

Preparation and Characterization of Tin Oxide Nanowires

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Abstract

The aim of this research is preparation of SnO₂ nanowires by means of Thermal chemical reaction vapor transport deposition (TCRVTD) method from SnO powders. The morphology, chemical composition and microstructure properties of the nanowires are characterized using field emission scanning electron microscope (FE-SEM), EDS, and XRD. The XRD diffraction patterns reveal that the SnO₂ nanowires have been grown in the form of tetragonal crystal structures with the lattice parameter of a=b=0.440 nm, and c=0.370 nm. The SEM images reveal that SnO₂ nanowires have successfully been grown on the Si substrate. The EDS patterns show that only elements of Sn, O and Au are detected. Prior to the VLS process the substrate is coated by a thin layer of Au. The diameter of nanowires is measured to be something between 20-100 nm.

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1. Introduction

In the last decade, semiconducting oxide 1D nanomaterials have attracted considerable attention because of their unique electrical, optical, and mechanical properties as a result of their low dimensionality and the quantum confinement effect. Among these semiconductors, the rutile form of SnO₂ is one of the interesting materials. It is an n-type semiconductor with a wide band gap of 3.6 eV at room temperature. It is well known for its applications in gas sensors, capacitors, transistors, and solar cells. It has very large exciton binding

energy (130 meV), even larger than that of ZnO (60 meV). Some of the synthesized semiconductor nanowires are based on the vapor-liquid-solid (VLS) mechanism of anisotropic crystal growth. This mechanism was first proposed for the growth of single crystal silicon whiskers 100 nm to hundreds of microns in diameter.

Metal oxide semiconductor nanowires such as: SnO₂, TiO₂, WO₃, ZnO, Fe₂O₃ and In₂O₃ have attracted significant attentions of the researchers due to their fundamental and wide range of applications in the nano-devices [1-2]. Among these

semiconductors, tin oxide is in the particular interest and it widely used in the gas sensors, because of its high mobility of conduction electrons, good chemical and thermal stability under the operating conditions [3]. SnO_2 is also used in capacitor, transistors, and solar cells [4].

The proposed growth mechanism involves the absorption of source material from the gas phase into a liquid droplet of catalyst (a molten particle of gold on a silicon substrate in the original work). Upon supersaturation of the liquid alloy, a nucleation event generates a solid precipitate of the source material. This seed serves as a preferred site for further deposition of material at the interface of the liquid droplet, promoting the elongation of the seed into a nanowire or a whisker, and suppressing further nucleation events on the same catalyst [5].

In this research, SnO_2 nanowires have been synthesized by *thermal chemical reaction vapor transport deposition* (TCRVTD) method from SnO powders. This material has a potential application to make gas sensor.

2. Experiments

Vapor liquid solid is a process in which the powder material source is vaporized at an elevated temperature and the resultant vapor phase condensed under certain conditions (temperature, pressure, atmosphere ...) to form the desired products. In this work VLS process carried out in a home made horizontal tube furnace with quartz tube (50 mm in diameter and about 60 cm in length). SnO powder (Alfa Aesar, 99.9%) served as the source and was placed in a quartz boat. N-type silicon wafers (1cm×1cm) coated with thin layers of gold (prepared by evaporation technique) were used as substrates. The Au layer thickness was about 5 nm. Prior to the growth process, the gold coated silicon substrates were annealed in the temperature

of 500°C for 30 minutes in order to break the continuous Au layer to several separated islands. Because of temperature gradient in the tube furnace, the optimum distance between powder and substrate was chosen to be 12 cm. The powder source was placed in the furnace tube closed to the substrate. Prior to the Ar flow, the furnace tube is evacuated using a rotary pump (Fig.1). The nanowires growth was carried out at temperatures, varying between 700 and 900°C for 60-180 minutes with a constant flow of argon at the rate of 60-100 sccm.

The field-emission scanning electron micrographs (FE-SEM) of the grown samples were recorded using a Hitachi S4160 (Cold Field Emission) system. Energy dispersive spectroscopy (EDS) diagrams were recorded by a VEGA\\TESCAN-LMU scanning electron microscope. X-ray diffraction spectra were recorded by a Philips X-Pert PRO diffractometer with $\text{CuK}\alpha$ ($\lambda = 0.1548$ nm) radiation operated at 45 kV and 40 mA with a grazing incidence of 2.0°.



