

## Growth of tetragonal SnO<sub>2</sub> microcubes and their characterization

O. Lupan<sup>a,b,\*</sup>, L. Chow<sup>a</sup>, G. Chai<sup>c</sup>, H. Heinrich<sup>a,d</sup>, S. Park<sup>a</sup>, A. Schulte<sup>a</sup>

<sup>a</sup> Department of Physics, University of Central Florida, P.O. Box 162385, Orlando, FL 32816-2385, USA

<sup>b</sup> Department of Microelectronics and Semiconductor Devices, Technical University of Moldova, Stefan cel Mare Blvd. 168, Chisinau MD-2004, Republic of Moldova

<sup>c</sup> Apollo Technologies, Inc. 205 Waymont Court, S111, Lake Mary, FL 32746, USA

<sup>d</sup> Advanced Materials Processing and Analysis Center, Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA

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### ABSTRACT

Single-crystalline SnO<sub>2</sub> microcubes were grown using the hydrothermal method without any catalyst. X-ray diffraction (XRD) patterns and energy dispersive X-ray (EDX) analysis verified that the cubes are tin dioxide SnO<sub>2</sub>. Their morphology and structure was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and Raman spectroscopy. It is revealed that the cube-shaped SnO<sub>2</sub> crystal have dimension varying from 500 nm to 5 μm as a function of chemical concentration and hydrothermal temperatures regimes. According to TEM results the cube axes are [001] direction and the side surfaces are {110} planes. A growth mechanism of SnO<sub>2</sub> cube-shaped crystals has been proposed.

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## 1. Introduction

Tin oxide (SnO<sub>2</sub>) microcrystals have attracted researchers attention due to their unique properties [1] and because of their wide applications in the field of optical waveguides [2], ultra-sensitive gas sensors [3], transistors [4], photosensors and solar cells [3,5]. Uniform shape and size controls are of fundamental and practical importance due to their unique shape-dependent properties of material [6–8]. Different strategies, such as, laser ablation, thermal evaporation, carbothermal reduction have been investigated in order to grow cubes of transition metal oxides [9,10], chalcogenides [11], transition metals [12]. So far only one report on SnO<sub>2</sub> microcubes from self-assembled nanorods [13] was reported. Recently, researchers' attention were focused on the hydrothermal technique and aqueous solution synthesis of various metal oxides [14,15]. These methods have been note-

worthy as a new fabrication technique of functional materials at relatively low-processing temperatures. By controlling the nucleation sites, the coordination states of coexisting species, supersaturated and kinetic growth regime in aqueous system it is possible to enable the construction of novel architecture through crystal growth.

In this paper, we report the results of a hydrothermal synthesis of SnO<sub>2</sub> cubes (which are not reported till date) and size-control of these cubes by varying reaction condition. The importance of the present technique is its simplicity and no sophisticated equipments are required.

## 2. Experimental procedure

In a typical synthesis route, SnCl<sub>2</sub> · 2H<sub>2</sub>O and NH<sub>4</sub>OH (29.5%) solution (from Fisher Scientific) were dissolved in a 100 ml aqueous solution (deionized water with resistivity about 18.2 MΩ cm added with a 5 ml of HCl (36%)). The solution was stirred for 5 min at room temperature until it became homogeneous. A silicon wafer and microscopic glass slide cleaned according to previous work [16,17] were used as substrates. After mixing, the

\* Corresponding author at: Department of Physics, University of Central Florida, P.O. Box 162385, Orlando, FL 32816-2385, USA. Tel.: +1407 823 5217; fax: +1407 823 5112.

E-mail address: [lupan@physics.ucf.edu](mailto:lupan@physics.ucf.edu) (O. Lupan).

