



Synchrotron radiation photoemission study of the thermal annealing and atomic hydrogen cleaning of native oxide covered InAs(1 0 0) surfaces



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ABSTRACT

Changes induced in the surface chemical composition of native oxide covered InAs(1 0 0) by both thermal annealing and atomic hydrogen cleaning have been investigated by soft X-ray photoemission spectroscopy. Annealing up to 450 °C shows a reduction in the intensity of the In and As oxides, however this anneal is not sufficient to produce an oxide and carbon free surface. Exposure to a beam of atomic hydrogen at 360 °C results in the removal of both native oxides and surface carbon contamination resulting in a clean In rich surface. The chemical stability of the cleaned InAs surface to prolonged atomic hydrogen exposure times at temperatures up to 420 °C has also been investigated and shown to have no effect on the surface stoichiometry.

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1. Introduction

High mobility III–V channel materials such as InAs are being considered as potential candidates to improve transistor performance beyond the 22 nm technology node. However, the high mobilities of these materials are difficult to realize because of the relatively high interface state densities between the gate insulator and transistor channel in metal oxide semiconductor field effect transistor (MOSFET) devices. The III–V oxides which form at the interfaces have been implicated as possible sources for the high defect states. This observation has been reinforced by the reported finding that an arsenic oxide free high- κ /III–V semiconductor interface can show unpin Fermi level behaviour indicative of low interface state densities [1,2]. Several approaches to prepare an oxide free InAs surface have been reported including sulphur passivation [3], wet chemical hydrochloric acid (HCl) cleaning [4,5], sputtering with low energy ions [6,7], and molecular hydrogen cleaning (MHC) [8,9]. However preserving the stoichiometry of the InAs surface after wet or dry cleaning treatments has proved to be a significant challenge [5,8]. The use of atomic hydrogen (AH) as a method for oxide removal and surface cleaning of III–V semiconductors has been proposed due to the relatively low temperature needed to instigate the oxide removal, [10,11] which is important due to the low decomposition

temperature of III–V semiconductor materials. This treatment has been used to prepare an atomically clean GaAs surface at ≤ 430 °C without any residual surface oxides [12,13]. However, when the same cleaning procedure was studied on native oxide covered InGaAs, the complete removal of the surface oxides resulted in the loss of indium which could have implications for device operation, as majority carrier mobility in InGaAs scales with indium content [10]. Previous studies have shown the complete removal of surface oxides from both polar and non-polar InAs surfaces upon atomic hydrogen exposure around 400 °C substrate temperature using high resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy measurements [14,15] however, details of the surface chemical interactions were not investigated. In this study the changes in the surface chemical composition of the native oxide covered InAs surface up to an annealing temperature of 450 °C are compared with the atomic hydrogen cleaning at 360 °C using high surface sensitivity synchrotron radiation based soft X-ray photoemission spectroscopy.

2. Experimental

The soft-X ray photoemission spectra were acquired from *n*-InAs(1 0 0) samples mounted on a molybdenum sample holder in an ultra high vacuum with the base pressure of 1×10^{-10} mbar. The measurements were made on the SX 700 beam line at the ASTRID synchrotron in Aarhus University, Denmark. The photoemission spectra of As 3d, In 4d, O 1s, and C 1s core levels requiring photon energies ranging from 69 eV to 600 eV were taken after

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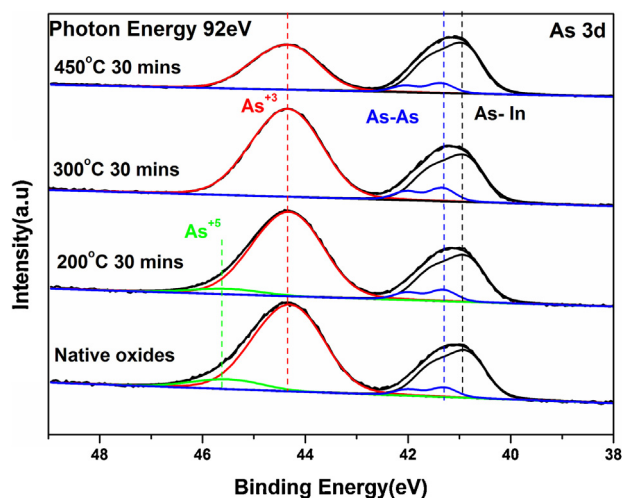


Fig. 1. Curve fitted As 3d core level spectra acquired at 92 eV photon energy for the native oxide surface and the successive anneals up to 450 °C.

successive vacuum anneals and atomic hydrogen cleaning steps. The photon energies of 69 eV and 92 eV were preferred for the In 4d and As 4d core level spectra as the photoemitted electrons from both core levels will have kinetic energy of ~50 eV to give an equivalent sampling depth of approximately 2 nm. The overall instrumental energy resolution was estimated as 0.7 eV at these photon energies. Work function measurements were carried out by biasing the samples with -9V through an external battery to collect the secondary photoemitted electrons. Thermal annealing studies of the native oxide covered InAs surface where performed up to 450 °C for 30 min. To generate an atomic hydrogen beam, molecular hydrogen was supplied to an Oxford Applied Research TC50 thermal cracker operating at 45 W and the system base pressure was maintained at 1×10^{-7} mbar. A minimum substrate temperature of 360 °C was used during the cleaning cycles. The curve fitting parameters such as doublet ratio, spin-orbit-splitting and Gaussian/Lorentzian ratios were derived from the atomically clean InAs surface consistent with previous report values [16,17]. The As 3d(In 4d) peak profile was curve fitted with a spin orbit splitting of 0.7 eV (0.85 eV), a doublet ratio of 0.66 (0.67) and the bulk component peak full width at half maximum (FWHM) was 0.7 eV (0.75 eV) which was composed of the square root of the sum of the squares of the Gaussian 0.7 eV (0.73 eV) and Lorentzian 0.07 eV (0.2 eV) line width values [16,17]. These parameters were then used for the bulk component peaks throughout this study and the FWHM of oxidation component peaks were allowed to vary to investigate any change in the chemical states.

