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NANOSTRUCTURED INDIUM OXIDE THIN FILMS DEPOSITED AT ROOM TEMPERATURE

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ABSTRACT

Nanostructured indium oxide thin films deposited at room temperature by reactive magnetron sputtering and annealing in a reducing atmosphere are investigated. The as deposited indium oxide (In_2O_3) films showed a dominating randomly oriented nanocrystalline structure of cubic In_2O_3. The grain size decreased with increasing oxygen concentration in the sputtering gas. Annealing in reducing atmospheres (vacuum, nitrogen and argon), besides improving the crystallinity, led to a partial cubic to rhombohedral phase transition in the indium oxide films.

Index Terms **-** cubic indium oxide, rhombohedral indium oxide, reactive magnetron sputtering, structural analysis, chemical and optical properties

1. INTRODUCTION

Transparent conducting oxides are widely used in various applications thanks to their low resistivity, high optical transparency and wide band gap. The application of these material ranges from transparent electrodes in various optoelectronic devices, barrier layers in tunnel junctions to active layers of gas sensors, especially in ozone sensors. Indium oxide (In_2O_3) is a potential material for use in solar cells, for ultraviolet lasers and sensor applications [1]. Therefore, there have been a lot of works on investigation of their growth conditions and optimizing their properties in dependence on the synthesis methods ranging from such as evaporation, sputtering, sol-gel process and chemical pyrolysis to metal organic chemical vapour deposition.

In_2O_3 thin films have a good adherence to the substrate surface and high chemical inertness [2]. In general, undoped binary oxide films are insulators in their stoichiometric form. On the other hand, this property can be changed by suitable doping and controlling the concentration of oxygen vacancies [2]. In_2O_3 can appear in two stable modifications as body-centered (bcc) cubic (a=10.118 Å) and rhombohedral (rh) (a=5.478 Å and c=14.51 Å) (crystallographic data are taken from [3]). They can be stabilized by choosing appropriate deposition conditions or synthesis methods [4-6]. The band gap of both is currently a subject of discussion and it seems to be that this material exhibits indirect transitions [7]. The values for the indirect and direct gaps of the cubic phase are between 2.1 to 3.1 eV and between 3.1 to 3.7 eV, respectively (data taken from [8-10]). In the case of the rhombohedral In_2O_3 phase the indirect gap was estimated to be in the range from 3.0 to 3.3 eV, whereas the direct gap can be expected 3.3 and 3.4 eV (data taken from [9, 10]). Recently, it was shown that the weak nature of the absorption around 3 eV can be attributed to transitions between the highest valence band states and the conduction band minimum being dipole forbidden or having only a very weak dipole intensity [9, 10].

In the present work it will be shown that annealing of cubic indium oxide films will cause, besides recrystallization of the film, partial phase transition from the cubic into the rhombohedral phase.

2. EXPERIMENTAL

The In_2O_3 films were deposited by dc reactive magnetron sputtering from an In target (4" in diameter, 99.99% pure) in a mixture of oxygen and argon onto unheated Si and oxidized Si substrates. A sputtering power of 75 W was used. Both argon inert flow and oxygen reactive flow were controlled by mass flow controllers. The flow of oxygen in the reactive mixture O_2-Ar was changed in the range of 40-80 sccm. The relative partial pressure of oxygen, defined as $\xi = p(O_2) / p(O_2+Ar)$, varied from 10 to 30%. The total gas pressure and the deposition time were kept constant. Some of the

deposited films were post-growth annealed in a tube furnace for 1 hour at temperatures 400 and 500°C in N_2 and Ar atmospheres and in vacuum.

The crystal structure was investigated by X-ray diffraction (XRD) using a D 5000 diffractometer with Cu Kα radiation. The structure refinement process was calculated using the program EVA Diffract Plus. Raman measurements were conducted on a micro-Raman spectrometer DILOR-JOBIN YVON-SPEX, type LabRam, in backscattering configuration, equipped with an optical Olympus microscope and a moveable xy-table. The excitation source was a He-Ne laser (632.8 nm, 15 mW). Some samples were investigated by high-resolution transmission electron microscopy (HRTEM) using TECNAI 20 S-TWIN operated at 12 kV acceleration voltage and selected area electron diffraction (SAED). The Raman spectrometer was calibrated using the 520.7 cm^{-1} Raman band of silicon. All measurements were performed at room temperature in a spectral range between 200 and 800 cm^{-1}.