Fig. 1. Experimental set-up for synthesis of SnO_2 nanowires.

3. Results and discussion

Structural studies

The nanowires were grown at two different growing temperatures i.e. 700 and 900°C. Fig. 2 shows the FE-SEM micrograph of SnO_2 samples grown at temperature of 700°C for 60 min. As the figure shows at this growth condition no nanowire has been grown. However some grains consisting of

the SnO₂ molecules have been formed. Although increasing temperature to 900°C does not still lead to nanowire growth but make the grains more uniform.

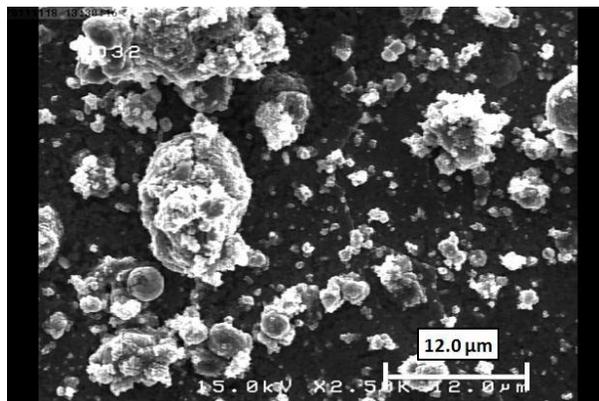


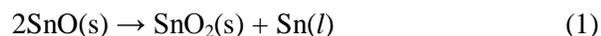
Fig. 2. Forming SnO₂ grains after annealing the sample at temperature of 700 °C for 60 min.

Effect of temperature and time on nanowires growth

In order to study the effect of temperature on the nanowire synthesis, the samples were annealed at temperature of 900°C for much longer time (up to 180 minutes). Increasing annealing temperature eventually leads to nanowire growth. The longer the annealing time the longer nanowires have been achieved. In this process as the temperature increases, gold droplets move on the surface and the vapors have been condensed and the nanowires begin to growth. Fig. 3 shows the SEM pattern of a sample annealed at temperature of 900°C for 180 minutes.

Effect of gas flow rate and vacuum pressure on nanowires growth

The source material (SnO) is thermodynamically unstable. The following reaction occurs at a temperature as low as 370°C:



where the symbols of *s* and *l* represent the *solid* and *liquid* states respectively. Under our experimental conditions (annealing at the temperature of 900°C),

the reaction product, Sn, remains in a liquid state because of its low melting point (231.9°C).

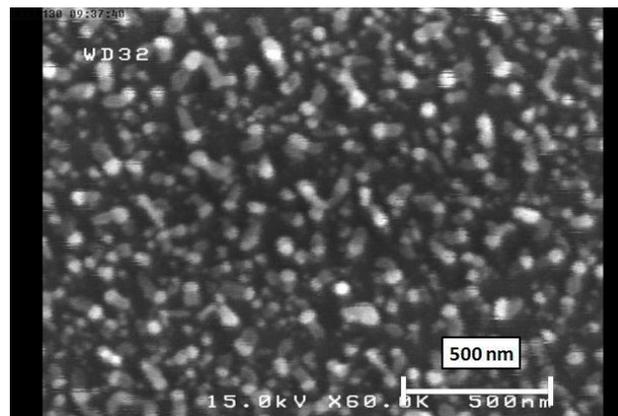


Fig. 3. start of nanowires growth during 180 min and 900°C.

Therefore, Sn will be easily vaporized at high temperature, and by carrier gas be transferred into the substrate place. The Sn steam is condensed on the local substrate due to the temperature gradient and absorbed by gold nano-particles, forming Sn-Au alloy droplets. These droplets are good sites for adsorbing the Sn steam and oxygen molecules. The final precipitation occurs when the liquid droplets become supersaturated with the metal source, and the SnO₂ nanowires are formed. The light spots on the nanowires tip observing on the SEM images (Figs. 4 and 6), are due to the gold nano-particles, indicating that the nanowire growth process is VLS. EDS diagrams confirm that the presence of some gold on the nanowire tips' and Au particles are not agglomerated and nor mixed with the wires (Fig.7).

