

ELECTRICAL PROPERTIES OF NONSTOICHIOMETRIC $\text{In}_2\text{O}_{3-x}$ THIN FILMS

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Received 22 February 2011; revised 23 March 2011; accepted 23 March 2011

Thin films of indium oxide were grown heteroepitaxially by dc magnetron sputtering onto (110) faces of crystalline yttria-stabilized zirconia. Resistance versus temperature of the films was measured *in situ* in a wide temperature range during film heating and cooling under various oxygen pressure conditions. Insulator–metal (I–M) phase transition induced in the nonstoichiometric oxide material with oxygen content variation has been indicated. The characteristic activation energy of oxygen diffusion in the material has been estimated by analysing temperature and oxygen content-dependent resistance kinetics.

Keywords: In_2O_3 films, electroresistivity, magnetron sputtering, oxygen diffusion, insulator–metal transition

PACS: 66.47.Gh, 73.20.Hb

1. Introduction

Thin films of both indium oxide In_2O_3 (IO) and tin-doped indium oxide, $\text{In}_2\text{O}_3\langle\text{Sn}\rangle$ (ITO), demonstrating relatively high electrical conductivity and optical transparency in the visible spectra range, are widely used as transparent electrodes in different optoelectronic devices [1]. It is well known, however, that electrical properties of both oxides depend strongly on oxygen content.

Stoichiometric indium oxide (In_2O_3) is known as an insulator with a wide band-gap ($\varepsilon_g \sim 3.5$ eV). At the same time the oxide with reduced oxygen content ($\text{In}_2\text{O}_{3-x}$) may exhibit great variety of electrical properties. Thus, there is an interesting possibility to vary electrical properties of the compound by varying its oxygen content rather than by introducing additional dopants such as Sn. Undoped IO films may have some technological advantages. For example, undesirable process of Sn diffusion from ITO film into light absorbing surface of solar cells may be avoided by using similar nonstoichiometric $\text{In}_2\text{O}_{3-x}$ films [2].

IO films can be fabricated by different methods such as dc and rf sputtering, thermal oxidation of indium films, atomic-layer epitaxial growth, pulsed laser deposition, and other methods. [3] Electrical and optical properties of the IO films may be tuned by their annealing either in an atmosphere of oxygen, ozone or vacuum and also by irradiation of the films by ultraviolet

light. It is worth noting, however, that both electrical and optical properties of the films remain stable at low temperatures, i. e. up to about 500 K due to reduced oxygen diffusion process.

To optimize growth conditions of both IO and ITO films, it is important to know major parameters of oxygen diffusion in the films and to reveal the role of oxygen concentration on their physical properties in a wide temperature range.

In this work, we investigated electrical properties of epitaxial IO films in a wide temperature range during their heating and cooling in a gas chamber under certain oxygen pressure conditions and in vacuum. A method based on a gradual temperature change of the samples with time at a fixed oxygen pressure and *in situ* film resistance measurements have been applied in this work [4]. Modelling of oxygen diffusion processes in the films has been employed to explain the observed resistance kinetics and to evaluate oxygen diffusion parameters from the measured resistance kinetics.

2. Experiment

Epitaxial IO films used for the investigations were prepared by a dc magnetron sputtering. Disk of high purity metallic indium with the diameter of 25 mm was used as a target. Pressure of the discharging gas consisting of Ar and O_2 mixture (1:1) was kept at 5 Pa during film deposition. The films with thickness varying

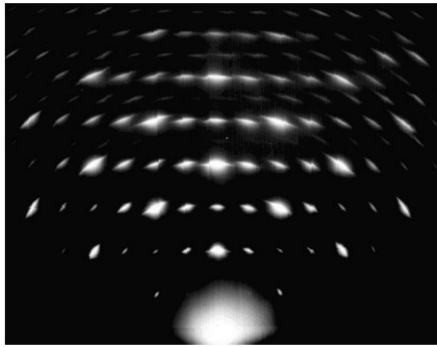


Fig. 1. Patterns of reflection high energy electron diffraction of IO film magnetron-sputtered onto lattice-matched YSZ (110) substrate.

from about 100 up to 500 nm were grown onto polished (110) planes of yttrium-stabilised zirconia (YSZ) ($10 \times 10 \times 0.5 \text{ mm}^3$) heated up to 600°C . Epitaxial quality of the as prepared IO films has been confirmed by point-like patterns seen in their reflection high energy electron diffraction images (see the corresponding RHEED patterns displayed in Fig. 1).

