

Indium tin oxide nanowires growth by dc sputtering

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Abstract Indium tin oxide nanowires have been grown by dc sputtering on different substrates without the use of catalysts or oblique deposition. The nanowire length was of the order of several μm , while their diameter was ~ 50 – 100 nm. Small side branches on the nanowires were frequently observed. The nanowires were characterized by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The growth mechanism of the nanowires is discussed.

1 Introduction

Transparent conductive oxide films are materials that are both conductive and have high transmittance in the visible spectral range [1–3]. Therefore, they are of interest as functional coatings, for example in energy efficient windows [2], as well as contacts in solar cells [2] and light-emitting diodes [3]. They are typically deposited in thin film form, by various techniques such as sputtering, pulsed laser deposition, evaporation, chemical vapor deposition, solution-based methods, spray pyrolysis, etc. [1, 2]. Among various transparent conductive materials, indium doped tin oxide (ITO) has been demonstrated to have low resistivity for a range of different deposition methods [1]. Consequently, it is widely

used in optoelectronic devices, such as displays, solar cells and light-emitting diodes [4].

Although ITO used in practical applications is mainly in the thin film form, there is considerable interest in ITO nanostructures [4–16], since they can result in very low resistivity [4], as well as enable improved performance of solar cells due to improved charge collection [6]. Growth of ITO nanostructures using different methods has been reported [4–16], such as chemical vapor deposition [4, 8, 10, 14, 15], chemical synthesis [5], oblique-incidence electron-beam (e-beam) deposition [6, 13], sol electrophoresis [7], sputtering [9, 11], and thermal treatment [12]. Some of these methods, such as chemical vapor deposition [4, 8, 10, 14, 15] and thermal treatment [12], require a high growth temperature and thus would not be suitable for growth on glass substrates, which are of interest for low cost optoelectronic device applications. On the other hand, low temperature methods like chemical synthesis [5] result in free-standing nanostructures instead of nanorod/nanowire arrays/networks on the substrate. In some cases, the use of templates was needed for the ITO nanostructure growth [7, 11], while reports on the ITO nanorod/nanowire growth using conventional techniques such as e-beam deposition [6, 13] and sputtering [9] have been scarce. While e-beam deposition was performed at oblique incidence [6, 13], dc sputtering deposition was simpler, but it resulted in relatively low density of ITO “whiskers” with diameters 10–20 nm and lengths 500 nm–1 μm [9]. In this work, we report preparation of dense arrays of long ITO nanowires on different substrates by dc sputtering. The growth mechanism of the nanowires is discussed.

2 Experimental details

Glass substrates were standard microscope slide glass. ITO/glass was obtained from Varitronix Ltd., Ti foil

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(0.127 mm thick, 99.7% purity) was obtained from Sigma-Aldrich, while Si ((100), p-type) was obtained from Silicon Materials Inc. Ti foil was polished before use. All the substrates were ultrasonically cleaned in acetone, ethanol and de-ionized water for 5 minutes each. The substrates were finally dried with nitrogen flow. The ITO nanowires were fabricated by dc sputtering using an Advanced System Technology Peva-400ES system. The sputtering target was an indium oxide/tin dioxide (90/10 wt%) target (Kurt J. Lesker Company, purity: 99.99%). The substrates were placed at a fixed position 14 cm above the target and the substrate holder was not rotating. Before the introduction of Ar gas, the chamber pressure was 7×10^{-6} Torr and the temperature was 350°C. Then 19 sccm Ar was introduced into the chamber, and sputtering was performed at a fixed current of 0.7 A for 20 min. For Ti foil and Si substrates, ITO film was deposited on the substrates before further deposition of the ITO nanowires. To fabricate the ITO film, the substrates were rotating about the center of rotation during sputtering. The working pressure and temperature were 7×10^{-6} Torr and 350°C, respectively, while the Ar flow rate was 10 sccm.

To characterize the ITO nanowires, a JEOL JSM-7001F field emission scanning electron microscope (FESEM) was used to examine the morphologies of the ITO rods. X-ray diffraction (XRD) measurements were performed using a Bruker AXS SMART CCD diffractometer. The growth directions and morphologies of the ITO nanostructures were examined using transmission electron microscopy (TEM) and selected area electron diffraction (SAED) with a Tecnai G2 20 S-Twin TEM. The sheet resistances were measured using a four-point probe with a Keithley 2400 sourcemeter.

