the presence of hydrocarbons on the surface. The shoulder on the high binding energy side may be due to the presence of alcohols, carbonates formed after the adsorption of atmospheric CO_2, and bicarbonates (Wolan *et al* 1997). The presence of In-oxide and As_2O_3 is indicated by reference to the binding energies of peaks in the In 3d, As 2p and 3d, and O 1s XPS spectra (Moulder *et al* 1992). The precise nature of the In-oxide could not be identified by XPS because the different oxides are indistinguishable because of the small chemical shifts of the In 3d lines - the peak positions are consistent with the presence of In_2O_3, the most common In-oxide, and sub-oxides such as In_2O. As there is no component of the As 3d spectrum at ~ 46 eV, the presence of the other common As-oxide, As_2O_5, above the XPS detection limit is ruled out. This oxide has previously been reported to be unstable in ultra-high vacuum, decomposing into As_2O_3 and oxygen within a few hours of formation (Schäfer *et al* 2000).

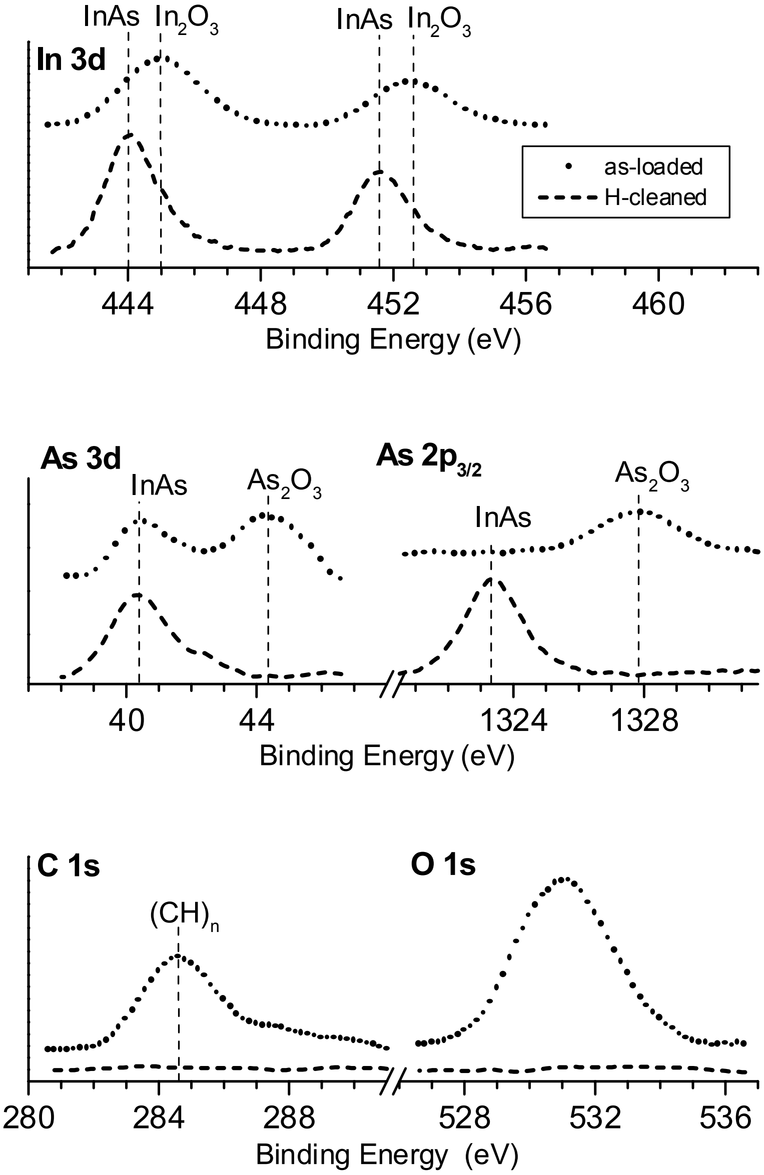

Figure 1. In 3d, As 3d, As $2p_{3/2}$, C 1s and O 1s XPS spectra from as-loaded InAs(110) (dotted lines) and from clean InAs(110) prepared by an AHC dose of 120 kL with a sample temperature of 400°C (dashed lines). All y-axes are in arbitrary units.

An approximate surface composition was determined from the relative intensities of various photoelectron peaks by applying the appropriate atomic sensitivity factor (ASF) for each core level. Errors in determining the surface atomic composition result from the fact that photoelectron lines for the different elements present occur at different binding energies. Consequently, the photoelectrons analysed have different kinetic energies and mean free paths. This means that information contained in the XPS spectra is integrated over different depths for the different elements and makes the assessment of uncertainty in the binding energies difficult. However, from straightforwardly applying the ASF values and using the As 3d line for As because its associated mean free path is closer to that of the In 3d, O 1s and C 1s photoelectrons than that of the $2p_{3/2}$ line, the elemental surface composition before cleaning is 47 % O, 37 % C, 9 % In, and 7 % As.

