Surface structure of Sn-doped In$_2$O$_3$ (111) thin films by STM

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Abstract. High-quality Sn-doped In$_2$O$_3$ (ITO) films were grown epitaxially on yttria stabilized zirconia (111) with oxygen-plasma assisted molecular beam epitaxy (MBE). The 12 nm thick films, containing 2–6% Sn, are fully oxidized. Angle-resolved x-ray photoelectron spectroscopy (ARXPS) confirms that the Sn dopant substitutes In atoms in the bixbyite lattice. From XPS peak shape analysis and spectroscopic ellipsometry measurements it is estimated that, in a film with 6 at.% Sn, $\sim$1/3 of the Sn atoms are electrically active. Reflection high energy electron diffraction (RHEED) shows a flat surface morphology and scanning tunneling microscopy (STM) shows terraces several hundred nanometers in width. The terraces consist of 10 nm wide orientational domains, which are attributed to the initial nucleation of the film. Low energy electron diffraction (LEED) and STM results show a bulk-terminated (1 × 1) surface, which is supported by first-principles density functional theory (DFT) calculations. Atomically resolved STM images are consistent with Tersoff–Hamann calculations that show that surface In atoms are imaged bright or dark, depending on the configuration of their O neighbors. The coordination of surface atoms on the In$_2$O$_3$(111)–1 × 1 surface is analyzed in terms of their possible role in surface chemical reactions.

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1. Introduction

In$_2$O$_3$ is a wide band-gap semiconductor and, when doped with Sn, becomes a transparent conducting oxide (TCO) [1]. This material is commonly called Sn-doped In$_2$O$_3$ (ITO) and finds vast uses in many technical fields, e.g. in flat panel displays, solar cells, ‘smart windows’ using oxide electrochromics and organic light emitting diodes. Despite its popularity as a substrate, and the importance of the substrate–overlayer interface in many of these applications, surprisingly little is known about the surface properties of In$_2$O$_3$. Typically, polycrystalline films are used, which makes it difficult to determine fundamental surface properties such as the geometrical and electronic structures. Recently, growth of epitaxial In$_2$O$_3$ and ITO films has been promoted as a way to produce films with superior electrical and optical properties [2]. Such films are also well suited for identifying atomic-scale surface characteristics. For example valence-band x-ray photoelectron spectroscopy (XPS) studies of epitaxial films strongly suggest that the commonly accepted value of 3.75 eV for the direct band gap of In$_2$O$_3$ needs to be revised [3]. To the best of our knowledge, virtually nothing is known about the geometrical structure for either pure or ITO surfaces. Except for an (experimentally unconfirmed) theoretical prediction for In$_2$O$_3$ (100) [4], no reports exist for atomic surface structures. Obtaining a reliable structural model of the surface represents the basis for atomic-scale models of molecular arrangements at interfaces and is a first step towards a molecular understanding of the surface chemistry, which is important for indium oxide’s role as a gas sensor and oxidation catalyst [5]. This paper shows firm experimental evidence for a bulk-terminated (1 $\times$ 1) structure of In$_2$O$_3$ (111). The findings are supported by first-principles density functional theory (DFT)-based calculations.

In$_2$O$_3$ has the bixbyite crystal structure [6]. The lattice is body-centered cubic, with the space group Ia3. The unit cell, with a lattice parameter $a$ of 1.0117 nm, contains 80 atoms, see figure 1(a). Every In atom is six-fold coordinated to neighboring oxygen atoms (In(6c)). All 48 oxygen atoms have a tetrahedral coordination to four In neighbors, O(4c). There are two nonequivalent positions for In atoms; In$_1$ and In$_2$, see figure 1(a). The dark green spheres represent In$_1$ sites, 8 per unit cell, with an In$_1$–O bond length of 0.2174 nm. The 24 In$_2$ atoms within the unit cell are shown in light green. The bond length from In$_2$ to O varies between 0.2127 and 0.2230 nm, making this an irregular octahedron.
The few surface [3, 4, 7] studies that have been reported so far have focused predominantly on the In₂O₃ (100) surface and polycrystalline films. Possible surface terminations (figure 1(a)) contain either exclusively In or O atoms, categorizing this as a polar surface (type 3 according to Tasker’s criteria [8]). Polar surfaces are generally unstable [9, 10]. In fact, we found that the surfaces of epitaxial In₂O₃ (100)-oriented films undergo faceting [11]. As shown in the (111)-oriented side view in figure 1(b), the structure can also be regarded as consisting of stacks of O–In–O trilayers with a net zero dipole moment. Surfaces with such a ‘Tasker type 2’ configuration often have a low surface energy, and it is possible that they lend themselves to producing very smooth films with a well-ordered surface structure. These considerations have motivated us to focus on (111)-oriented ITO films. In fact, Ohta et al [2] reported that (111)-oriented ITO films prepared by pulsed laser deposition have superior crystallinity compared to (100)-oriented films. The fact that Brinzari et al [12] have found unusual adsorption properties for CO on In₂O₃ (111) further motivates us to investigate this particular surface orientation.
2. Experimental and theoretical methods

