# $IrO_2$ Nano Structures by Metal Organic Chemical Vapor Deposition


Fengyan Zhang*, Robert Barrowcliff*, Greg Stecker*, Deli Wang**, Sheng Teng Hsu*

* Sharp Laboratories of America, Inc.
5700 NW Pacific Rim Blvd, Camas, Washington 98607, USA, Fzhang@sharplabs.com
** Department of Electrical & Computer Engineering
University of California, San Diego
9500 Gilman Drive, Mail Code 0407, La Jolla, CA 92093-0407, USA, dwang@ece.ucsd.edu


## ABSTRACT


This paper will discuss the fabrication of three different shapes of $IrO_2$ nano structures, nanorods, nanotubes and nanowires, using (methylcyclopentadienyl) (1, 5-cyclooctadiene) iridium (I) as the precursor and using Metal Organic Chemical Vapor Deposition (MOCVD) method with no template. Vertically aligned dense array of $IrO_2$ nanorods were fabricated with 100nm in diameter and 500nm-2μm long and with sharp tips at the end. Square shape hollowed $IrO_2$ nanotubes have also been fabricated by tuning the growth conditions. The wall of the nanotubes is only 10-20 nm thick. Also we have successfully grown high aspect ratio single crystal $IrO_2$ nanowires at about 10-50nm in diameter and 1-2 um long. The sharp tip at the end of the nanowire is about 5nm. Detailed experiment conditions for growing these different nano structures will be discussed. Furthermore, single $IrO_2$ nanowire test structure has been fabricated and the electrical properties of $IrO_2$ nanowires were studied.



***Keywords***: $IrO_2$, nanorods, nanotubes, nanowires, MOCVD


## 1 INTRODUCTION

Nano structures, such as semiconductor nano rods and nano wires, have draw more and more attention due to their potential application for nanoelectronics [1-7], optoelectronics [6, 8-11], and sensorics [12-14]. On the other hand, metallic nano structures can be used in nanoscale interconnects [15] and field emission devices [16]. Nano structures can be grown with or without templates using CVD or PVD methods [17-22], the shapes, compositions and crystal structures strongly depend on the processing conditions, the substrates and the catalysts on the substrate surface. A subtle change in any of the above conditions can results in dramatic changes on the physical forms of the nano structures. It will also affect the electrical, mechanical, chemical, and thermal properties of the nano structures that are important properties for integrating them into future nano devices and systems.

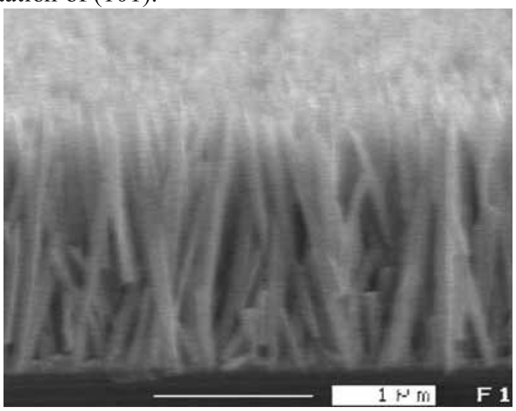
$IrO_2$ is a conductive metal oxide that has stable electrical and chemical properties even at high temperature in $O_2$ ambient [23, 24]. $IrO_2$ can also be used as pH sensor material [25]. This paper will discuss the deposition of varies shapes of $IrO_2$ nano structures using (methylcyclopentadienyl) (1, 5-cyclooctadiene) iridium (I) as the precursor and using Metal Organic Chemical Vapor Deposition (MOCVD) method with no template. Three different shapes of $IrO_2$ nano structures have been successfully synthesized: they are $IrO_2$ nanorods [26], $IrO_2$ nanotubes and high aspect ratio $IrO_2$ nanowires [27]. The $IrO_2$ nanorods and nanowires are good candidates for field emission and sensor applications. $IrO_2$ nanotubes also have the potential to carry chemicals and medicines in bio and medical fields.