The gas flow rate is an important parameter on nanowire growth and it should kept constant in an optimum value. If the gas flow rate is too high, the vapor might be removed from the substrate and no SnO powder can be deposited on the gold substrates. Thus blowing low gas flow rate in the furnace is a crucial parameter in the nanowire synthesis. Fig. 4 shows the FE-SEM micrograph of some nanowires grown in the above described conditions.

The optimum growth condition was found to anneal the sample at 900°C for 180 min under constant Ar flow of 60 sccm and tube vacuum pressure of 300 torr. In order to reaction 1 takes place, presence of the oxygen molecules is also necessary. However, the required oxygen molecules are very low (less than 10%) which usually exist in the tube environment, no need to flow the oxygen gas.

Growth mechanism

There is a well established method for the growth of nanowires, i.e. the catalyst assisted vapor–liquid–solid (VLS) [6, 7] method. VLS mechanism of SnO₂ nanowires growth starts as follow (reaction 1): Solid SnO will be transform to liquid Sn and solid SnO₂. They then evaporate molecularly in the temperature near the SnO melting point and forward on gold layer by Ar flow. In the VLS process, the thin layer of deposited Au catalyst breaks up to form liquid nanodroplets at high temperature. These metal droplets form a liquid phase with the incoming molecular vapors above the eutectic temperature. Finally, upon the supersaturation of the solute species, nanowires start growing with the metal nanoparticles at their tips. Thus, a key signature of the VLS growth process is the presence of the metal nanoparticles at the tips of the nanostructures.

As mentioned earlier, the observed Au metal nanoparticles at the end of each nanowire, confirms the vapor–liquid–solid mechanism. Fig. 5(a) shows the schematic diagram of the proposed growth mechanism of SnO₂ nanowires by VLS process. However, a number of nanowires with branched structure have been observed. Interestingly, the metal gold tips are still observed at the end of each branches of the nanowire. The schematic diagram of formation mechanism of branched nanowires is depicted in Fig. 5(b).

