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Growth and characterization of indium oxide films for ozone detection

FUNCTIONALIZATION OF MATERIAL SURFACES

Abstract

The indium oxide (In_2O_3) films were deposited by DC reactive magnetron sputtering from an In target on unheated silicon substrates at power of 75 W. The flow of oxygen in the reactive mixture O_2-Ar was changed in the range of 40-80 sccm. The deposited films were post-growth annealed in a tube furnace for 1 hour at temperature of 500°C in H_2+N_2 atmosphere and for 8 hours at temperature of 400°C in N_2 atmosphere, respectively. The energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and atomic force microscopy (AFM) were employed in order to investigate the effect of the process parameters and post-deposition thermal annealing on the chemical composition, the microstructure and the surface morphology of In_2O_3 thin films. Changes due to different preparation conditions were observed. The electrical response of In_2O_3 -based structure, as a function of ozone concentration has been measured.

1. Introduction

Transparent conducting oxides are widely used in various applications due to their low resistivity, high optical transparency and wide energy band gap. Therefore, there has been a lot of works on investigation their growth conditions and optimizing their properties. In general, undoped binary oxide films are insulators in its stechiometric form. On the other hand, this property can be changed by suitable doping and controlling of oxygen vacancies [1]. Indium oxide In_2O_3 (E_g = 3.5–3.7 eV) is a potential material for using in solar cells, for ultraviolet lasers and sensor applications [2]. It is widely used as a material for transparent electrodes in various optoelectronic devices

and as a barrier layer in tunnel junctions. Highly resistive In_2O_3 thin films are utilized as active layers of gas sensors, especially in ozone sensors. In_2O_3 occurs in two crystal structures: body-centered cubic (a=10.118 Å) and rhombohedral (a=5.478 Å and c=14.51 Å), although there were only few reports in the literature concerning rhombohedral In_2O_3 synthesis [3]. In_2O_3 thin films have a good adherence to the substrate surface and high chemical inertness [1]. Polycrystalline In_2O_3 films can be prepared by various methods such as evaporation, sputtering, sol-gel process and chemical pyrolysis [1,3]. In_2O_3 nanoparticles can be obtained by metal organic chemical vapour deposition [4].

2. Experimental

The In_2O_3 films were deposited by DC reactive magnetron sputtering from an In target (3" in diameter, 99.99% pure) in a mixture of oxygen and argon onto unheated Si substrates. A sputtering power of 75W 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 16% to 30%. The total gas pressure was kept at 0.5 Pa. The thicknesses of the resulting layers were in the range of 40-80 nm. Some of the deposited films were post-growth annealed in a tube furnace for 1 hour at temperature of 500°C in H_2+N_2 atmosphere and for 8 hours at temperature of 400°C in N_2 atmosphere, respectively. Details of preparation conditions are listed in *Table 1*.

Table 1. List of samples:

sample no.	Oxygen content in working gas (%)	Oxygen flow (sccm)		Annealing
1	16	40		-
1a400				400°C, 8 hours, N_2
2	20	60		-
2a400				400°C, 8 hours, N_2
2a500				500°C, 1 hour, H_2+N_2
3	24	70		-
3a400				400°C, 8 hours, N_2
3a500				500°C, 1 hour, H_2+N_2
4	30	80		-
4a400				400°C, 8 hours, N_2

4a500				500°C, 1 hour, H_2+N_2

Chemical composition of the In_2O_3 thin films was determined using a FEI XL30 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyzer based on a silicon detector (EDAX) and a S-UTW-Window operating at 10 kV acceleration voltage. The crystal structure was identified with a Theta - Theta X-ray diffractometer (XRD) D 5000 with a Goebel mirror in grazing incidence geometry with Cu Kα radiation. The structure refinement process was calculated using the program EVA Diffract Plus. The surface morphology was observed by atomic force microscopy (AFM) using NT-MDT Solver under normal air conditions in non-contact mode. 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 electrical response of In_2O_3 -based structure, as a function of ozone has been measured.

3. Results

3.1 EDX spectra

Chemical analysis of prepared In_2O_3 thin films was performed by energy dispersive X-ray spectroscopy (EDX). EDX spectra were acquired from different places of all samples and then were averaged. X-ray counts per second (cps) were normalized to silicon peak in order to suppress the influence of the samples' thickness and unequal measurement conditions. EDX spectra of as-grown samples (Fig.1) and annealed samples (Fig.2) reveal the presence of indium and oxygen atoms in all In_2O_3 films. Carbon originates from the thin carbon layer on top of all samples, sputtered due to SEM investigation.