An estimate of the thickness of the oxide layer was obtained by virtue of the attenuation of the substrate signal by the oxide overlayer. The As 3d spectrum is suitable for this analysis as the chemical shift between substrate and oxide peaks is large, allowing the substrate signal alone to be examined before and after oxide layer removal. The attenuated signal from the substrate beneath the oxide layer I_s is given by

$$I_s = I_{s0} \exp(-z/\lambda) \qquad (1)$$

where I_{s0} is the unattenuated clean surface signal obtained after AHC, z is the thickness of the oxide layer, and λ is the inelastic mean free path of the As 3d photoelectrons 27.5 Å (Schaefer *et al* 1990). Allowing for the error associated with determining the peak areas, this gives an oxide layer thickness of 30 ± 5 Å. This is qualitatively consistent with the information given by comparing the as-loaded spectra of the As 3d and As $2p_{3/2}$ photoelectrons and considering their different inelastic mean free paths. The lower kinetic energy (higher binding energy) As $2p_{3/2}$ electrons have a mean free path of ~ 7.5 Å (Schaefer *et al* 1990), compared with the ~ 27.5 Å of the higher kinetic energy (lower binding energy) As 3d electrons. Because of the exponential attenuation, over 98 % of each signal comes from within four mean free path lengths of the surface. The fact that no As $2p_{3/2}$ signal from the InAs substrate is visible in the as-loaded spectrum indicates that the oxide layer is at least 30 Å (4 × 7.5 Å) thick.

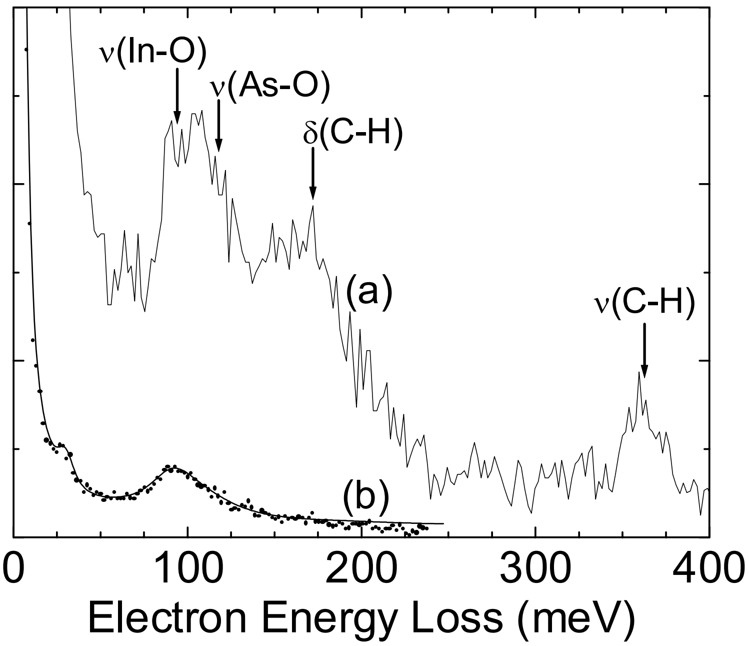

Figure 2. Specular HREEL spectra, recorded at 15 eV, with an instrumental broadening of 10 meV FWHM, from (a) an as-loaded InAs(110) sample; (b) after annealing for one hour at 360ºC and a total of 120kL of atomic hydrogen cleaning at a sample temperature of 400ºC. The dotted line of spectrum (b) depicts the experimental points and the solid line is the simulated spectrum calculated using semi-classical dielectric theory.

