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In-adlayers on non-polar and polar InN surfaces: Ion scattering and photoemission studies

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Abstract

The surface structure of In-polarity *c*-plane InN has been investigated by low energy ion scattering spectroscopy. Comparison of ion scattering spectra recorded along the [1 0 0 0] azimuth with model calculations indicates that the clean In-polarity *c*-plane InN surface is terminated by In-adlayers with a laterally contracted topmost In layer. This is consistent with previous X-ray photoemission and electron diffraction results. Additionally, the surface properties of *a*-plane InN have been investigated using core-level and valence band X-ray photoemission spectroscopy (XPS). From the ratio of the In and N core-level XPS signal intensities, the clean *a*-plane InN surface has also been found to be terminated by In-adlayers. Photoemission measurements of the valence band maximum to surface Fermi level separation for *a*-plane InN indicate the existence of an electron accumulation layer at the surface. This observation of electron accumulation at non-polar InN surfaces in the presence of In-adlayers is in agreement with the predictions of previous first-principles calculations.

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Keywords: Indium nitride; Surfaces; Photoemission; Ion scattering

1. Introduction

Electron accumulation occurs at the surface of InN as a result of its very low Γ-point conduction band minimum with respect to the charge neutrality level, allowing donor-type surface states to donate their electrons into the conduction band [1–4]. However, while this explains the phenomenon from a bulk band structure perspective, a microscopic origin has only very recently been proposed. Based on first principles calculations, it has been suggested that the donor-type surface states on clean InN surfaces are associated with the In–In bonds in a surface In-adlayer [5–7]. Experimentally, however, the influence of the InN film polarity, orientation, surface reconstruction and surface stoichiometry on the electron accumulation has received very little attention. Previous photoemission studies have revealed ~3.4 and ~2.0 monolayers (ML) of In on the In- and N-polarity *c*-plane InN surfaces, respectively [8]. Here, an ion scattering spectroscopy investigation of the In-polarity *c*-plane InN surface structure confirms the findings of the earlier photoemission study. Additionally, photoemission spectroscopy of *a*-plane InN indicates the presence of both In-adlayers and surface electron accumulation.

2. Experimental details

The *c*-plane InN film was grown by molecular beam epitaxy (MBE) to a thickness of 1500 nm on a *c*-plane sapphire substrate, incorporating a GaN/AlN buffer layer. It was found to be In-polarity (i.e. (0 0 0 1) orientation) from scanning electron microscopy after KOH etching [9]. The *a*-plane ($(1\,1\,\bar{2}\,0)$ orientation) InN film was MBE grown to a thickness of 2600 nm on an *r*-plane sapphire substrate incorporating an AlN buffer layer. Details of the growth methods are reported elsewhere [10,11]. Hall effect

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measurements indicated average free electron densities and mobilities of $1.8 \times 10^{18}\,cm^{-3}$ and $1200\,cm^2\,V^{-1}\,s^{-1}$ for the *c*-plane film and $4.8 \times 10^{18}\,cm^{-3}$ and $470\,cm^2\,V^{-1}\,s^{-1}$ for the *a*-plane film.

The ion scattering experiments were carried out at room temperature in an ultrahigh vacuum chamber equipped with low energy electron diffraction (LEED), a dual anode X-ray source, a 100 mm concentric hemispherical electron energy analyzer, and a co-axial impact collision ion scattering spectroscopy (CAICISS) system (described elsewhere [12]). The data presented here are of the polar scans of the [1 0 0 0] azimuth. The two-dimensional periodicity of the InN surfaces was determined by LEED, enabling azimuthal alignment of the sample to be achieved for the CAICISS experiments.

The high resolution X-ray photoemission spectroscopy (XPS) measurements were performed at room temperature using a Scienta ESCA300 spectrometer at the National Centre for Electron Spectroscopy and Surface analysis, Daresbury Laboratory, UK. Details of the spectrometer and its arrangement are reported elsewhere [13]. The energy scale is given with respect to the Fermi level and was calibrated using the Fermi edge of an ion-bombarded silver reference sample.