2.1. Experimental details

Yttria stabilized zirconia (YSZ) is an ideal substrate for ITO growth, as it exhibits cube-on-cube epitaxy and a small lattice mismatch with In$_2$O$_3$. The YSZ lattice parameter ($a = 0.5125$ nm) is almost exactly half that of In$_2$O$_3$, and the lattice mismatch is $-1\%$. We have used oxygen-plasma assisted molecular beam epitaxy (MBE) to grow high-quality single crystalline ITO films on YSZ(111). The ITO films were grown in an ultrahigh vacuum (UHV) chamber with a base pressure of $10^{-10}$ mbar. In order to fully oxidize the films, an oxygen plasma source (Oxford Scientific, OSMiPlas) was operated with a current of 15 mA and an oxygen background pressure of $6 \times 10^{-6}$ mbar. Activated oxygen is necessary for fully oxidizing the film; growth in a background of molecular oxygen resulted in non-stoichiometric films. The samples were heated radiatively and the temperature was monitored with an infrared pyrometer. A sample temperature of 700 $^\circ$C produced the flattest films; higher temperatures resulted in considerable re-evaporation during growth and very small deposition rates. Growth was monitored with reflection high energy electron diffraction (RHEED, electron energy of 25 keV). A Knudsen cell was used to co-evaporate Sn while depositing In from a single pocket e-beam evaporator with a growth rate of $5 \times 10^{-4}$ nm s$^{-1}$. Film deposition was monitored with a quartz crystal monitor, and the film thickness was calibrated by x-ray reflectivity measurements and profilometry. Results from 12 nm thick films are reported here. The concentration of the Sn dopant was examined with XPS (non-monochromatized Mg–K$\alpha$ source), taking into account Sn and In 3d photoelectrons peak intensities. Atomic sensitivity factors were calculated from published atomic cross sections [$^{13}$] and values for the inelastic mean free path [$^{14}$] as well as the transmission function given by the vendor of the electrostatic analyzer (SPECS PHOIBOS 100). A sputter-cleaned In foil and In$_2$O$_3$ powder (Aldrich) were used for taking reference spectra. Ex situ film characterization was performed by spectroscopic ellipsometry (SE) in the photon energy range 0.75–4.50 eV at angles of light incidence of 65$^\circ$, 70$^\circ$ and 75$^\circ$ using a VASE spectroscopic ellipsometer (JA Woolam Co., Inc., USA). The free electron density is obtained from SE data using the Drude–Lorentz parameterization of the film optical constants [$^{15}$–$^{17}$].

Low energy electron diffraction (LEED) was performed to check for surface reconstructions. The STM experiments were carried out using a UHV-STM (SPECS GmbH) with W tips. All STM images were taken in the constant-current mode imaging empty states (sample bias between +1.2 and +1.8 V and tunneling currents from 0.4 to 0.8 nA) at room temperature.

2.2. Theoretical details

The DFT calculations were performed using all electron first-principles DFT. After studying the dependence of the calculated bulk properties on the density functional, i.e. local density approximation (Perdew Wang functional) (LDA (PWC)) [$^{18}$] versus Perdew Burke Ernzerhof (PBE) [$^{19}$] and scalar relativistic treatment all-electron-non-relativistic versus density functional semicore pseudopotential (DSPP) [$^{20}$] and scalar relativity with DMol$^3$ [$^{21}$, $^{22}$], it was found that the PWC-DSPP lattice constant comes closest to the experimental one (0.2%), as expected. The Kohn–Sham bandgap (1.3 eV) was too small, also as expected. A four O–In–O trilayers-thick slab, containing 160 atoms per unit cell, was studied, using the experimental lattice constant and the PWC-DSPP functional. For the Tersoff–Hamann (TH) calculations [$^{23}$] a $6 \times 6 = 8$ symmetry unique k-points mesh was used.

