Review Article

Well-Aligned IrO₂ Nanocrystals

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Received 27 February 2007; Accepted 16 August 2007

Recommended by Berger Shlomo

We review the results of synthesis of well-aligned IrO₂ nanocrystals (NCs) on sapphire (SA), LiNbO₃ (LNO), LiTaO₃ (LTO) substrates via reactive magnetron sputtering and metal-organic chemical vapor deposition. The surface morphology and structural properties of the as-deposited NCs were characterized. Field emission scanning electron microscopy micrographs reveal that NCs grown on SA(100)/LNO(100) are vertically aligned, while the NCs on SA(012)/LTO(012) and SA(110) contain singly and doubly tilted alignments, respectively, with a tilt angle of $\sim 35^\circ$ from the normal to the substrates. NCs grown on SA(001) show in-plane alignment with mosaic structure. The X-ray diffraction results indicate that the NCs are (001), (101), and (100) oriented on SA(100)/LNO(100), SA(012)/LTO(012)/SA(110), and SA(001) substrates, respectively. A strong substrate effect on the alignment of the IrO₂ NCs deposition has been demonstrated. The roles of different substrates in the formation of various textures of nanocrystalline IrO₂ are studied and the possible mechanisms have been discussed.

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1. INTRODUCTION

Recently, one-dimensional (1D) nanoscaled materials in the form of wires, rods, belts, and tubes have become the focus of intensive research owing to their fundamental interests in science and potential in fabrication nanodevices [1–3]. The development of nanodevices should benefit from the unique morphology, huge surface area, and high aspect ratio of nanocrystals (NCs). A wide range of the nanosized oxide materials is currently the focus of a rapidly growing scientific community. The electrically insulating and/or semiconducting oxides of nanostructured SiO₂ [4], TiO₂ [5], SnO₂ [6], GeO₂ [7], Ga₂O₃ [8], and VO_x [9] have been synthesized and studied. Among the numerous metallic oxides, the electrically conducting iridium dioxide (IrO₂) belongs to a class of materials with unique properties [10], whose nanophase are not well cultivated and required extensive investigation.

IrO₂ belongs to the family of conductive oxides crystallized in the tetragonal rutile structure [11]. Single-crystalline IrO₂ shows metallic behavior in electrical and optical properties [12–14]. Owing to the conductive nature, high thermal

and chemical stability, and oxygen diffusion resistance, IrO₂ has been an attractive candidate for sensing material in pH sensors [15–18], for acidity and basicity determination in a nonaqueous industrial lubricant environment [19], durable electrodes for chlorine and oxygen evolution [20–22], excellent diffusion barrier and suitable electrode material in ferroelectric for nonvolatile memory devices [12, 23, 24], optical switching layers in electrochromic displays [25, 26], as an emitter material in field emission cathodes for vacuum microelectronic devices and field emission displays [27–30].

As a result of these diverse applications, there is a growing need to develop simple and reliable methods for synthesizing different IrO₂ phases in micro- or nanophase forms. Various methods such as reactive magnetron sputtering [13, 14, 31], pulsed laser deposition [32, 33], solution growth [21, 34], thermal preparation [35, 36], and metal-organic chemical vapor deposition (MOCVD) [37, 38] have been employed for this purpose. Recently, MOCVD have been successfully implemented for the growth of IrO₂ one-dimensional nanostructures on different substrates by Chen et al. [39–41]. However, MOCVD generally requires multiple processing steps to fabricate nanostructures. It is difficult to have proper control

FIGURE 1: Schematic diagram of the RF magnetron sputtering system.

of these processes, for example, the properties of the precursor might change during deposition or after a few runs of the growth process. On the other hand, the method of reactive radio frequency magnetron sputtering (RFMS) has demonstrated its potential applicable for the synthesis of nanostructured materials [42, 43] as it possesses the advantage of being a single-step fine control growth conditions technique.

In this article, we review the efforts to develop RFMS and MOCVD techniques for deposition of nanostructural IrO_2 during the past few years. A strong substrate effect on the alignment of the IrO_2 NCs deposition has been demonstrated. The roles of different substrates for the formation of various textures of nanocrystalline IrO_2 are reported and the probable mechanisms for the formation of these NCs are discussed. Section 2 reviews the results of the deposition of IrO_2 NCs on different substrates by RFMS using Ir metal target. A substrate effect on the alignment of the IrO_2 NCs has been discussed, and the possible explanation for the formation of oriented IrO_2 nanostructures has been provided. Section 3 reviews the results of synthesis of IrO_2 NCs on different substrates via MOCVD using $(\text{MeCp})(\text{COD})\text{Ir}$ as the source reagent. The successful growth of vertically aligned IrO_2 nanotubes (NTs) on $\alpha\text{-Al}_2\text{O}_3(100)$ [sapphire(100)] (SA(100)) and $\text{LiNbO}_3(100)$ (LNO(100)) substrates are presented in Section 3.1. An interesting tilted growth of well-aligned IrO_2 NTs on the $\text{LiTaO}_3(012)$ (LTO(012)) and SA(012) substrates is shown in Section 3.2. In Section 3.3, a morphological study showing the formation conditions and mechanism for various 1D nanostructures of IrO_2 including NRs and NTs is presented. In Section 3.4, area-selective growth of IrO_2 NRs has been demonstrated on SA(012) and SA(100) substrates, which consist of patterned SiO_2 as the nongrowth surface. The study of the initial growth of IrO_2 nuclei is also presented. Section 4 is the summary.

2. DEPOSITION OF WELL-ALIGNED IrO_2 NANOCRYSTALS VIA RFMS

In this section, we review the growth of well-aligned IrO_2 NCs via RFMS on different oriented single-crystal oxide substrates [42, 43]. Reactive sputtering was carried out using a

high vacuum RFMS system in a mixture of argon (5 sccm) and oxygen (2.5 sccm) gases. A schematic diagram of the system is shown in Figure 1. The sputtering target was a 1-inch Ir (99.95%) metal. A working pressure of $\sim 5 \times 10^{-2}$ Torr, power of the RF generator at 65 W, substrate temperature T_s at 300–350°C, and deposition time of 60–90 minutes were used in the deposition process. The surface morphology and structural properties of the as-deposited NCs were characterized. The growth behavior of IrO_2 NCs is highly correlated with the growth conditions and orientations of the substrates. A strong substrate effect on the alignment of the NCs has been observed, and the possible explanation for the NCs' structure formation has also been given. RFMS has been demonstrated to be a simple method to fabricate large-area structures, which has several advantages including better control of the growth conditions and a single deposition step to obtain the nanostructures of IrO_2 .

