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# Iridium L<sub>3</sub>-edge and oxygen K-edge x-ray absorption spectroscopy of nanocrystalline iridium oxide thin films

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## ABSTRACT

Structural investigations of the short range order around iridium and oxygen ions in nanocrystalline iridium oxide thin films, prepared by dc magnetron sputtering technique, were performed by x-ray absorption spectroscopy. The Ir L<sub>3</sub>-edge extended x-ray absorption fine structure (EXAFS) and the O K-edge x-ray absorption near edge structure (XANES) signals were measured at room temperature and analysed within ab initio multiple-scattering and full-multiple-scattering approaches, respectively. The x-ray absorption spectroscopy results indicate the presence in the films of ordered regions - nanocrystals, having a size of about 10 Å and a structure rather close to that in crystalline iridium oxide IrO<sub>2</sub>. Such evidence agrees well with observations by x-ray diffraction, suggesting that the thin films are x-ray amorphous.

**Keywords:** IrO<sub>2</sub> thin films, Ir L<sub>3</sub>-edge, O K-edge, EXAFS, XANES

## 1. INTRODUCTION

Iridium oxide is technologically important material with wide range of applications. These include ion storage electrodes in electrochromic devices, oxygen barriers in advanced memory technology, electrocatalysts for water electrolyses, solar-cells-electrolytic systems, optical disk-storage memory, pH sensors and electrodes for neural stimulation [1-4]. Note that in all cases, the useful properties of iridium oxide are strongly determined by its local atomic and electronic structure.

Crystalline IrO<sub>2</sub> has the rutile structure with the tetragonal space group P4<sub>2</sub>/mnm and the lattice parameters a=b=4.4983 Å and c=3.1547 Å [5]. The positions of oxygen atoms are additionally determined by the parameter u=0.308 [5]. From the local point of view, iridium atoms are octahedrally coordinated by oxygens with R(Ir-O)≈1.98 Å and R(O-O)≈2.44-2.79 Å. The shortest Ir-Ir distances, equal to 3.15 Å, are within chains of IrO<sub>6</sub> octahedra joined across opposite edges. IrO<sub>2</sub> has metallic conductivity with the Fermi level lying within 5d(Ir)-subband [6]. In iridium oxide thin films one can expect strong modification of both long and short range orders due to a decrease of the crystallites size and a presence of defects.

The local atomic structure around iridium ions in thin films has been studied previously by x-ray absorption spectroscopy at the Ir L<sub>1,3</sub>-edges [5,7-9]. It has been found that iridium ions are located in rather symmetric surrounding [8] and are coordinated by six oxygen ligands, located at the distances close to that in crystalline IrO<sub>2</sub> [7]. A relaxation of the local environment around iridium atoms during the electrochemical process has been also observed in [9]. It appears in a strong decrease of the average Ir-O distance from 2.011 to 1.963 Å with increasing iridium oxidation state from 3.03 to 3.85 [9].

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In this work we discuss results of edge x-ray absorption spectroscopy and x-ray diffraction studies of the short range order around iridium and oxygen ions in nanocrystalline iridium oxide thin films, prepared by dc magnetron sputtering technique.

## 2. EXPERIMENTAL AND DATA ANALYSIS

Iridium oxide thin films were deposited on glass and polyimide film substrates by dc magnetron sputtering from iridium metal target in oxygen atmosphere. The distance between the target and the substrate was 8.5 cm. The films thickness was in the range of 60-100 nm.

The crystallinity of the films was probed by x-ray diffraction. The measurements were performed at room temperature using  $\text{CuK}\alpha$  radiation from x-ray tube, mounted on a conventional Bragg-Bretano  $\theta$ - $2\theta$  powder diffractometer. Polycrystalline iridium oxide ( $\text{c-IrO}_2$ ) powder was also measured for comparison.