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3. Results

Following a recipe given by Ohta et al [2], the YSZ(111) substrate was prepared by annealing in air at a temperature of 1350 °C for about 40 min. As shown in figure 1(c), this results in a RHEED pattern with sharp Kikuchi lines and first Laue zone diffraction spots; evidence for an excellent substrate surface quality. The ITO film also shows Laue zones (see figure 1(d)), indicative of a high surface quality with low roughness.

YSZ is an insulator and charges up when irradiated with low-energy electrons. It was possible to perform LEED measurements (figure 1(e)) by heating the substrate for 2 min at 400 °C and quickly taking a picture right after turning off the heating filament. A LEED pattern of the ITO(111) film (figure 1(f)), taken with the same electron energy as for the YSZ substrate, shows sharp spots with double periodicity, consistent with an epitaxial film with a lattice unit cell twice that of the substrate. The LEED spots from the film are sharp, indicating good surface crystallinity. We tested the effects of standard cleaning treatments, commonly used to prepare clean surfaces in UHV. A few cycles of Ar sputtering (Ar⁺ ion dose of 8 × 10¹³ cm⁻²) and annealing between 550 and 670 °C did not affect the sharpness of the LEED pattern or the overall appearance in STM. Brinzari et al [12] reported the appearance of extra spots after annealing films at 320 °C in oxygen, indicating a possible reconstruction. This was not observed in our experiments.

The composition of the In₂O₃ (111) films, doped with 2.4, 4.1 and 6.2 at.% Sn, was investigated with XPS. The line shape of the x-ray induced MNN Auger transition is a sensitive indicator of the chemical state of In atoms; the films are fully oxidized. Auger line MNN of ITO(111) film with 4.1% Sn is shown in figure 2(a). The Auger parameter of the Sn: In₂O₃ films was 851.9 eV, close to the value reported in the literature (850.8 eV [24]) and measured in our own setup for In₂O₃ powder (850.9 eV); a plasma-oxidized In foil gave an Auger parameter of 851.6 eV. The In 3d₅/₂ binding energy (444.4 eV) for the as-grown film is the same as that from untreated In₂O₃ powder. Upon heating in UHV a small shift (0.1–0.2 eV) to higher binding energy is observed, potentially because desorption of excess oxygen leads to flatter bands. The O 1s binding energy is 530.2 eV, confirming no charging effects (see figure 2(d)). Following a procedure outlined in [25] the photoemission peaks are fitted using two Voigt curves. One contribution comes from regular photoemission (‘screened’) and the other one, at higher binding energy and with broader line shape, from inelastically scattered photoelectrons (‘unscreened’), (see [26]). This second part is attributed to interaction of the photoelectron with electrons in the s-like conduction band and the creation of plasmons (figures 2(b) and (c)). Its peak position can be used to estimate the electron density of free charge carriers within the film. Using the core levels from a UHV-annealed films with 6.2% Sn, the plasmon energy is found to be 0.52–0.77 eV, which translates into a free electron concentration of 4 ± 2.5 × 10²⁰ cm⁻³. Such a high concentration of free electrons is corroborated independently by SE, which shows substantial optical absorption in the near-infrared spectral range. The Drude–Lorentz parameterization yields a value of (7.5 ± 0.2) × 10²⁰ cm⁻³, which agrees reasonably well with the estimates based on the XPS data and suggests that between one-third and one-half of the incorporated Sn atoms are electrically active. Angle-resolved XPS (figure 2(e)) shows that the Sn 3d₅/₂ peak intensity closely tracks the one for In 3d₅/₂, indicating that the Sn is located in substitutional sites within the film. The fact that the measured Sn concentration is not dependent on the exit angle of the photoelectrons (figure 2(f)) is strong evidence that Sn is not segregating to the surface.
Figure 2. XPS results of ITO(111) films. (a) X-ray induced Auger MNN line of a (4.1% Sn), (b) In 3d (6.2% Sn) showing Voigt curve fitting, (c) Sn 3d (6.2% Sn), (d) O 1s (6.2% Sn). (e) Angle resolved (AR) XPS (2.4% Sn) taken along the [1\bar{2}1] azimuth, and (f) angular dependence of Sn concentration.