The samples were transferred through air from the growth chamber to the CAICISS and high resolution XPS instruments. Prior to CAICISS and XPS analysis, the InN surfaces were prepared *in situ* by atomic hydrogen cleaning (AHC). Molecular hydrogen was thermally cracked with an efficiency of ~50% by passing it through a tungsten capillary heated to ~2000 °C. The AHC process consisted of a 10–20 kL dose of hydrogen at a sample temperature of 200 °C. Finally, the samples were annealed without exposure to hydrogen at 275 °C for 1–2 h. Because excessive exposure to atomic hydrogen is known to etch InN and produce indium droplets [14], all samples were analysed by scanning electron microscopy after the CAICISS and XPS measurements. Only results from samples where no indium droplets were produced are presented.

3. Ion scattering from *c*-plane InN

The CAICISS data recorded from an In-polarity *c*-plane InN sample and corresponding simulations are shown in Fig. 1. From the variation of the energy and flux of the scattered ions as a function of incidence or azimuthal angle, it is possible to analyse the surface structure of the epilayer. To interpret the data, trial structures are simulated using the FAN simulation program developed by Niehus [15] until agreement is achieved between the experimental data and the simulated intensity as a function of polar angle.

The simulated polar angle-dependence of the CAICISS signal is shown in Fig. 1 for In-terminated bulk In-polarity *c*-plane InN. Comparison of this calculated spectrum with the experimental data reveals many differences. The peaks

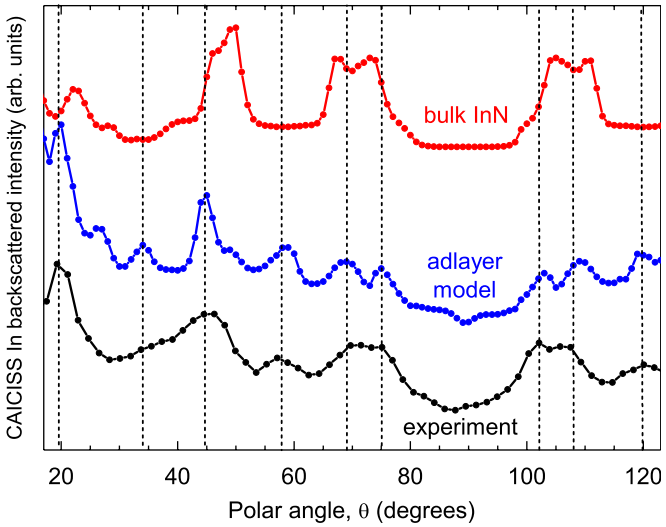

Fig. 1. (Colour online) Experimental CAICISS In-backscattered intensity as a function of polar angle for the [1 0 0 0] azimuth. Simulated CAICISS spectra are also shown for bulk-like In-terminated In-polarity InN(0 0 0 1) and InN(0 0 0 1) terminated with In-adlayers, as depicted in Fig. 2.

at ~33°, ~58° and ~120° in the experimental data are not reproduced in the calculated spectrum for the bulk-like termination of InN. Additionally, features at ~20°, ~45°, ~69−75° and ~102−108° in the experimental spectrum appear a few degrees away from similar features in the calculated spectrum for bulk termination.

Due to the lack of agreement between the measured ion scattering spectrum and that calculated for bulk-terminated InN, the ion scattering spectra for other trial structures were calculated. These consisted of various models containing In-adlayers, the structure of which was based on analogies with Ga-adlayers on Ga-polarity GaN and previous photoemission and reflection high energy electron diffraction (RHEED) results from InN [8]. The best agreement between the experimental data and a simulated spectrum was obtained for the structure shown in Fig. 2. This structure consists of three layers of In on top of the bulk-terminated In-polarity InN, with $\frac{4}{3}$ ML of In in the topmost layer with $(\sqrt{3} \times \sqrt{3})$R30° periodicity as shown in Fig. 2. The registry shown is required to produce, for example, the 58° peak in the spectrum which results from shadowing of In in the topmost layer onto atoms in the second layer. The best fit structure is consistent with both the observation of ~3.4 ML of In-adlayers determined from the In:N ratio in core-level photoemission spectra and the $(\sqrt{3} \times \sqrt{3})$R30° reconstruction previously observed by RHEED [8,9]. Only integer order diffraction spots with relatively high background intensity were observed by LEED in the CAICISS chamber, indicating a relatively disordered surface but not ruling out the presence of regions of $(\sqrt{3} \times \sqrt{3})$R30° periodicity.