The tape-like platinum coatings (patterned by masking) have been deposited preliminary onto the top side of the YSZ substrates by DC magnetron sputtering to be used as contacts for the electrical measurements. The distance between a couple of the as prepared planar Pt contacts was about 2 mm. During electrical measurements, temperature of the films was either increased gradually from 300 up to 840 K or reduced back down to 300 K by varying the temperature of samples linearly with time: $dT/dt = \pm 9 \text{ K/min}$. Resistance of the films was measured *in situ* in a vacuum chamber both under vacuum conditions ($p = 5 \cdot 10^{-4} \text{ Pa}$) and under oxygen ambient with partial oxygen pressure of $5 \cdot 10^4 \text{ Pa}$.

3. Results and discussion

It has been found in this work that electrical properties of the prepared epitaxial $\text{In}_2\text{O}_{3-x}$ films are governed by oxygen vacancies and therefore the resistance of films may be varied in a wide range depending on temperature, oxygen pressure, as well as on heating and cooling conditions.

One can expect that in the stoichiometric compound ($x = 0$) the concentration of oxygen vacancies should be low. Taking into account that oxygen vacancies in indium oxide are doubly charged donors, one can estimate from resistivity measurements that the highest x value in oxygen reduced films may be of about 0.07, while the variation of oxygen content in the films could

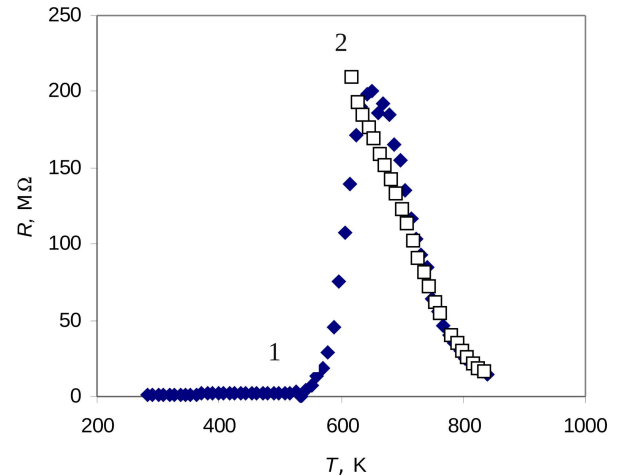


Fig. 2. Resistance versus temperature measured for $\text{In}_2\text{O}_{3-x}$ film ($d = 220 \text{ nm}$) during heating (curve 1) and subsequent cooling (curve 2). Pressure of oxygen $p = 5 \cdot 10^4 \text{ Pa}$. $dT/dt = \pm 9 \text{ K/min}$.

be related to oxygen in- and out-diffusion processes. To control the stoichiometry of the $\text{In}_2\text{O}_{3-x}$ films we further attempted to measure the resistance kinetics and to evaluate the oxygen diffusion parameters for the films investigated.

In order to study the oxygen diffusion, a common way to investigate the resistance kinetics via a set of $R(t)$ curves measured at various temperatures [5, 6] was chosen. It is worth to note, however, that at high temperatures ($T > 650 \text{ K}$) the oxygen in- and out-diffusion for $\text{In}_2\text{O}_{3-x}$ is relatively fast. One can expect therefore that in the case of slow temperature variation, resistance of the films (measured *in situ*) should depend mainly on temperature-dependent oxygen content rather than on cooling or heating conditions. Thus one can conclude that at high temperature (using relatively slow linear temperature variation with time) one can get information on oxygen in- and out-diffusion processes in the films by measuring their $R(T)$ dependences.

In Fig. 2 we show typical plots of resistance versus temperature measured *in situ* for the $\text{In}_2\text{O}_{3-x}$ film during film heating (see curve 1) and subsequent cooling (curve 2) in oxygen atmosphere ($p = 5 \cdot 10^4 \text{ Pa}$) with $dT/dt = \pm 9 \text{ K/min}$.

Three different regions in the measured $R(T)$ plots can be seen from the figure. In the first region, i. e., at relatively low temperatures (up to about 540 K), certain resistance increase with temperature demonstrates metallic conductivity. In this temperature range, oxygen diffusion processes are slow enough, and concentration of vacancies in the film remains unchanged. The observed metallic behaviour in this temperature region is typical of most of the highly doped semiconductors and can be explained taking into account that

self-doping of the film material is high enough and the impurity band (caused by oxygen vacancies) is overlapping with a conduction band. Film resistance in this case is governed mainly by carrier mobility variation due to scattering of electrons by doubly charged oxygen vacancies.

In the intermediate temperature range (540–650 K), the sharp resistance increase with temperature can be explained assuming that oxygen in-diffusion processes are governing the self-doping of film material, i. e. the cause is variation of oxygen content (density of oxygen vacancies). One may conclude that resistance of the film in this temperature range should depend on the oxygen exchange between film and gas ambient and the resultant density of carriers (electronic holes) substituted by doubly charged oxygen vacancies.

