EPITAXIAL In_2O_3 LAYERS FOR CHEMICAL SENSORS: STRUCTURAL AND SURFACE CHARACTERIZATION

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1. INTRODUCTION

Indium oxide is one of the basic oxides, which have been extensively studied [1-3] due to its prominent applications for gas sensor design, and as modeling material, possessed of some interesting chemical and structural peculiarities such as polar surfaces and systematic anion vacancies. Like conductometric gas sensor material it demonstrates enhanced sensitivity to oxidizing gases (O_3, NO, etc.). During our own experiments the interesting and unusual effects concerned with surface and gas sensing properties of undoped In_2O_3 thin films were revealed [4-6]. Nevertheless of rather great efforts in the direction of basic understanding it can be stated the lack of generalized pattern in description of sensitivity mechanism on that oxide. Thorough study of fundamental sensing properties needs well-characterized surfaces like in single crystals or epitaxial layers. Thus we make an attempt to prepare and characterize epitaxial layers of In_2O_3 with (100) orientation. As it is known (100) plane is the most stable in the In_2O_3 crystal.

2. EXPERIMENTAL DETAILS

In_2O_3 films were grown on optically polished substrates of (100)YSZ (yttria stabilized zirconia) using a conventional d.c. sputtering method [7]. The film growth rate and the total thickness were equaled 0.2 nm/s and 120 nm respectively. Morphological, structural and surface characterizations were carried out using AFM (atomic force microscopy), RHEED (reflection high-energy electron diffraction) X-ray and ultraviolet PES (photoelectron spectroscopy), as well as XPD (X-ray photoelectron diffraction). AFM scans were taken in taping mode in air. RHEED pattern was recorded in UHV system with background pressure $8x10^{-8}$ Pa and energy of primary electron beam of 25 keV at grazing angle geometry. PES and XPD experiments were carried out in UHV system equipped with an Omicron EA 125 multichannel analyzer, Mg (1253.6 eV) and HeI (21.218 eV) sources. XPD patterns were acquired using computer-controlled rotation of sample in azimuthal and polar directions. Zero polar angle corresponds to escaping photoelectrons along the surface normal. Two kinds of diffraction pattern were recorded, namely for In3$d_{5/2}$ and O_{1s} core levels, that allowed to recognize contribution from each element. Surface cleaning by soft Ar-ion sputtering (500 eV; 1 μA; 10^{-4} Pa), and in-situ annealing were performed to see the surface structure evolution.

3. RESULTS AND DISCUSSIONS

The AFM image of (100) In_2O_3 epitaxial film is presented in the Fig.1. The RMS roughness of the surface estimated from these data is equaled 4.6 nm. It is seen that the growth occurs in stepped-terrace mode. The average size of terrace is equaled about 200 nm. RHEED pattern and its interpretation shown in the Fig.2 confirm the monocrystalline quality of the grown films, accordance to the symmetry of the substrate surface and belonging to cubic C type rare earth oxide structure (bixbyite). Slightly elongated spots in the direction perpendicular to the sample surface indicate on the relatively high roughness of the film surface that corresponds to the results of AFM measurements.

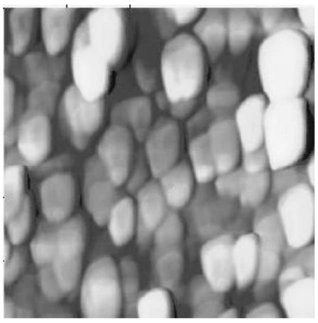

Fig.1 AFM image of In_2O_3 epitaxial layer, scan size 1x1μm

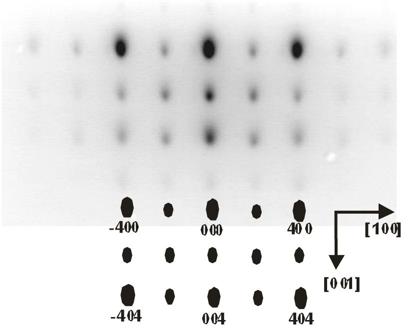

Fig.2 RHEED diffraction pattern and its interpretation. The primary beam is parallel to [010] direction

The lattice constant obtained from experiments is 1.012 nm that is in good coincidence with referred value [2]. High surface sensitivity about few atomic layers of RHEED method suggests on no phase transformations in this vicinity. However this do not refuse the possible reconstruction in the outermost plane. If to look on crystallographic structure of this surface (see Fig.3), then it means that some amount of topmost oxygen atoms (from oxygen subplane) may remove the surface under some ambient conditions due to a large surface dipole moment and rather small binding energies. There are three kinds of oxygen atoms with different binding energies in the In_2O_3 lattice [5]. First of all oxygen with the smallest energy leaves the surface, results in the rearrangement of residuary atoms. Besides heating and ambient conditions with oxygen deficiency this process to a great extent is caused by hydroxylation of the surface [8]. Results of XPD measurements have shown the distinct difference in the diffraction images correspondent to In and O atoms (see Fig.4). Note that given zero-order diffraction of photoelectrons, which means forward scattering geometry, probes chemical bond directions between atoms constitute the lattice.

