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Abstract. We present the results of an investigation of ultraviolet, visible, near-infrared (UV-Vis-NIR) and X-ray absorption spectroscopy absorption spectra for zinc-iridium oxide (Zn-Ir-O) thin films with various iridium concentrations deposited by reactive DC magnetron sputtering. It is found that the absorption spectra of zinc-iridium oxide thin films contain a broad band with maxima at 446 nm and 710 nm in the visible region, bands with maxima at about 1100 nm and 3300 nm, and a low-intensity absorption band at 1570 nm in the near-infrared region. The obtained absorption bands are associated with iridium ions at valences of Ir^{3+}, Ir^{4+} and Ir^{5+}. Changes in the oxidation state of iridium ions from 5+ to 4+ are observed.

1. Introduction

The physics of iridium-based transition metal oxides has sparked significant interest, since iridium oxide has many unique properties that make it an ideal material for applications in electrochromism, bio-sensing and water electrolysis. For most optoelectronic devices such as flat panel displays, it is essential to use a transparent electrode consisting of a thin film of a transparent conducting oxide (TCO) semiconductor. Kawazoe et al. [1] reported *p*-type conductivity in highly transparent thin films of copper aluminum oxide. In this publication, a variety of *p*-TCOs were investigated. Despite these results, the insufficient transparency and low conductivity of the *p*-TCOs continue to restrict their technological applications [2]. Several precious-metal-based transparent oxides have also shown *p*-type conductivity, including polycrystalline ZnM_2O_4 (*M*= Ir, Rh. Co) films [3-5]. An increase in the Ir concentration of the Zn-Ir-O thin films from 12 to 16 at. % changes the conductivity type from *n*- to *p*-type [6].

Iridium has the ability to form compounds in many different oxidation states, the most stable of which are +3 and +4. The mixed-valence nature of Ir^{3+} and Ir^{4+} ions has been observed in several compounds; Ir^{5+} and Ir^{6+} can also be obtained [7-10].

Theoretical calculations of the substitution defects of Ir^{2+}_{Zn} and Ir^{3+}_{Zn} in Ir-doped ZnO predict localised energy states in the band gap, which is expected to reduce the transmittance of ZnO: Ir films [11, 12]. A decrease in the transmittance of the films is observed experimentally [6, 13].

In this paper, UV-Vis-NIR and X-ray absorption spectroscopy are used to investigate the valence states of Ir ions in Zn-Ir-O films deposited by reactive DC magnetron co-sputtering.

2. Experimental methods and materials

Zinc-iridium oxide thin films were deposited on glass, Si and polyimide tape substrates by reactive DC magnetron co-sputtering in an Ar + O_2 atmosphere. Two types of sputtering methods were used to deposit the films studied here. The detailed experimental procedure of both methods can be found in [6, 14, 15]. An elemental analysis of the films was carried out using an Eagle III X-ray fluorescence spectrometer. Since it is difficult to quantify elements lighter than sodium with XRF, our measurements include only the Zn and Ir concentration ratios. To determine the influence of the substrate temperature on the structure and properties of the films, two sets of samples were deposited: one set without

intentional substrate heating during the deposition process, and a second with additional heating at a temperature of 300°C.

The Zn K-edge (9659 eV) and Ir L_3-edge (11215 eV) X-ray absorption spectra (XAS) were measured in transmission mode at the SOLEIL synchrotron bending-magnet SAMBA beamline [16] under ambient conditions. More details of this experiment can be found in [6].

For the UV-Vis absorption spectra measurements at room temperature, we employed a Specord 210" (Analytikjena), a double-beam spectrophotometer operating in the spectral region of 190–1100 nm. The FTIR spectra were also measured at RT using a VERTEX 80v vacuum FTIR spectrometer with an actively aligned UltraScan™ interferometer