3. RESULTS

The improvement of the crystalline structure was confirmed by the carried out XRD diffraction measurements. A typical XRD pattern taken from the indium oxide layer in the as deposited case and annealed at 500°C for 1 h in nitrogen is shown in Fig. 1. The XRD patterns revealed a clear polycrystalline structure. The diffraction patterns consist of diffraction peaks related to the (bcc) structure of In_2O_3 and corresponding to (211), (222), (400), (440) and (622) lattice planes correlating with the results obtained in [2, 11]. The strongest diffraction peak is the peak related to the (222) lattice plane indicating corresponding preferential orientation along this direction. After annealing all diffraction peaks were shifted towards higher 2 angles by 0.5° - 0.9°, as depicted in Fig. 1. This implies that the process of post-deposition annealing at 500°C has shrunk the lattice constant or caused a change in the residual strain between the lattice planes, resulting in a decrease of the lattice parameter. The obtained lattice plane values extracted from the diffraction peaks before and after annealing are given in Fig. 2. In the as deposited case the lattice constants are increases compared with the unstrained value of the lattice parameter for (bcc) In_2O_3 which is 1.0118 nm [3]. The experimental obtained lattice parameters are in the range between 1.021 and 1.026 nm for as-deposited samples.

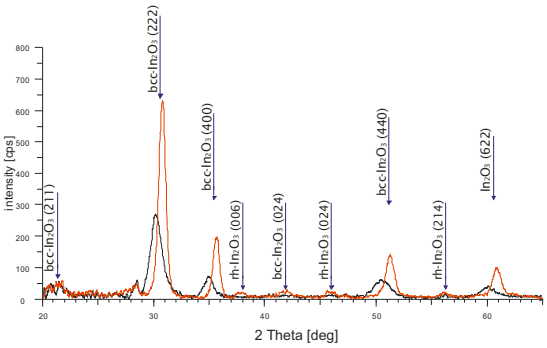

Fig. 1: XRD patterns of In_2O_3 films: as-deposited and annealed at 500°C (black line – as deposited sample, grey line – annealed sample).

After annealing the lattice parameter drops below the theoretical value and is within the range of 1.001 and 1.006 nm. Such drastic changes are a common effect in sputtered oxide films [2, 12] and can be attributed to out-diffusion of the implanted sputter gases, defect annealing and defect-defect interaction. Further reasons for the change in the lattice constants can be oxygen vacancy formation and differences in the thermal expansion coefficients between the substrate and the thin film. The intensities of the diffraction peaks were also significantly higher (at least two times in comparison with as-deposited) for all annealed samples. Moreover, the values of the full-width at half-maximum (FWHM) of the annealed samples were smaller, indicating better crystallinity of the indium oxide film due to the carried out annealing procedure. Additionally, another remarkable change was observed. Namely, the appearance of weak additional diffraction peaks in the diffraction pattern of the annealed sample. The peak positions correspond to the (006), (024) and (214) lattice planes of the rhombohedral modification of indium oxide. Therefore, in consequence of the thermal annealing, the initial cubic structure was partially transformed into a rhombohedral structure. The rhombohedral polymorphic modification of indium nitride is the so-called high pressure phase [8], i.e., this phase is metastable at normal pressures. At 3.8 GPa a phase transition from the (bbc) modification into the (rh) modification of indium oxide can be expected. If we recalculate the lattice constants obtained after annealing into lattice strain, compressive strain in the range between 0.011 and 0.005 nm can be obtained. Taking into account the elastic properties of indium oxide [8], compressive strain 1.7 and 0.86 GPa can be estimated, which is close to the predicted pressure value of the (bbc) to (rh) phase transition.

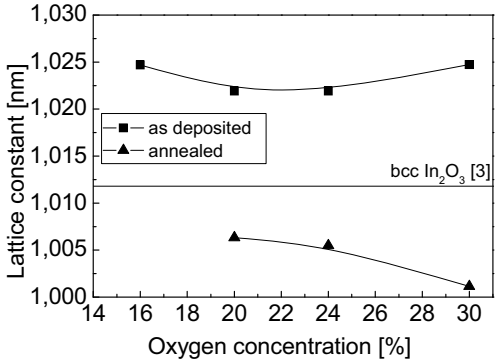

Fig. 2: Lattice constants of the (bcc) indium oxide fraction in the film in dependence on the oxygen content in the working gas for as deposited and annealed at 500°C samples.