3 Results and discussion

Figures 1 and 2 show SEM images (top view and side view, respectively) of ITO nanowires (NW) grown on glass and ITO/glass substrates. It can be observed that on both types of substrates we obtained dense growth of nanowires with similar morphology and dimensions, with one difference: that nanowires are longer on glass ($\sim 5 \mu\text{m}$) compared to ITO/glass substrates ($\sim 3 \mu\text{m}$). The sheet resistance of the nanowires on glass is $20 \Omega/\text{sq}$, while for ITO NW/ITO samples, the sheet resistance is $8 \Omega/\text{sq}$, lower than that of the ITO substrate ($14 \Omega/\text{sq}$), illustrating that they have excellent electrical properties. Furthermore, some of the nanowires exhibit smaller branches, which are growing at an angle close to 90° to the main body of the nanowire. Branched nanowires (In_2O_3 on ITO backbone) were previously grown by CVD, but it required two deposition processes (growth of ITO backbone, deposition of Au catalyst, and then growth of branches) [4]. Branched ITO whiskers were also previously obtained by dc sputtering [9].

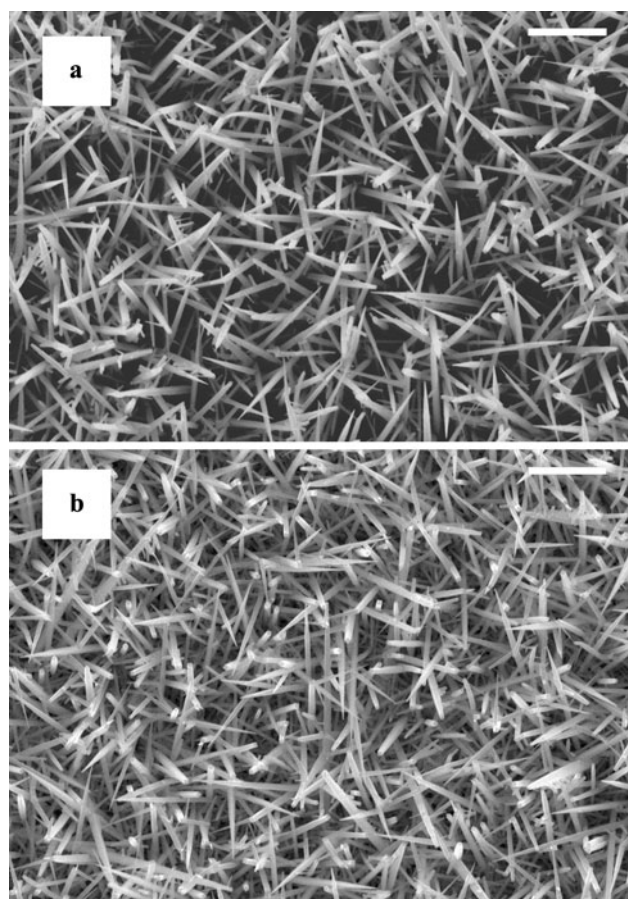


Fig. 1 SEM images (top view) of ITO nanowires on (a) glass, (b) ITO glass. The scale bars are $1 \mu\text{m}$

To obtain more information about the growth of these structures, we performed XRD, TEM and SAED measurements. Figure 3 shows the XRD patterns from the ITO nanowires on different substrates. The peak positions were indexed according to JCPDS file No. 89-4598, and they are in good agreement with other reports on ITO nanostructures [5, 7, 8]. It can be observed that the peak intensity is different for different substrates, which likely occurs due to differences in nanowire orientation. From TEM and SAED images, as shown in Fig. 4, we can determine that the nanowire growth direction is [100] and the growth direction is the same for both substrates. This growth direction is in agreement with previous reports on the growth of ITO nanowires [4, 10], although other growth directions such as [211] [8], [222] [9], and [001] [15] have also been reported. Although the deposition method in our work is similar to that previously reported [9], from the lattice spacings (0.51 nm) in TEM images and SAED patterns we can clearly identify the growth direction as [100] rather than [222]. Considering that the growth along [100] direction is faster than that along [222] direction [16], growth of nanostructures with [100] growth direction would be expected. The branches are also single crystalline and exhibit same lattice spacings

