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Surface structure of $In_2O_3(111)$ (1×1) determined by density functional theory calculations and low energy electron diffraction

K. Pussi [a], A. Matilainen [a], V.R. Dhanak [c], A. Walsh [d], R.G. Egdell [b],*, K.H.L. Zhang [b]

[a] Department of Mathematics and Physics, Lappeenranta University of Technology, FIN-53581 Lappeenranta, Finland
[b] Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK
[c] Department of Physics, University of Liverpool, Liverpool L69 3BX, UK
[d] Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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ABSTRACT

The surface structure of $In_2O_3(111)$ has been investigated by dynamical analysis of low energy electron diffraction data, in conjunction with first principles calculations using density functional theory. The experimental data set consisted of eight independent beams whose intensities were measured for incident energies in the range between 25 eV and 250 eV. In fitting the experimental data it was essential to treat the radii of In and O spheres as variable parameters: following this procedure a final Pendry R factor of 0.31 was obtained. The LEED results are compatible with the calculations and both analyses suggest that the surface structure involves only small vertical relaxations in the outermost of the $\{[O^{2-}]_{12}^{24-}[In^{3+}]_{16}^{48+}[O^{2-}]_{12}^{24-}\}$ quadrupolar units that define the (111) surface. The *ab initio* slab calculations also confirm that lateral relaxations not considered in fitting the experimental data are of very minor importance.

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1. Introduction

Sn-doped In_2O_3 is a prototype transparent conducting oxide (TCO) with important applications in heat reflecting mirrors [1], thin film display devices [2] and solar cells [3,4]. Although surface and interface properties are often important to the technological performance of TCOs in these areas, very little is known about the structure of In_2O_3 surfaces. This is in part because of the limited availability of bulk In_2O_3 single crystals. However, there have been important developments in recent years in the epitaxial growth of high quality In_2O_3 single crystals on cubic Y-stabilised ZrO_2 (Y-ZrO_2) substrates [5–13]. This has enabled preparation of ordered (001), (110) and (111) surfaces which have proved amenable to investigation by scanning tunnelling microscopy (STM) [14–16]. The body centred cubic bixbyite structure of In_2O_3 belongs to the space group $Ia\overline{3}$ and has a cubic lattice parameter $a=10.1170$ Å [17]. By contrast the face centred cubic fluorite structure of Y-ZrO_2 belongs to the space group $Fm\overline{3}m$ with lattice parameter $a=5.1423$ Å at the 17% Y doping level found in most commercial substrates [9]. The bixbyite structure is derived from a $2\times2\times2$ superstructure of fluorite but with ¼ of the anion sites vacant. In contrast to the 8-fold coordination of cations within the fluorite structure, the cation sites of bixbyite are all 6-fold coordinate. However two distinct cation sites can be identified: 8b sites with regular octahedral coordination defined by a single In–O bond length of 2.181 Å; and lower symmetry 24d sites where there are three distinct pairs of In–O bond lengths. There is a small mismatch on the order of only 1.6% between $2a$ for Y-doped ZrO_2 (10.2846 Å) and a for In_2O_3, with the epilayer under tensile stress. Moreover the close relationship between the cation arrangements within the two structures ensures that there is minimal chemical mismatch at interfaces between the two. Thus Y-doped ZrO_2 is an ideal substrate for growth of well-ordered thin films of In_2O_3.

In parent fluorite-type oxides such as Y-ZrO_2 [18,19] and UO_2 [20], the sequence of energies for the low index surfaces follows the order $\gamma(001)>\gamma(110)>\gamma(111)$ [21]. The high energy (001) surface is a polar Tasker type III surface with alternating cation and anion containing planes [22] whilst the intermediate (110) surface is Tasker type I with charge neutral layers. The lowest energy (111) surface is Tasker type II and is based on a sequence of anion and cation layers which may be grouped into charge neutral quadrupolar layers. The sequence of surface energies for bixbyite In_2O_3 is the same as for fluorite-like oxides, although there are small displacements in the ionic positions so that successive layers of ions are not rigorously coplanar as in fluorite itself but are characterised by a straddle of positions above and below the idealised fluorite positions [21]. Using the idealised layer description, the lowest energy (111) surface structure is based on repeating quadrupolar units with overall stoichiometry $\{[O^{2-}]_{12}^{24-}[In^{3+}]_{16}^{48+}[O^{2-}]_{12}^{24-}\}$: there are three of these repeat units before registry is restored in lateral positions in the fourth quadrupolar layer. It is possible to grow continuous (111) oriented epitaxial thin films with reasonably flat surfaces under a range of conditions, whereas in growth on (110) or (001) oriented substrates there is a propensity