ZAF correction was applied to data acquired by EDX detector in order to determine the relative atomic fractions of the chemical elements of indium and oxygen present in the InO_X thin films. ZAF correction includes an atomic number correction accounting for the fraction of electrons backscattered by the sample and the volume of X-ray generation (the Z factor); a correction for the absorption of the generated X-rays in the sample (the A factor); and a correction for secondary X-ray fluorescence in the sample (the F factor) [5]. The values of oxygen concentrations in the InO_X thin films after ZAF correction varied from 70% to 77.2%. These values have been used to illustrate the variation of the oxygen presence in InO_X thin films versus oxygen content

in working gas (Fig.3). The tendency of increasing oxygen concentration in the films with the oxygen content in the working gas was observed, excluding samples prepared

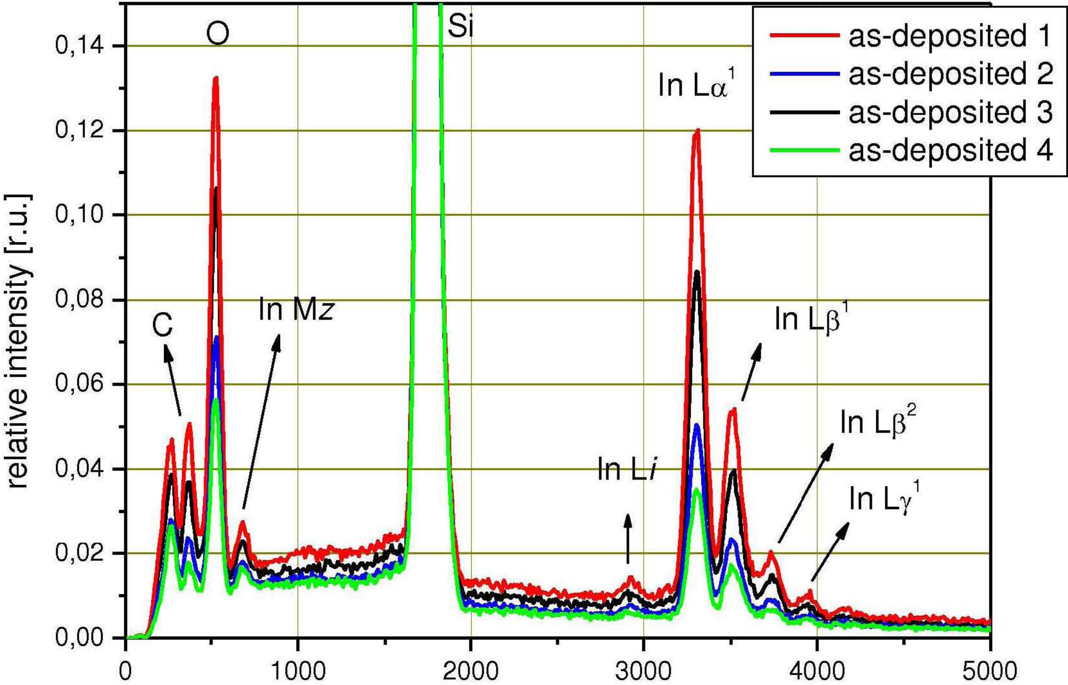


Fig.1 EDX spectra of as-grown samples.