The overall agreement between the simulated CAICISS intensity and the experimental spectrum is good, apart from the fact that the spectral features in the calculated spectrum are angularly narrower than those in the

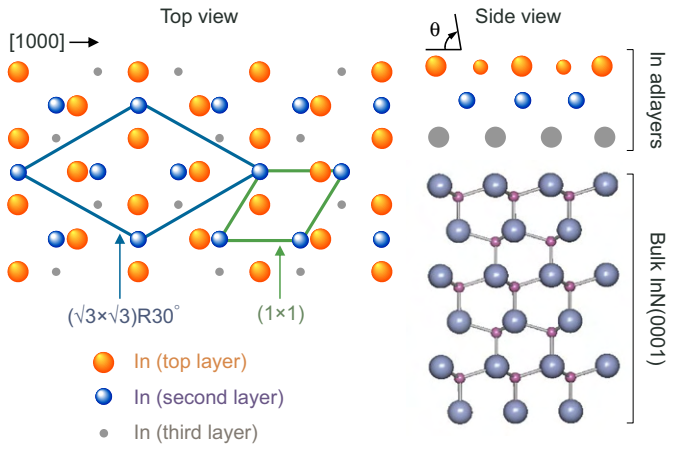

Fig. 2. (Colour online) Structural models showing the top and side views of the In-adlayer surface reconstruction for the In-polarity *c*-plane InN surface. There are three layers of In on top of the In-terminated bulk InN. The topmost layer consists of 4/3 ML of In with $(\sqrt{3}\times\sqrt{3})$R30° periodicity.

experimental data. The additional broadness in the experimental data compared with the simulation may be related to the In atoms in the topmost-layer being mobile. This could result in the presence of rapidly moving domain boundaries separating regions of the surface having different registries. This is consistent with the observed (1×1) LEED pattern with high background intensity. Evidence for this phenomenon has previously been found for Ga-adlayers at GaN surfaces which exhibit a pseudo-(1×1) surface reconstruction [16]. Such effects would broaden the features in the CAICISS spectra.

4. Photoemission from *a*-plane InN

Core-level XPS has been used to investigate the In-coverage on the clean surface of *a*-plane InN and thereby determine whether In-adlayers are present. The In:N XPS intensity ratio, calculated from the core-level peak areas divided by the atomic sensitivity factors for each core-level for the Scienta ESCA300 spectrometer, is 1.9 and 2.8 at 90° and 30°. The In:N ratio being greater for the more surface sensitive 30° emission indicates that the *a*-plane film has an In-rich surface.

To obtain a quantitative value of the In-coverage on the *a*-plane InN film from the XPS core-level results, the In:N intensity ratios have been compared with model calculations for different surface adlayer coverages. The calculations of the core-level photoemission intensity ratios use a layer-attenuation model based on photoelectron inelastic mean free paths (IMFPs) calculated using the TPP-2M predictive formula of Tanuma et al. [17]. The calculated intensity ratios are not sensitive to small variations in either these IMFPs or the spacings between layers. However, the intensity ratios vary significantly with both the number of surface indium layers and the concentration of indium within the layers.

Comparison of the model calculations with the measured XPS In:N ratios indicates that the *a*-plane InN has ~3 ML of In above the non-polar bulk-like termination. The surface In-coverage is therefore ~1.4 ML lower than for In-polarity *c*-plane InN where there is ~3.4 ML of In above the In-terminated bulk. A similar In-coverage consisting of an In-bilayer on In dimers has been predicted from first principles calculations for the *a*-plane InN surface under In-rich conditions [18].

