



Local structure and optical and electrical properties of amorphous Zinc-Iridium oxide thin films



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Introduction

ZnO is a widely studied material due to its suitable properties for short wavelength optoelectronic devices, such as blue or ultraviolet (UV) light emitting diodes (LEDs) and lasers [1-5]. Group-V and group-I dopants are usually used for p-type doping [1,3]. It has been reported [2,6] that even nano-crystalline films ZnO-IrO₂ possess p-type transparent semiconductor. p-type conductivity in the spinel type ZnIr₂O₄ structure has been interpreted within the ligand field theory [2]. Typical challenges for p-type doped ZnO are reproducibility and insufficient long term stability of electrical resistivity [3,7].

This paper reports on characterisation of elemental, structural, electrical and optical properties of ZnO-IrO₂ thin films deposited by DC reactive magnetron sputtering, with the main focus on the influence of the iridium concentrations in films. The films have been deposited by reactive DC magnetron sputtering at room temperature, suitable for deposition on polymer substrates.

Experimental details

ZnO-IrO₂ thin films were deposited on glass substrates by DC reactive magnetron sputtering from a metallic Zn target with Ir pieces on the target surface in an Ar+O₂ atmosphere. Vacuum chamber was pumped to base pressure below 1 · 10⁻⁵ Torr. During the deposition the substrate was kept at room temperature, the sputtering was conducted at 20 mTorr working pressure and 100W sputtering power. The target to substrate separation was 5 cm. Argon and oxygen gas flows were kept constant at 50 sccm and 10 sccm, respectively. A set of samples was deposited with the iridium fraction on target erosion zone ranging from 1 to 23 % (Table 1).

Elemental, structural, electrical and optical properties of ZnO-IrO₂ thin films were studied by XRF, XRD, EXAFS, Raman spectroscopy, profilometry, Hall effect, impedance spectroscopy and two beam optical spectrophotometry.

Results and discussion

Table 1. Deposition parameters and properties of ZnO-IrO₂ thin films.

Sample Nr.	Iridium fraction on target erosion zone (%)	Iridium concentration in film (atomic %)	Voltage (V)	Deposition rate (nm/min)	Resistivity 10 ⁻³ (Ωcm)	Transmittance at 550 nm (%)
1	1.4	~5.0	306	14.0	>100	57.3
2	8.4	36.7	343	23.2	13.3	33.1
3	11.2	41.4	361	27.0	5.9	22.9
4	16.9	50.4	353	33.6	3.1	13.7
5	19.7	61.7	363	38.2	1.4	6.3
6	22.5	61.5	364	37.2	1.5	5.5

Figure 1(a) shows that iridium atomic concentration (n_{Ir}) in the films is 3 to 4 times higher than the relative amount of iridium on the target surface (S_{Ir}/S_{Target}). Deposition rate increases from 23 to 38 nm/min with the iridium fraction on the target erosion zone increasing from 8 to 23 % (Fig.1(b)).

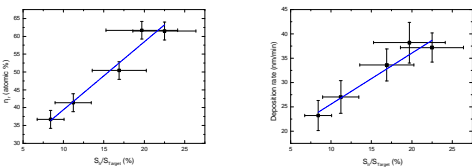


Fig.1. Iridium concentration in the films (a) and the deposition rate (b) as a function of iridium fraction in the erosion zone of the target.

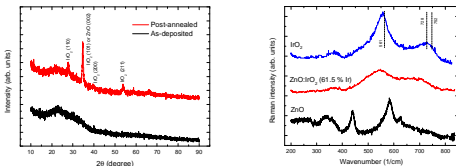


Fig. 2. XRD spectrum of as-deposited and post-annealed ZnO-IrO₂ (61.5% Ir) thin film (a) and Raman spectrum of a-IrO₂, ZnO and a-ZnO-IrO₂ (61.5% Ir) thin films deposited on titanium substrates (b).

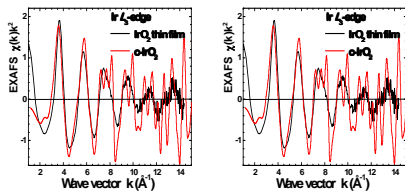


Fig. 3. EXAFS signal and Fourier transforms.