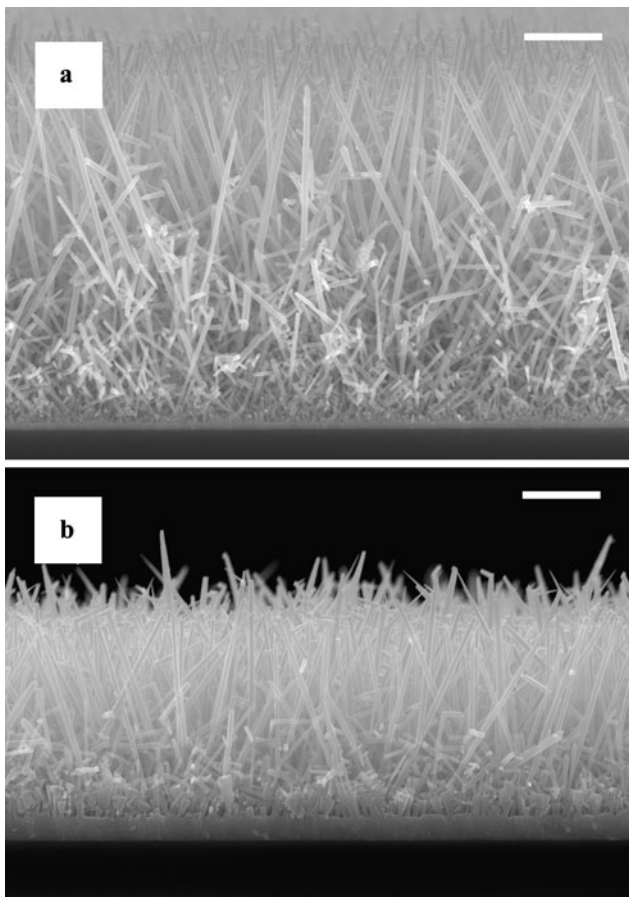


Fig. 2 SEM images (side view) of ITO nanowires on (a) glass, (b) ITO glass. The scale bars are 1 μm

and diffraction patterns as the nanowire backbone. Furthermore, no segregation into core-shell structures was observed in both branches and backbone nanowires, unlike the ITO nanorods grown by e-beam deposition [6].

Concerning the growth mechanism of the nanowires, oxygen-deficient environment and rapid growth rate are

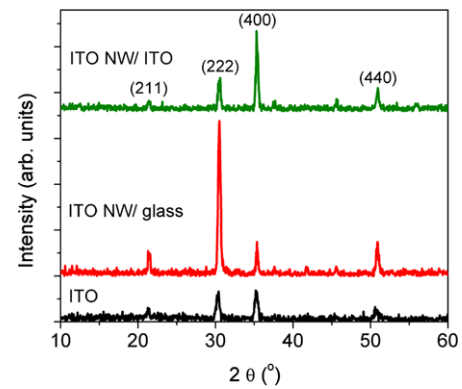


Fig. 3 XRD patterns of ITO nanowires on glass and ITO substrates. ITO substrate is also shown for comparison

likely significant factors in the nanowire formation. It was previously reported that the formation of ITO whiskers occurs more readily when In/Sn alloy target was used compared to ITO target, and that it occurs at increased sputtering power [9]. The formation of branched structures is also likely facilitated by high growth rate resulting in secondary nucleation and branch growth. In a previous report on ITO whisker growth, branched structures occurred at higher sputtering power, which would result in a higher growth rate. It should also be noted that no catalysts were used for nanowire deposition. However, the lack of catalyst does not necessarily exclude the possibility of vapor-liquid-solid (VLS) growth mechanism. It was proposed that the growth mechanism of ITO nanorods by e-beam deposition is self-catalytic VLS growth [6, 13]. Metals with low melting point can easily form droplets for self-catalyzed VLS growth of the nanowires [17], so that it is possible that the growth mechanism is indeed self-catalyzed VLS. The formation of tin-indium catalyst droplets is further facilitated by the oxygen-deficient environment [6, 13]. However, no catalyst droplets were observed at the tips of the nanowires after 20 min. growth.