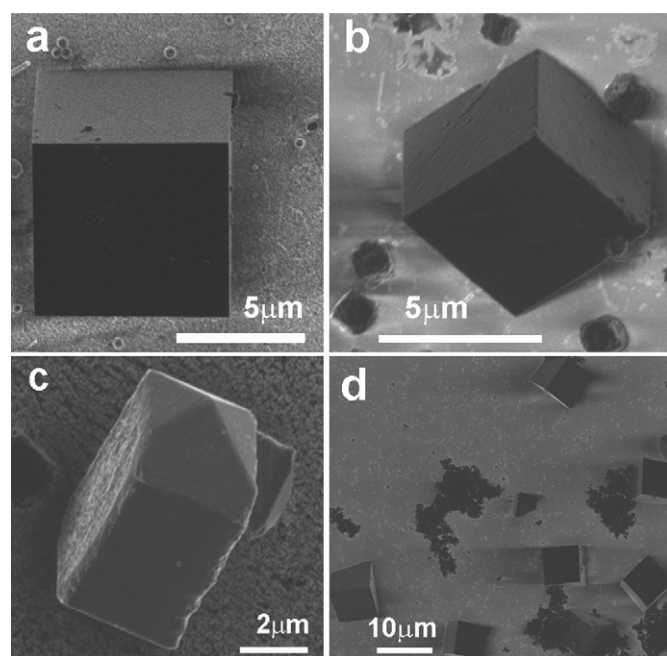
solution was transferred in a glass beaker with a sphericalconcave cap with the radius of curvature of the surface of 10 cm and an orifice (1 mm in radius) on the side [14]. The system was heated to 98 °C and kept for 15 min, then was allowed to cool to 40 °C naturally. The products synthesized by described method were then annealed at 370 °C for 10 min.

Synthesized material was analyzed and characterized by scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM) (a FEI Tecnai F30 TEM), X-ray diffraction (XRD), (Rigaku) and Raman spectroscopy. For the TEM observation, the products were collected on a carbon holey grid. The Raman spectra were obtained using a Horiba Jobin Yvon LabRam IR system with a spatial resolution of 2 μm. He–Ne laser was used as an exciting source. This unit delivers <4 mW at the sample at 633 nm and was used in this study with a spectral slit width of approximately 2 cm<sup>-1</sup>.

### 3. Results and discussion

Fig. 1(a) displays SEM images of the cube-shaped SnO<sub>2</sub> crystals grown by a hydrothermal method on silicon (100) substrates using 15–25 mM SnCl<sub>2</sub>·2H<sub>2</sub>O. Fig. 1(a) and (b) shows, respectively, SEM of tin oxide microcubes with length of each side about 5–8 μm and smaller cubes with length of each side about 500 nm. Different sizes were obtained by changing the concentration using 30–40 mM SnCl<sub>2</sub>·2H<sub>2</sub>O and by varying the kinetic growth regime, thus for sample shown in Fig. 1(b) temperature gradient was lower by 0.5 °C/s, than for sample shown in Fig. 1(a).

Each face of the SnO<sub>2</sub> microcubes is a square. Evidence of the faultless shape is given by the SEM image (Fig. 1(a) and (b)) where eight vertices and six faces can be observed. Every face is not only flat and smooth, but also is perpendicular to its adjacent faces.

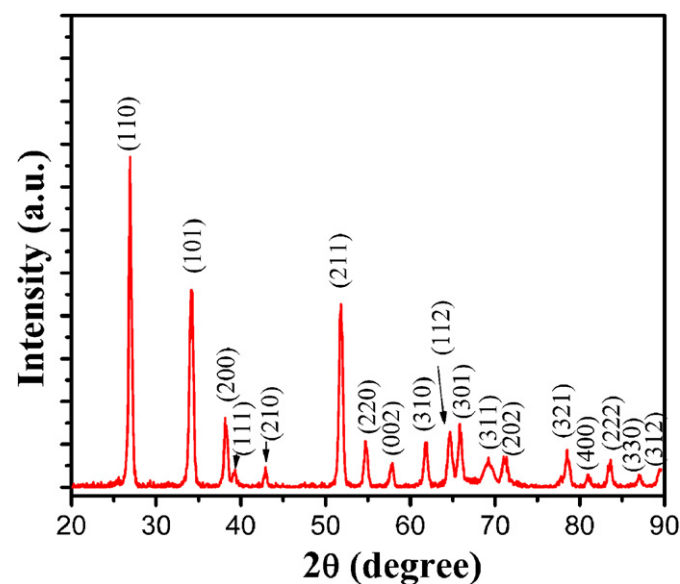


**Fig. 1.** SEM images of the (a) typical as-synthesized SnO<sub>2</sub> microcube grown by using 15–25 mM SnCl<sub>2</sub>·2H<sub>2</sub>O in aqueous solution; (b) different sizes SnO<sub>2</sub> microcubes grown by using 30–40 mM SnCl<sub>2</sub>·2H<sub>2</sub>O in aqueous solution; (c) SnO<sub>2</sub>-pyramided architecture obtained by second process at 80 °C and (d) lower magnification view showing monodisperse SnO<sub>2</sub> cubes distributed on substrate surface.

