Microwave Conductivity Investigations of AZO Films Deposited by Atomic Layer Deposition Method at a Low Temperature

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AZO (ZnO:Al) are deposited by atomic layer deposition method for applications as transparent conductive oxide films (transparent electrode) in photovoltaics. In the present work we evaluate uniformity of such films when deposited on polymer substrate at low temperature. The latter is important for new generations of photovoltaics devices based on temperature sensitive organic materials. Results of DC and AC conductivity measurements are compared to evaluate uniformity of Al distribution in AZO films.

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1. Introduction

Possible applications of thin films of oxides deposited by the atomic layer deposition (ALD) include applications in electronic industry — in particular applications in photovoltaics. New generation of transparent conductive oxides (TCO) materials are intensively studied, aimed to replace too expensive indium tin oxide (ITO) layers. For such application we need highly uniform films with large electron concentration, high transparency, and good carriers mobility. In the present work we show that such properties have ZnO:Al (AZO) films deposited at low temperature by the ALD. Low deposition temperature is important for solar cells based on temperature sensitive materials (polymers, perovskites, etc.). For evaluation of electrical properties of the films and of their uniformity we compare DC and AC conductivity of AZO layers.

Formally, measurements of microwave AC conductivity (see below description of the method) should give the same results as DC investigations. However, when performed on samples with large uniformity fluctuation, inclusions of foreign phases or in-depth inhomogeneities, AC conductivity may considerably differs from a DC one [1]. This we recently observed for ZnCoO films with large fluctuations of Co-distribution [2, 3].

In the case of ZnCoO films use of microwaves was particularly useful. The method turned out to be highly sensitive to detection of small Co metal inclusions with a high conductivity. Such inclusions explain puzzle of magnetic properties of ZnCoO films [2]. We demonstrated that observation of ferromagnetic response of ZnCoO samples correlates with an appearance of Co metal inclusions. Correlation between AC conductivity and FM response of the films [2] was demonstrated. The AC conductivity increases for the layers with a non-uniform Co-distribution. The AC conductivity is large for samples showing a large FM response, strongly indicating an important, if not a dominant, role of metallic inclusions. The observed discrepancy between DC and AC measurements correlates with an alloy (ZSnCoO) nonuniformities [2].

In the present work we apply microwaves AC conductivity technique for evaluation of uniformity of Al doped ZnO (AZO) films deposited by the ALD on polymer films at a low temperature. AZO films are intensively investigated for applications in photovoltaics (PV) as transparent top electrodes [4–6]. For this application highly uniform samples are required with a high transparency and a high conductivity (metallic one). To evaluate uniformity of deposited samples we compare their DC (Hall effect) and AC conductivity.

2. Experimental

2.1 Samples

ZnO:Al (AZO) samples were deposited by ALD method using the Savannah-100 reactor (Ultratech Company) and double-exchange chemical reactions. Organic Zn and Al precursors were used — diethylzinc as zinc precursor, trimethylaluminum as aluminum precursor and deionized water as an oxygen precursor. Between doses of metal precursors growth chamber was purged with a nitrogen gas. Further details on growth conditions and precursors used can be found elsewhere [5, 6]. For microwave measurements samples were deposited on dielectric PET foil (circular with 5 mm diameter) and in parallel on glass substrate for controlled Hall effect measurements. Prior to AZO deposition on selected foils (see Table I) thin layers of Al_2O_3 were deposited to improve AZO adhesion.

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Al fraction was selected close to that found in previous investigation to be optimal to get samples with a high electrical conductivity and Al uniformity [4]. To get a given Al fraction after a sequence of Zn precursor–O precursor of the ALD cycles we replaced Zn precursor pulse with an Al one [4]. Such sequence was repeated several times to get an AZO film of a required thickness. The method was successfully used by us to get uniform ZnMnO [7, 8] and ZnCoO [2, 9] samples. To get uniform alloys growth temperature was also crucial [2, 7–9]. The process temperature should allow elements diffusion and their intermixing to get an uniform alloy. To get such good uniformity and high conductivity AZO films were previously deposited by us at higher temperature than in the present case [4–6]. However, for application in new generations of PV devices (based on temperature sensitive organic materials) the process temperature should be lowered, as we done in the present case. This fact opened the question on samples uniformity, investigated in the present case. Low growth temperature was selected between 80 and 120 °C, since a temperature sensitive PET foil was used as a substrate. These conditions are not optimal to get highly conductive AZO films. This is why resistivities shown in Table II are higher than the one for AZO films deposited at increased temperature [4–6]. Thickness of AZO films was varied between 150 and 500 nm, the range of thicknesses investigated by us to get best performance photovoltaic cells [5, 6].