X-ray absorption spectroscopy was used to study the short range order around iridium and oxygen atoms. The Ir  $L_3$ -edge ( $E=11210$  eV) extended x-ray absorption fine structure (EXAFS) and the O K-edge ( $E=530$  eV) x-ray absorption near edge structure (XANES) signals were recorded at room temperature at the LURE DCI (D44 beamline, energy resolution 3 eV) and SuperACO (SA22 beam line, energy resolution 0.2 eV) synchrotron radiation storage rings (Orsay, France), respectively. The transmission mode was used for iridium  $L_3$ -edge, while total electron yield (TEY) mode for oxygen K-edge. The absorption spectra were treated by the EDA software package [10] and analysed using ab initio multiple-scattering (MS) and full-multiple-scattering (FMS) approaches, based on the calculations by the FEFF8 code [11].

## 3. RESULTS AND DISCUSSION

### 3.1. X-ray diffraction

X-ray diffraction pattern of iridium oxide thin films does not exhibit any Bragg peaks (Fig. 1), in contrast to polycrystalline iridium oxide  $\text{c-IrO}_2$ , used as a reference. Therefore, the thin films, studied in this work, are x-ray amorphous. This suggests the mean crystallites size of less than  $\sim 20$  Å.

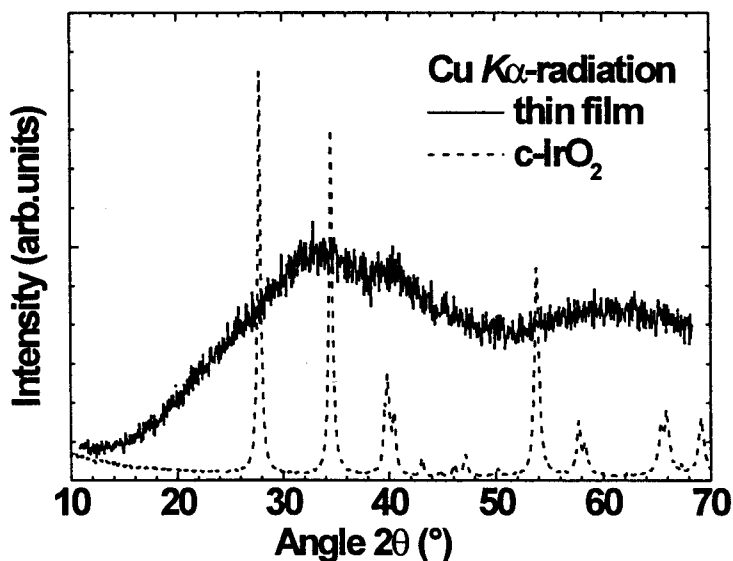


Figure 1: Room temperature x-ray diffraction patterns of polycrystalline iridium oxide ( $\text{c-IrO}_2$ ) and iridium oxide thin film.