The general morphology of the different sizes microcubes are shown in Fig. 1(b), which shows that in addition to the larger microcubes, there are also smaller cubes. Growth of two types of cubes bigger (length of each side 5–8 μm) and smaller (length of each side 0.5 μm) for the anisotropic crystal can be adjusted by balance between the thermodynamic and the kinetic growth regimes. Also, as the quantity of the nuclei depends on the concentration of the precursor we observed that by increasing the concentration of Sn(OH)<sub>6</sub><sup>2+</sup> generated more nuclei, which benefits the formation of nanocrystals with smaller cubes as displayed in Fig. 1(b). The hydrothermal route was performed at 80 and 98 °C. The crystals grown at 80 °C have curved and imperfect faces, irregular shape, corners and rough surface (Fig. 1(c)). Fig. 1(c) shows the SEM image of a tin oxide pyramided architecture grown at 80 °C for the same duration of heating. In Fig. 1(d) a lower magnification image of SnO<sub>2</sub> cubes synthesized on silicon substrate is presented.

The chemical composition of the microcubes was determined by EDX to be pure tin oxide. The XRD pattern is shown in Fig. 2, which reveals the crystal structure and phase purity of the as-synthesized microcubes. All of the diffraction peaks can be indexed to the tetragonal SnO<sub>2</sub> structure with lattice parameters  $a = b = 4.738 \text{ \AA}$  and  $c = 3.188 \text{ \AA}$  (JCPDS 041-1445). No characteristics peaks of other forms of tin oxide were detected.

Fig. 3(a) shows a typical high-resolution (HRTEM) image of one edge of the cube-shaped SnO<sub>2</sub> crystal. In the inset in Fig. 3 is the selected area electron diffraction (SAED) pattern of SnO<sub>2</sub> microcubes. The spacing between the lattice planes along the cube height and the width are 0.32 and 0.33 nm, which are in agreement with distance between (001) and (110) planes of rutile SnO<sub>2</sub>, respectively. The growth direction for the cubes can be determined from SAED patterns. This confirmed that it grew along [110] direction in lateral sides (indicated with an arrow, perpendicular to the axis of a microcube). The distance separation between lattice layers are found to be 0.33 nm corresponding to lattice parameters of the rutile structure of SnO<sub>2</sub> [110] reflection. No dislocations or other planar defects were detected in the examined area of SnO<sub>2</sub> cubes. The growing is along [001] and [110] directions in vertical and horizontal planes, respectively, which is in accordance with the “lowest energy” argument.



**Fig. 2.** A typical X-ray diffraction (XRD) pattern obtained by using CuK $\alpha$  radiation 1.5406 Å of SnO<sub>2</sub> microcubes obtained by the aqueous solution method.

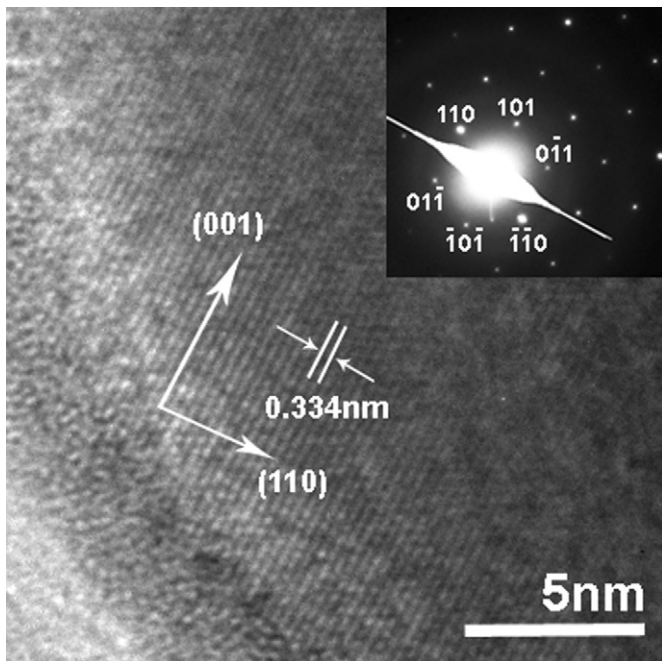


Fig. 3. (a) HRTEM micrograph of SnO<sub>2</sub> microcubes grown at 95 °C and (b) SAED image of SnO<sub>2</sub> microcubes.