## 2 EXPERIMENT

$IrO_2$ nano structures are fabricated using an in house cold wall MOCVD system. (methylcyclopentadienyl) (1, 5-cyclooctadiene) iridium (I) was used as the precursor. The growths were conducted at different pressures and temperatures that are in the range of 10-50 torr and 200-500°C. Oxygen gas was used directly as the carrier gas. The precursor and delivery line were maintained at 80°C. Ti has been used as buffer metal on Si substrate. The $IrO_2$ nano structures were imaged using JEOL JSM 6400F field emission scanning electron microscopy (SEM) with an accelerating voltage of 5 kV. The phase and composition of the nano structure were analyzed by Philips X'pert XRD. For transmission electron microscopy (TEM) studies, the NWs were suspended in ethanol, dispersed onto a lacey carbon film substrate (Ted Pella), and imaged with a JEOL 2010F TEM with an accelerating voltage of 200 kV. The electrical properties of $IrO_2$ nanowires and its temperature dependency were researched by fabricating $IrO_2$ single nanowire test structures. To fabricate the devices, the $IrO_2$ nanowires were dispersed on the $SiO_2$ wafer, followed by Ti metal deposition at 300°C and patterning by photolithography using a regular metal pad arrays. The I-V characteristics were collected using a HP 4156A precision semiconductor parameter analyzer.

## 3 RESULTS AND DISCUSSION

We found that the shapes of $IrO_2$ nano structures are strongly depend on the processing conditions and substrates. In order to grow $IrO_2$ nanorods, the pressure needs to be in the range of 30-50 torr and the growth temperature in the range of 300-400°C. If the pressure is lower than 10 torr or the temperature below 250°C or higher than 450°C, Ir or $IrO_2$ films will be formed. Also sufficient supply of the precursor is critical in order to obtain large array of vertically aligned $IrO_2$ nanorods. Figure 1 shows the SEM images of the $IrO_2$ nanorods. They are aligned vertically and densely with about 100nm in diameter and 500nm-2um long. There are naturally formed sharp tips that make them more ideal for field emission application. The XRD spectrum confirmed that the nanorods are polycrystalline $IrO_2$ with a preferred orientation of (101).

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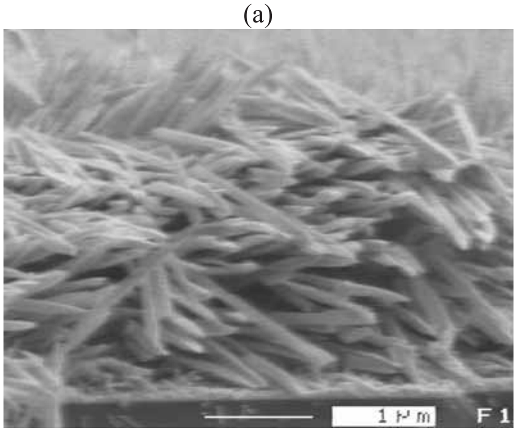


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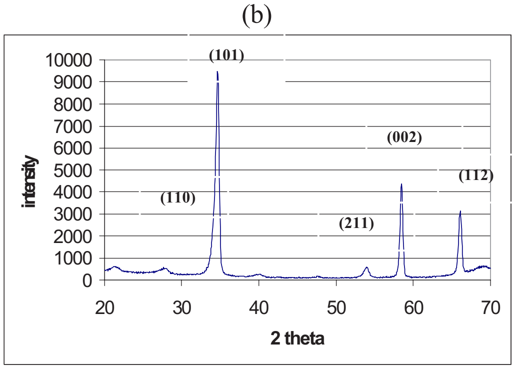


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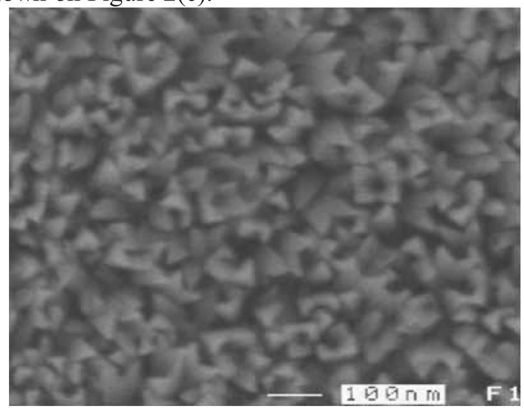
Figure 1. $IrO_2$ nanrods grown by MOCVD
(a) vertically aligned $IrO_2$ nanorods
(b) intentionally bended $IrO_2$ nanorods at the edge to show the sharp tips
(c) XRD spectrum of $IrO_2$ nano rods

We also found that by increasing the initial chamber pressure, hollowed square shape $IrO_2$ nano tubes can be formed. By carefully studying the forming process, we found that these hollowed nanotubes actually started by four nanorods to grow in clusters as shown on Figure 2(a). More interestingly, individual $IrO_2$ nanotubes can be formed on Si substrate with a tube wall as thin as 10-20 nm as shown on Figure 2(c).