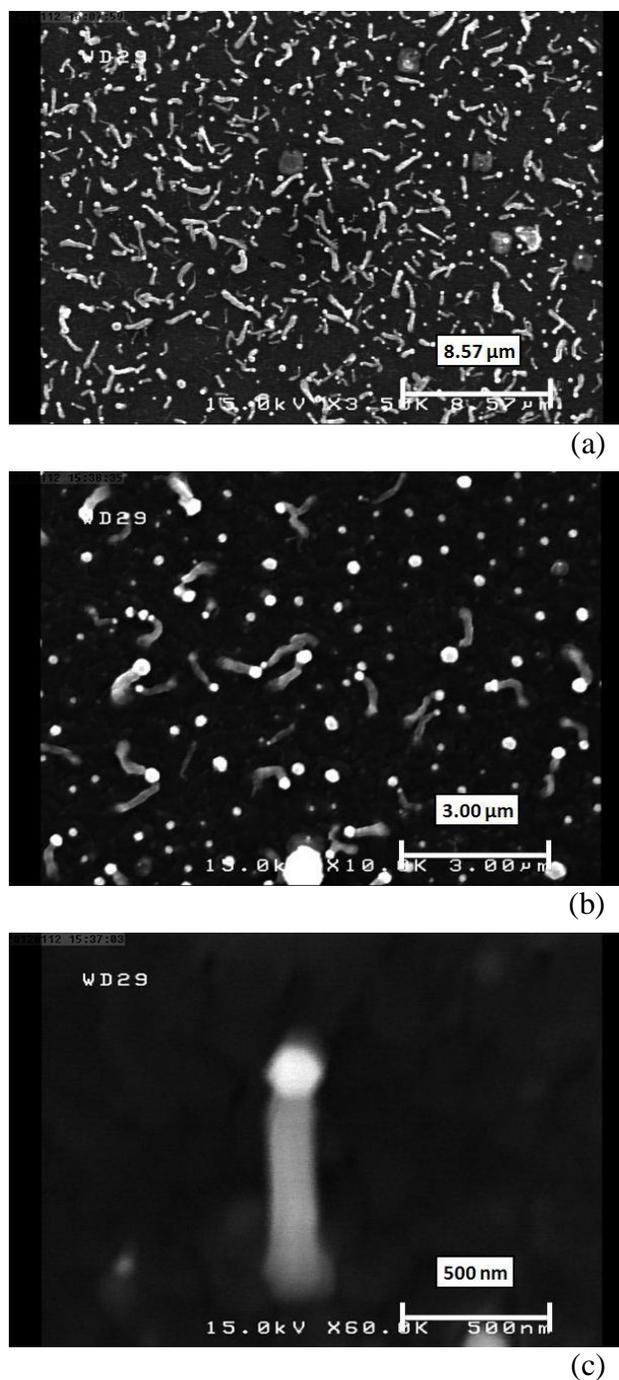


Fig. 4. The SEM images of substrate surface and grown nanowires in different magnifications. Presence of gold in the nanowires' tip justifies VLS mechanism. The images were taken at (a) 8.57 μm, (b) 3 μm, and (c) 500 nm scales.

These Au droplets act as secondary nucleation centers on the nanowire surfaces, which then grow by VLS process.

Unsuitable condition of Ar flow is higher than 100 or less than 60 sccm. In higher or less than this interval, molecular vapors cannot condense on the substrate. In the higher flow rates, the vapors fly above the substrate and in the lower flow rates they cannot push the vapors.

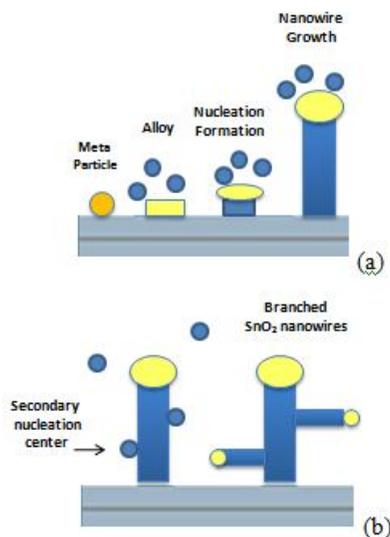


Fig. 5. (a) Schematic diagram of SnO₂ nanowires growth (b) branched of SnO₂ nanowires.

The sample position in the furnace is an important parameter which can influence on the nanowires growth. This matter is illustrated in Fig. 6. Fig. 6 shows the nanowires on the edge of substrate. Unlike many research groups who found that the nanowires mainly grow when the substrate is horizontal [8-20], we surprisingly observed SnO₂ nanowires growth on diagonal substrate, and presence of them in the substrate edges, is dominated.

Fig. 7(a) confirms that the compositions of the SnO₂ nanowire tips' consist of Sn and O. The O peak comes from the surface oxide of nanowire tips'. Fig. 7 (b) shows that the gold particles act as catalyst. Presence of oxygen in the furnace tube leads to mixture of Au and O₂ gases. The Si peak in the EDS spectra could be due to the sample substrate.

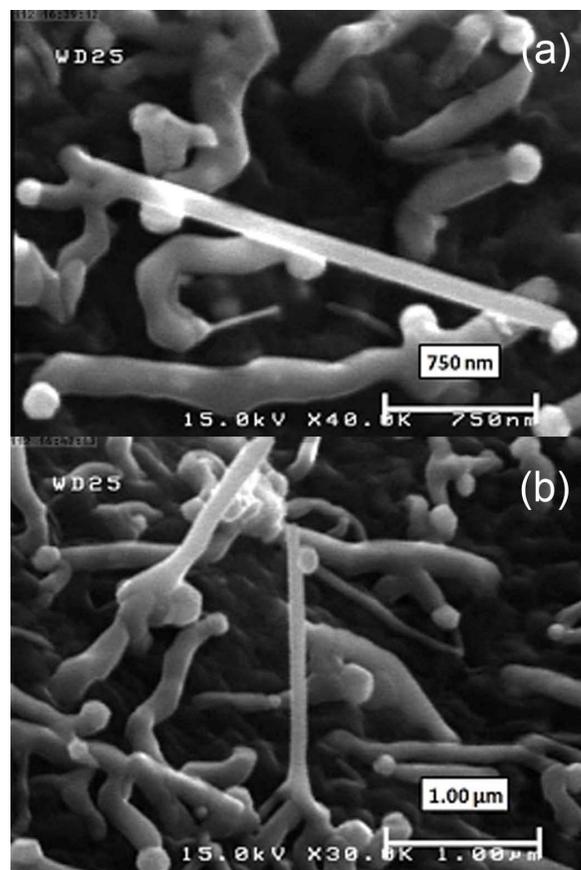


Fig. 6. Nanowire growth on cross section of substrates. Figures (a) and (b) show long nanowires with 100 nm in diameter and 2 μm in length (in two different magnifications).