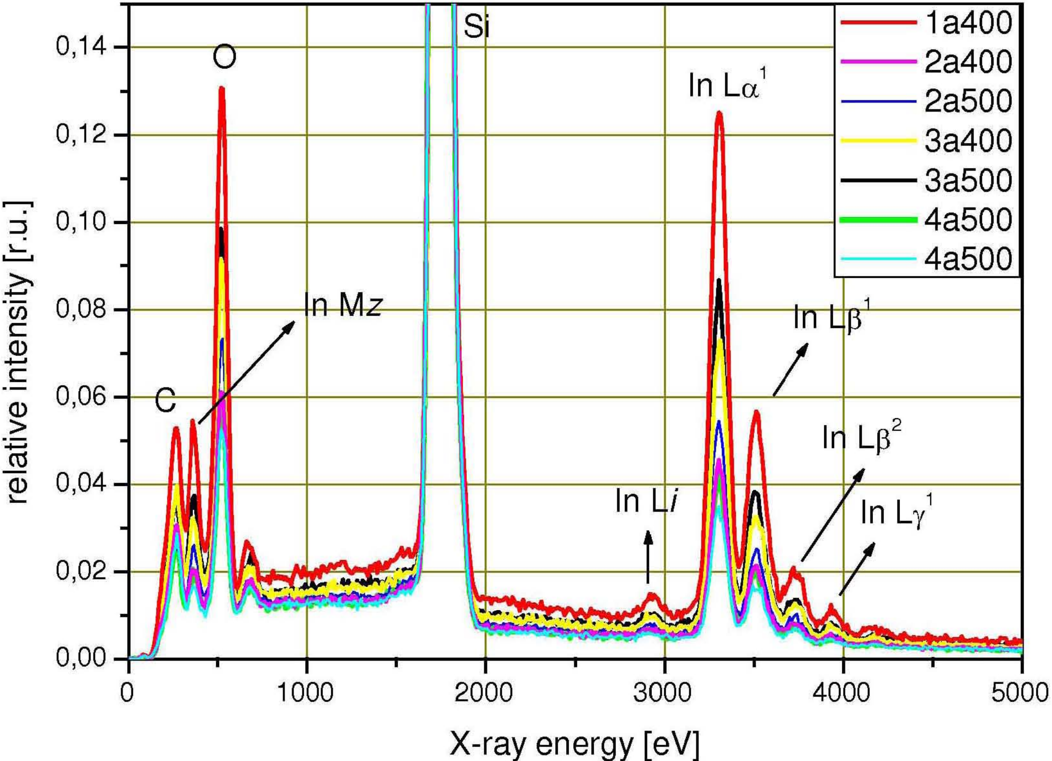


Fig.2 EDX spectra of annealed samples.

in working gas with oxygen content of 24%. The correlation between amount of oxygen in the prepared InO_X films and oxygen content in working gas in the chamber during film preparation is similar as was achieved by Al-Ajili and Bayliss [6]. To sum up, results (Fig. 3) show that the deposition conditions and process of post-deposition thermal annealing had influence on concentration of oxygen in the InO_X films.

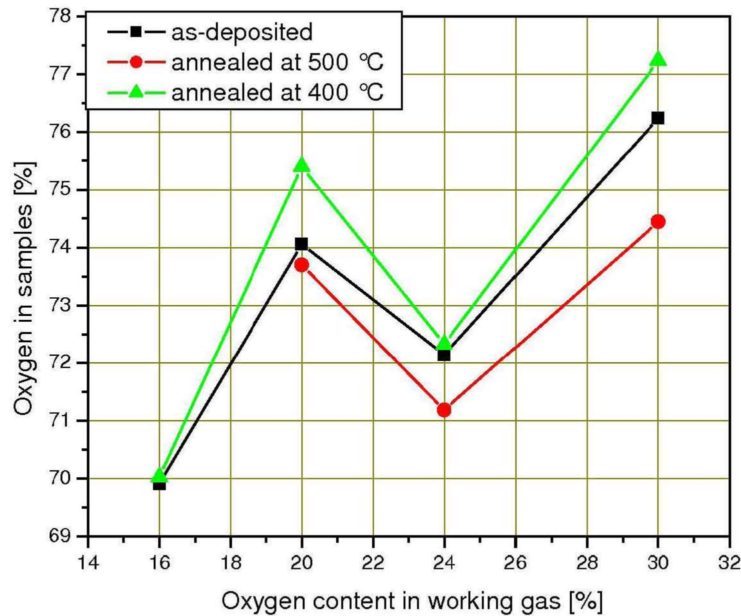


Fig.3 Variation of the oxygen presence in InO_X *thin films versus oxygen content in working gas.*

3.2 XRD observation

Fig. 4 presents the XRD diffraction patterns of the as-deposited samples (prepared at different oxygen contents in the working gas) and annealed samples (annealed for 1 hour at 500°C in H_2+N_2 atmosphere). From XRD spectra it was found that all examined In_2O_3 thin films had polycrystalline structure. The diffraction patterns from In_2O_3 thin films showed the presence of diffraction peaks from the (222), (400), (440) and (622) lattice planes, which were also reported by *Prathap et al.* [1]. In_2O_3 films have body-centred cubic structure and exhibit (222) as the preferential orientation. All diffraction peaks of annealed samples were shifted towards higher 2θ angles by 0.5°-0.9°, as depicted in *Fig. 5.* It implies that process of post-deposition annealing at 500°C has caused residual strain between the lattice planes, resulting in the decrease of lattice parameter. Theoretical value of lattice parameter for cubic In_2O_3 is 1.0118 nm.