The valence band XPS spectra recorded from *a*-plane and In-polarity *c*-plane InN thin films after surface cleaning are shown in Fig. 3. The intensity ratio of the two valence band peaks is different for the two orientations, with the 6.5 eV valence band peak reducing in relative intensity on going from *a*-plane to In-polarity *c*-plane InN. First-principles calculations of the surface valence band density of states are required to investigate these differences.

Additionally, the near-Fermi level emission provides another qualitative indication that the In-coverage is lower on the surface of the non-polar *a*-plane InN than for the In-polarity *c*-plane film. The emission close to the Fermi level is associated with the metallic In-adlayers on the surface. A similar feature in XPS spectra from GaN(0 0 0 1) surfaces has previously been attributed to the presence of Ga-adlayers [19]. The intensity of the feature decreases on going from *a*-plane to In-polarity *c*-plane InN, consistent with the lower surface In-coverage on the *a*-plane InN indicated by the core-level spectra.

As well as the information about the surface structure, the valence band spectra also contain the VBM to surface Fermi level separation. By extrapolating the leading edge of the valence band emission to the baseline, the valence band maximum (VBM) to surface Fermi level separation is found to be 1.32 ± 0.10 eV for both samples. Although this method is known to slightly underestimate the VBM to

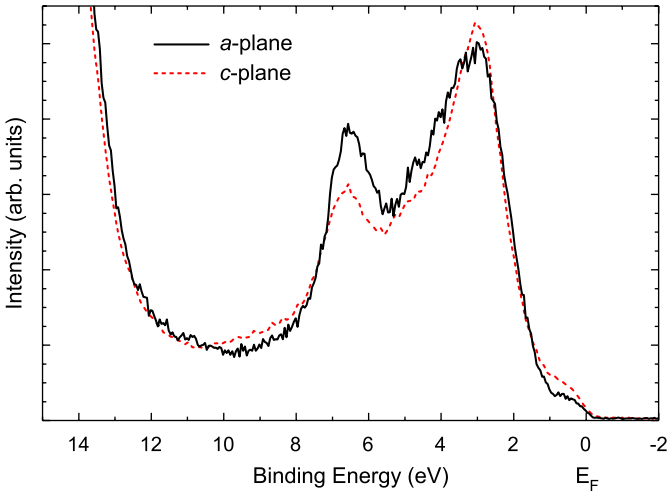

Fig. 3. (Colour online) The valence band spectra from *a*-plane (solid line) and In-polarity *c*-plane (dashed line) InN samples after AHC. The extrapolation of the leading edge of the valence band emission to the baseline indicates that the VBM to surface Fermi level separation is 1.32 ± 0.10 eV for both samples.

surface Fermi level separation in InN [20], these results indicate a lack of orientation dependence of the surface Fermi level. This has been confirmed by comparisons of the valence band spectra with valence band density of states calculated using density functional theory, where the surface Fermi level was found to be 1.53 ± 0.10 eV for In- and N-polarity *c*-plane InN and *a*-plane InN [21]. Since the bulk Fermi levels in these films lie in the range 0.75–0.82 eV above the VBM, this surface Fermi level position indicates the presence of downward band bending and surface electron accumulation. The observation of electron accumulation at *a*-plane InN surfaces in the presence of In-adlayers is in agreement with the predictions of first principles calculations [5]. Electron accumulation has also recently been observed at the *m*-plane surfaces of InN nanocolumns grown under In-rich conditions [22] and at the (0 0 1) surface of zincblende InN [21].

5. Conclusions

Using low energy ion scattering spectroscopy, the In-polarity *c*-plane InN surface has been found to be terminated by In-adlayers with a laterally contracted and rotated topmost In layer. This is consistent with previous diffraction and X-ray photoemission results which indicated a surface In-coverage of ~3.4 ML. Additionally, using core-level XPS, the *a*-plane InN surface has also been found to be terminated by In-adlayers with an In-coverage of ~3 ML. Photoemission measurements of the VBM to surface Fermi level separation for *a*-plane InN indicate the existence of an electron accumulation layer at the surface. This observation of electron accumulation at non-polar InN surfaces in the presence of In-adlayers is in agreement with the predictions of previous first-principles calculations.

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