Fig. 8. shows the schematic of the samples positions in the furnace. The substrates are not laid horizontally.

As it shows in Fig. 6 a large number of nanowires (with diameter of 100 nm) have been grown in the edges of substrate. The lengths of many of them are longer than 1 μm. The average size of wires diameters and lengths were measured using software called "Particle Size Measurement". Since the substrates are coated by a thin layer of gold, the substrate edges are also coated by gold, making them suitable places for nanowires growth.

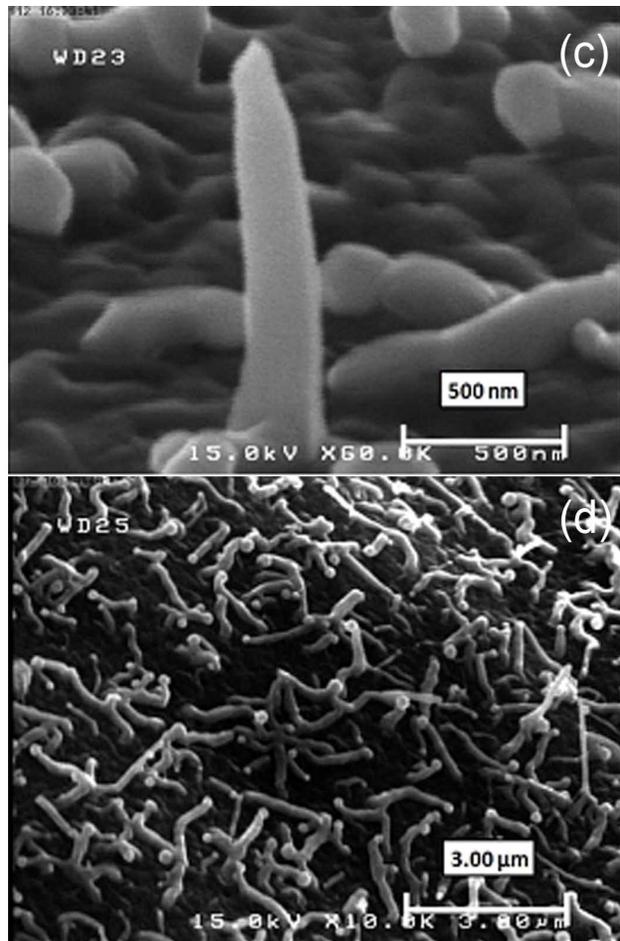


Fig. 6. Figure (c) shows the vertically grown nanowires. Figure (d) shows a large number of nanowires grown on the edge of substrate.

Cutting the silicon substrate in smaller pieces, makes the substrate edge rough. This could be the reason for observation of rough surface in the neat of the nanowires in Fig. 6. Interestingly, due to the existence of a temperature gradient in the furnace, some wires have been grown vertically.

Fig. 9 (a) shows X-ray diffraction patterns of the nanowires grown at 900°C at the grazing incidence (2.0°). The X-ray diffraction patterns in comparison to peak list (Fig.9 (b)) reveal that the SnO₂ nanowires have been grown in the form of tetragonal crystal structures whit the lattice parameter of a=b=0.440 nm, and c=0.370 nm.