3. Results and discussion

3.1. Impact of vacuum annealing

The As 3d and In 4d core level spectra acquired from the native oxide covered InAs surface and following thermal vacuum annealing are shown in Figs. 1 and 2, respectively. The As 3d core level spectrum for the native oxide sample was curve fitted with four components consisting of a bulk As peak at 40.8 eV, an elemental As peak shifted 0.5 eV to higher binding energy and two oxidation states of arsenic As^{+3} (As_2O_3) and As^{+5} (As_2O_5) shifted to 3.2 eV and 4.4 eV higher binding energy, respectively, consistent with previous assignments [16]. Annealing at 300 °C results in the complete attenuation of the As_2O_5 without any other significant difference observed in the other oxidation state intensities. Subsequent annealing at 450 °C for 30 min results in a significant attenuation

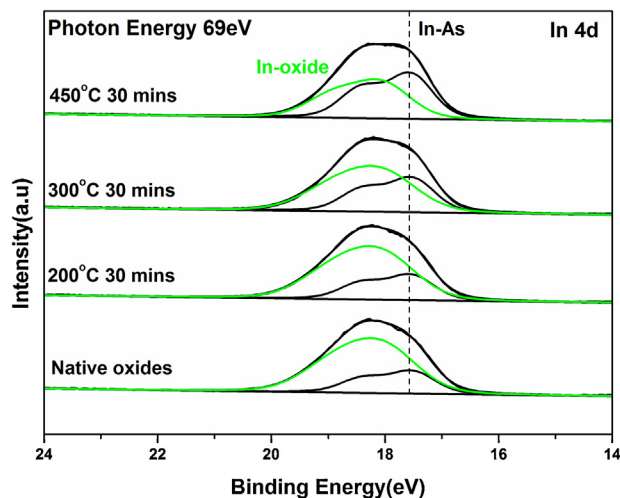


Fig. 2. Curve fitted In 4d core level spectra acquired at 69 eV photon energy for the native oxide surface and the successive anneals up to 450 °C.

of the As_2O_3 peak intensity as was reported for a similar study on InGaAs [16]. The Indium (In) 4d signal for the native oxide sample, shown in Fig. 2, was peak fitted with a bulk indium peak at 17.5 eV and a peak shifted to higher binding energy is attributed to oxidized indium [16,18]. Annealing up to 450 °C results in the progressive reduction in the intensity of the In oxidation state, however, a considerable oxidized indium signal is still detected at the highest temperature anneal. The change in the intensity of both the As and In oxidation species as a function of successive anneals expressed as a ratio to the substrate signal intensities is plotted in Fig. 3. This shows that the As^{+5} state is completely attenuated at 300 °C and there is a corresponding increase in the intensity of As^{+3} and the elemental arsenic signals attributed to the partial loss of oxygen from the surface, as has been reported by Brennan and Hughes [16] for the thermal anneal of native oxide covered InGaAs substrate. The presence of elemental arsenic and the As^{+3} state have been suggested as the cause of Fermi level pinning in high- κ /GaAs MOS devices [1,2,19,20]. At 450 °C, As^{+3} state and elemental arsenic species have decreased in intensity, however there is still a significant amount present which is inconsistent with the reported desorption temperature of As^{+3} at 200 °C [21]. The gradual attenuation of the oxidized indium signal suggests the relatively high

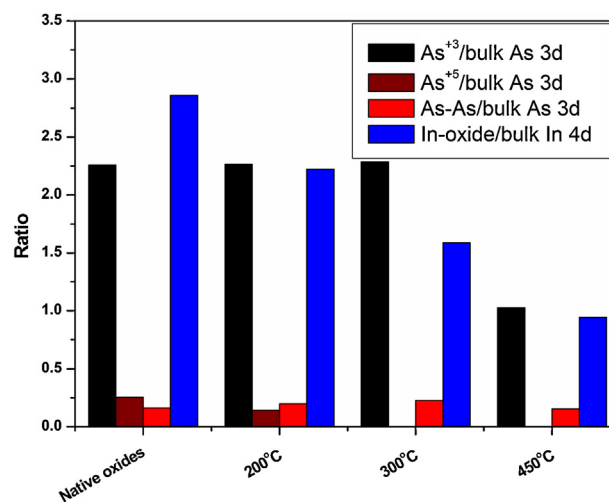


Fig. 3. Ratio of arsenic oxidation states to bulk arsenic and indium oxidation state to bulk indium calculated from the As 3d at 92 eV and In4d at 69 eV for the native oxide surface and the subsequent annealing treatments.

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