XRD data shows that all deposited ZnO-IrO₂ thin films are x-ray amorphous (Fig. 2). The film with $n_{Ir} = 61,7 \%$ was annealed at 500°C for 20 h in air. XRD spectrum of the post-annealed film shows (110), (101), (200) and (211) planes of IrO₂. Since the peak at 34.34° corresponding to ZnO (002) plane overlaps with IrO₂ (101) peak, presence of ZnO crystalline phase in the films cannot be ruled out. However, no unambiguous evidence for such a presence was found. A strong amorphous phase is still observed as well. Profilometer measurements show that RMS roughness of the surface increases from 45.6 nm for as-deposited film to 60.2 nm for post-annealed film.

Raman spectrum of ZnO and ZnO-IrO₂ (61.5% Ir) films is shown in Fig. 2. Dashed vertical lines in Fig. 2 show the positions of the characteristic peaks of IrO₂ [8]. Due to amorphous ZnO-IrO₂ structure Raman peaks are extremely wide. The spectrum of the ZnO-IrO₂ film resembles the spectrum of IrO₂, without any distinct features of wurtzite ZnO detected.

The Ir L3-edge EXAFS (Extended X-ray absorption fine structure) signals $\chi(k)k^2$ of c-IrO₂ and the thin films were extracted and analyzed. Comparative analysis of the Fourier transforms (FTs) of the EXAFS signals (Fig. 4) for the thin film and crystalline c-IrO₂ indicates that the FT peaks amplitude for the thin film decreases relative to that for c-IrO₂ when the distance increases [9].

Fig. 4(a) shows that the electrical resistivity of the films decreases considerably with the iridium content. Yet, the resistivity is by four orders of magnitude higher than that of pure IrO₂, which can show a close to metallic conductivity if deposited at elevated temperatures [8]. The resistivity decrease with the temperature (Fig. 4(b)) corresponds to the typical semiconductor conductivity behavior with a negative temperature coefficient.

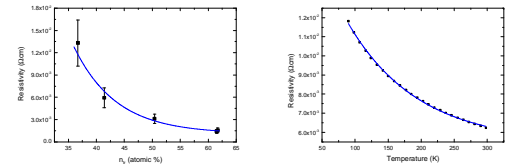


Fig. 4. Resistivity as a function of iridium atom concentration (a) and temperature at $n_{Ir}=41.4 \%$ (b).

Impedance spectrum (Fig. 6a) shows typical semi-circles common for semiconductor materials [10]. The spectrum was fitted by an equivalent circuit diagram consisting of one single resistor and two RC elements. It is assumed that the single resistor accounts for the core of the grains, and the two RC elements are related to grain-electrode and grain-grain contacts. The first RC element describes the impedance spectrum at lower frequencies with the characteristic relaxation time of 10⁻⁵ s, the second one at higher frequencies with the relaxation time of 2.4 · 10⁻⁹ s. The films of pure IrO₂ showed a typical ohmic behaviour.

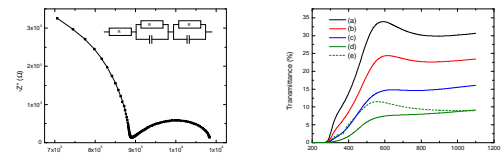


Fig. 5. Nyquist plot of impedance spectrum and the equivalent circuit diagram (a) and Transmittance of ZnO-IrO₂ thin films. $n_{Ir} = 36.7 \%$ (a), 41.1 % (b), 50.4 % (c), 61.7 % (d) and 61.7 % with post-annealing (e).

Conclusion

Preferential sputtering of iridium compared with zinc is observed: the iridium oxide sputtering yield is significantly higher than the zinc oxide sputtering yield.

All as-deposited ZnO-IrO₂ thin films at room temperature are x-ray amorphous without any crystalline oxide or spinel ZnIr₂O₄ structure. The films crystallize upon post-annealing in air, leading to an increase in optical transmittance without any noticeable change in resistivity. Increase in iridium concentration leads to lower resistivity of the films. Yet, the resistivity of a-ZnO-IrO₂ is considerably higher than that of pure crystalline IrO₂. The electrical impedance spectrum can be approximated by an equivalent circuit, accounting for the bulk resistance, the grain-grain resistance and capacity, and the grain-electrode resistance and capacity.

Acknowledgments

The work has been performed within the ERAf Projects 2010/0272/2DP/2.1.1.1.0/10/APIA/VIAA/088. The authors would like to thank Dr. Rocca University of Trento for XRD measurements.

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