TABLE I

ALD samples

Sample	Al [%]	Growth temp. [°C]	Al_2O_3 thickness [nm]	AZO thickness [nm]
B370	3	80	0	250
B371	1.5	80	0	250
B380	3	100	50	500
B382	3	120	50	500
B392	3	100	50	350
B393	3	120	50	350
B401	3	120	50	150
B423	3	100	50	150

TABLE II

DC electrical parameters

Sample	Al [%]	Resistivity [Ω cm]	Free electron concentration at room temp. (RT) [cm^{-3}]	Electron mobility at RT [$cm^2/(V\ s)$]
B370	3	26.7	2.4×10^{17}	0.9
B371	1.5	80.1	2.7×10^{16}	2.7
B380	3	1.3×10^{-1}	5.8×10^{19}	0.8
B382	3	2.3×10^{-2}	1.1×10^{20}	2.5
B392	3	3.7×10^{-2}	6.3×10^{19}	2.6
B393	3	1.3×10^{-2}	9.1×10^{19}	5.2
B401	3	3.5×10^{-2}	5.3×10^{19}	3.4
B423	3	1.6×10^{-1}	2.9×10^{19}	1.4

In the previous studies uniformity of AZO films was evaluated from secondary ion mass spectrometry (SIMS) investigations [10]. However, this is not highly sensitive method. This is why we apply in the present work the method tested by us for investigations of ZnCoO samples. Results of DC and AC conductivity measurements are compared.

Details on samples used in the present study are given in Table I, whereas Table II summarizes results of their Hall effect measurements.

2.2. DC measurements

Before microwave investigations Hall effect was measured for samples selected for AC investigations. For these measurements electrical contacts of Ti(15 nm)/Au(40 nm) to the AZO layers were deposited in corners of the samples by an e-beam evaporation system (PVD 75, Kurt Lesker). The area of the ohmic contacts was $\approx 0.1 \times 0.1$ cm^2. Then, the electrical parameters of AZO films were extracted from the RT Hall effect measurements performed in dark in the van der Pauw configuration using RH2035 PhysTech system with permanent 0.4 T magnet. The relevant data are summarized in Table II.

2.3. AC measurements, microwave AC conductivity system

For AC conductivity measurements we used the X-band system described in Ref. [6] — a cylindrical cavity of the diameter $d = 49$ mm and height $h = 35.5$ mm was used, working in the TE_{112} mode with a resonant frequency of 9.2 GHz. Samples were placed in the electric field maximum in the plane perpendicular to the cavity axis at the distance $h = 4$ mm from the cavity bottom. The cavity resonance curve consisting of about 400 points was recorded both for an empty cavity and a cavity containing a sample. Next, the resonance curve was fitted to a standard Lorentzian shape. The fitting parameters allowed to determine precisely both the frequency shift and the cavity mode bandwidth change. Filling factors were calculated as the ratio of a layer (substrate) volume to an effective volume of the cavity, dependent on its dimensions and actual distribution of the electromagnetic field for a given resonant mode.

3. Results and discussion

3.1. Microwave measurements — introduction

We used microwave cavity perturbation techniques to study uniformity of doping of AZO films. A perturbation method applied was first introduced in Refs. [11, 12] and then generalized for samples with an ellipsoidal shape [13], and applied to describe samples with a wide range of conductivities [14, 15]. Details of the method can be found in our previous publication on highly inhomogeneous ZnCoO samples [2] and also in a forthcoming publication [16].

3.2 Results of the AC investigations

Figure 1 shows comparison between DC and AC conductivity of ALD deposited AZO films. A very good correlation is observed indicating that films deposited at low temperature in the ALD process are highly uniform. For films with a nonuniform Al distribution AC conductivity (see earlier investigations of nonuniform ZnCoO films) should be considerably higher than DC one. This result means that contactless microwaves AC conductivity method is suitable for investigation of thin films and evaluation of their doping uniformity potentially also in mass-production industrial environment. Importantly, AZO films deposited at low temperature on dielectric substrate are of a good quality to be applied as top electrodes in organic materials based PV devices.

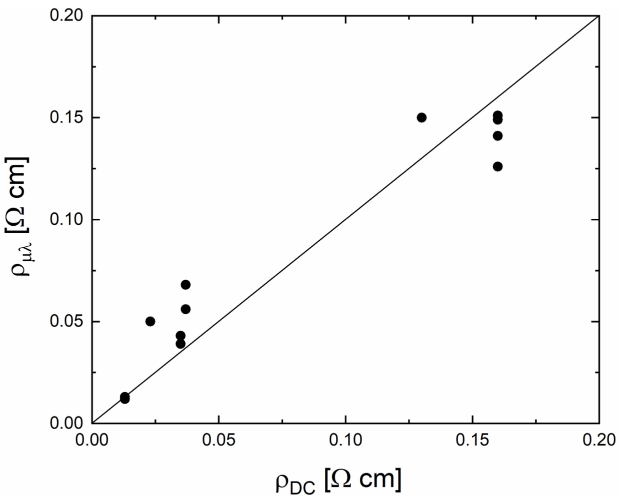

Fig. 1. Comparison of DC (ρ_{DC}) and AC ($\rho_{\mu\lambda}$) resistivity of AZO samples deposited by the ALD on foils, as described in Table I.

4. Summary

For uniform films DC and AC conductivity measurements give similar samples electrical parameters. The AC method used by us allows verification of films uniformity and turned out to be highly advantageous (no contacts required) for fast evaluation of films electrical parameters.

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