Nanostructural characterization of samples deposited at an oxygen concentration in the working gas of 10 and 20 % has been carried out by TEM, HRTEM and SAED. HRTEM observations (Fig. 3) of as-deposited In_2O_3 films confirmed that they were polycrystalline with fine-grained, different size and shape nanostructure. The size of the nanocrystals forming the layer ranges about 20 nm for samples prepared at 10% oxygen content in sputtering gas while the film deposited at 20% oxygen content the size of crystallites decreased into the range of ~10 nm. The phase formation was investigated by scanning the transparent regions of the indium oxide film with SAED as well as by FFT analysis HRTEM patterns of indium oxide grains. In both cases it was possible to obtain diffraction features and lattice plane spacings corresponding to the rhombohedral polymorphic modification. It has to be mentioned here that this was possible only on selected regions in the layer. Nevertheless, this is a hint that even during the deposition position process rhombohedral crystallites were formed. During the annealing of the film at 400°C a coalescence of In_2O_3 nanocrystals could be detected and the structures with smaller particles sizes than in the as-deposited film has been observed.

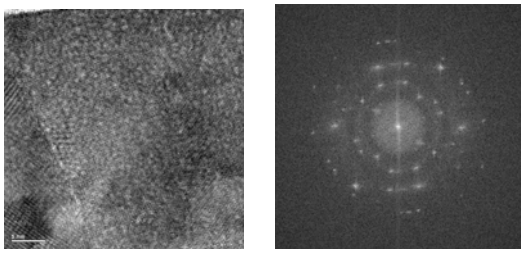

Fig. 3 HRTEM images and FFT patterns of as-deposited and annealed sample prepared at 10% oxygen content in sputtering gas.

The obtained Raman spectra in dependence on the annealing atmosphere are shown in Fig. 4. Independently on the annealing and deposition conditions they showed one prominent Raman peak located at 302 cm^{-1} and 303 cm^{-1} for the as deposited and annealed sample, respectively. This peak is a typical Raman peak of the (bcc) polymorphic modification of indium oxide [5, 13, 14]. The peak shift to higher wave numbers indicates a change in the residual strain of indium oxide from higher tensile to lower tensile or from tensile to compressive strain. Unfortunately, a clear conclusion cannot be drawn from the Raman spectra because the unstrained peak position is not known. The feature at the wave number range from 420 to 430 cm^{-1} can be also assigned to indium oxide [15] but does not appear in materials with pronounced crystallinity [5]. Therefore, this peak might be related to specific defects in the film structure which were not annealed out. At the lower wave number side of the main peak a weak shoulder appears. This shoulder could be caused by two weak Raman peaks originating from the rhombohedral In_2O_3 phase formed in the film during annealing. They are indicated in Fig. 4 and located at 220 and 275 cm^{-1} [5].

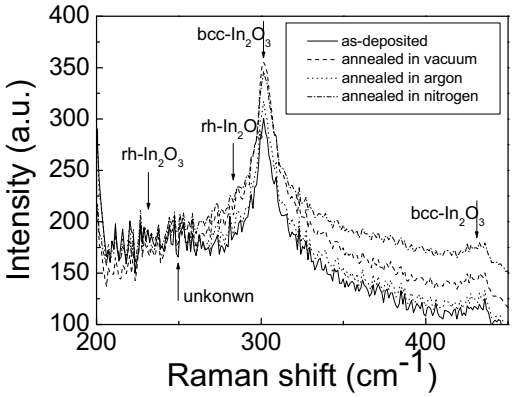

Figure 4 Raman spectra of In_2O_3 films prepared at 17.5% oxygen content and annealed at 400°C in various atmospheres.

4. CONCLUSIONS

Structural evolution of indium oxide thin films deposited at room temperature by reactive magnetron sputtering and annealing in a reducing atmosphere are investigated. Increased oxygen concentration in the working gas during magnetron sputtering at lower and higher oxygen contents causes a decrease of the growth rate due to surface reaction and sputter limitation. Annealing in a reducing atmospheres shrinks the layer thickness and improves the crystallinity due to recrystallization and out-diffusion of incorporated gases as a consequence the residual strain in the

layer changes from tensile to compressive, which causes a partial phase transition from the (bcc) polymorphic modification into the rhombohedral modification of indium oxide.

5. ACKNOWLEDGMENT

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