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* Corresponding author. Tel.: +44 1 865 2 85157.
E-mail address: Russell.egdell@chem.ox.ac.uk (R.G. Egdell).

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toward development of islands with low energy (111) side facets [5,9,21,23]. Thus as a first step toward systematic investigation of the structures of low index In_2O_3 surfaces, a study of $In_2O_3(111)$ is an obvious starting point.

We present here a determination of the structure of the (1×1) reconstruction of Sn-$In_2O_3(111)$ by analysis of intensity/voltage (I/V) curves in low energy electron diffraction (LEED). In_2O_3 has 80 atoms in the unit cell and fitting the LEED data to an experimental structure is not trivial. However we have reached an acceptable Pendry R factor of 0.31. It transpires that the experimental structure is derived from a simple bulk termination with relaxations normal to the surface which cause a small reduction in the spacings between the In and O atoms in the outer quadrupolar layer. Reasonable agreement is found between the experimental surface structure and that derived from *ab initio* density functional theory calculations, which suggest that both vertical and lateral relaxations are small.

2. Experimental section

To minimise the effects of sample charging, LEED studies were conducted on lightly n-type doped In_2O_3 (with Sn as the dopant) rather than nominally undoped material. It has also been shown that Sn doping leads to improvement in the smoothness of In_2O_3 thin films [24]. Epitaxial thin films of 3% Sn-doped In_2O_3 were grown on 1 cm × 1 cm Y-stabilized $ZrO_2(111)$ substrates in an ultrahigh vacuum oxide MBE system (SVT, USA) with a base pressure of 5×10^{-10} mbar. This incorporated a hot lip indium Knudsen cell, a conventional Sn Knudsen cell and a radio frequency (RF) plasma oxygen atom source operated at 200 mW RF power with an oxygen background pressure of 3×10^{-5} mbar. Substrates were heated radiatively using a graphite filament. The nominal growth rate was 0.035 nm s^{-1}, as calibrated from the film thickness derived from HRTEM measurements. The Y-ZrO_2 substrates were cleaned by exposure to the oxygen atom beam at a nominal substrate temperature of 900 °C. Films were then grown to a thickness of 210 nm at a substrate temperature of 700 °C. *In situ* display LEED was carried out in an analysis chamber connected to the growth chamber, which revealed a well ordered (1×1) reconstruction. This reconstruction was easily regenerated in a second ultra high vacuum (UHV) system. The *ex situ* experiments were conducted in a standard UHV surface science chamber containing a PSP Vacuum Technology electron energy analyser, dual anode X-ray source, rear view LEED optics from OCI Vacuum Microengineering and an Omicron scanning tunnelling microscopy module (STM1) operating at room temperature. The base pressure of the system was less than 2×10^{-10} mbar, with hydrogen as the main residual gas in the chamber. The Sn doped In_2O_3 samples were cleaned by repeated cycles of bombardment with 500 eV argon ions followed by annealing at 500 °C for 30 min in ultrahigh vacuum (UHV). The cleanliness of the final surface was confirmed by x-ray photoelectron spectroscopy (XPS), where no C 1 s signal could be observed. There was no evidence of pronounced surface segregation of Sn and from the observed ratio of intensities between In 3*d* and Sn 3*d* core lines (Fig. 1) it was estimated that the Sn/In ratio in the near surface probed by XPS was very close to the nominal bulk value of 0.03. The occupation of some In sites by Sn introduces extra complexity into an already complex problem, but it was impossible to obtain LEED data from undoped samples of a quality comparable to that from doped samples.