2.1. Deposition of vertically aligned IrO_2 nanocrystals on $\alpha\text{-Al}_2\text{O}_3(100)$ and $\text{LiNbO}_3(100)$ substrates by RFMS

The FESEM images illustrated in Figures 2(a), 2(b) show the IrO_2 NCs, grown on SA(100) and LNO(100) substrates with vertically aligned growth behavior. The rod-like densely populated IrO_2 NCs have the edge size and length of about 40 ± 5 nm and 450 ± 50 nm, respectively. The typical XRD patterns of the vertically aligned IrO_2 NCs grown on SA(100) and LNO(100) depicted in Figure 2(c), show the preferable orientation of the nanostructures along $\text{IrO}_2[001]$ ($2\theta \sim 58.5^\circ$). For the IrO_2 NCs on LNO(100) substrate, a weak diffraction signal indexable to the $\text{IrO}_2(301)$ plane ($2\theta \sim 69.3^\circ$) can be distinguished. This fact proves the predominantly (001) oriented growth on SA(100) and LNO(100) with a small presence of (301) growth orientation on LNO(100) substrates, which can be predicted according to lattice relationship of substrates and nanostructures interfaces.

The preferable oriented growth of $\text{IrO}_2(001)$ along [001] can be explained by examining and correlating the epitaxial relation between the rutile lattice IrO_2 and the underlying SA(100)/LNO(100) planar structures at the atomic level.

The main assumption is that the SA(100) and LNO(100) surfaces are terminated by dislocated oxygen atoms as in the single crystals. The schematic diagrams illustrated in Figure 3 show the atomic arrangements of $\text{IrO}_2(001)$ on SA(100) and LNO(100) planes. The lattice parameters for IrO_2 are $a = b = 4.50 \text{ \AA}$ and $c = 3.16 \text{ \AA}$ [JCPDS no. 15-0870], for sapphire $a = b = 4.76 \text{ \AA}$ and $c = 12.99 \text{ \AA}$ [JCPDS no. 10-0173], and $a = b = 5.15 \text{ \AA}$ and $c = 13.86 \text{ \AA}$ for LiNbO_3 [JCPDS no. 20-631]. The incoming Ir atoms have sufficient mobility to minimize the lattice misfit and align themselves in $\text{IrO}_2(001)$ arrangement because the oxygen arrangement of the underlying substrates is similar to that of $\text{IrO}_2(001)$ oxygen atoms. Thus, the growth relationship can be described as: $\text{IrO}_2(001)[001] \parallel \text{SA}(100)[010]$ and $\text{IrO}_2(001)[100] \parallel \text{LNO}(100)[010]$. These alignments produce residual stress due to lattice mismatch values of -5.46% , that is, $[(4.50 - 4.76) \text{ \AA} / 4.76 \text{ \AA}] \times 100\%$ along $\text{IrO}_2[100]$, $+3.69\%$ $[(4.50 - 4.34) \text{ \AA} / 4.34 \text{ \AA}] \times 100\%$ along $\text{IrO}_2[010]$ for the NCs grown

FIGURE 2: The typical FESEM images (30° perspective-view and cross-sectional view) of the vertically aligned IrO_2 nanorods grown by RFMS on (a) $\text{SA}(100)$, (b) $\text{LiNbO}_3(100)$ substrates, and their (c) X-ray diffraction patterns.

FIGURE 3: The schematic plots of the lattice relationships between IrO_2 and sapphire(100), and $\text{LiNbO}_3(100)$ substrates: (a) $\text{IrO}_2(001)$ plane; (b) sapphire(100) plane; (c) $\text{LiNbO}_3(100)$ plane; (d) $\text{IrO}_2(001)$ on sapphire(100); and (e) $\text{IrO}_2(001)$ on $\text{LiNbO}_3(100)$.

on $\text{SA}(100)$, and -12.62% , that is, $[(4.50-5.15) \text{ \AA} / 5.15 \text{ \AA}] \times 100\%$ along $\text{IrO}_2[100]$, -3.02% $[(4.50-4.64) \text{ \AA} / 4.64 \text{ \AA}] \times 100\%$ along $\text{IrO}_2[010]$ for the NCs grown on LNO(100). Therefore, the c -axis directional growth of $\text{IrO}_2[001]$ with

the lattice mismatch minimizing mechanism can explain the vertical growth of IrO_2 NCs on $\text{SA}(100)$ and LNO(100) substrates which exhibit the templates for the $\text{IrO}_2(001)$ planes formation.

FIGURE 4: The typical FESEM images (30° perspective-view and cross-sectional view) of the tilted IrO₂ NCs grown by RFMS on (a) SA(012), (b) SA(110) substrates, and their (c) X-ray diffraction patterns. (Reprinted from [43] with permission from Institute of Physics Publishing.)

FIGURE 5: The schematic plots of the lattice relationships between IrO₂ and SA(012) and SA(110) substrates: (a) IrO₂(101) plane; (b) SA(012) plane; (c) SA(110) plane; (d) IrO₂(101) on SA(012); and (e) IrO₂(101) on SA(110). (Reprinted from [43] with permission from Institute of Physics Publishing.)

2.2. Deposition of IrO₂ nanocrystals on α -Al₂O₃(012) and α -Al₂O₃(110) by RFMS

The micrographs of self-assembled densely packed IrO₂ NCs on SA(012) and SA(110) are illustrated in Figure 4. These

rod-like nanostructures exhibit regularly tilted NCs with identical tilt-angle ($\sim 35^\circ$) from the normal to substrate. Moreover, the NCs on SA(110) substrate reveal symmetrically aligned, doubly tilted directions. The possible explanation of these unique directional growths will be discussed

FIGURE 6: (a) The typical FESEM images (30° perspective-view and cross-sectional view) and (b) their X-ray diffraction patterns of the mosaic IrO₂ NCs grown by RFMS on a SA(001) substrate. (Reprinted from [43] with permission from Institute of Physics Publishing.)

below. The FESEM images reveal that IrO₂ NCs have an average diameter and length of 40 ± 5 nm and 400 ± 40 nm, respectively.