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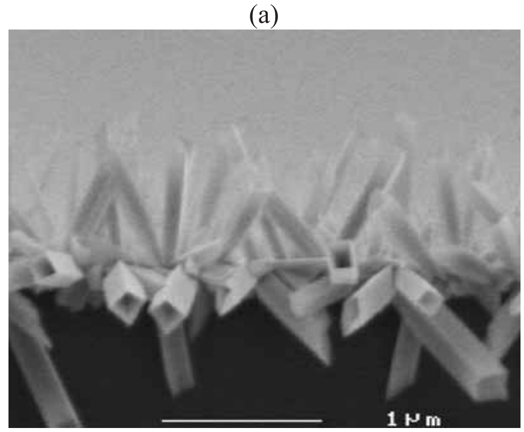


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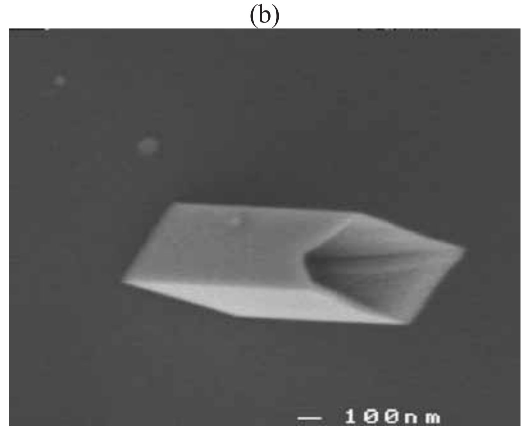
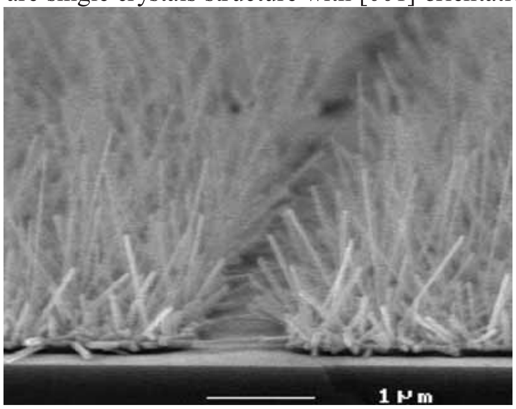



(c)

Figure 2. $IrO_2$ nano tubes grown by MOCVD
(a) cluster growth of $IrO_2$ nanorods
(b) $IrO_2$ nanotubes grown at the wafer edge
(c) Individual $IrO_2$ nanotube grown on Si substrate

Furthermore, by increasing the deposition temperature to 400°C and using Si substrate with a very thin Ti buffer layer, we have obtained very high aspect ratio $IrO_2$

nanowires with naturally formed sharp tips. The nanowires are about 10-50nm in diameter and 1-2 um long. The sharp tip is about 5nm under the HRTEM analysis. Selective growth of $IrO_2$ nano wires has also been achieved by patterning the Ti buffer layer. Unlike the $IrO_2$ nanorods and nanotubes that are polycrystalline structure with some dislocations and defects, HRTEM show that the $IrO_2$ nano wires are single crystals structure with [001] orientation.

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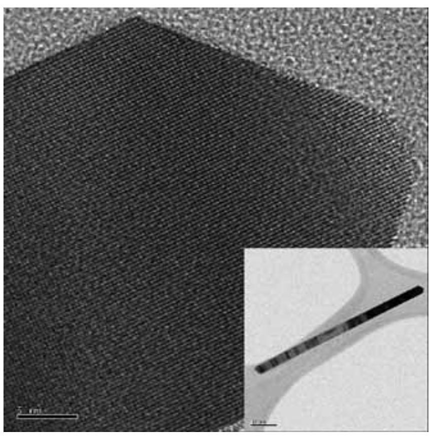