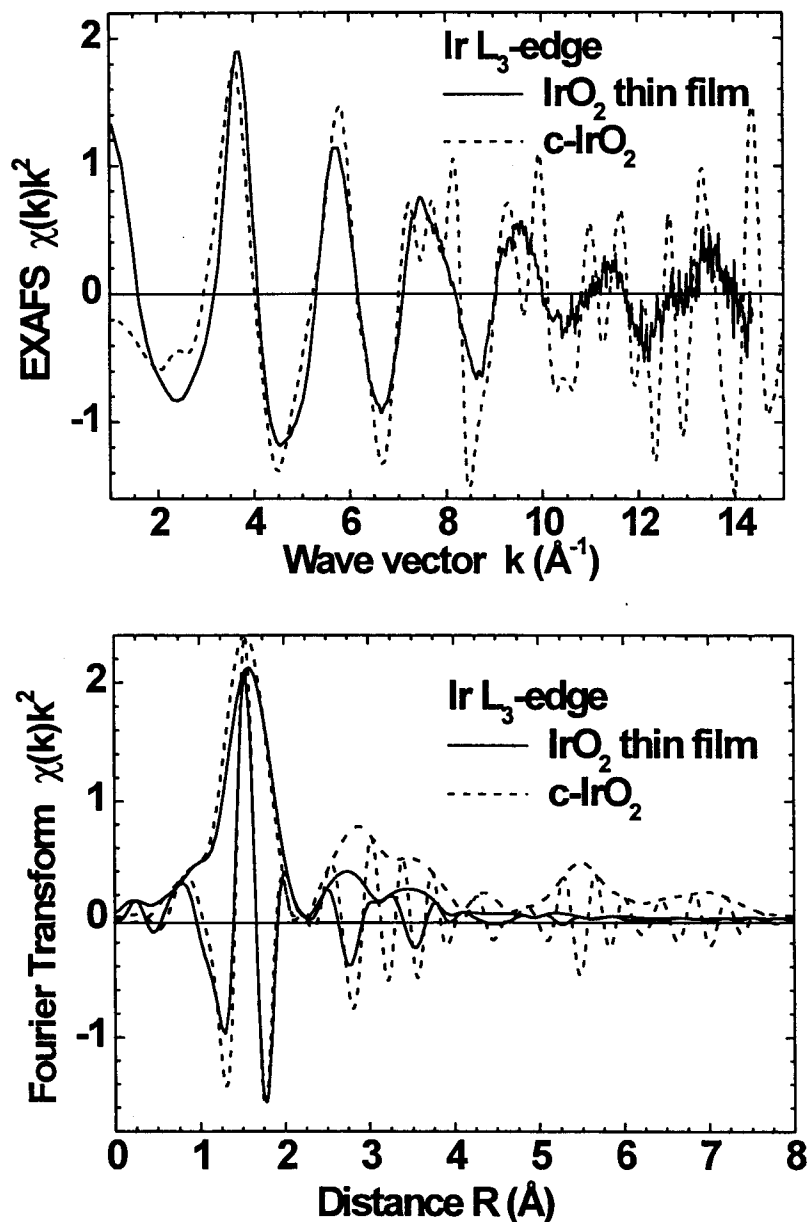


Figure 2: Room temperature Ir L<sub>3</sub>-edge EXAFS signals  $\chi(k)k^2$  (upper panel) and their Fourier transforms (FTs) (lower panel) for polycrystalline iridium oxide (c-IrO<sub>2</sub>) and iridium oxide thin film. Note that the positions of peaks in FTs differ from true crystallographic values

### 3.2. Ir L<sub>3</sub>-edge EXAFS and O K-edge XANES

The Ir L<sub>3</sub>-edge EXAFS signals  $\chi(k)k^2$  ( $k$  is the photoelectron wave vector) of c-IrO<sub>2</sub> and the thin films were extracted and analysed following standard procedure [10] and are shown in Fig. 2. Comparative analysis of the Fourier transforms (FTs) of the EXAFS signals for the thin film and crystalline c-IrO<sub>2</sub> indicates that the FT peaks amplitude for the thin film decreases relative to that for c-IrO<sub>2</sub> when the distance increases. Such behaviour is typical for nanocrystalline materials [12] and is due to the loss of a periodicity at the crystallites boundaries. The radius of the ordered region in the films can be approximately estimated from Fig. 2 to be around 4-5  $\text{\AA}$ , that corresponds to the crystallites size of about 10  $\text{\AA}$ .

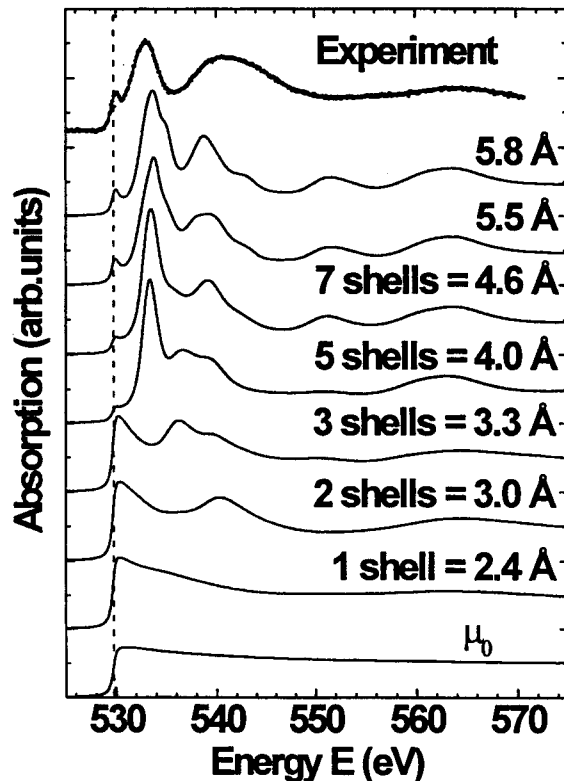


Figure 3: Comparison of the experimental O K-edge XANES signal in iridium oxide thin film (upper curve) with the FMS calculations for several clusters, having different size (up to 5.8 Å) and centred at the absorbing oxygen atom. Vertical dashed line indicates the position of the Fermi level, and  $\mu_0$  denotes atomic (oxygen) absorption coefficient.