Figure 4(c) shows the typical XRD patterns of the regularly tilted IrO₂ NCs deposited on SA(012) and SA(110). Two peaks can be indexed as (101) and (202) diffraction planes at $2\theta \sim 34.7^\circ$ and $\sim 73.2^\circ$, respectively, indicating parallel in-plane IrO₂(101) orientation. Here, we observe anisotropic growth and as a result, film formation is restricted by the in-plane mismatch. Thus, the deposited Ir and O atoms are stacked into a 1D nanostructure in *c*-direction with IrO₂ plane formation following the substrate orientation. The probable allowed orientations of the NCs to the substrate interfaces are IrO₂(101) // SA(012) or SA(110).

To determine the directions of planar deposition, we have to examine the atomic arrangements of the appropriate surfaces. Figure 5 illustrates the schematic plots of the atoms arrangements and lattice relationships between IrO₂ and SA(012), SA(110) surfaces. According to the argument on minimization of the oxide sublattice structural mismatch, the possible NCs-substrates alignment can be described as IrO₂(101)[010] // SA(012)[100]. The relationship of IrO₂(101) and SA(110) oxide sublattices reveals the possibility to form two equivalent structural domains with 180° rotation symmetry, and, in this way, it leads to doubly tilted nanostructures formation with the following orientations: IrO₂(101)[$\bar{1}01$] // SA(110)[$1\bar{1}0$] and with IrO₂ [$\bar{1}\bar{1}1$] or IrO₂ [$1\bar{1}\bar{1}$] // SA[$2\bar{2}1$].

The alignments mentioned above produce directional mismatches on SA(012) of -5.46% $[(4.50-4.76) \text{ \AA} / 4.76 \text{ \AA}] \times 100\%$, $+7.02\%$ $[(5.49-5.13) \text{ \AA} / 5.13 \text{ \AA}] \times 100\%$ along IrO₂[010] and IrO₂[$10\bar{1}$], respectively; and on SA(110) along

IrO₂[010] of $+3.68\%$ $[(4.50-4.34) \text{ \AA} / 4.34 \text{ \AA}] \times 100\%$; the mismatches are -4.36% $[(5.49-5.74) \text{ \AA} / 5.74 \text{ \AA}] \times 100\%$ on one side and $+2.23\%$ $[(5.49-5.37) \text{ \AA} / 5.37 \text{ \AA}] \times 100\%$ on the other side of the unit cell along IrO₂[$10\bar{1}$], and $+1.42\%$ $[(7.10-7.00) \text{ \AA} / 7.00 \text{ \AA}] \times 100\%$ along IrO₂[$\bar{1}\bar{1}1$]. The minimization of the oxide sublattice structural mismatch together with the *c*-directional growth mechanism are the two main driving forces for forming either the tilted or vertical IrO₂ 1D NCs. The substrate orientation combining with the temperature of substrate can also influence the internal factor such as energetically favorable surface for the incoming atoms (*c*-directional growth mechanism) and initiate the preferable plane orientation of IrO₂ NCs whereby the incoming atoms will stick onto the lower energy sites. The *c*-directional growth mechanism comes from the anisotropy of the crystal structure that results in different growth rate for the different directions of NCs.

2.3. Deposition of IrO₂ nanocrystals on α -Al₂O₃(001) by RFMS

FESEM micrographs shown in Figure 6 display images of IrO₂ NCs deposited on SA(001) substrate which contains a threefold symmetry surface. FESEM perspective view and cross-sectional pictures of NCs on SA(001) (Figure 6(a)) exhibited a nanowall-like mosaic structure containing three equivalent structural domains. The estimated dimensions of the nanowalls (NWs) are: height ~ 200 nm, thickness and length of the NWs are, respectively, $\sim 20-45$ nm and $\sim 100-200$ nm. XRD patterns of the IrO₂ NWs grown on SA(001) substrate are shown in Figure 6(b). The IrO₂(200) diffraction peak at $2\theta = 40.03 \pm 0.02^\circ$ and its higher-order reflection of (400) at larger angles $2\theta = 86.40 \pm 0.02^\circ$ exhibit a preferential crystalline alignment of IrO₂ NWs along [100] for the sample grown on SA(001).

Heteroepitaxy of IrO₂(100) on SA(001) (Figure 7) becomes understandable by examining the atomic arrangement of the relevant epitaxy surfaces. The SA(001) surface contains oxygen atoms that exhibit threefold symmetry, and represent the template onto which the NWs are deposited. To compensate for the residual negative charge, the first layer of the IrO₂ should compose of iridium ions. In the IrO₂ lattice, each Ir⁴⁺ is octahedrally coordinated, but termination of the IrO₂ lattice with a layer of cations would leave them with a coordination number of three. By centering the metal over a threefold hollow on the oxide surface of SA, each iridium ion can achieve a favorable coordination number of six. The distances between the corner positions in IrO₂ are 3.16 Å and 4.50 Å corresponding, respectively, to the [001] and [010] directions. On SA(001) layers, the distance between the nearest threefold hollow sites is 2.88 Å. Another threefold hollow site in the SA(001) lattice appears every 4.76 Å along the [010], [100], and [110] directions. Thus, if IrO₂ NCs are set to grow over SA(100), then the best structural match is to position the IrO₂(100) NWs structure such that IrO₂[010] // SA[100], resulting in a directional mismatch of $+9.72\%$ along the IrO₂[001] $[(3.16-2.88) \text{ \AA} / 2.88 \text{ \AA}] \times 100\%$, and -5.46% along the IrO₂[010] $[(4.50-4.76) \text{ \AA} / 4.76 \text{ \AA}] \times 100\%$. Schematically, this is marked by the IrO₂ unit cell in

FIGURE 7: The schematic plots of the lattice relationships between IrO_2 and $\text{SA}(001)$ substrate: (a) $\text{IrO}_2(100)$ plane; (b) $\text{SA}(001)$ plane; and (c) $\text{IrO}_2(100)$ on $\text{SA}(001)$. (Reprinted from [43] with permission from Institute of Physics Publishing.)

FIGURE 8: Schematic diagram of a vertical-flow cold-wall MOCVD system.