Calculated lattice parameter has changed from 1.018 nm – 1.025 nm for as-deposited samples to 1.005 nm – 1.007 nm for annealed ones. The decline of lattice parameter due to thermal processes is in agreement with the work of *Prathap et al.* [1]. Intensities 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 annealed samples were smaller, indicating better polycrystalline structure of annealed samples.

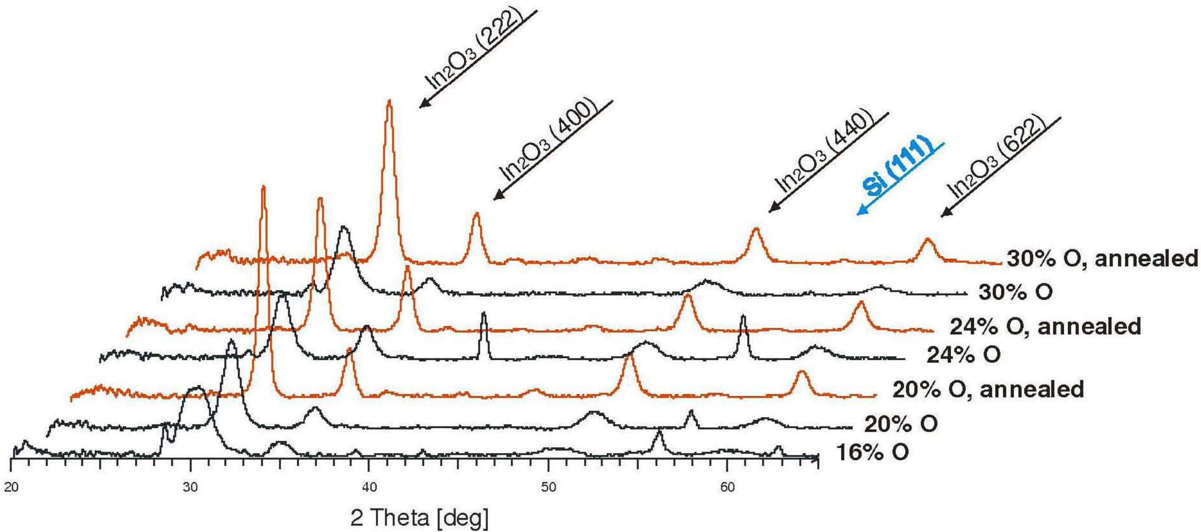


Fig. 4. XRD patterns of In_2O_3 films: as-deposited and annealed at 500℃.