The as-loaded samples gave a very weak and broad specular elastic peak in HREELS, with an angular spread of 15° full width at half maximum (FWHM); they exhibited no ordered LEED pattern. Figure 2 (a) shows a specular HREEL spectrum from an as-loaded sample and features a peak at 106 meV - almost twice the width of the elastic peak. This is attributed to a combination of In-O and As-O vibrational modes. These are known to be at ~ 87 and ~ 118 meV respectively (Ibach and Mills *et al* 1982). However, it is apparent that the broad peak at 106 meV in spectrum (a) of Figure 2 cannot be solely due to the combination of two symmetric peaks centred at 87 and 118 meV. However, when the character of an intramolecular bond changes, relatively large frequency shifts can occur (Ibach and Mills *et al* 1982). It is therefore suggested that the origin of the low loss energy side of this peak is In-O vibrational modes of several different frequencies in the range 87 to ~ 100 meV resulting from the various intramolecular bonds present in the different In-oxides likely to exist in the native oxide, including In_2O_3 and suboxides such as In_2O. The peak centred at ~ 170 meV on the HREEL spectrum recorded from the as-loaded InAs (100) surface is due to the combined hydrocarbon deformation modes, δ(C-H) (Aquino *et al* 1995), whilst the peak at 360 meV is attributed to the well known hydrocarbon stretching mode, ν(C-H) (Ibach and Mills *et al* 1982). The as-laoded spectrum is quite noisy and has low resolution because of the disordered nature of the atmospheric contamination present. As a result, the presence of alcohols and carbonates suggested by the C 1s XPS spectrum cannot be unambiguously confirmed because their vibrational modes occur at around the same part of the spectrum as the δ(C-H) modes (Jones *et al* 1989). The intensity of all the peaks in the as-loaded spectrum of Figure 2 decreased as the incident electron energy was increased, confirming that they are due to vibrational modes and not collective excitations.

A clean surface was obtained after a total of 120 kL of AHC. The XPS spectra recorded from the clean surface are shown in Figure 1 (dotted lines). As shown in this figure, the C 1s and O 1s signals were below the detection limit of XPS. The binding energy of the In 3d lines has shifted down by 1 eV, indicative of the removal of In oxide and the presence of InAs at the surface. The As_2O_3 peaks in the As 3d and As $2p_{3/2}$ spectral regions disappeared, with the InAs peak becoming stronger in the As 3d spectrum and appearing for the first time in the As $2p_{3/2}$ region. Bearing in mind the caveats mentioned earlier with regard to determination of surface atomic composition using photoemission results, these XPS spectra suggest that the clean surface consists of 53 % In and 47 % As, close to the 1:1 stoichiometry expected for the non-polar (110) surface.

In the case of GaAs(100), it has been proposed that the removal of As_2O_3 occurs by the formation and desorption of AsH_3, whilst the oxygen generated in this process reacts with surface gallium to form *more* Ga_2O_3 (Mikhailov *et al* 1992). A similar mechanism is proposed here with the formation of more In_2O_3 which is corroborated by vibrational spectroscopy results (Veal and McConville, 2000). The proposed reaction for As_2O_3 removal and creation of additional In_2O_3 is

$$As_2O_3 + 2InAs + 12H^* \rightarrow In_2O_3 + 4AsH_3 \uparrow,$$

where H* represents thermally excited hydrogen atoms and ↑ indicates the desorption of the reaction product. Upon further AHC treatment, it is suggested that the In_2O_3 is eventually removed, by analogy with the case of Ga_2O_3 (Mikhailov *et al* 1992, Yamada *et al* 1993), according to the reaction

$$In_2O_3 + 4H^* \rightarrow In_2O \uparrow + 2H_2O \uparrow.$$

The clean surface exhibited the clear, sharp (1×1) LEED patterns shown in Figure 3 with the rectangular spacing of diffraction spots characteristic of the (110) surface. Increased surface ordering was also apparent from the more intense specular elastic peak in HREELS, with a much reduced angular spread (3° FWHM). An HREEL spectrum recorded from the clean surface is shown in Figure 2. Whilst the clean surface spectrum shown does not extend to the loss energies of all the contaminant vibrational modes, it was independently confirmed that their intensities had been reduced to below the detection limit. A series of normalised specular HREEL spectra were recorded with a range of incident electron energies from a clean InAs(110) surface prepared by annealing at 360ºC followed by a 120 kL dose of AHC with a sample temperature of 400ºC. The peak at ~ 90 meV in all the spectra is due to the conduction-band electron plasmon excitation. The width of this feature decreases at higher incident electron energies, whilst its intensity increases relative to the elastic peak. As the incidence energy is reduced, the plasmon peak becomes more asymmetric and less well defined on the high loss energy side; a small shift towards higher loss energy also occurs. The shoulder on the elastic peak at ~ 29 meV is assigned to Fuchs-Kliewer surface optical phonon excitations (Mönch *et al* 1993): this feature does not change in loss energy, but its intensity decays rapidly with increasing incidence energy, disappearing completely above 60 eV.