3. Results and discussion

The absorption spectra for zinc-iridium oxide thin films deposited on a glass substrate at various iridium concentrations are shown in Figure 1. Zinc-iridium oxide thin films are transparent in the visible region. An increase in the iridium concentration leads to the attenuation of film transparency. This increase also shifts the absorption edge towards the shorter wavelengths compared to crystalline ZnO, leading to higher absorption coefficient in the visible range. The results of curve fitting (the band shapes are assumed to be Gaussian) give a bands with maxima at 446 and 710 nm. The intensities of the bands increase with the iridium concentration of the thin films.
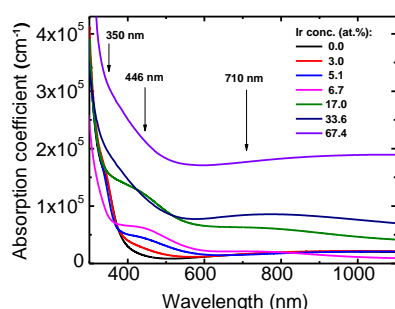
Figure 1. Absorption spectra of Zn-Ir-O thin films with different iridium concentrations.
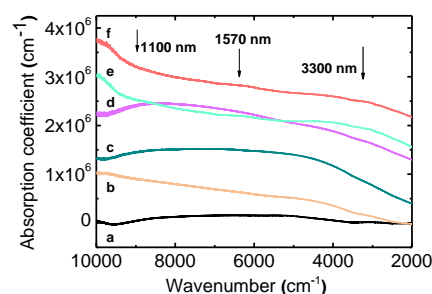
Figure 2. Near infrared absorption spectra of Zn-Ir-O thin films with different iridium concentrations (at.%): 7 (a), 16 (b), 29 (c), 41(d), 47 (e), and 54 (f).

In the near-infrared and infrared regions, the absorption spectra of zinc-iridium oxide thin films with different iridium ion concentrations show two broad bands with maxima at about 1100 and 3330 nm (Figure 2). The intensity of the 1100 nm band in the zinc-iridium oxide thin films increases with the iridium concentration, reaching a maximum at an iridium concentration of 29%. A further increase in the iridium concentration to 41% leads to an increase in intensity of the 3330 nm band. At an iridium concentration of between 47% and 56%, the ratio of the intensities of the 1100 and 3330 nm bands remains unchanged. A low-intensity absorption band at ~1570 nm is also observed.

The 5d transition-metal ions are known to be present in different valences in many compounds. A very complex situation can occur when a certain ion is present in more than one valence state and when these ions occupy both tetrahedral and octahedral sites. The valence and site occupation of these ions are mainly determined by the growth conditions and the current impurities

It has been reported in the literature that the low-spin state of Ir 5d electrons is preferred. Comparing the obtained results with the Tanabe-Sugano diagram [17], we conclude that the absorption spectra bands correspond to the Ir^{3+} ion transition from the ground to the excitation state: band 3300 nm $^1A_{1g} \rightarrow$ $^5T_2$ transition, band 1100 nm $^1A_{1g} \rightarrow {}^3T_{1g}$ transition, band 710 nm $^1A_{1g} \rightarrow {}^3T_{2g}$ transition, and band 446 nm $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The transitions $^1A_{1g} \rightarrow {}^5T_{2g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ are forbidden and have low intensities. The restrictions imposed by the selection rule are removed due to the exchange

interaction. The transition $^1A_{1g} \rightarrow {}^1T_{1g}$ is allowed. An analogous absorption band associated with the trivalent ion iridium has observed in prior papers [18].

Tetravalent iridium has the electronic configuration of $5d^5$, which corresponds to a half-filled d-sub-shell and is particularly most stable. In the ground state of the d^5 ion in the low-spin state, ^6S transforms into the $^2T_{2g}$ state. The transitions from the ground to the quartet and sextet states are forbidden, and hence are too weak. The bands observed in the absorption spectra of zinc-iridium oxide thin films may belong to the transitions from the ground state $^2T_{2g} \rightarrow {}^6A_{1g}$ (band at 3330 nm), $^2T_{2g} \rightarrow {}^4T_{1g}$ (band at 710 nm) and $^2T_{2g} \rightarrow {}^4T_{2g}$ (band at 446 nm) to the excited state of the iridium ions. The intensity of the 710 nm band is less than that of the 446 nm band. A significant intensity increase in the band at 710 nm is observed at an iridium concentration of more than 20%. This indicates the oxidation of Ir^{3+} to Ir^{4+}. The same process was observed in [19].

