DIFFUSION AND CRYSTAL GROWTH IN PLASMA DEPOSITED THIN ITO FILMS*

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Tin-doped indium oxide (ITO) films were deposited by means of DC-planar magnetron sputtering. A metallic In/Sn (90/10) target and an Ar/O_2 gas mixture were used. The oxygen flow was varied between 0 and 2 sccm. Substrate voltages between 0 and -100 V were used. With increasing oxygen flow film structure and composition change from crystalline metallic In/Sn to amorphous ITO. Simultaneously the deposition rate decreases and the film density increases. The diffusion of oxygen into metallic In/Sn films and the amorphous-to-crystalline transformation of ITO were studied using in situ grazing incidence X-ray diffractometry (GIXRD), grazing incidence reflectometry (GIXR), and AFM. From the X-ray integral intensities diffusion constants, activation energies of the diffusion, reaction order and activation energy of the crystal growth process were extracted.

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1 Introduction

Tin doped indium oxide (ITO) films are an integral part of sophisticated optoelectronic devices, e.g. solar cells, heat mirrors, LCDs etc. The macroscopic film properties such as conductivity and transmission strongly depend on microstructure, stoichiometry and crystallinity and can be influenced by the deposition conditions. Magnetron sputtering is a mature and often used technology for ITO film formation.

In this article we present a study of the influence of oxygen flow and low energy ion bombardment to DC-magnetron sputtered ITO film growth processes and film properties like composition and structure degradation. In addition oxygen diffusion and solid state crystallization of amorphous ITO in thin films were investigated.

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2 Experimental

In/Sn as well as ITO films were deposited on Si (100) wafer by means of DC planar magnetron sputtering. A metallic In/Sn target was used. Power, pressure and Ar flow were kept constant. The standard deposition conditions were DC power: 30 W, inert gas flow: 15 sccm Ar (5N), sputter pressure: $5.6 \cdot 10^{-3}$ mbar. The oxygen flow was varied between 0 and 2 sccm. Bias voltages between 0 and -100 V were used. The film thickness was between 5 and 50 nm [1], [2].

The films were investigated by grazing incidence X-ray diffractometry (GIXRD) and grazing X-ray reflectometry (GIXR) with a $\Theta - \Theta$ diffractometer. For in situ GIXRD measurements the diffractometer was equipped with a special parallel beam attachment and with a high temperature chamber. For diffusion studies X-ray patterns were recorded isothermally in a vacuum of 10^{-6} mbar between 100 °C and 300 °C . The crystallization process was investigated using the integral intensity of the In_2O_3 (222) reflection. Film thickness and density were determined by GIXR at room temperature before and after annealing. The composition of the films was determined by means of XPS. Surface morphology investigations were carried out with AFM.

To calculate the diffusion coefficients a model for the time dependence of the X-ray integral peak intensity during diffusion of oxygen and cristallization was developed. The kinetic of the crystallization process was studied by the JOHNSON-MEHL-AVRAMI equation: $I_m(t) = 1 - e^{-(kt)^n}$. I_m is the measured integral intensity of phase m (In_2O_3), n is termed the reaction order and k is the rate constant. In case of diffusion limited processes n should be 0.5. An n value between 1 and 2 indicates one-dimensional growth with rapid nucleation while two-dimensional growth generally has a growth mode parameter between 2 and 3 [4], [5]. The activation energies for both the diffusion and the crystallization were determined from ARRHENIUS plots.

3 Results and Discussion

3.1 Film Deposition

During the deposition the oxygen flow influences the chemical and phase composition, film density, growth rate and coating morphology. Deposition without oxygen forms crystalline metallic In/Sn films. No preferred orientation was observed. The intensity ratios are similar to the pattern of polycrystalline bulk In [3]. With increasing oxygen flow the observable particle sizes of crystalline metallic In/Sn decreases (Tab. 1). XPS measurements support this result. In Fig. 1 the film density and the growth rate in dependence on the oxygen flow are shown. The deposition rate decreases with increasing oxygen partial pressure. Oxygen flows more than 1 sccm led to film densities similar to the X-ray density of In and In_2O_3 (7.28 g cm^{-3} and 7.12 g cm^{-3} respectively). The low density suggest a high amount of voids in the metallic films. Increasing oxygen flows effect more compact layers. From GIXR measurements and AFM images additionally a drop of the substrate roughness follows. The metallic films shows large particles forming a rough film surface. Increasing oxygen flow causes a smooth surface without clearly observable particles.