At high temperatures ($T > 650$ K), both oxygen out- and in-diffusion processes are fast enough to ensure a thermodynamical equilibrium, i. e. the resultant concentration of vacancies in the case of low heating (cooling) rates should depend on oxygen pressure and temperature rather than on cooling or heating rates. Gradual resistance decrease with temperature seen in Fig. 2 at $T > 700$ K is typical of semiconductors. It seems likely that at a fixed partial pressure of oxygen (in a gas ambient), oxygen content in the films should not depend strongly on temperature. Therefore we argue that the semiconductor-like $R(T)$ dependence observed in this work for the IO films at the highest temperatures can be explained taking into account the emerging temperature-dependent energy gap between the impurity band of vacancies and the conduction band. Then the exponential increase of resistance is observed while cooling the film (curve 2).

Similar resistance variation caused both by oxygen in- and out-diffusion processes and the appearing energy gap between impurity band and conductivity band have been observed in this work also for thin films of tin-doped indium oxide (ITO). Typical resistance versus temperature plots obtained for the ITO film during heating and subsequent cooling under a fixed oxygen pressure ($p = 5 \cdot 10^4$ Pa) is displayed in Fig. 3. Before the measurements, the film was annealed for 2 h at 650 K in vacuum. It can be seen from the figure that resistance of the film increases with heating in oxygen (curve 1), while only slight resistance variation below 600 K (see curve 2) has been recorded with cooling. Relatively low resistance of the ITO film measured after the heating and cooling cycle may be understood taking into account the presence of dopants (Sn ions).

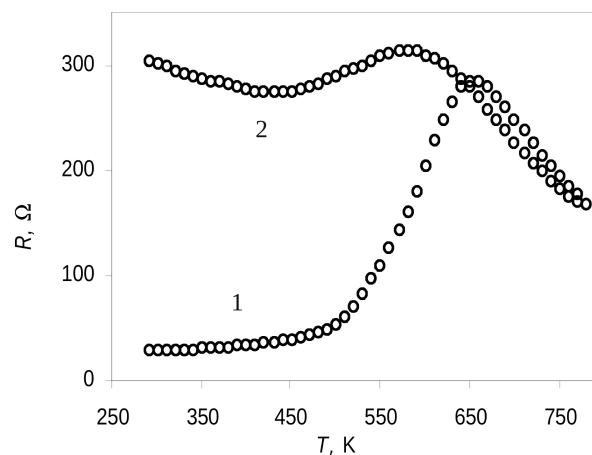


Fig. 3. Resistance versus temperature measured for the ITO film during heating (curve 1) and subsequent cooling (curve 2). Partial pressure of oxygen $p = 5 \cdot 10^4$ Pa. $dT/dt = \pm 9$ K/min.

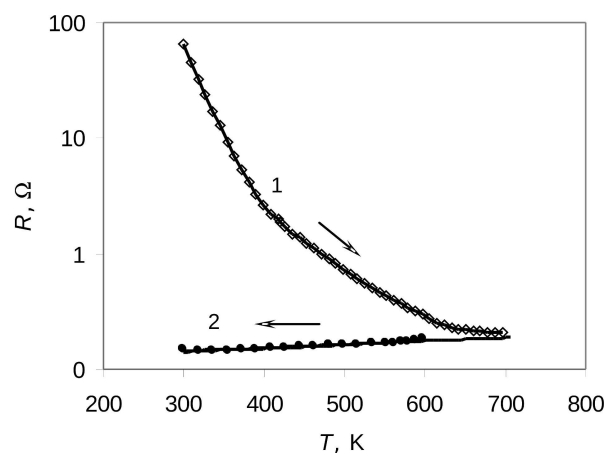


Fig. 4. Resistance versus temperature of In_2O_3 film measured *in situ* during heating (curve 1) and cooling (curve 2) in vacuum ($dT/dt = \pm 9$ K/min).

Figure 4 demonstrates resistance versus temperature of the stoichiometric IO film saturated preliminary in oxygen. Resistance of the film was measured *in situ* during film heating (curve 1) and subsequent cooling (curve 2) in vacuum. Gradual decrease of the film resistance (curve 1) during film heating in vacuum may be understood taking into account oxygen out-diffusion resulting in significant decrease of oxygen content and substantial increase of carrier density. At the same time the observed slight additional resistance decrease with subsequent cooling of the same film down to room temperature in our opinion is due to carrier mobility variation.