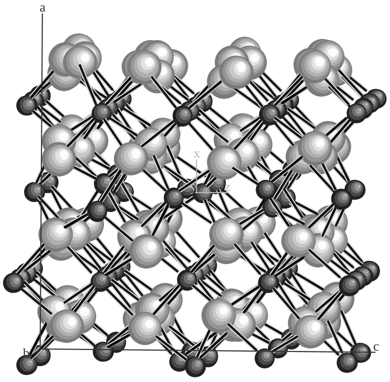

Fig.3 Crystallographic structure of (100) In_2O_3 surface (side view). Large balls – oxygen atoms, small balls – indium atoms

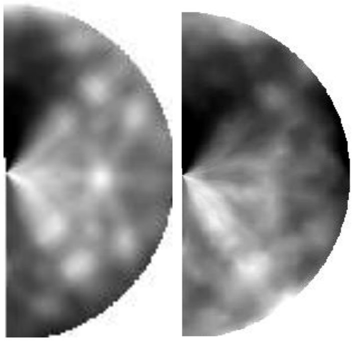

Fig.4. XPD patterns from $In3d_{5/2}$ (BE=442.7 eV) – on the left and O_{1s} (BE=532.5eV) –on the right, core level photoelectrons. Azimuthal and polar scans are of 0-180^o and 0-80^o respectively.

There is not such regular symmetry for oxygen spots as for indium ones. Some spots are smeared and others are missing. Additionally, the total background level is higher. Presented pictures were obtained on the sample after cleaning in the UHV conditions by heating (up to 500^o C) and soft Ar sputtering. Surface cleaning was done in some steps implying successive cycles of heating and sputtering from lower to higher temperatures and sputter times. It should to be noted that we did not observe any sufficient changes in In-XPD patters like in RHEED patterns during surface cleaning procedure, but rather considerable improving of the O-XPD pattern towards to an appearance of some spot ordering took place. To elucidate this question we examined the evolution of valence band (VB) spectra with above treatments using UPS method. The results of these experiments are presented in the Fig.5. As one can see spectra undergo crucial transformations. Typical for In_2O_3 VB structure [1,2,6] with O2p derived peak and some features at higher BE appears only after annealing at 500^{o}C. At the same time the band gap emission caused by surface oxygen vacancies [9,10] drastically increases. Such behavior both of VB spectra and O-XPD patterns can be explained if to take into account the above-mentioned reconstruction of topmost oxygen layer under conditions of dehydroxylation during applied treatments. Initial state of the surface is characterized by considerable amounts of adsorbed water (~1ML) that mask the signal (escaping photoelectrons) from the regular lattice atoms. Desorption of water molecules from In_2O_3 [4] with annealing or sputtering is accompanied by the loss of these kinds of oxygen atoms with weak bond energy and following rearrangement of remaining. The next step on sensitivity mechanism elucidation is to examine the reactivity of this surface to oxygen chemisorption, its possible forms and to study the interaction of such modified surface with reducing gas.

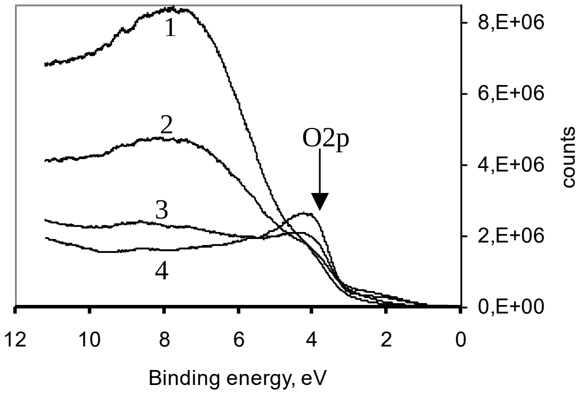

Fig.5. UPS valence band spectra of In_2O_3 epitaxial layer. Treatments: 1 – without treatment, 2 – 300°C, 3 – 500°C, 4 – Ar^+ sputtering , 15min

4. ACKNOWLEDGEMENTS

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