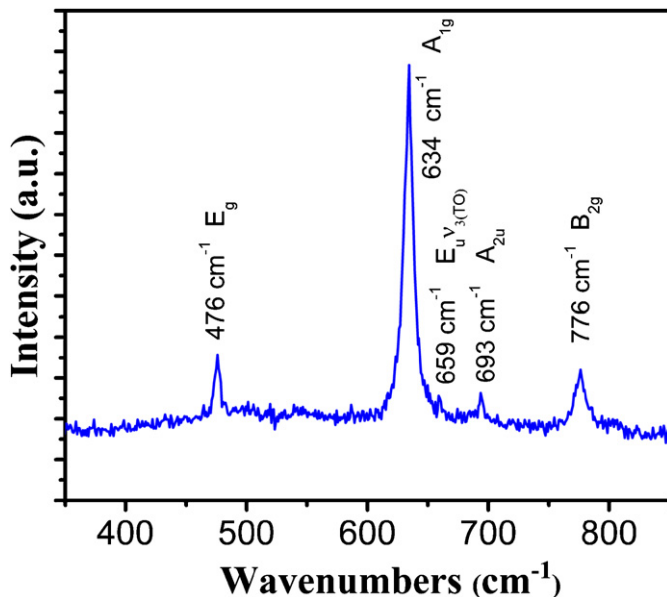


Fig. 4. Micro-Raman scattering spectra of the cube-shaped tin oxide crystal.

Fig. 4 shows micro-Raman spectra of the as-grown SnO<sub>2</sub> cube at room temperature. The tetragonal structure of SnO<sub>2</sub> belongs to the space group D<sub>4h</sub><sup>14</sup> (P4<sub>2</sub>/mm) with square pyramid as its thermodynamically stable crystallographic form and has two SnO<sub>2</sub> molecules per unit cell. It has a ditetragonal bipyramid type of symmetry and according to group theory [18] the normal lattice vibration at the  $\Gamma$  point of the Brillouin zone is as follows [19]:

$$\Gamma = \Gamma_1^+(1A_{1g}) + \Gamma_2^+(1A_{2g}) + \Gamma_3^+(1B_{1g}) + \Gamma_4^+(1B_{2g}) + \Gamma_5^-(1E_g) + \Gamma_1^-(1A_{2u}) + 2\Gamma_4^-(B_{1u}) + 3\Gamma_5^+(E_u) \quad (1)$$

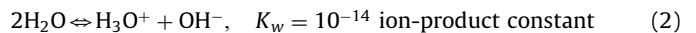
where the A<sub>1g</sub>, B<sub>1g</sub>, A<sub>2g</sub> and E<sub>g</sub> modes are Raman active and A<sub>2g</sub> and B<sub>1u</sub> modes are inactive.

In Fig. 4, there are peaks at 476, 634, 659, 693, and 776 cm<sup>-1</sup> in the Raman spectrum which are in agreement with those of a rutile

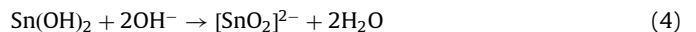
SnO<sub>2</sub> single crystal [20] and are in agreement with the data from group-theory analysis also [21,22]. These peaks are attributed to the E<sub>g</sub>, A<sub>1g</sub>, (A<sub>u</sub>)v<sub>3(TO)</sub>, A<sub>2u</sub>, and B<sub>2g</sub> vibrational modes of SnO<sub>2</sub> [23]. These modes confirm the rutile structure of SnO<sub>2</sub> cubes. In comparison with the SnO<sub>2</sub> powder, additional Raman bands at 659 and 693 cm<sup>-1</sup> can be observed in the SnO<sub>2</sub> micron cube-shaped crystals, which can be attributed to the (E<sub>u</sub>)v<sub>3(TO)</sub>, IR-activated (A<sub>2u</sub>)v<sub>(LO)</sub> for LO, calculated theoretically [24] and also observed experimentally [25].

#### 4. A proposed growth mechanism

A proposed growth mechanism for SnO<sub>2</sub> micron cube-shaped crystals, in terms of chemical reactions and crystal growth is described here. From the crystallization point of view, the formation of an oxide during of an aqueous solution reaction is expected to experience a hydrolysis–condensation (nucleation–growth) process. The growth process of SnO<sub>2</sub> microcubes can be simplified as the following reactions [26,27]:



At the beginning in aqueous solution with an OH<sup>-</sup> excess, a higher Sn<sup>2+</sup> ion concentration accelerates the nucleation process [27] and nuclei are formed

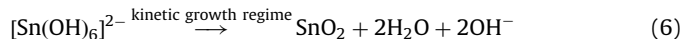


The amphoteric hydroxide dissolves in excess of ammonia solution and forms [Sn(OH)<sub>4</sub>]<sup>2-</sup> anions



The amphoteric hydroxide [Sn(OH)<sub>4</sub>]<sup>2-</sup> dissolves in ammonia solution and forms [Sn(OH)<sub>6</sub>]<sup>2-</sup> anions.

