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High temperature thermal stability studies of ultrathin Al_2O_3 layers deposited on native oxide and sulphur passivated InGaAs surfaces

Lalit Chauhan [a,*,1], Durga Rao Gajula [b], David Mc Neill [b], Greg Hughes [a]

[a] School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland
[b] School of Electronics, Electrical Engineering and Computer Science, Queen's University Belfast, UK

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ABSTRACT

High resolution synchrotron radiation core level photoemission measurements have been used to undertake a comparative study of the high temperature stability of ultrathin Al_2O_3 layers deposited by atomic layer deposition (ALD) on both sulphur passivated and native oxide covered InGaAs. The residual interfacial oxides between sulphur passivated InGaAs and the ultrathin Al_2O_3 layer can be substantially removed at high temperature (up to 700 °C) without impacting on the InGaAs stoichiometry while significant loss of indium was recorded at this temperature on the native oxide InGaAs surface.

1. Introduction

High indium content InGaAs is a leading III–V semiconductor candidate to realise high performance for n-channel metal oxide semiconductor (MOS) devices. Significant progress has been recently made in improving the electrical quality of the high-k dielectric-InGaAs interface by the atomic layer deposition (ALD) of high-k materials on passivated surfaces [1–3]. Controlling III–V surface oxidation, which leads to the formation of a high density of extrinsic defect states (D_{it}) at the high-k/InGaAs interface, is a major challenge to optimum device operation. Passivation procedures aimed at controlling D_{it} by removal of the native oxide have been developed [4–8]. The use of sulphur based chemicals such as ammonium sulphide $(NH_4)_2S$ [1,9] have been extensively investigated due to its effectiveness at removing native oxides and passivating the surface thereby improving the electrical characteristics of devices [1,3,10,11]. Different thermal treatments, like post deposition forming gas annealing at temperatures of 400–500 °C, have been reported to improve the electrical characteristics of Al_2O_3/InGaAs based MOS structures [12,13]. Therefore, understanding of the effects of these high temperature anneals on the Al_2O_3/InGaAs interface chemistry is important as some studies have shown evidence of inter diffusion across the interface [14,15]. In previous annealing studies Chauhan et al. [16,17] have observed a much higher indium loss from the *in situ* sulphur passivated InGaAs surface compared to the atomically clean InGaAs surface at 530 °C. Since majority carrier mobility in InGaAs scales with indium content, the thermal stability of the InGaAs surface is an important consideration in that preserving the stoichiometry in the near surface region has implications for channel mobility. In this study high resolution synchrotron radiation based photoemission has been used to observe the effects of high temperature annealing on the Al_2O_3/InGaAs interface for sulphur passivated and native oxide covered surfaces.

2. Experimental

An n-type Be doped $In_{0.53}Ga_{0.47}As$ epilayer 0.5 μm thick (5×10^{17} cm^{-3}) lattice matched to an InP substrate was degreased for 1 minute in acetone followed by 1 minute rinse in methanol prior to being immersed in 10% ammonium sulphide ($(NH_4)_2S$) solution for 20 minutes at room temperature (290 K). Both sulphur passivated and native oxide covered samples were then immediately loaded into an atomic layer deposition (ALD) chamber load lock within 1 minute to minimize the air exposure. Approximately 1 nm (10 cycles) of alumina (Al_2O_3) was deposited at 300 °C using trimethyl aluminium (TMA) and water as the precursors. The ALD was carried out at Queen's University Belfast, UK

* Corresponding author.
[1] Present address: School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan, South Korea.

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and the samples were stored under a nitrogen atmosphere before being transferred to the synchrotron for measurement. Samples were subsequently secured to a molybdenum holder and measured on the soft X-ray photoemission SX700 beam line at the Astrid synchrotron in the University of Aarhus in an ultra high vacuum (UHV) system which had a base pressure of 5×10^{-10} mbar. Photoemission core level spectra were subsequently acquired for In 4d, Ga 3d, As 3d, Al 2p, O1s and S 2p core levels following thermal anneals up to 700 °C for a period of 20 minutes. A photon energy of 92 eV was chosen for As 3d to allow comparison with previous studies and a photon energy of 105 eV was chosen for the In 4d/Ga 3d core level spectra which gives almost equal intensity to the Ga 3d and In 4d core level peaks [17]. The spectra were curve fitted using Voigt profiles composed of Gaussian and Lorentzian line shapes and using a Shirley-type back ground as previously reported [17]. The total energy resolution in these photoemission experiments is estimated to be ~0.7 eV.