The analysis of the EXAFS signals was performed within ab initio MS model [11]. The scattering amplitude and phase shift functions, required to simulate the EXAFS signal, were calculated by the FEFF8 code [11] using self-consistent potential with complex Hedin-Lundqvist exchange-correlation part. The EXAFS spectrum of crystalline  $\text{IrO}_2$  was used for calibration purposes of model parameters. The first shell peak at 1.5 Å (Fig. 2) was analysed within Gaussian and cumulant models [10], that allowed us to determine the first shell radial distribution function (RDF) around iridium atoms. The iridium atoms are coordinated to  $6.0 \pm 0.3$  oxygen atom in both c- $\text{IrO}_2$  and the thin films. The RDF in c- $\text{IrO}_2$  has Gaussian shape with the mean distance  $R(\text{Ir-O}) = 1.98 \pm 0.01$  Å and the mean square relative displacement (MSRD) or Debye-Waller factor  $\sigma^2 = 0.0018 \pm 0.0005$  Å<sup>2</sup>. Note that according to XRD data [5], there are two sets of Ir-O distances in c- $\text{IrO}_2$ : two at 1.959 Å and four at 1.995. In the thin films, the mean distance is shorter  $R(\text{Ir-O}) = 1.94 \pm 0.01$  Å, and the RDF is broader ( $\sigma^2 = 0.005 \pm 0.001$  Å<sup>2</sup>) and asymmetric with a tail at shorter distances (cumulant  $C_3 = -0.0008 \pm 0.0002$  Å<sup>3</sup> < 0). This left-hand side asymmetry is probably the consequence of the first shell splitting into two sub-shells, having shorter and longer distances similar to that found in c- $\text{IrO}_2$  [5]. Thus, the  $\text{IrO}_6$  octahedra in the thin films are more distorted, compared to crystalline c- $\text{IrO}_2$ .

The analysis of the O K-edge XANES signal [13] within the FMS formalism [11] is shown in Fig. 3. The ab initio FMS calculations were performed by the FEFF8 code [11] using self-consistent potential with complex Hedin-Lundqvist exchange-correlation part. By increasing the size of the cluster, having c- $\text{IrO}_2$  structure, around central oxygen atom, one can estimate the required number of coordination shells to reproduce the experimental spectrum. Our calculations are able to account for all main features of the experimental signal. However, the clusters with less than 5 shells are not able to describe the high peak at 533 eV, but the clusters with more than 6 shells have additional feature at 552 eV, which is not present in the experiment. The best agreement is found for the clusters of 5-6 shells, having a radius of 4-4.5 Å, but also in this case the agreement is not perfect: there is some difference in the amplitude of the peak at 533 eV

and in the shape of the next peak at 540 eV. We attribute this disagreement mainly to a relaxation of the thin film structure from that of c- $\text{IrO}_2$ , which was found by EXAFS and was not taken into account in our FMS calculations. Thus, XANES analysis suggests that the thin films consist of crystallites with a size of about 4.5 Å in radius. This result agrees well with our findings by EXAFS and XRD. Besides, taking into account our scanning probe microscopy studies [14], we can conclude that several crystallites form grains with a size of about 20-50 nm.

#### 4. CONCLUSIONS

Good quality nanocrystalline  $\text{IrO}_2$  thin films can be prepared by dc magnetron sputtering in oxygen atmosphere. According to XRD, the thin films are x-ray amorphous that agrees well with the crystallites size, estimated by x-ray absorption spectroscopy, to be about 10 Å. Detailed analysis of the Ir  $L_3$ -edge EXAFS and O K-edge XANES signals shows that the structure of crystallites is close to that in crystalline  $\text{IrO}_2$ , but is relaxed already within the first coordination shell of iridium atoms. Our complementary investigations by scanning probe microscopy [14] suggest that these small crystallites form nanosized grains.

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