Figure 7(c), which illustrates the growth of $\text{IrO}_2(100)$ NWs on $\text{SA}(001)$. In other words, the mismatch is not as energetically favorable along the $\text{IrO}_2[001]$. The experimental observation that the IrO_2 NWs take on a mosaic structure consisting of three equivalent domains would be consistent with an epitaxy structure in which IrO_2 unit cells are distributed on the $\text{SA}(001)$ surface such that the match along $\text{IrO}_2[010]$ is maximized, while that along $\text{IrO}_2[001]$ is minimized. Schematically, this is illustrated by the three equivalent unit cells of IrO_2 , rotated 120° from each other, as depicted in Figure 7(c). The maximized/minimized match of IrO_2 along $[010]/[001]$ can explain the reason of producing discontinuous growth and forming the nanowalls-like structure instead of an epitaxial film. The c-directional growth behavior aligns NWs along $[001]$ direction whereas a higher degree of lattice mismatch along the c-direction tends to impede the growth process of producing a structure with shorter NWs.

3. GROWTH OF IrO_2 NANOCRYSTALS BY MOCVD

In this section, we review the growth of IrO_2 nanocrystals utilizing a vertical-flow cold-wall MOCVD system. A

schematic diagram of the system is shown in Figure 8. The low-melting and highly volatile iridium precursor (methylcyclopentadienyl) (1,5-cyclooctadiene) iridium (I), $(\text{MeCp})(\text{COD})\text{Ir}$, was used for the chemical vapor deposition of IrO_2 samples [37].

3.1. Growth of vertically aligned IrO_2 nanotubes on $\alpha\text{-Al}_2\text{O}_3(100)$ and $\text{LiNbO}_3(100)$ substrates

In this section, growth and a detailed characterization of vertically aligned single-crystalline IrO_2 NTs on $(\text{SA})(100)$ and $(\text{LNO})(100)$ substrates [10] via MOCVD will be presented. The synthesis parameters for the growth of vertically aligned IrO_2 nanotubes are as follows: both the temperatures of transfer line T_{tl} and the precursor reservoir T_{pr} were kept at a constant temperature of $100\text{--}110^\circ\text{C}$, high-purity oxygen was used as both carrier and reactive gas with a flow rate of 100 sccm, the substrate temperature and pressure of the CVD chamber were at 350°C and 10–50 Torr, respectively.

The FESEM images illustrated in Figures 9(a), 9(b) show that most of the IrO_2 crystals grown on $\text{SA}(100)$ substrates reveal hollow square cross-section and exhibit vertically aligned growth. The estimated edge size and tube length of the nanotubes (NTs) are around $40\text{--}100\text{ nm}$ and $0.2\text{--}2.0\text{ }\mu\text{m}$, respectively. Similar results were also found in the growth of the IrO_2 NTs using $\text{LNO}(100)$ substrate as shown in Figures 9(c), 9(d). The vertically aligned tubes grown on $\text{LNO}(100)$ have edge size and length around $50\text{--}100\text{ nm}$ and $0.5\text{--}1.0\text{ }\mu\text{m}$, respectively. Nonetheless, some differences in the uniformity of growth alignment and orientation between the samples on $\text{SA}(100)$ and $\text{LNO}(100)$ can still be observed. The top-view images of the overall tubules on $\text{SA}(100)$ (Figure 9(a)) are clear open squares with the edges parallel to each other. This result indicates that the tubules standing on substrate are perfectly vertical and follow the same in-plane orientation. On the other hand, the top-view image for the tubules on $\text{LNO}(100)$ (Figure 9(c)) shows some degrees of deviation as compared to that on $\text{SA}(100)$, indicating the probable occurrence of other growth planes.

The TEM images, depicted in Figures 10(a)–10(d), show the tubular morphology of the IrO_2 nanocrystals on

FIGURE 9: FESEM images of the vertically aligned IrO_2 nanotubes grown by MOCVD on SA(100) substrate: (a) top view; (b) cross-sectional view, and on $\text{LiNbO}_3(100)$ substrate: (c) top view; and (d) cross-sectional view. (Reprinted from [10] with permission from Elsevier).

FIGURE 10: TEM images of the IrO_2 nanotubes focused on (a) two individual tubes; (b) the front end; (c) the middle; and (d) the bottom: (e) the high-resolution TEM image and its SAD pattern taken from the tube-wall marked in (b); (f) a schematic diagram of the IrO_2 nanotube. (Reprinted from [10] with permission from Elsevier).

SA(100). TEM images focused on the front end, middle, and bottom end of the nanotube are depicted in Figures 10(b), 10(c), and 10(d), respectively, showing the nonuniform tube wall thickness, which tends to decrease from the bottom to the open-end. As shown in Figure 10(e), a high resolution TEM image taken from the tube wall marked in Figure 10(b) exhibits clear lattice planes of the IrO_2 NT and the lattice spacing between adjacent lattice planes for both the (001) and (110) planes is about 0.31 nm. The corresponding selected-area electron diffractometry (SAD) pattern (inset, Figure 10(e)) is identified to be the [110] zone pattern, indicating that the tube walls belong to the {110} facets and the preferential growth direction of the IrO_2 tubes is along the [001] direction (c-axis). A schematic of the tubular crystal of IrO_2 is illustrated in Figure 10(f). The results also confirm

the tetragonal rutile structure and single-crystalline quality of the IrO_2 NTs.

The typical XRD patterns of the well-aligned IrO_2 NTs grown on SA(100) and LNO(100) substrates are shown in Figures 11(a) and 11(b), respectively. The single $\text{IrO}_2(002)$ diffraction peak at $\sim 58.5^\circ$, together with the TEM analysis confirm the uniquely single-directional growth of IrO_2 NTs along [001] for the sample grown on SA(100). For the sample on LNO(100) substrate, a weak $\text{IrO}_2(301)$ diffraction signal at $\sim 69.3^\circ$ in addition to the $\text{IrO}_2(002)$ peak were also observed, indicating a small presence of (301) growth orientation within predominantly (001) oriented IrO_2 NTs grown on LNO(100) substrates.

Growth with (001) orientation of IrO_2 nanotubes on the SA(100) and LNO(100) substrates can be understood based

FIGURE 11: XRD patterns of the vertically aligned IrO_2 nanotubes grown on the (a) sapphire(100) and (b) LiNbO_3 (100) substrates by MOCVD. (Reprinted from [10] with permission from Elsevier).

on the lattices relationship as described in Section 2.1. Lattice misfit at interface produces strain energy when IrO_2 is nucleated. The orientation that minimizes the lattice misfit and produces the smallest strain energy will be preferred. The overall orientation relationship between the nanotubes and substrates can be described as: $\text{IrO}_2(001) [100] \parallel \text{SA}(100) [010]$ and $\text{IrO}_2(001) [100] \parallel \text{LNO}(100) [010]$. A higher degree of lattice mismatch for IrO_2 grown on $\text{LNO}(100)$ is probably the reason for the generation of the two preferential orientations of (001) and (301), with the former being the dominant. The higher lattice mismatch and formation of the (301) plane also explain why the IrO_2 NTs on $\text{LNO}(100)$ substrate grow with lesser uniformity in alignment.