Pentavalent iridium has the electronic configuration d^4. The ground state of the d^4 ion in the low-spin state is $^3T_1$. The transitions from the ground to the excited ^5E, $^1T_2$, ^1E and $^1A_1$ states are forbidden, and hence are too weak. The allowed transitions ^3E, $^3T_1$, $^3T_2$, $^3A_1$ and $^3A_2$ lie in the region above ~ 330 nm (~ 30000 cm^{-1}) [20]. A low-intensity absorption band is observed for thin films of zinc-iridium oxide in the near-infrared region at a maximum of ~ 1570 nm. The d^4 electron configuration is shown by Cr^{2+} ions, and in the absorption spectra for the $ZnS:Cr^{2+}$ compound, its observed band is at ~ 1600 nm [21]. We assume that the band at 1570 nm in the zinc-iridium oxide films is connected with the $^3T_{1g} \rightarrow {}^5E$ transition of the Ir^{5+} ions.
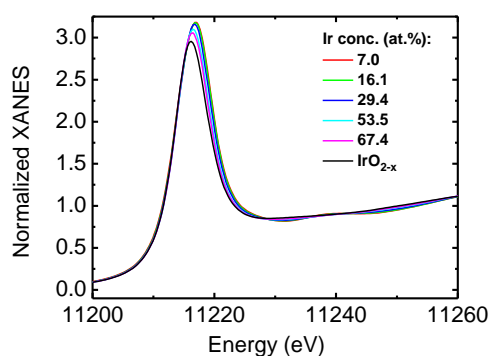
Figure 3. XANES spectra at the Ir L_3-edge of the deposited films.
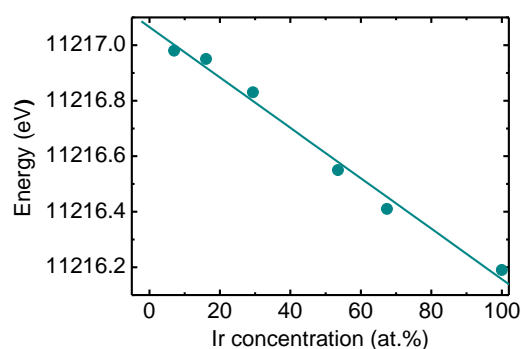
Figure 4. Plot of the maximum position energy of the XANES spectra as a function of iridium concentration in the zinc-iridium oxide films

X-ray absorption spectroscopy (XAS) is typically one of the most optimal techniques for this work. In order to investigate the local atomic structure, we need the bounding characteristics, oxidation and valance state of the atom of interest. This technique can be separated into two regimes based on the absorbed energy: (i) the X-ray absorption near the near-edge structure (XANES), which extends up to nearly 40 eV and is very sensitive to the charge density (i.e. the evolution of the oxidation sate) and bounding traits of the absorbing atom; and (ii) the extended X-ray absorption fine structure (EXAFS), which is specific to the local environment of the selected atom for energies higher than 40 eV. As emphasised above, in this research we investigate the oxidation state of the Ir atom by analysing the bounding energy shift of core level electrons [22]. For the XANES L-edge ($L_{2,3}$, $2P_{1/2}$ and $2P_{3/2}$ states) absorption profiles, the magnitude of the absorption intensity indicates the available vacant states in the d-orbital, and it is therefore proportional to the oxidation state of the absorbing atoms [23]. Figure 3 depicts the XANES spectra for the Ir L_3-edge from the zinc-iridium oxide thin film. A plot of the energy position as a function of iridium concentration in zinc-iridium oxide thin films is given in Figure 4. The distribution of energy positions is significantly larger in the higher oxidation states. We observe a change in the oxidation state of iridium ions in zinc-iridium oxide thin films from 5+ to 4+, as indicated in [24].

4. Conclusion
The research has been applied to the ultraviolet, visible and near infrared (UV-Vis-NIR) absorption spectra of zinc-iridium oxide (Zn-Ir-O) thin films with various iridium concentrations deposited by reactive DC magnetron sputtering It was found out that the absorption spectra of zinc-iridium oxide thin films include a broad band with maxima 446 and 710 nm in the visible region and bands with maxima at about 1100, 3300 nm and the low intensity absorption band 1570 nm in near infrared region. The obtained bands are shown to be associated with iridium ions with different valence states Ir^{3+}, Ir^{4+} and Ir^{5+}. Changes in the oxidation state of iridium ions from 5+ to 4+ are observed.

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