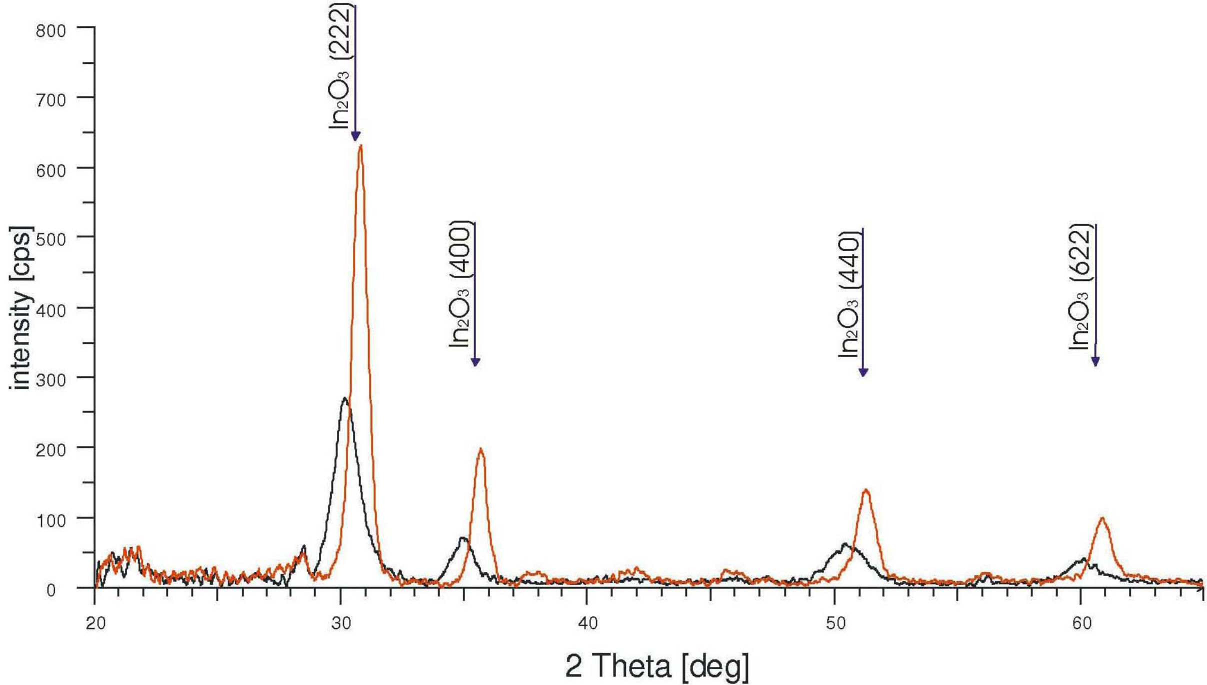
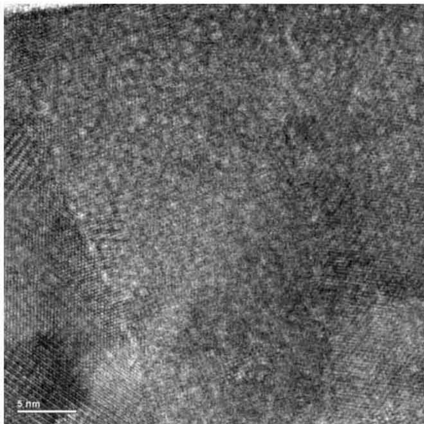


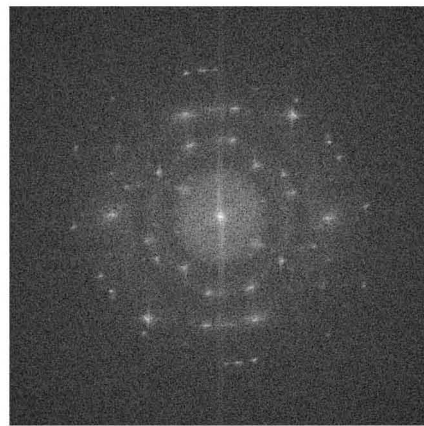
Fig. 5. XRD patterns of as-deposited and annealed samples – shift of diffraction peaks due to annealing.

3.3 TEM *observation*

Nanostructural characterization of samples 1 and 4 has been carried out via TEM, HRTEM and SAED. HRTEM observations (Fig. 6) 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 15% oxygen content in sputtering gas while the film deposited at 30% oxygen content the size of crystallites decreased into the range of ~10 nm. Confirmation of the presence of In_2O_3 in the deposited film has been obtained from SAED analyses. The FFT patterns of both as-deposited films were of a continuous ring type indicating a polycrystalline nature of film. The majority of reflexes correspond to rhombohedral In_2O_3 phase although any single reflexes could associate with body-centered cubic phase. During the annealing of the film at 400℃ a coalescence of In_2O_3 nanocrystals and the structure with smaller particles than in as-deposited has been observed.

a)





b)

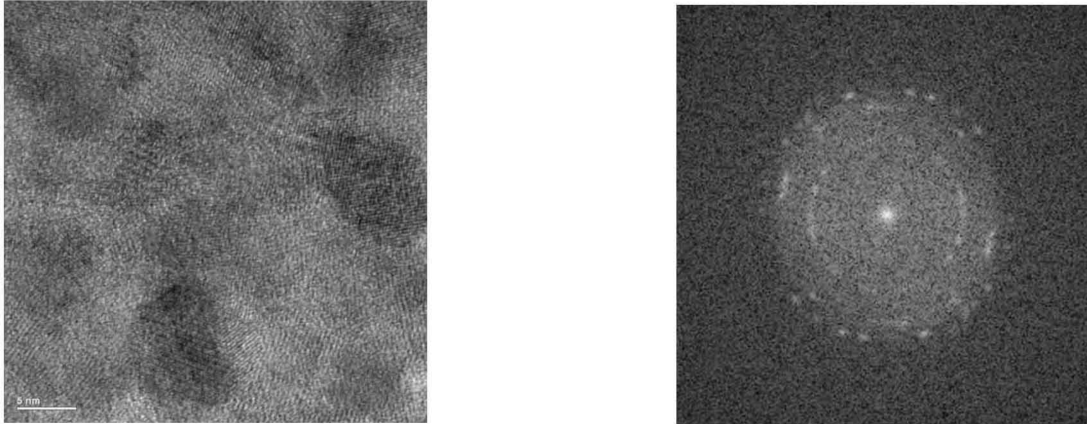


Fig. 6. HRTEM images and FFT patterns of as-deposited (a) and annealed sample prepared at 15% oxygen content in sputtering gas.