The layer growth is determined by the sputter yield on the target and by the reaction of indium and oxygen on the substrate surface, too. As the oxygen flow is increased the cathode is partially covered by an oxide layer which results in a drop of the sputter yield. Another reason for the drop of the deposition rate is the different crystal growth. Indium grows in crystallites which

O_2-flow [sccm]	domain sizes In(101) [nm]	
	0 V	-50 V
0.0	26.4	24.6
0.5	6.9	25.2
1.0	-	16.6
1.5		14.3
2.0		-

Tab. 1. Domain sizes of metallic In/Sn for films deposited at 0 V and -50 V substrate.

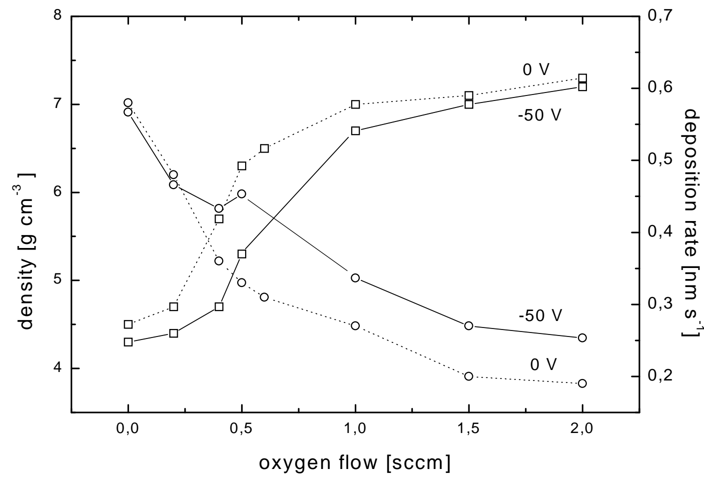

Fig. 1. Density (□) and deposition rate (○) of samples deposited at 0 V (· · ··) and -50 V (——) substrate voltage vs. oxygen flow.

include a lot of voids particularly in the initial stage. In_2O_3 grows presumably amorphous (X-ray amorphous), i.e. in very small particles, which are closely packed [1], [2]. To obtain further information on the effect of energy flux due to ion energy, the substrate potential U_{sub} was varied from 0 V to -50 V. There are appreciable differences in the microstructure. An increased amount of metallic In/Sn was detected in films deposited with -50 V substrate voltage and oxygen flow (see Tab. 1). Film density and growth rate show a different behavior from the 0 V films (Fig. 1). In principle the slop of the curves are similar. However, the densities are smaller and the growth rates higher for -50 V substrate voltage. XPS measurements show that the amount of oxygen

O_2-flow [sccm]	U_{sub}[V]					
	0		-50		-100	
	D [cm^{2}s^{-1}]	f	D [cm^{2}s^{-1}]	f	D [cm^{2}s^{-1}]	f
0.0	$6.0{\cdot}10^{-16}$	0	$1.3{\cdot}10^{-15}$	0	$9.4{\cdot}10^{-16}$	0
0.5	$5.5{\cdot}10^{-16}$	0.5	$1.7{\cdot}10^{-15}$	0	$9.1{\cdot}10^{-16}$	0
1.0	$6.0{\cdot}10^{-16}$	0.75	$1.4{\cdot}10^{-15}$	0.3	$9.6{\cdot}10^{-16}$	0.5
1.5	-	1	$1.5{\cdot}10^{-15}$	0.5	$9.6{\cdot}10^{-16}$	0.65
2.0	-	1	$1.6{\cdot}10^{-15}$	0.7	$9.6{\cdot}10^{-16}$	0.8

Tab. 2: Diffusion constants D and fractions f of amorphous ITO films.

in the layer is decreased. We assume that the additional energy flux to the growing film causes more frequently resputtering of oxygen. The growth of In is preferred although the oxygen flow is unchanged.

3.2 Diffusion

Two sets of annealing experiments were carried out. At first, films deposited with oxygen flows of 0, 0.5, 1.0, 1.5 and 2 sccm and bias voltages of 0, -50V and -100V were annealed at 250 °C. Table 2 contains the oxygen flows, the bias voltages, the diffusion constants D and the factors f, which represent the amorphous ITO fraction in the investigated films. It is obvious that D is depending on the bias voltage but not on the oxygen flow and the amorphous ITO fraction. The diffusion constants increase considerably from 0 to -50V reaching a maximum at -50 V and diminishing again at -100V.

The D values of thin films are strongly influenced by the film microstructure. Thus films with identical chemical composition have a wide spread of D values if different microstructures or defect structures are present [6]. Especially imperfections of the second type such as domain sizes or dislocations modify the diffraction line shape. In the near future we are going to investigate the lattice defects in more detail. With these results it will be possible to discuss the influence of the plasma on film growth and diffusion mechanism in more detail. In a second set of experiments the activation energy of the diffusion process was determined in metallic In/Sn layers. Films deposited with substrate voltages of 0 V, -50 V and -100 V were annealed in the temperature range from 100 °C to 300 °C (see Fig. 2). Two activation energies were estimated: 25 kJ/mol for $T < 156$ °C and 12.4 kJ/mol for $T > 156$ °C. This suggests that, depending on the temperature, two different diffusion mechanisms occur, which were not changed by the bias voltage.