3.2. Tilted growth of the well-aligned IrO_2 nanotubes on $\text{LiTaO}_3(012)$ and $\alpha\text{-Al}_2\text{O}_3(012)$ substrates

In this section, growth and characterization of the well-aligned IrO_2 NTs on the $(\text{LTO})(012)$ [40] and $\text{SA}(012)$ [44] substrates with a tilt angle of 35° will be presented. Detailed synthesis parameters for the growth of tilted IrO_2 nanotubes are as follows: the temperatures of transfer line T_{tl} and the precursor reservoir T_{pr} were kept at a constant temperature of $100\text{--}110^\circ\text{C}$, oxygen flow rate at 100 sccm, substrate temperature at 350°C , and the chamber pressure in the range of 10–30 Torr. The deposition rate of the 1D crystal with tubular morphology was estimated to be 5–10 nm/min.

As illustrated in Figure 12, the FESEM images show high density and well-aligned IrO_2 NTs grown on a $\text{LTO}(012)$ substrate. The self-assembled NTs were grown with an identical tilt angle from the normal to the substrate. Unlike the cylindrical symmetry of most of the NTs reported so far, the IrO_2 tubes show open ends with square cross-section. The estimated edge size, length, and packing density are 50–80 nm, 1.0–1.5 μm , and $75 \pm 5 \mu\text{m}^{-2}$, respectively. Energy dispersive X-ray spectroscopy EDS measurements indicate that the tubules have an average atomic ratio of Ir to O of 1 : 2.

The cross-sectional TEM image in Figure 13(a) shows that all of the IrO_2 NTs grow with a tilt angle of $\sim 35^\circ$ from

the normal to the substrate surface. By separately focusing on the NTs and substrate, the tetragonal $\text{IrO}_2[\bar{1}11]$ and rhombohedral $\text{LTO}[2\bar{2}1]$ zone patterns are obtained and shown in Figures 13(b) and 13(c), respectively. Furthermore, a mixed SAD pattern at the interface region, depicted in Figure 13(d), indicates that the $\text{IrO}_2(101)$ layers are heteroepitaxially deposited on the $\text{LTO}(012)$ substrate. This result is further confirmed by XRD measurements. Figure 14 shows a typical XRD pattern of the well-aligned IrO_2 NTs grown on $\text{LTO}(012)$ substrate. Two peaks at around 35° and 73° are indexed as (101) and (202), respectively, of rutile IrO_2 , indicating that all the $\text{IrO}_2(101)$ planes are parallel to the substrate plane. In addition, these results also provide a reasonable explanation of the substrate effect on the tilted growth of the IrO_2 NTs. Initially, the deposition of IrO_2 starts from the epitaxy of the {101} planes on the $\text{LTO}(012)$ surface. Since the long axis of NT is along the [001] direction, the growth rate of (001) planes should be the highest in this case. Then the tilted growth occurs along the [001] direction which is $\sim 35^\circ$ from the normal to the $\text{LTO}(012)$ substrate or $\text{IrO}_2(101)$ plane. Figure 13(e) illustrates the schematic diagram of the orientation relationship between IrO_2 NTs and the $\text{LTO}(012)$ substrate. The allowed probable orientation of the nanotube to substrate interface is $\text{IrO}_2(101)[010] \parallel \text{LTO}(012)[100]$. Similar results were also found in growth of the IrO_2 NTs using $\text{SA}(012)$ substrates [44] (see Figure 15).

The obtained heteroepitaxy could be interpreted by examining the planar atomic arrangement of the $\text{IrO}_2(101)$ and $\text{LTO}(012)/\text{SA}(012)$ planes [44] (Figure 16). The crystal formation follows the substrate orientation at conditions when the surface mobility of the oxygen atoms constructing IrO_2 is just sufficient to maintain and 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. In accordance with the argument of the minimization of the oxide sublattice structural mismatch mechanism, the best match of $\text{IrO}_2(101)$ and $\text{LTO}(012)$ ($\text{SA}(012)$) planes should appear along $\text{IrO}_2[010] \parallel \text{LTO} [100]$ ($\text{IrO}_2[010] \parallel \text{SA} [100]$) direction. This heteroepitaxy produces directional mismatches of -12.62% (-5.46%) along $\text{IrO}_2[010]$ and -0.37% ($+7.02\%$) along $\text{IrO}_2[10\bar{1}]$, respectively. Where the lattice parameters are $a = b = 5.1530 \text{ \AA}$ and $c = 13.755 \text{ \AA}$ for LTO [JCPDS no. 29-836]. The formation of tilted NTs were the consequence of the overall two mechanisms, in which one is based on the lattice mismatch termed as the axial screw growth mechanism and another, the c-axis directional growth mechanism [40].

3.3. Morphological evolution of IrO_2 one-dimensional nanocrystals

In this section, we present the results of direct observation of the morphological evolution from solid-triangle NRs via hollow-square NTs to solid-square NRs for a tetragonal rutile material of IrO_2 by precisely controlling the growth rate of these 1D nanocrystals via MOCVD [41].

For a CVD process, the surface morphology of the as-deposited structures is determined by the complex interplay between mass transport and surface kinetics of the system,

FIGURE 12: FESEM images of the well-aligned IrO_2 nanotubes grown on the LiTaO_3 (012) substrate by MOCVD: (a) and (b) top view; (c) cross-sectional view; (d) focus on a typical IrO_2 nanotube. (Reprinted from [40] with permission from The American Chemical Society).

FIGURE 13: (a) The cross-sectional TEM image of the IrO_2 nanotubes on LiTaO_3 (012) substrate and its corresponding SAD patterns taken separately from the regions of (b) IrO_2 nanotubes, (c) LiTaO_3 substrate, and (d) interface along the zone axes of IrO_2 $\bar{1}11$ and LiTaO_3 $2\bar{2}1$. (e) The schematic diagram of the orientation relationship between the nanotube and substrate. (Reprinted from [40] with permission from The American Chemical Society).

FIGURE 14: Typical XRD pattern of the well-aligned IrO₂ nanotubes grown on LiTaO₃(012) by MOCVD. (Reprinted from [40] with permission from The American Chemical Society).

