

# THE GROWTH AND CHARACTERIZATION OF IrO<sub>2</sub> 1D NANOCRYSTALS ON SAPPHIRE SUBSTRATES

<sup>1,3</sup>Korotcov Alexandru, <sup>1,\*</sup>Huang Ying-Sheng, <sup>2</sup>Tsai Dah-Shyang

<sup>1</sup> Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei, 106, Taiwan

<sup>2</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 106, Taiwan

<sup>3</sup> Department of Physics, State University of Moldova, Chisinau, MD-2009, Moldova

\* Tel.: + 886-2-2737-6385; fax: +886-2-2737-6424; e-mail: [ysh@et.ntust.edu.tw](mailto:ysh@et.ntust.edu.tw)

**Abstract:** Well-aligned IrO<sub>2</sub> nanocrystals (NCs) have been grown on sapphire (SA) substrates by rf magnetron sputtering using Ir metal target. The surface morphology and structural properties of the as-deposited NCs were characterized using field-emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). FESEM micrographs reveal that vertically aligned NCs were grown on SA (100), while the NCs on SA (012) and (110) show single and double aligned-directions, respectively, with a tilt angle of ~35° from the normal to the substrates. The XRD results indicate that the IrO<sub>2</sub> NCs are (002) oriented on SA (100), and (101) oriented on SA (012) and (110) substrates. A strong substrate effect on the alignment of the IrO<sub>2</sub> NCs growth has been demonstrated and discussed.

**Keywords:** iridium dioxide, nanocrystals, reactive sputtering, field emission scanning electron microscopy, X-ray diffractometry.

## 1. INTRODUCTION

Fabrication of one-dimensional (1D) nanoscaled materials has gained considerable attention owing to their fundamental interests in science and potential in developing nanodevices [1,2]. IrO<sub>2</sub> belongs to the family of rutile-type conductive oxides, whose nanocrystals (NCs) are not well cultivated and solicit extensive investigation [3]. Owing to the conductive nature, high thermal and chemical stability, effective diffusion barrier for oxygen, IrO<sub>2</sub> 1D NCs have been an attractive material for field emitters, sensors, displays, interconnects, etc. [4,5]. Metal-organic chemical vapor deposition (MOCVD) has been successfully employed for the growth of IrO<sub>2</sub> 1D NCs on different substrates [6,7]. In this work, we report the deposition of 1D well aligned IrO<sub>2</sub> NCs deposited on

sapphire (SA) substrates by reactive sputtering using an Ir metal target which has several advantages such as a single deposition step to obtain the NCs and better control of the growth conditions.

The surface morphology and structural properties of the as-deposited NCs were examined by using field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD). A strong substrate effect on the alignment of the IrO<sub>2</sub> NCs is observed and discussed.

## 2. EXPERIMENTAL DETAILS

The study was performed using a home-made high vacuum rf magnetron sputtering system. The sputtering gun has a standard circular planar magnetron. The sputtering target was a 1-inch Ir (99.95%) metal. IrO<sub>2</sub> NCs were deposited on the different sapphire substrates: SA (100), SA (012) and SA (110). The sputtering chamber was maintained at a base pressure of  $\sim 3 \times 10^{-5}$  mBar. Reactive sputtering was carried out in a mixture of argon and oxygen. The sputtering parameters for all the data reported in this paper were O<sub>2</sub>/Ar = 1 : 2; rate of O<sub>2</sub> flow 2.5 sccm; sputtering pressure  $6.5 \times 10^{-2}$  mBar; power of the rf generator 65 W; distance between gun and substrate 45 mm; substrate temperature 400 °C.

The micrographs of IrO<sub>2</sub> samples were recorded using a JEOL-JSM6500F FESEM. The dimensions and growth rates of various IrO<sub>2</sub> samples were estimated according to the 90° cross-sectional FESEM images. X-ray diffraction patterns were recorded on a Rigaku D/Max-RC diffractometer to examine the growth orientation over a large area.