Large area STM images were obtained in constant-current mode with a chemically etched tungsten tip at room temperature. These revealed that the prepared surfaces contained large flat terrace areas separated by steps of a height $a/2\sqrt{3}=2.9$ Å, corresponding to the separation between successive In layers (Fig. 2).

The surfaces gave sharp (1×1) LEED patterns with a low background (Fig. 3). The intensities of the diffraction spots as a function of the energy of the incident electrons (LEED I–V spectra) were measured at normal incidence of the primary beam. The spectra were background subtracted and normalised with respect to the primary beam current. The intensities of the symmetrically equivalent spots were averaged in order to reduce experimental noise. The data set that was gathered at 300 K consisted of 8 beams, ranging in energy from 20 eV to a maximum of 250 eV. The cumulative energy range was 1270 eV. The useful energy range was limited by two factors. Firstly owing to the large lateral size of the surface unit cell, low order spots converged into the electron gun at fairly low kinetic energies. Secondly higher order spots rapidly faded into the background for kinetic energies much in excess of 200 eV, thus imposing further limitations on the data range.

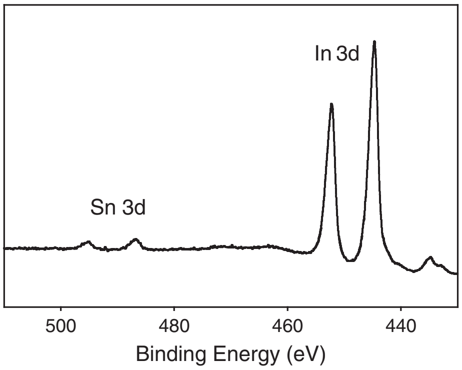

Fig. 1. Core level XPS of Sn-doped $In_2O_3(111)$ film in the In 3*d* and Sn 3*d* core level region measured *in situ* in the LEED system.

3. Density functional theory calculations on $In_2O_3(111)$

The relaxed surface structure of $In_2O_3(111)$ was calculated using density functional theory (DFT), within the generalized gradient approximation using a Perdew–Burke–Ehrnzerhof (PBE) functional [25], as implemented in the VASP package [26,27]. The plane-wave kinetic energy threshold (500 eV) and *k*-point density (4×4×4) were both well-converged for the bulk system. Starting from the relaxed bulk bixbyite lattice ($a=10.293$ Å), 2D surface models were constructed using a periodic arrangement of slabs, separated with a 20 Å vacuum region. Convergence of the surface energy γ with respect to slab thickness resulted in a model containing 48 formula units (i.e. 6 quadrupolar layers) for the (111) surface. Ions in the top two quadrupolar units were allowed

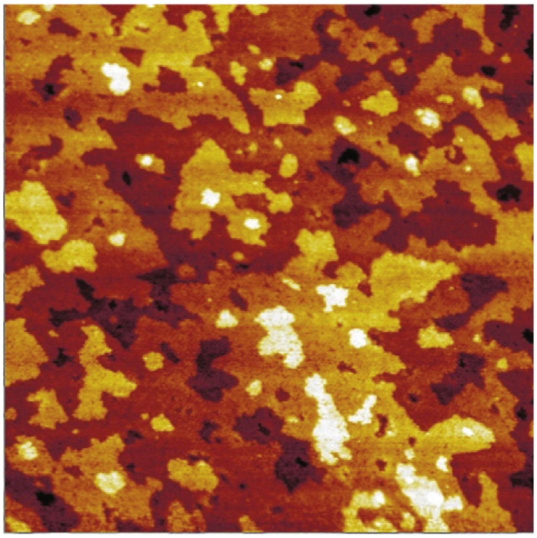

Fig. 2. (Colour online) STM image (200 nm×200 nm) of Sn-In_2O_3 epilayer measured after completion of LEED I/V experiments showing atomic scale steps of height 0.291 nm, corresponding to $a/2\sqrt{3}$. $V_{sample}=+1.5$ V; $I_{current}=0.1$ nA.

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