3.4 Surface morphology

The two and three dimensional AFM images taken at a scan area of 2 μm x 2 μm (Fig. 7-9) represent the surface morphology of the In_2O_3 thin films. After acquiring an AFM images, the images were subjected to a flattening procedure using the NOVA image processing software. The AFM topography of the prepared thin films reveals that the film surface is rather smooth and compact, copying the surface of polished silicon substrate. According to a quantitative analysis of the roughness deduced from AFM measuring (Table 2), the values of average roughness (R_a), root mean square (RMS) and coefficients of kurtosis (R_{KU}) changed in dependence on the deposition conditions. AFM images indicate that the topography of the samples annealed at 500℃ was modified in comparison to the as-deposited samples. On the other hand, the samples annealed at 400℃ exhibit a less rough surface compared to the as-deposited samples. A quantitative roughness analysis also confirmed that the process of post-deposition thermal annealing did not increase the values of average roughness and RMS. Carcia et al. obtained similarly small surface roughness (RMS < 1nm) by magnetron sputtering of InO_X on polyethylene terephthalate (PET) substrate [7]. The samples annealed at 500℃ have significantly higher coefficient of kurtosis R_{KU}, which means that these samples have infrequent extreme deviations of measured height. This is clearly seen as spikes in the 3D picture of the sample no. 2a500.

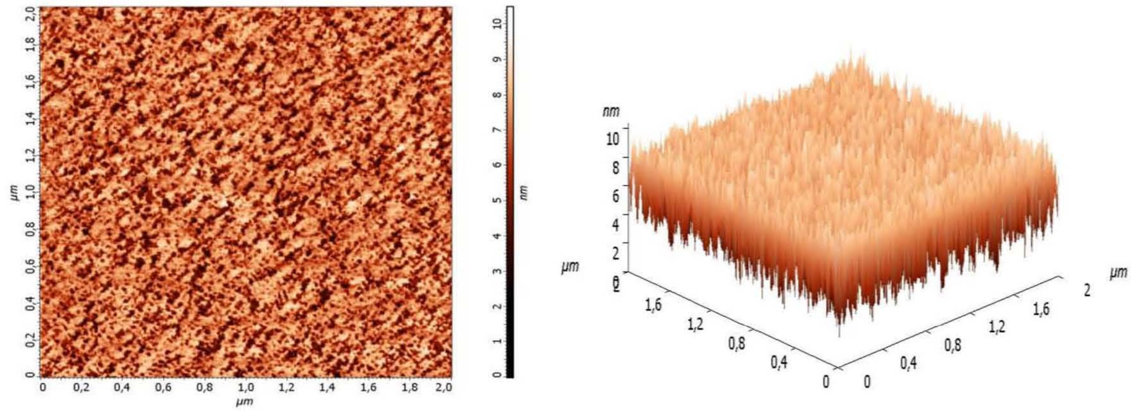


Fig. 7 AFM images of as-grown sample no. 2.