## 3. RESULTS AND DISCUSSION

The FESEM images illustrated in Fig. 1a show vertically well aligned IrO<sub>2</sub> NCs grown on SA (100) substrate. The estimated edge size and the length of the NCs are around 35 nm and 0.4 μm, respectively. The perspective view and cross section images of the overall NCs reveal a wedge-shaped geometry and almost all of them have sharp tips. The results indicate that the NCs standing on substrate are perfectly vertical orientated. The typical XRD patterns of the IrO<sub>2</sub> 1D NCs grown on SA (100) is shown in Fig. 2(a). The single IrO<sub>2</sub> (002) diffraction peak at  $\sim 58.5^\circ$  confirms the unique directional growth of IrO<sub>2</sub> NCs along [001]. A schematic plot of the IrO<sub>2</sub> NCs on SA (100) is illustrated in Fig. 3(a). Figure 1(b) shows the FESEM images of high density and well aligned IrO<sub>2</sub> NCs grown on a SA (012) substrate. The self-assembled regularly tilted rod-like NCs were grown with identical tilt angle ( $\sim 35^\circ$ ) from the normal to the substrate. XRD patterns of the IrO<sub>2</sub> NCs on SA (012) are depicted in Fig. 2(b) show two peaks at around  $34.7^\circ$  and  $73.2^\circ$  indexed as (101) and (202) planes of rutile IrO<sub>2</sub>, respectively. The results indicating that all the IrO<sub>2</sub> (101)

planes are parallel to the substrate plane (Fig. 3(b)). The IrO<sub>2</sub> 1D NCs on the SA (110) (Fig. 1(c)) exhibit a similar tilted-aligned growth behavior as that on the SA (012) and reveal symmetrically double aligned-directions (Fig. 3(c)) rather than single one.

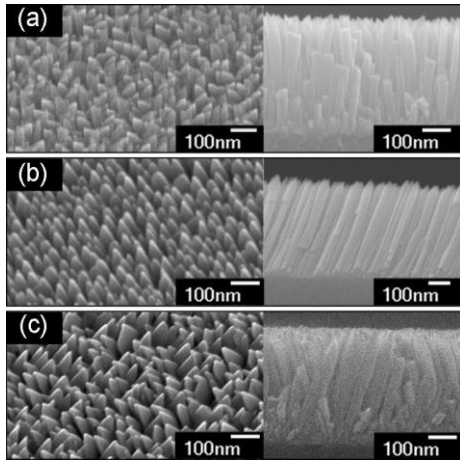


Fig. 1. FESEM images (30° perspective- and cross section view) of the IrO<sub>2</sub> 1D NCs on: (a) SA (100); (b) SA (012); (c) SA (110).

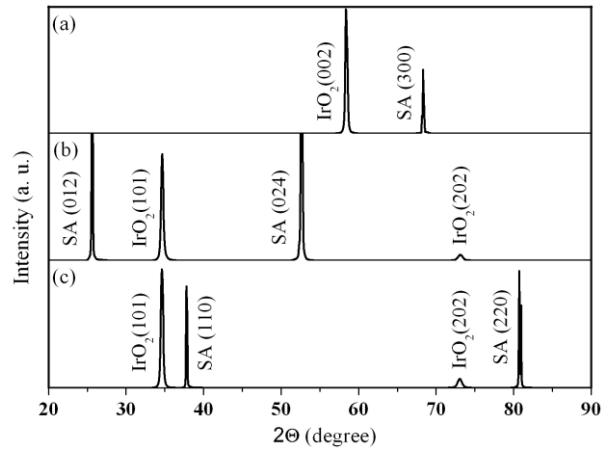


Fig. 2. The typical XRD patterns of the IrO<sub>2</sub> NCs grown on the different SA substrates: (a) SA (100); (b) SA (012); (c) SA (110).

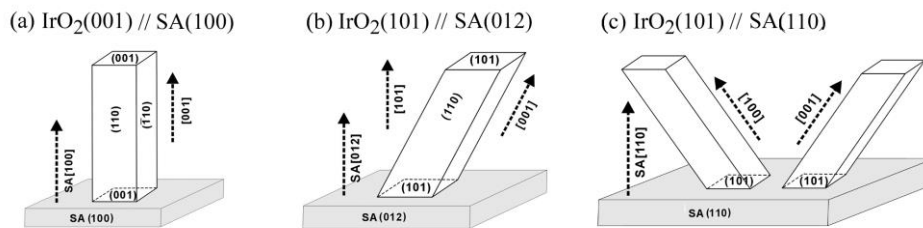


Fig. 3. The schematic drawing of the orientation relationship between IrO<sub>2</sub> and SA. (a) IrO<sub>2</sub> (001) on SA (100); (b) IrO<sub>2</sub> (101) on SA (012); (c) IrO<sub>2</sub> (101) on SA (110).