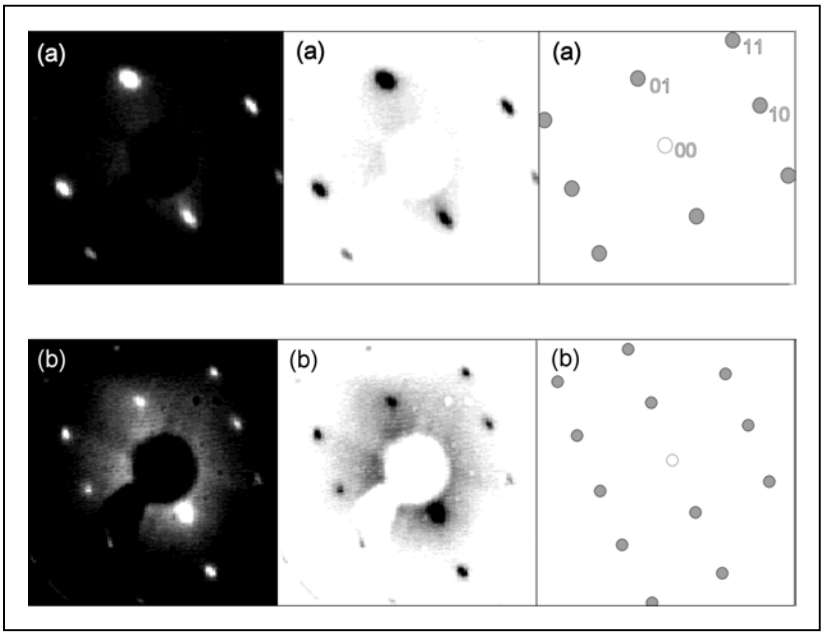

Figure 3. (1×1) LEED patterns (left) recorded using beam energies of (a) 31 eV and (b) 49 eV from InAs(110) prepared by an AHC dose of 120 kL with a sample temperature of 400ºC. The inverted images (centre) and schematic diagrams (right) are also shown. The diffraction spots obscured by the electron gun are shown unshaded in the schematic pattern.

The HREEL spectra of the atomic hydrogen cleaned surface were analysed using the semi-classical dielectric theory of HREELS (Lambin *et al* 1990). The plasma dielectric function was based on the hydrodynamic model, with the plasma frequencies, plasmon lifetimes, and spatial dispersion coefficients as parameters (Bell *et al* 1996b). A three-layer model was used to simulate the experimental spectra across the entire incident-electron energy range, consisting of a plasmon-free surface "dead" layer, accumulation layer, and a semi-infinite bulk. Below the 35 Å dead layer, the 55 Å accumulation layer had a carrier concentration of 6.7×10^{18} cm^{-3}, above a semi-infinite bulk with a carrier concentration of 3.9×10^{18} cm^{-3}: that is, unchanged from the nominal bulk doping value given by the sample manufacturer. The band bending was estimated to be 115 meV, with a triangular potential well width of 140 Å, giving a surface charge density of $6.3 \pm 2.0 \times 10^{11}$ cm^{-2}. This is in agreement with the values of 10^{11}-10^{12} cm^{-2} found on other faces of InAs (Olsson *et al* 1996, Bell *et al* 1997) and on hydrogen terminated InAs(110) (Chen *et al* 1989).

The spatial dispersion coefficient for the simulations was calculated using the Thomas-Fermi model (TFM), giving a value of 0.43×10^{6} ms^{-1}, which successfully reproduced the observed plasmon peak dispersion in the experimental spectra. This indicates that the hydrogen cleaning treatment does not cause subsurface damage: for ion bombarded and annealed samples spatial dispersion coefficients are significantly lower than those predicted by the TFM because of additional defect scattering (Bell *et al* 1996b). The carrier mobility of AHC InAs(110) deduced from the plasmon lifetimes used in the simulations is five times higher than for samples from the same wafer subjected to grazing incidence 500eV IBA (Veal and McConville 2001), providing further evidence in favour of AHC as a surface preparation technique.

An accumulation layer has also been observed on InAs(110) cleavage surfaces after good mirror-like cleavages, as seen by visual inspection and LEED (Karlsson *et al* 1998). Whilst an "ideal" cleavage gives a flat band condition on the InAs(110) surface with no electron accumulation, the surface electronic structure is extremely sensitive to the presence of contamination and defects, resulting in downward band bending and accumulation layer formation.

From cleave to cleave large changes in step densities, and consequently adsorption properties and defect densities occur, resulting in significant variations in surface properties. Atomic hydrogen cleaning is an effective alternative method of obtaining clean, undamaged InAs(110) surfaces prior to further *in situ* processing.

In conclusion, it has been demonstrated that clean, ordered InAs(110) surfaces can be obtained by exposing the atmospherically contaminated substrates to atomic hydrogen at 400ºC with a molecular hydrogen dose of 120 kL. During atomic hydrogen cleaning, the As_2O_3, In-oxides and hydrocarbons are removed completely. Furthermore, this process produces no detectable damage: dielectric theory simulations of the plasmon excitations in the HREEL spectra indicate carrier mobilities and spatial dispersion coefficients significantly higher than those of samples prepared by IBA; and below the accumulation layer the carrier concentration was found to be that of the nominal S-doping.

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