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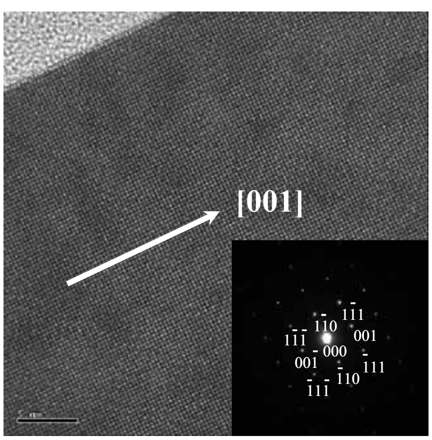
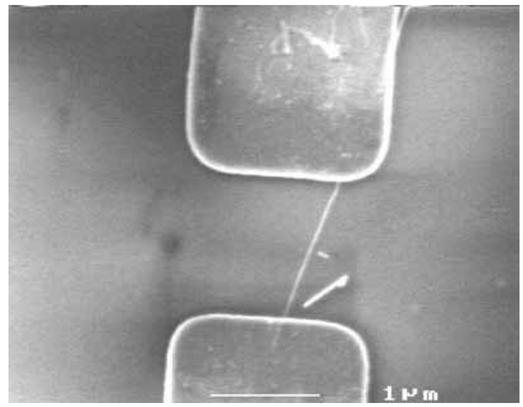



Figure 3. $IrO_2$ nanowires and the TEM analysis
(a) Selective growth of $IrO_2$ nanowires
(b) LRTEM and HRTEM of the tip region of $IrO_2$ nanowires
(c) HRTEM and the diffraction pattern of the $IrO_2$ nanowires

Single $IrO_2$ nanowire test structure has been successfully fabricated. Electrical measurements on $IrO_2$ single nanowire show ohmic contact were achieved between $IrO_2$ nanowire and Ti metal pads with no annealing. The $IrO_2$ nanowires are metallically conducting with a resistance of 2-10 Kohm for a nanowire at about 1 um long and 30-40 nm in diameter. The resistivity of $IrO_2$ nanowire is around 300-400 μohm•cm, which is higher compared to that of bulk $IrO_2$ (32-51 μohm•cm) and $IrO_2$ thin film (80 μohm•cm), most likely due to the surface scattering effect. We also measured the temperature coefficient of resistivity from -40°C to 60°C. As shown on Figure 3(c), the temperature coefficient of resistivity of $IrO_2$ nanowire is about 3 x $10^{-3}$ $K^{-1}$.

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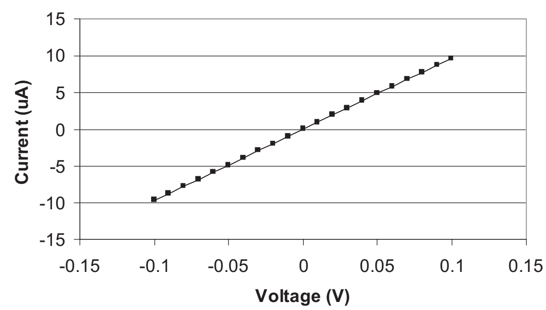


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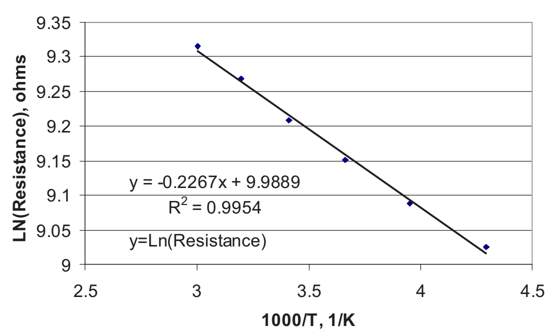


(c)

Figure 3. Electrical characterization of $IrO_2$ nanowires
(a) test structure of single $IrO_2$ nanowire
(b) IV characteristics of $IrO_2$ nanowire
(c) temperature coefficient of resistivity of $IrO_2$ nanowire

## 4 CONCLUSION

We have successfully fabricated three different shapes of $IrO_2$ nanostructures using MOCVD methods without any template. The $IrO_2$ nanorods are vertical aligned dense array with sharp tips at the end that make it a good candidate for field emission applications. The interesting hollowed $IrO_2$ nanotubes has a square shape and a thin wall at 10-20 nm that have a potential application in bio and medical field. High aspect ratio and single crystal $IrO_2$ nanowires can be selective deposited on a patterned Ti buffer layer on Si. It will also have a wide potential application in nanoelectronics, optoelectronics, sensorics and field emission devices.

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