The growth results in smooth films, see figure 3. The center of the wide-scale STM image in figure 3(a) shows a typical terrace, about 100 \times 70 \text{nm}^2 in size. Neighboring terraces are separated by mono-atomic steps, 0.3 nm high (see the line labeled ‘b’ and the corresponding profile in figures 3(a) and (b), respectively). The step edges are predominantly oriented along high-symmetry directions. Note that the terraces, while flat and large, consist of small domains with an average width of 10 nm (figure 3(c)). Neighboring domains show a lateral shift in their atomic-scale structure. We attribute this to the nucleation during the initial stages of growth. The substrate unit cell is half that of the film, hence independently nucleating islands can assume various lateral registries with the YSZ substrate, which can produce a half unit cell shift for neighboring domains. This results in many domain boundaries, which will reduce the residual strain within the film and contribute further to a smooth, epitaxial growth. Despite the relatively large number of domains the films are very smooth, indicating a quasi layer-by-layer growth, once the initially formed islands have merged together. Sn atoms within the lattice could not...
Figure 3. Empty-states STM results (I_{Tunnel} = 0.4 nA and V_{sample} = +1.7 V) of an ITO(111) film. (a) Wide-scale image with an rms roughness of 0.1 nm. The white line indicates the position of the line profile across a monoatomic step edge, displayed in (b). (c) Smaller scale image showing terraces with 10 nm-wide domains. (d) Atomically resolved STM image with the unit cell indicated. The black line shows the position of the line profile displayed in (e).

be distinguished in our atomically resolved STM images. Undoped In$_2$O$_3$ (111) thin films show a (1 × 1) bulk-terminated periodicity in LEED [11], but they were not conductive enough to perform STM measurements.

The high resolution image in figure 3(d) shows the periodicity of the atomic-scale structure. In empty-states STM it consists of a repeating pattern of triangular, clover-shaped black spots, surrounded by a bright contour. Taking a profile along the line labeled ‘e’ in figures 3(d) and (e) shows a corrugation of 0.06 nm. The size of the surface unit cell (indicated with dashed lines in figures 3(d) and 4(a)) is 1.4 nm, consistent with a (1 × 1) periodicity.

4. Discussion

As mentioned in the introductory paragraphs, the surface chemistry and surface electronic structure of ITO is key to many of its applications. We thus analyze the consequences of the atomic-scale atomic structure of the In$_2$O$_3$ (111) surface, both in terms of the coordination of surface atoms (and resulting likely role in surface chemical reactions) and how the structure is imaged in empty-states STM.

All experimental results point towards a simple, bulk-terminated form of the In$_2$O$_3$ (111) surface. Ball-and-stick models of such a (111) surface in both top and side-view are shown in figures 4(a) and (b), respectively. Each unit cell contains 12 five-fold coordinated In atoms (green) and 12 three-fold coordinated O atoms (red). Thus the same number of In → O and O → In bonds are broken, fulfilling the criterion for auto-compensation [27] or a stoichiometric,
Figure 4. Ball-stick model of In$_2$O$_3$ (111) surface (1 × 1) terminated. Arrows mark In and O atoms with their corresponding coordination (a) top view where the unit cell is marked with a broken line and (b) side view.

non-polar surface [8]. Calculated surface relaxations are small, confirming the stability of the In$_2$O$_3$ (111) surface. In addition, 4 six-fold coordinated In atoms (light blue) and 12 four-fold coordinated O atoms per unit cell are present; the latter reside in a layer underneath the In atoms and are shaded in a lighter color. These atoms have the same coordination as in the bulk. For large classes of molecules, adsorption on oxide surfaces follows acid/base behavior [28], where undercoordinated cation sites serve as electron donors (Lewis base), and neighboring undercoordinated oxygen atoms as proton acceptors (Brønsted base). A relatively large part of the In$_2$O$_3$ (111) consists of O(3c) atoms connected to In(6c) atoms; the latter will not participate in such reactions. On the other hand, oxidation reactions (e.g. the oxidation of CO, which is important in gas sensing), require surface oxygen atoms that are easily removed through reaction with an adsorbate. It is possible that the O(3c) atoms that are coordinated to the In(6c) atoms are more facile and would participate in such a reaction. The lateral separation of areas with distinct surface chemical properties is unusual for an oxide surface, and could give rise to an interesting nanoscale organization of surface chemical reactions.