During the hydrothermal reaction, the [Sn(OH)<sub>6</sub>]<sup>2-</sup> ions decomposed into SnO<sub>2</sub>



The formation of cube-shape SnO<sub>2</sub> structures was fundamentally achieved with the progress of the crystal growth. The concentration of tin ions in solution is of influencing to the size of cubes. The kinetic growth regime during the hydrothermal reaction is a decisive factor in formation of cube-shaped crystals. Also, the hydrothermal temperature is an important factor affecting tin oxide growth. In Fig. 1 images of different SnO<sub>2</sub> cubes and architectures synthesized on substrate are presented. We also observed that increasing the temperature and extending the heating duration will lead to an increase of the volume sizes of cubes. Different shapes cubes were obtained at 80 °C (pyramided architecture shown in Fig. 1(c)), but no crystals deposition occurred at temperatures lower than 80 °C.

In our experiments, the hydrothermal process using described reaction media allows a slow nucleation and growth at low-interfacial tension conditions, which favors the generation of cube-shaped SnO<sub>2</sub> crystals. The growth mechanism of perfect shaped SnO<sub>2</sub> microcubes can be explained on base of its rutile structure, which is 6:3 coordinated and the bonding between atoms has a strong ionic character. The synthesized material is a cube-shaped crystal because of the tetragonal unit cell containing two tin atoms and four oxygen atoms. As was determined experimentally, the crystal growth is enclosed by the stable (110) facets, thus the rutile structure is built up from neutral stacked layers of the following planes (O), (2Sn+O), and (O) with

ionic charges 2–, 4+, and 2–, respectively, in the surface unit cell. In this way, a termination is possible with these planes of the tin oxide (110) called a stoichiometric surface. According to our results tin oxide can grow from solutions in well-defined cubic edges and giving a proper morphology. Understanding of the growth mechanism of cubic structure is very important for the synthesis of new materials as well as for device applications.

Thus, by carefully adjusting the balance between the thermodynamic and kinetic growth regimes, crystals with geometrical morphology consistent with their crystallographic structure can be formed. Also by controlling the kinetic growth regime the anisotropic growth along the high-energy crystallographic face can be promoted [28]. It is known that tin oxide with rutile structure belongs to the (P4<sub>2</sub>/mnm) space group with square pyramid as its thermodynamically stable crystallographic form [18,29]. According to theoretical studies [30,31] it is suggested that the surface energy sequence of SnO<sub>2</sub> is  $E(110) < E(100) < E(101) < E(001)$ . Thus, the (110) surface which is the most thermodynamically stable [30] and the plane (110) with the lowest surface energy for SnO<sub>2</sub> has preferential growth and would be expected to feature predominantly in the cube morphology. In this way the (110) lateral growth can be explained and cube-shaped tin oxide crystals can be realized through the chemical reaction in a non-equilibrium kinetic regime using a hydrothermal process.

## 5. Conclusion

In summary, SnO<sub>2</sub> microcubes were successfully synthesized by a simple hydrothermal method. XRD, TEM, SEM, EDX and Raman spectroscopy reveal that the SnO<sub>2</sub> cubes surfaces are very smooth, and are of a crystalline rutile structure. The vertical growth direction is [001] and the side-faces of SnO<sub>2</sub> are {110} planes. The obtained structures can be used for further studies of lattice dynamics of rutile. Peaks at 476, 634, 659, 693, and 776 cm<sup>-1</sup> in the Raman spectrum which are in agreement with those of a rutile SnO<sub>2</sub> single crystal [20] and they are attributed to the E<sub>g</sub>, A<sub>1g</sub>, (E<sub>u</sub>)v<sub>3(TO)</sub>, A<sub>2u</sub>, and B<sub>2g</sub> vibrational modes of SnO<sub>2</sub> [23]. These modes confirm the rutile structure of SnO<sub>2</sub> cubes. Proposed synthesis process is easy and cost-effective, as the microcubes growth was carried out in an aqueous solution, which does not require any sophisticated equipment. Also, a crystal growth mechanism for cube-shaped SnO<sub>2</sub> crystals has been proposed. These findings have significant scientific and technological implications in crystal growth topic may gain greater importance due to the necessity in controlling shape and size of the synthesized materials.

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