(a)

(b)

FIGURE 15: (a) A typical FESEM image of the well-aligned IrO₂ nanotubes and (b) x-ray diffraction pattern of the single-direction tilted IrO₂(101) nanotubes grown on sapphire(012) by MOCVD. (Reprinted from [44] with permission from Institute of Physics Publishing.)

which is critically dependent on the temperature of precursor reservoir T_{pr} , the substrate temperature T_s , the flow rate of the carrier gas J_0 , and chamber pressure P_c , and so forth. Usually, T_s is chosen to be higher than the pyrolysis temperature of the reactants to ensure their rapid decomposition and heterogeneous reaction at the growth interface. In addition, T_s also plays an important role in surface kinetics and strongly influences the surface morphology. To study the growth kinetics, a surface morphology diagram in terms of the degree of supersaturation $\Delta\mu$ versus $1/T_s$ can be used to interpret the morphological evolution [45]. From a crystal grower's point of view, a larger $\Delta\mu$ and a lower T_s can result in an instability of surface morphology of the as-deposited structures.

At first, by fixing all other parameters ($T_s = 350^\circ\text{C}$, $J_0 = 100$ sccm, and $P_c = 15\text{--}20$ Torr) and by only adjusting T_{pr} from 70 to 140°C , the partial pressure of the incoming source vapor (MeCp)(COD)Ir is changed. Because the vapor pressure of (MeCp)(COD)Ir near the growth interface is not available, the actual $\Delta\mu$ of the corresponding CVD system cannot be determined. Hence, the notation of $\Delta\mu(T_{pr})$ at various T_{pr} is then taken as a reference for our discussion. Different values of $\Delta\mu$ would result in different morphologies and lead to different growth rates of the IrO₂ 1D nanostructures. The growth rate R is defined as the increase in length of the long axis per unit growth time for the 1D crystal. All the samples in this study were grown on SA(100) substrates to make the IrO₂ crystals uniformly arrange in vertically aligned arrays [39].

In the largest $\Delta\mu$ region ($T_{pr} = 125\text{--}140^\circ\text{C}$) and $R(=18\text{--}40$ nm/min), the IrO₂ NRs with nearly triangular (Figures 17(a)–17(c)) and wedge-like (Figures 17(d)–17(f)) cross-sections are grown accompanying the formation of self-assembled sharp tips [38]. Usually, the former is preferred at larger $\Delta\mu$ than the latter. While reducing $\Delta\mu(T_{pr} = 110\text{--}125^\circ\text{C})$ and $R(15\text{--}22$ nm/min), the first morphological evolution occurs. The wedged rods evolve new walls and tend to complete a square loop. However, under this condition, IrO₂ crystals always evolve into incompletely enclosed tubes (Figures 18(a)–18(c)) and the scrolled tubes (Figures 18(d)–18(f)). The second stage of evolution is from the incomplete and scrolled tubes to the square NTs. Figures 19(a)–19(c) show that further reducing $\Delta\mu(T_{pr} = 100\text{--}110^\circ\text{C})$ and $R(=8\text{--}17$ nm/min) could make the wedged NR enclose a perfect square loop and evolve into the NT rather than its incomplete counterparts (Figure 18). The edge sizes of these NTs on the SA(100) substrate are around 50–100 nm. The tube walls of the square NTs will become thickened and be filled inside upon further decreasing $\Delta\mu$ or R as depicted in Figures 19(d)–19(f). The third evolution is from the hollow-square tubes to the solid-square rods under even smaller $\Delta\mu(T_{pr} = 85\text{--}95^\circ\text{C})$ and $R(=3\text{--}5$ nm/min), as shown in Figures 19(g)–19(i). In addition to the evolution between the 1D nanocrystals, a transformation from anisotropic 1D to isotropic 3D growth was also observed. Figure 20(a) shows that in the lowest $\Delta\mu(T_{pr} = 70\text{--}80^\circ\text{C})$ region the as-grown IrO₂ mixture is comprised of continuous grains and a few short rods protruding from the film surface. The growth rate range of this sample estimated from the thickness of film

FIGURE 16: The schematic plots of the lattice relationships between IrO_2 and LiTaO_3 (012) and sapphire(012) substrates: (a) IrO_2 (101) plane; (b) LiTaO_3 (012) plane; (c) sapphire(012) plane; (d) IrO_2 (101) on LiTaO_3 (012); (e) a schematic drawing of the orientation relationship between IrO_2 (101) and LiTaO_3 (012); and (f) IrO_2 (101) on sapphire(012). (Reprinted from [44] with permission from Institute of Physics Publishing.)

FIGURE 17: The top and 30° perspective view FESEM micrographs and the corresponding schematic plots for (a)–(c) the nearly triangular nanorods and (d)–(f) the wedge-like nanorods of IrO_2 . (Reprinted from [41] with permission from Institute of Physics Publishing.)

layer and length of the rod is around 1–2 nm/min which is also the lowest R in this study. Above results suggest that the self-mediated 1D growth habit of IrO_2 could be gradually retarded by reducing $\Delta\mu$.

From a surface kinetics point of view, a lower value of $\Delta\mu$ or R means that the adhered surface atoms have sufficient time to make the surface diffusion. Thus, the morphology of the as-grown structures becomes more stable. Similarly, a higher value of T_s , which provides sufficient surface diffusion energy for the adhered surface atoms, also plays an important role in determining the shape of the as-grown structures. Accordingly, as the second part of this work, T_s is

varied from 350 to 500°C. The study of the morphological evolution can then be carried out by adjusting T_{pr} from 70–140°C to change $\Delta\mu$ of the corresponding MOCVD system. The morphology distribution of IrO_2 in terms of $\Delta\mu$ and T_s is schematically illustrated in Figure 21(a). Overall, the NRs and NTs with square cross-section are more energetically favorable among these 1D nanostructures. The film, composed of continuous 3D grains (Figure 20(c)), is formed under the highest T_s and the lowest $\Delta\mu$ condition, which is the most morphologically stable condition. Figure 21(b) summarizes the entire trend of morphological evolution of IrO_2 in terms of $\Delta\mu$ and $1/T_s$. These results have been repeated and further

FIGURE 18: The top and 30° perspective view FESEM micrographs and the corresponding schematic plots for (a)–(c) the incomplete nanotubes and (d)–(f) the scrolled nanotubes of IrO_2 . (Reprinted from [41] with permission from Institute of Physics Publishing.)