The growth of IrO<sub>2</sub> 1D NCs on SA substrates can be explained on the basis of the lattice relationship. The lattice parameters are  $a = b = 0.449$  nm and  $c = 0.315$  nm for IrO<sub>2</sub>,  $a = b = 0.476$  nm and  $c = 1.299$  nm for sapphire [8]. Lattice misfit at interface produces strain energy when the IrO<sub>2</sub> is nucleated and an axial stress determined the driving force for 1D growth. The crystallinity formation follows the substrate orientation at conditions when the surface mobility of the sputtered atoms is just sufficient to maintain sustain the formation of the plane with lowest energy. The orientation that minimizes the lattice misfit and produces the smallest strain energy will be preferred.

The tilted growth of IrO<sub>2</sub> NCs can be understood as follows: initially, the deposition of IrO<sub>2</sub> starts from the epitaxy of {101} planes on the SA (012) or SA (110) surfaces. Since the long axis of NCs is along the [001] direction, the growth rate of (001) planes should be the highest in this case.

Then the tilted growth occurs along [001] direction which is  $\sim 35^\circ$  from the normal to the SA (012)/SA (110) substrates or IrO<sub>2</sub> (101) plane. This process also leads to the vertical 1D growth of IrO<sub>2</sub> NCs on the sapphire substrate and can be explained by the initial IrO<sub>2</sub> (001) nucleation on the SA (100) plane. Since the IrO<sub>2</sub> (001) plane is normal to the SA (100) plane, under this anisotropic growth condition, the IrO<sub>2</sub> (001) nuclei should elongate along {001} orientation and form vertically aligned 1D NCs in the same direction.

#### 4. CONCLUSION

IrO<sub>2</sub> 1D nanocrystals have been grown on SA (100), SA (012) and SA (110) substrates via the rf magnetron sputtering deposition technique. The results of the structural study reveal that the single-crystalline vertically aligned IrO<sub>2</sub> (001) 1D NCs were grown on SA (100), while the NCs on the SA (012) and SA (110) were grown with a tilted angle of  $\sim 35^\circ$  (IrO<sub>2</sub> (101)) from the normal to substrates. Moreover, the well-aligned IrO<sub>2</sub> 1D NCs on SA (110) reveal symmetrically double aligned-directions rather than single one on SA (012). A strong substrate effect on the alignment of the IrO<sub>2</sub> NCs growth has been demonstrated and the probable mechanism for the formation of these 1D NCs has been discussed.

#### ACKNOWLEDGEMENT

The authors acknowledge the support of the National Science Council of Taiwan under the project No. NSC93-2120-M-011-001.

#### REFERENCES

- [1] Patzke G.R., Krumeich F., Nesper R.; (2002); *Angew. Chem. Int. Ed.*; 41; 14; 2446- 2461;
- [2] Xia Y., Yang P., Sun Y., Wu Y., Mayers B., Gates B., Yin Y., Kim F., Yan H.;(2003); *Adv. Mater.*; 15; 5; 353-389;
- [3] Chen R.S., Chang H.M., Huang Y.S., Tsai D.S., Chattopadhyay S., Chen K.H.; (2004); *J. Cryst. Growth*; 271; 1-2; 105-112;
- [4] Kuratani Y., Morikawa Y., Okuyama M.; (1998); *Jpn. J. Appl. Phys.*; 37; 9B; 5421-5423;
- [5] Chiang D., Lei P.Z., Zhang F., Barrowcliff R.; (2005); *Nanotech.*; 16; 3; S35-S40;
- [6] Chen R.S., Huang Y.S., Tsai D.S., Chattopadhyay S., Wu C.T., Lan Z.H., Chen K.H.; (2004); *Chem. Mater.*;16; 12; 2457-2462;
- [7] Chen R.S., Chang H.M., Huang Y.S., Tsai D.S., Chiu K.C.; (2005); *Nanotech.*; 16; 1; 93-97;
- [8] JCPDS card No. 15-870 (IrO<sub>2</sub>); No.10-0173 (Al<sub>2</sub>O<sub>3</sub>); International Centre for Diffraction Data, Newtown Square, PA, USA.