It is well-established that the STM contrast on semiconducting metal oxide surfaces is heavily influenced, and sometimes even dominated, by electronic effects [29]. For example, in empty-states images of TiO$_2$ (110), only five-fold coordinated Ti atoms appear bright, and the geometrically protruding two-fold coordinated O atoms, which, in turn, are bound to Ti(6c) atoms, appear black [30]. However, in other cases STM images closely follow the geometric morphology of surfaces. For example in empty-state images of V$_2$O$_5$ (001) with a surface containing O(1c), O(2c) and O(3c), only the O(1c) protruding above the main surface plane are imaged bright [31, 32].

To elucidate the tradeoff between electronic structure and topography on the In$_2$O$_3$(111) surface TH calculations [23] were performed using the relaxed (1 × 1) surface. The results for empty states (integrating 1–2 eV above the conduction band edge) are displayed in a 2 × 2
Figure 5. TH plots of the empty states DOS, integrated up to 1–2 V above the conduction band edge, above a relaxed In$_2$O$_3$ (111) surface. (a) The contours are chosen in 0.1 Å intervals such that the most protruding point (white) is 4.4 Å above the surface. (b) Overlay of the TH results from (a) with an experimental STM image. (c) TH plot overlaid with a ball-and-stick model of the relaxed coordinates (color code of atoms as in figure 4; i.e. In$_{1(1)}$(5c) dark green; In$_{2(1)}$(5c) light green, In(6c) light blue, O(3c) (located above neighboring In) red and O(4c) (located below neighboring In) light red. Red and blue areas in the Tersoff–Hamann (TH) plot would translate into higher and lower-lying areas, respectively.

Supercell (figure 5(a)); dark triangular areas are surrounded by white circular regions surrounded by lighter blue. By superimposing a ball-stick model with TH results in figure 5(c) it becomes apparent that both the darker (blue) and the lighter (red) areas are centered at rings of three In$_2$(5c) atoms. The In atoms in the darker areas are connected by O(4c) atoms and in the brighter areas they are connected by O(3c) atoms, located underneath and above the main In plane, respectively. TH calculation is also superimposed with experimental STM image and similarities are apparent, figure 5(b).

The TH plots show little change when varying the energy cutoff, as expected from the mainly In 5s-derived nature of the conduction band [33–35]. The shape and orientation of contours surrounding both the bright and dark areas do change with the position above the sample, however. For distances very close to the sample, the brighter areas break up into three bright spots, marked red in figure 5(c). As an experimental test, the same area of the ITO(111) was imaged with a constant tunneling current ($I = 0.4$ nA) while changing the sample bias voltage from +1.4 to +0.4 V. (Note that this will also move the tip closer to the sample as fewer states for tunneling are available for smaller bias voltages.) The results are displayed in an STM ‘movie’ available from stacks.iop.org/NJP/10/125030/mmedia. For high bias voltages a fuzzy white contour surrounds the dark, clover-shaped spots (see also figure 3(d)). This contour breaks up into three bright spots at a bias voltage around 0.7 V (marked with a ring in the movie). Additional bright features also appear, consisting of an arrangement of three more distinct bright spots. These are located at imperfections on the sample surface (imaged as larger dark areas for high bias voltages, enclosed by white rectangles in the movie). These STM results provide good support for the TH calculations.

Coming back to figure 5 it is interesting that the In(5c) atoms in the bright and dark regions of the STM images are located at roughly the same z position and distinguish themselves only...
by the orientation and coordination of the neighboring O atoms. For the development of current optoelectronic and future molecular electronic devices the charge injection into ITO substrates is a critical issue; thus a further analysis of the nature of the STM image contrast (hence tunneling probability) could go beyond a mere academic interest as to which atoms are imaged in STM experiments.

5. Conclusion

In summary, we have grown epitaxial, (111)-oriented ITO thin films. The high surface quality of the films allows their structure to be investigated with atomic-scale detail for the first time. The films exhibit large, atomically smooth surfaces, which consist of small, laterally shifted domains. The surface is stoichiometric and has a \((1 \times 1)\) surface termination. Empty-states STM images can be explained by a bulk-terminated surface that shows an interesting lateral separation of fully coordinated and undercoordinated surface In atoms. TH calculations are in good agreement with empty-states STM images. Interestingly, the tunneling probability into \(\text{In}_{12}(5c)\) atoms changes depending on the orientation and undercoordination of neighboring O atoms.

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