FIGURE 19: The top and 30° perspective view FESEM micrographs and the corresponding schematic plots for (a)–(c) the square nanotubes, (d)–(f) the intermediate 1D nanocrystals and (g)–(i) the square nanorods of IrO_2 . (Reprinted from [41] with permission from Institute of Physics Publishing.)

FIGURE 20: The 30° perspective view FESEM micrographs and the corresponding schematic plots for (a) and (b) the mixture comprised of continuous grains and partial short rods, and (c) and (d) the thin film of IrO_2 . (Reprinted from [41] with permission from Institute of Physics Publishing.)

FIGURE 21: (a) The morphology distribution of various IrO₂ 1D nanocrystals in terms of supersaturation degree $\Delta\mu$ and substrate temperature T_s . (b) The schematic diagram showing the trend of the morphological evolution of IrO₂ in terms of $\Delta\mu$ and $1/T_s$. Here, 3D means the individual crystallite performing isotropic 3D growth. (Reprinted from [41] with permission from Institute of Physics Publishing.)

FIGURE 22: XRD patterns for the four typical 1D nanocrystals and a thin film of IrO₂ grown on the sapphire(100) substrates. (Reprinted from [41] with permission from Institute of Physics Publishing.)

confirmed using other substrates including LiNbO₃(100) and LiTaO₃(012). Similar phenomena have been observed in a solution-phase growth for the transition of nanorods to nanotubes with respect to different solute concentrations (i.e., different values of $\Delta\mu$) [46] and in thermal evaporation method for the size variation of box-beams with respect to substrate temperatures [47].

For the four typical IrO₂ 1D nanostructures and a thin film grown on sapphire (100) substrates, their corresponding XRD patterns (Figure 22) show the nearly single-crystalline quality and the same [001] long-axis directions for the vertically aligned NRs and NTs [38, 39] according to the unique (002) diffraction signal. The results also suggest that the orientation and crystallinity of the as-grown IrO₂ samples are not influenced by varying T_{pr} and T_s , while the morphology is highly dependent on the variations of CVD conditions. Therefore, the evolution begins from a spiral growth mode

on the plane perpendicular to the [001] long-axis directions with wedged NRs as embryos. Under the condition of highest morphological instability, these embryos grow and persistently remain as shown in Figures 18(a)–18(c). By reducing the degree of morphological instability, via the growth mode, wedged NRs composed of two side walls can evolve new walls and encloses spirally into various tubular structures. Square NTs formed under lower $\Delta\mu$ and higher T_s show more energetically favorable than the incomplete and scrolled ones. The most energetically stable 1D structure is the solid-square rods. These results can be explained as follows: the tetragonal rutile IrO₂ has the relationship of the lattice constants $a = b > c$. In term of crystallography, the crystal morphology with square cross-section should be the most stable rather than the triangular, wedged, scrolled, spiral, and any other forms. With the implication of diffusion-limited aggregation (DLA) model [45], the protruding part of the as-grown structure can easily capture the vaporized reactants and can grow faster leaving the inner growth sites (shielded by the outer branches) vacant. Naturally, by increasing the degree of interface instability (i.e., increasing $\Delta\mu$ and reducing T_s), since most of the source atoms are enforced to elongate along the longitudinal length, the corresponding R increases. Triangular and wedged rods with the fastest growth rate are grown at the highest $\Delta\mu$ and the lowest T_s . Under this condition, because the adhered atoms prefer to stack along [001] directions, no sufficient atoms can build a new wall from the rod edges, and so the spiral growth will not occur to complete a square circumference which is energetically more favorable. After the square tubes are formed, further lowering $\Delta\mu$ and increasing T_s will provide surface atoms sufficient time and energy to arrange and diffuse into the center of the hollow structure, resulting in the thickening of the tube walls (Figures 19(d)–19(f)). The hollow structure will be filled up and solid structure will form, instead (Figures 19(g)–19(i)) when the deposition and diffusion conditions are suitable.

FIGURE 23: Variation of the surface area being covered, the number density (inset), and the average size (inset) of IrO₂ nuclei with growth time in the initial growth stage. The growth temperature is 450°C. (Reprinted from [48] with permission from The Royal Society of Chemistry).

FIGURE 24: Arranged IrO₂ nuclei on a SA(012) surface at a growth temperature of 450°C and growth times of (a) 30 s and (b) 60 s. (Reprinted from [48] with permission from The Royal Society of Chemistry).

3.4. Area-selective growth of IrO₂ nanorods on α -Al₂O₃(012) and α -Al₂O₃(100) substrates

In this section, area-selective growth of IrO₂ NRs will be demonstrated on SA(012) and SA(100) substrates which consist of patterned SiO₂ as the nongrowth surface [48]. The optimal substrate temperature for selective growth is 450°C at a chamber pressure of ~20 Torr. The two crystal planes are chosen to align the nanorods in a specific orientation. Origin of the selectivity along with other 1D morphological features are traced back to nucleation in its initial growth period.

FIGURE 25: IrO₂ nanorods on SA(012) patterned by the photolithographic method and selectively grown at 450°C; (a) a stripe pattern, (b) a corner of square patch, (c) a border of populated nanorods, and (d) a border of less-populated nanorods. (Reprinted from [48] with permission from The Royal Society of Chemistry).

Photolithography was employed in patterning a silicon thin layer on sapphire. It began with standard wafer cleaning, and followed by sputtering a 20 nm thick Si thin film on SA(012) and SA(100) substrates. Si patterns of stripe and square window were created by spin-coating a photoresist, exposure, and wet etching. After removing the photoresist, the substrate was transferred to an MOCVD chamber and heated in flowing oxygen at 480°C for 25 minutes so that the patterned Si thin film was oxidized. The area covered by non-crystalline SiO₂ thin film was always designated as the non-growth region and the exposed sapphire area was the growth region for iridium dioxide nanorods.

The starting point of IrO₂ selective growth on these two patterned sapphire substrates is the nucleation energy barrier difference between sapphire and noncrystalline silica surfaces. Figure 23 compares kinetics of IrO₂ initial growth on SA(012), SA(100), and noncrystalline silica surfaces at $T_s = 450^\circ\text{C}$. The low-energy barrier of IrO₂ nucleation on sapphire is manifested by its short incubation time, approximately 19 seconds on SA(012) surface and 9 seconds on SA(100) surface. On the contrary, the incubation time on the noncrystalline silica surface is much longer at 369 seconds. Here the incubation time is defined as the intercept extrapolated from the linear plot of surface area covered by IrO₂ nuclei versus growth time.