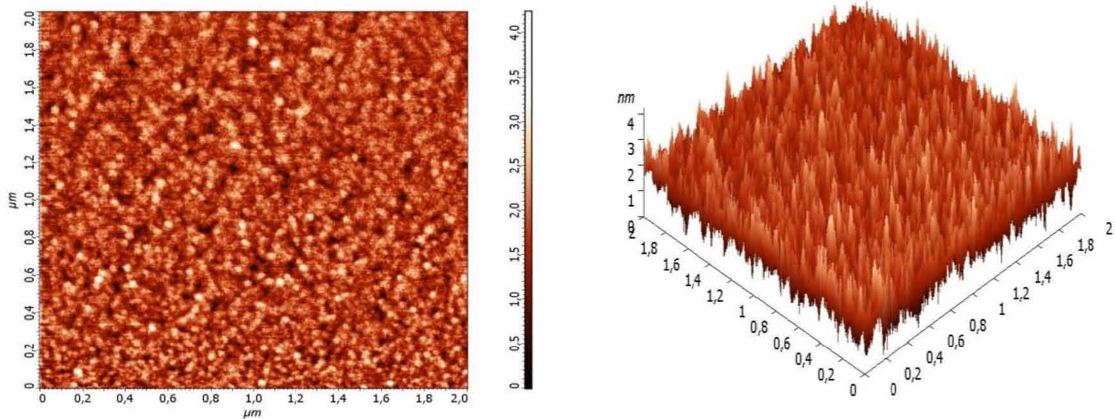


Fig. 8. AFM images of sample no. 2a400, annealed at 400 °C.

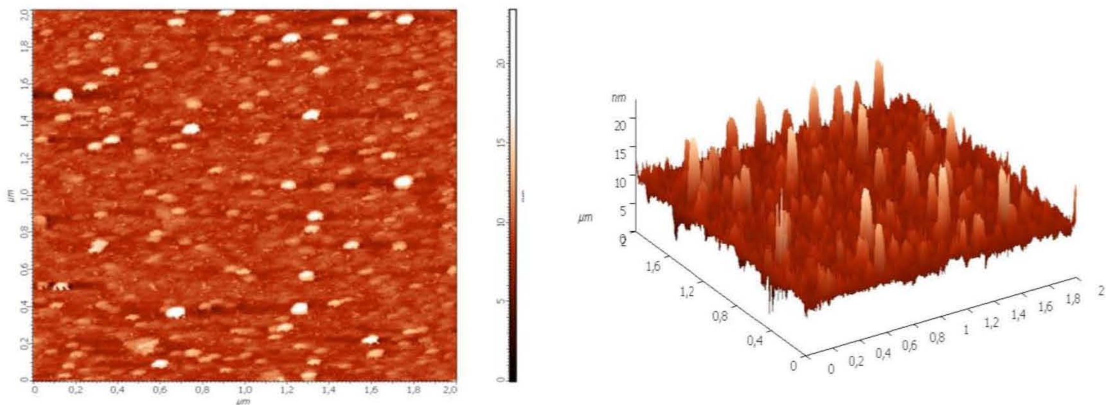


Fig. 9. AFM images of sample no. 2a500, annealed at 500 °C.

Table 2. Quantitative roughness analysis deduced from AFM:

sample no.	RMS [nm]	R_a [nm]	R_{KU}
2	1,580 nm	1,304 nm	0,38
2a400	0,468 nm	0,360 nm	0,41

2a500	1,483 nm	0,959 nm	11,06

3.5 Gas sensing properties

To check the ozone detection properties, In_2O_3 sensor structure towards ozone in the range of 500 ppb-150 ppm were measured. The ozone response of In_2O_3 sensor structure was defined as R_{O3}/R_{UV}, where R_{O3} and R_{UV} are the resistivity of the In_2O_3 layer after O_3 and UV light exposure, respectively. It was recorded that the resistance value of the In_2O_3 layer changes by two orders of magnitude between O_3 and UV light exposure. The sensor structures were found to be sensitive to O_3 concentrations as low as ~500 ppb. The optimal thickness of these In_2O_3 films was about 10 nm.

4. Conclusion

The deposition conditions and process of post-deposition thermal annealing had influence on concentration of oxygen in the InO_X films. The tendency of increasing oxygen concentration in the films with the oxygen content in the working gas was observed. From XRD spectra it was found that all examined In_2O_3 thin films had polycrystalline structure with (222) preferential orientation. The process of post-deposition annealing at 500°C improved the structure of In_2O_3 thin films towards better polycrystalline structure. At the same time annealing caused residual strain between the lattice planes, resulting in the decrease of lattice parameter. The HRTEM images showed the different crystalline structures sizes and shape. While in the low oxygen flow case the size of the crystallites is in the range of >20 nm and so in the FFT spots a clearly visible, for the higher oxygen case the particle size decreased into the range of ~10 nm and the polycrystalline structure was increased. The AFM topography of the prepared thin films reveals that the film surface is rather smooth and compact. The process of post-deposition thermal annealing did not increase the values of average roughness and RMS. Nevertheless, AFM images indicate that the topography of the samples annealed at 500°C was modified and have surface with sharp peaks. Further studies are in progress to improve and optimize the ozone detection properties.

Acknowledgments

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