3. Results and discussion

Fig. 1(a) and (b) show the changes in the As 3d curve fitted photoemission spectra at 92 eV for the ultrathin Al_2O_3 layer on sulphur passivated and native oxide InGaAs surface as a result of thermal annealing up to 700 °C. Although the deposited Al_2O_3 layer on the native oxide surface was thinner than on the passivated surface, current–voltage measurements made on metal oxide semiconductor structures fabricated on both sample types showed near identical characteristics, leading us to believe that the Al_2O_3 layer was continuous and closed in both cases. Due to the relatively small binding energy separation differences between the As 3d bulk peak and the various reported sulphur and oxygen oxidation states [9,17,19], no attempt has been made to distinguish between the chemical shifts of the two elements in the curve fitted data [20]. At room temperature, the As 3d peak was curve fitted with a bulk As component, an As dimer or dangling bond related component (shifted by $\Delta \sim -0.65$ eV), elemental arsenic ($\Delta \sim +0.55$ eV) and a mixed phase of interfacial arsenic oxides composed of As^{1+} ($\Delta \sim +1.4$ eV), As^{2+} ($\Delta \sim +2.7$ eV), As^{3+}($\Delta \sim +3.4$ eV) and As^{5+} ($\Delta \sim +4.4$ eV). Comparison with previous synchrotron radiation photoemission studies of oxidised InGaAs at these photon energies [18], indicate that the thickness of the interfacial oxide on the sulphur passivated surface is estimated to be no more than 0.3 nm while on the native oxide surface, the interfacial oxide is less than 0.5 nm thick. An initial anneal at 425 °C showed an increase in the higher oxidation state peak intensities (As^{1+}, As^{3+} and As^{5+}) and drop in the As dimer/dangling bonds As^{2+}, and As^{3+} signals on both samples. Thereafter, a thermal anneal at 485 °C resulted in a decrease in the higher oxidation state peak intensities (As^{2+}, As^{3+} and As^{5+}) with a concurrent increase in lower oxidation states (As^{1+}) for both samples. An increase in the intensity of the elemental As was also observed at this temperature which is attributed to the reduction of the arsenic oxides. This observed preferential removal of the higher oxidation states with thermal annealing is similar to the behaviour previously reported for the thermal anneal of native oxides on InGaAs [19]. Subsequent annealing at 545 °C showed a decrease in all arsenic oxidation states on both samples. Annealing at 635 °C removed all the higher As oxidation states (As^{3+}, As^{5+}) on the sulphur passivated sample with only traces of As^{1+} and As^{2+} states remaining, while residual evidence of all arsenic oxidation states was observed on the native oxide sample. A final anneal at 700 °C resulted in the removal of all higher oxidation states from both interfaces with only elemental As and As dimers/dangling bond related signals remaining.

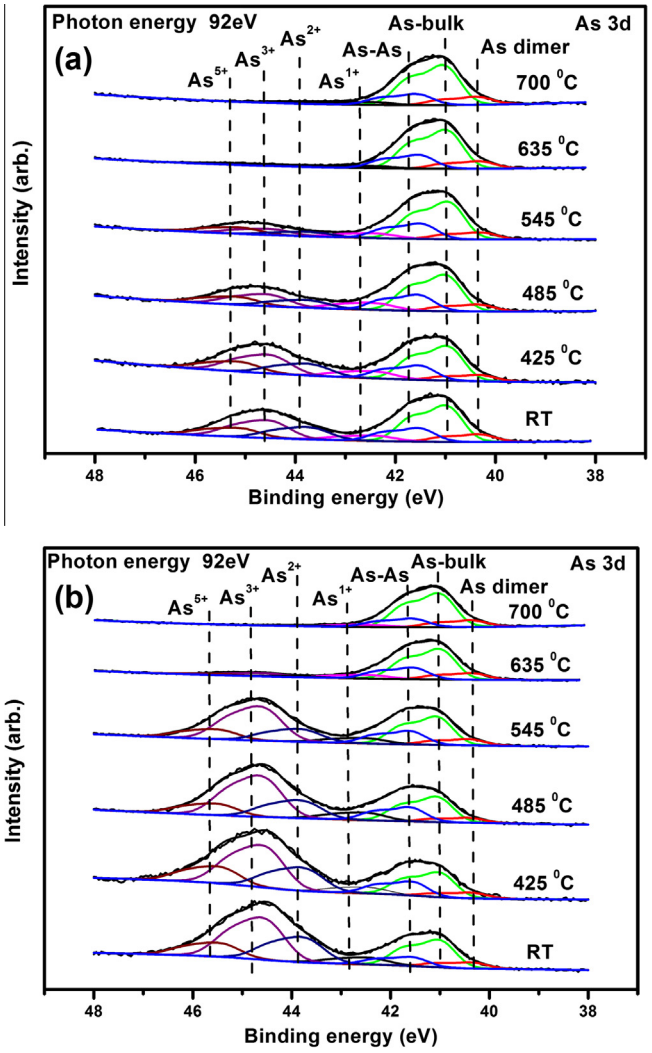

Fig. 1. Curve fitted core level spectra of As 3d acquired at a photon energy of 92 eV for Al_2O_3 on (a) sulphur passivated InGaAs and (b) native oxide InGaAs surfaces following thermal anneals showing the almost complete removal of the oxides following the 635 °C anneal.

The change in the intensity ratios of the individual arsenic oxidation states to the bulk arsenic signals are shown in Fig. 2(a) and (b) for both samples. The ratios reflect the larger initial interfacial oxide on the native oxide sample compared to the sulphur passivated surface which is attributed to the effectiveness of the sulphur treatment at removing the native oxide. As reported in the literature [21–24], the ALD deposition of Al_2O_3 results in the so-called "clean up effect", which consumes interfacial oxides during the initial stages of Al_2O_3 growth, however, the extent of this effect depends on the initial oxide thickness. The observed changes in the As oxides with thermal anneal are in agreement with a recent XPS study by Yoshida et al. [2] of the thermal annealing of ALD deposited Al_2O_3 on the InGaAs surface which showed a decrease in higher oxidation arsenic states with increased temperature. The high temperature thermal anneals essentially leave both interfaces chemically identical in relation to the As 3d spectrum and there is no evidence of arsenic out diffusion.

Fig. 3(a) and (b) show the changes in the In 4d/Ga 3d curve fitted photoemission spectra acquired at a photon energy of 105 eV for 1 nm Al_2O_3 on sulphur passivated and the native oxide InGaAs surfaces, respectively. Again, with these curve fits, no attempt has been made to separately identify oxide or sulphide