The upper inset of Figure 23 shows that the number density of nuclei increases rapidly on both sapphire surfaces, while the number density increases on the glassy silica surface much more slowly. The lower inset of Figure 23 is a plot

of average nucleus size versus growth time. These two insets indicate that the number density of nuclei on SA(012) and SA(100) is large, but its average size is small and increases quickly. On the other hand, the number density of nuclei on glassy silica surface is zero before incubation or small after incubation; and once IrO_2 nuclei appear on the silica surface, their sizes are comparatively large. Observation of a few large nuclei after considerably long incubation suggests that establishment of an IrO_2 nucleus on the glassy silica surface needs to collect a sufficient number of atoms. A nucleus of insufficient size tends to dissipate, diffuse or evaporate away.

Some morphological features of the IrO_2 nanorods can find their roots in the nucleation behavior on sapphire. Figure 24 illustrates IrO_2 nuclei at growth time 30 and 60 seconds on SA(012). The nuclei in Figure 24(a) appear to be lined up and develop several dotted lines along the diagonal direction. The distance between two dotted lines is approximately 100–130 nm. A few IrO_2 nuclei are present in the interval between two dotted lines. Lining up of these nuclei seems to be the consequence of preferential nucleation sites on sapphire at certain surface defects, such as steps and kinks. Figure 24(b) indicates that these earlier nuclei are evolving into short rods and simultaneously most of the gap is being filled by new nuclei resulting in a reduced nucleus free area. Even in an initial stage as shown in Figure 24(b), some nuclei have turned into short rods. These short rods are clearly evolved from the older nuclei. The head start of those rods persists throughout the growth period and develops a height advantage since a taller rod is in a superior position to receive more growth species in the gas phase.

Orientation of IrO_2 nanorods is a morphological feature that is easily affected by the pattern resolution at the border between sapphire and glassy silica regions. Figures 25(a) and 25(b) illustrate a stripe pattern and a square corner of tilted IrO_2 nanorods on SA(012) substrate, respectively. A sharp boundary in Figure 25(d) delineates the upper half (growth region) and lower half (nongrowth region) of micrograph. We would like to emphasize that a border of less-populated nanorods, such as Figure 25(d), is uncommon. Nevertheless, such an image allows us to see the boundary between sapphire and silica thin film clearly, which is generally hidden in the nanorods. Figure 25(c) illustrates a typical border image, in which rods are aligned along the border line. Occasionally, there are toppled rods sticking out from the nanorods forest. The toppled rods stem from nuclei whose growth are influenced by both sapphire and silica surfaces.

Figures 26(a) and 26(b) show well-defined images of four nongrowth squares and a corner of vertically aligned IrO_2 nanorods on SA(100) substrate. Although nanorods in Figures 25 and 26 are grown under the same CVD condition and patterned by the same procedure, morphological influence of SA(012) and SA(100) goes beyond rod orientation. There are more grains surrounding the roots of IrO_2 rods illustrated in Figures 26(c) and 26(d) compared with those in Figures 25(c) and 25(d). Those surrounding grains can be understood from the difference in nucleation behavior on SA(100) and SA(012) surfaces. Compared with SA(012), the incubation time is shorter and the nucleation rate is higher on SA(100). Not all nuclei on SA(100) are well oriented un-

FIGURE 26: IrO_2 nanorods on SA(100) patterned by the photolithographic method and selectively grown at 450°C ; (a) a pattern of four-square nongrowth patches, (b) a corner of square patch, along with images showing the nanorods and their surrounding grains at, and (c) a corner, and (d) a border line. (Reprinted from [48] with permission from The Royal Society of Chemistry).

der the CVD condition. The nuclei with their (001) planes parallel with the sapphire (100) plane will grow into vertical nanorods and stand out since they are in a favorite position to receive growth species from the gas phase. The nuclei that do not satisfy the epitaxial relation also grow, but their sizes are limited. As deposition proceeds, they turn into grains surrounding the roots of vertical rods. The size limitation occurs since most of the growth species are intercepted by the vertical rods. The IrO_2 crystals which satisfy the epitaxial relation display the 1D growth feature. The morphological results indicate that the SA(012) surface exerts a tighter control on IrO_2 nucleation than the SA(100) surface.

4. SUMMARY

We review the results of the synthesis of well-aligned 1D IrO_2 nanocrystals on different substrates via reactive radio frequency magnetron sputtering and metal-organic chemical vapor deposition. The 1D growth behavior of IrO_2 is found to be highly correlated to the oxygen-rich ambient, substrate temperature, and the crystal structure of substrates. A strong substrate effect on the alignment of the IrO_2 NCs has been discussed, and the possible explanation for the formation of the oriented IrO_2 NCs structure has been provided.

By designing a series of MOCVD experiments, a morphological evolution of IrO_2 1D nanocrystals has been studied. The as-grown 1D nanostructures have their origin from the interface instability driven by increasing the degree of

supersaturation $\Delta\mu$ and/or reducing substrate temperature T_s . By decreasing the degree of interface instability, the 1D nanostructures evolve from triangular/wedged NRs via incomplete/scrolled NTs to square NTs and square NRs according to their morphological stability. The results show that the 3D grains composing film belong to the most stable form as compared to the 1D nanocrystals and the sequential shape evolution has been found to be highly correlated to a morphological phase diagram based on the growth kinetics. The results could help material scientists and chemists to understand the mechanisms and to control the anisotropic 1D growth for solid and hollow nanostructures from bulk materials.

In addition, area-selective growth of IrO_2 nanorods have been demonstrated on silica-patterned SA(012) and SA(100) substrates by MOCVD. Area-selective chemical deposition is known as a chemical technique to realize patterned thin films, which are essential for many electronic and miniaturized electrical devices. The area-selective growth takes advantage of the nucleation barrier difference between glassy silica surface and sapphire surface. The glassy silica surface serves as the nongrowth surface and the sapphire surface as the growth surface in the selective growth process. The IrO_2 NCs which satisfy the epitaxial relation display the 1D growth feature. The morphological results indicate that the SA(012) surface exerts a tighter control on IrO_2 nucleation than the SA(100) surface.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of National Science Council of Taiwan under the Projects no. NSC95-2120-M-011-001, NSC94-2120-M-011-001, and NSC93-2120-M-011-001.

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