To evaluate the oxygen diffusion parameters from the obtained $R(T)$ dependences, we used the model proposed earlier in [7]. Taking into account that oxygen diffusion in the substrate material (YSZ) is relatively low at $T < 850$ K [8], it was assumed that oxygen

exchange between the YSZ substrate and IO film can be avoided in the calculations. In such a case the diffusion equation is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

which is solved for the following boundary conditions:

$$\begin{aligned} \frac{\partial C}{\partial x} \Big|_{x=0} &= 0, \\ D \frac{\partial C}{\partial x} \Big|_{x=d} &= k_1 \sqrt{p}(1 - C) \Big|_{x=d} - k_2 C \Big|_{x=d}, \\ C(x, 0) &= C_0 = \text{const.} \end{aligned} \quad (2)$$

Here $C = C(x, t)$ is the density of oxygen vacancies, D is diffusion coefficient, k_1 and k_2 are coefficients characterizing oxygen diffusion rates through free surface of the films, i. e., from a gas ambient into the film and out of it, correspondingly, p is oxygen pressure in the gas ambient, and d is film thickness.

In the case when temperature of the film is varied linearly with time, the $C(t)$ dependence may be replaced with the relationship $C(T)$, using the dependence $dR/dT = \beta = \text{const.}$ The diffusion coefficient D has been assumed to depend on temperature according to the well-known Arrhenius law: $D = D_0 \exp[-\varepsilon_a/(kT)]$, where ε_a is the activation energy of diffusion. In such a case, we get the following $R(T)$ expression [9]:

$$\begin{aligned} R(T) &= R_{\text{eq}} \left[1 - a_1 \left(1 - \frac{R_{\text{eq}}}{R_0} \right) \right. \\ &\quad \left. \times \exp \left(-D(T) K_1^2 \frac{T - T_0}{\beta} \right) \right]^{-1}, \end{aligned} \quad (3)$$

where R_0 is the film resistance at $t = 0$ and R_{eq} is the corresponding equilibrium value, $\beta = 9 \text{ K/min}$. $a_1 = 8/\pi^2$, $K_1 = \pi/(2d)$ when oxygen exchange between the film and a gas ambient is limited by oxygen diffusion in the bulk material, and $a_1 = 1$, $K_1 = \sqrt{(k_1 p^{1/2} + k_2)/(Dd)}$ when oxygen exchange is limited by oxygen diffusion through a surface barrier. By fitting the theoretical curve to experimental points plotted in Fig. 2, the activation energy of oxygen diffusion for the IO film ($d = 220 \text{ nm}$), ε_a , has been evaluated to be of $0.4 \pm 0.02 \text{ eV}$. Similar ε_a values estimated in this work for the IO films with $d = 120$ and 490 nm show that resistance kinetics in the nonstoichiometric IO films is determined mainly by oxygen diffusion in a bulk material.

4. Conclusion

It has been found in this work that electrical resistance of the IO films grown heteroepitaxially on YSZ substrates may be tuned in a wide range by their annealing under different oxygen pressure conditions. The films containing various concentrations of oxygen vacancies demonstrate stable physical properties in a wide temperature range. Significant change of film resistance with oxygen content indicated at high temperatures (540–650 K) has been associated to the insulator–metal phase transition. The observed phase transition has been explained assuming separation of the impurity band formed by oxygen vacancies from the conduction band of the oxide material. The activation energy of oxygen diffusion in the IO films ($\varepsilon_a = 0.4 \text{ eV}$) has been estimated by fitting theoretical dependences to the experimental data

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PLONUJŲ NESTECHIOMETRINIŲ $\text{In}_2\text{O}_{3-x}$ SLUOKSNIŲ ELEKTRINĖS SAVYBĖS

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Santrauka

Plonieji indžio oksido ($\text{In}_2\text{O}_{3-x}$) sluoksniai buvo užauginti nuostoviosios srovės magnetroninio dulkinimo būdu ant itriu stabilizuotų kristalinių cirkonio oksido padėklų. Tirti šių sluoksnių elektrinių savybių pokyčiai, keičiant juose deguonies vakansijų koncentraciją. Deguonies koncentracija sluoksniuose buvo

keičiama kaitinant ir vėsinant bandinius, esant įvairiems deguonies slėgiams vakuuminėje kameroje. Sluoksnių elektrinė varža matuota plačiame temperatūrų intervale tiesiogiai kaitinimo metu (*in situ*). Modeliuojant deguonies difuzijos procesus, lemiančius deguonies atomų pasikeitimą su dujine aplinka, nustatyta deguonies difuzijos aktyvacijos energija $\text{In}_2\text{O}_{3-x}$ sluoksniuose.