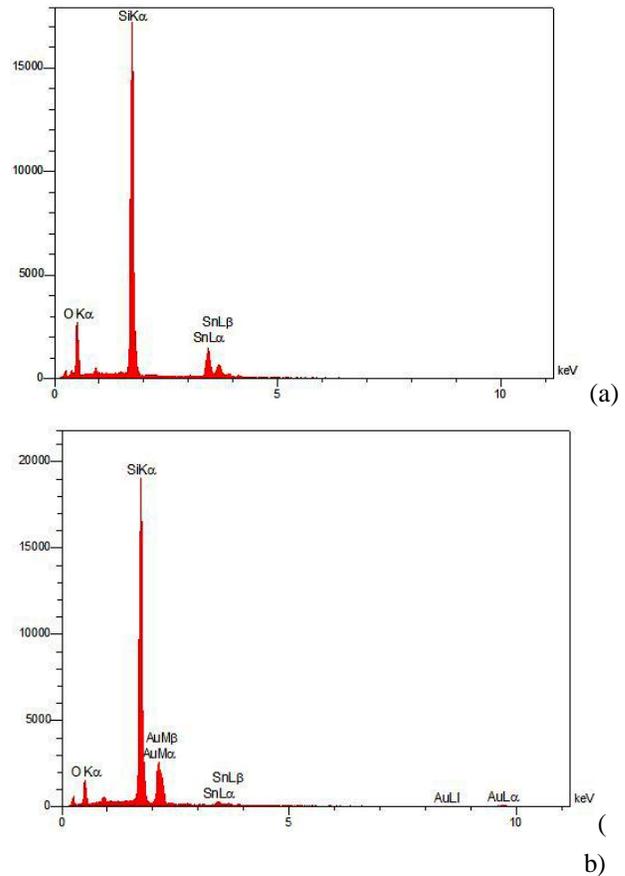


Fig. 7. EDS diagrams of SnO₂ nanowires. (a) captured from wires , (b) captured from Au tips.

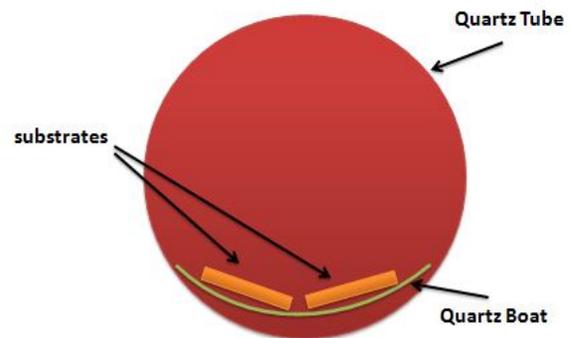
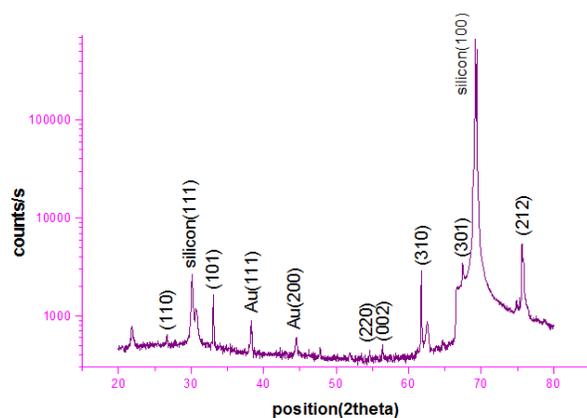


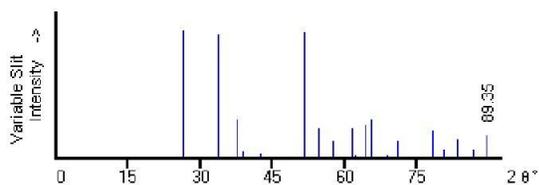
Fig. 8. Schematic of the samples positions in the furnace. The substrates are not laid horizontally.

All of the peaks can be attributed to the SnO₂ and there is no trace of SnO and Sn phases in these nanowires. The SnO₂ have low intensity; implying nanoscale size of nanowires. The (100)-Si peak is also appears that obviously due to the substrate. The

other peaks are due to gold which is used as the catalyst element.



(a)



(b)

Fig. 9. (a) XRD pattern of SnO₂ nanowires synthesized by VLS mechanism, (b) peak list of primitive lattice of SnO₂ in tetragonal phase.

4. Conclusions

We have successfully synthesized SnO₂ nanowires using thermal chemical reaction vapor Transport deposition technique. The effect of temperature, gas flow rate, pressure and growth time are extensively studies and optimized. It has been revealed that in temperatures lower than 700°C, growth times shorter than 90 min, pressures lower than 300 torr and gas flow rates higher than 60 sccm no nanowire would be grown. We also found that if the substrate is mounted in the furnace diagonally (faced to the flow of molecular vapor), a large number of wires are grown.

A possible explanation for this result could be due to displacement of gold drops on the substrate (due to the gravity force) and producing SnO₂ nanowires. The growth SnO₂ nanowires are characterized using field emission scanning electron microscopy and X-ray diffraction.

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