Grain boundary diffusion dominates at practically all temperatures in polycrystalline metal films with domain sizes of 500 nm or less. An activation energy of 25 kJ/mol for temperatures

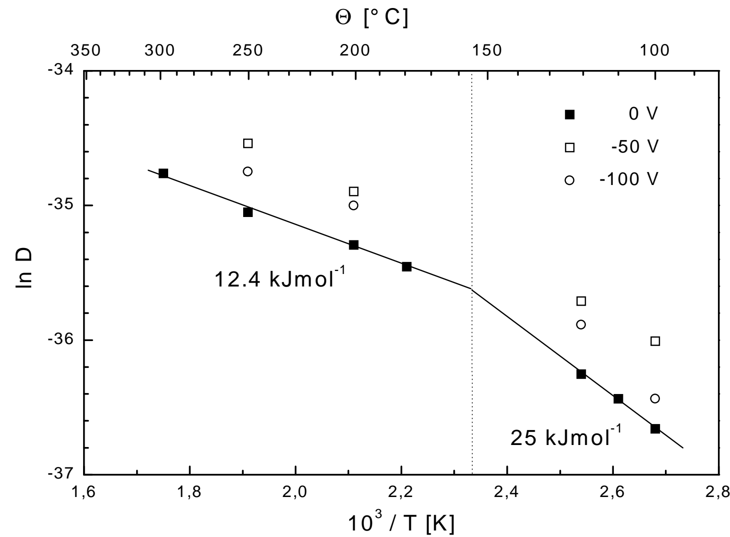

Fig. 2. Determination of the activation energies from the temperature dependence of the diffusion coefficients.

lower than 156 °C fits well into this assumption [7]. The melting point of indium is 156 °C. We assume that the layer is partially molten during annealing at higher temperatures. The activation energy for diffusion in liquids is expected to be smaller than in solids thus an activation energy of 12.4 kJ/mol was found for $T > 156$ ° C.

Film thickness and film density do not change during annealing. That means the grain distributions in the thin film remain preserved also at temperatures higher than 156 °C. We assume thin ITO layers surround the metallic In drops and prevent the formation of large liquid regions. The AFM images confirm this assumption.

3.3 Crystallization

The crystallization process was investigated in complete amorphous ITO films deposited without negative substrate voltage (Tab. 2). The time for a total amorphous to crystalline transformation is about 1/30 of the time necessary for the whole diffusion process. To determine the activation energy experiments at three different temperatures 220, 230 and 240 °C were made. Reaction orders between 2.4 and 3.0 were found representing a two-dimensional growth. An activation energy of 74 kJ/mol was estimated for the crystallization process.

In all annealing experiments the finally formed films consist of crystalline ITO in the bixbyite structure type. However, corresponding AFM images show differences in surface morphology. Large grain sizes with rounded edges are observed if the ITO growth is diffusion limited. Whereas cubic grains were formed in the fast crystallization process. The surface is very smooth.

4 Conclusions

Grazing incidence X-ray diffractometry (GIXRD) and grazing incidence X-ray reflectometry (GIXR) are well suited methods for a non destructive analysis of chemical, physical and crystallographic properties of thin films and can be used as in situ techniques for thermal induced processes. New information was obtained about the influence of oxygen flows and plasma conditions on ITO film properties.

Chemical composition and particle sizes of the films are strongly influenced by the deposition conditions. Indium/tin grows in crystallites which include voids, ITO grows preferably in very small and closely packed particles. From the results of negative substrate voltage experiments it can be concluded, that the resputtering of oxygen determines the reduced oxygen content in these films.

Two mechanisms determine the formation of crystalline ITO during the post deposition annealing procedure. A fast crystallization and a diffusion-limited reaction were observed. From the X-ray integral intensities the following kinetic parameters were extracted: diffusion constant, activation energy of the diffusion, reaction order and activation energy of the crystal growth process. The diffusion constants depend on the bias voltage in following manner: $D(0V) < D(-100V) < D(-50V)$. The oxygen flow during deposition does not influence the diffusion constant. The activation energy of the diffusion was determined in films deposited without oxygen. Two activation energies were found: 25 kJ/mol for processes below 156°C and 12.4 kJ/mol for diffusion higher than 156°C. The bias voltage does not influence the activation energy. Crystallization of amorphous ITO occurs via classical nucleation and growth mode parameter as described by the JOHNSON-MEHL-AVRAMI equation. Reaction orders between 2.4 and 3.0 were estimated. That is consistent with a two-dimensional transformation geometry. The activation energy is 74 kJ/mol.

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