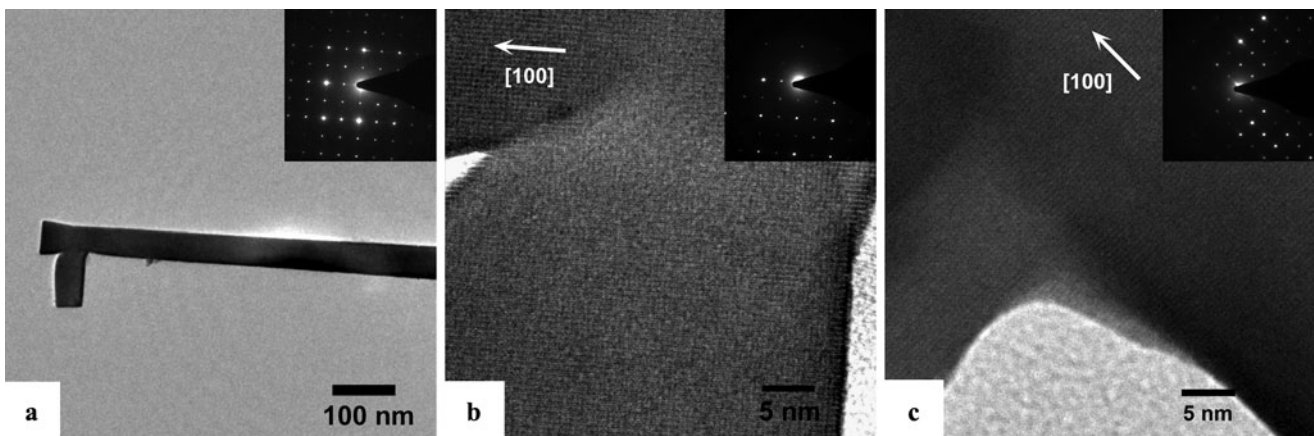


Fig. 4 TEM images of branched ITO nanowires at different magnification levels. The insets show corresponding SAED patterns

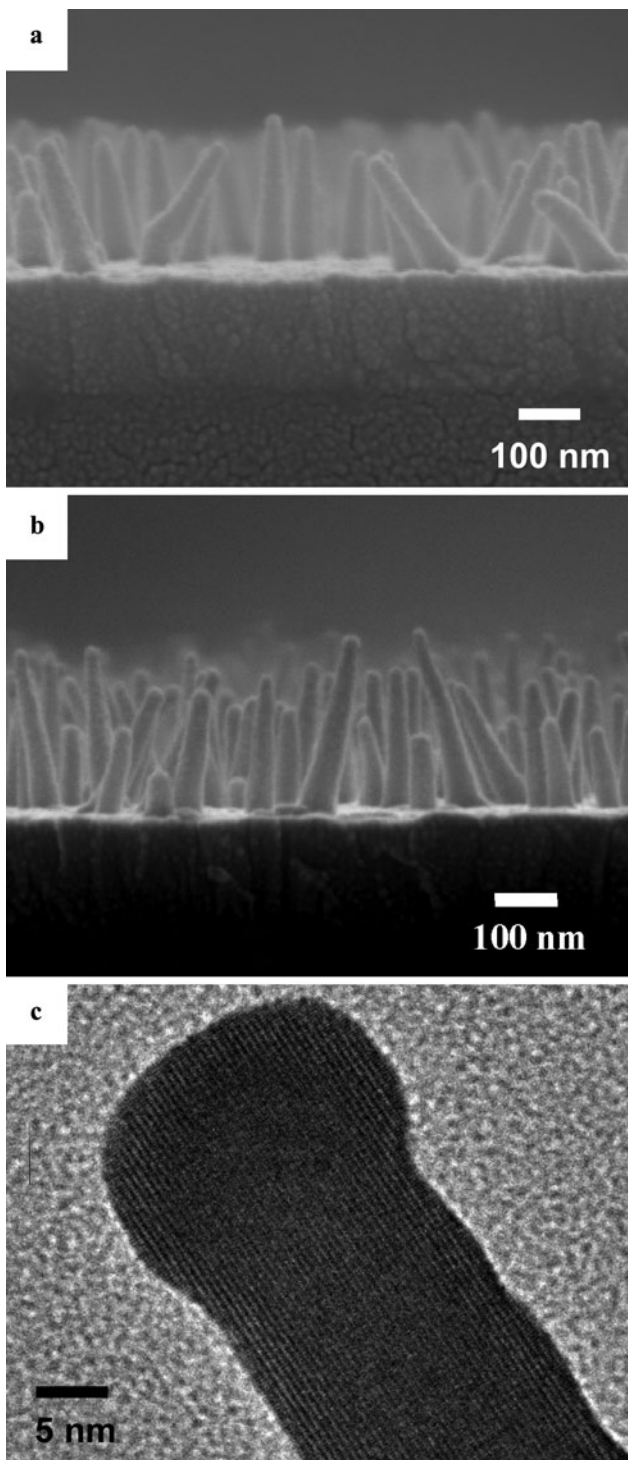


Fig. 5 SEM image of ITO nanorods for (a) 30 s, (b) 1 min sputtering time. (c) TEM image of ITO nanorod for 1 min sputtering time

To examine better the initial stages of the nanowire growth, samples with deposition times 30 s and 1 min. were prepared, and the obtained nanostructures are shown in Fig. 5. It can be observed that in early stages of growth (30 s) the growth of the nanorods is sparse. The nanorods

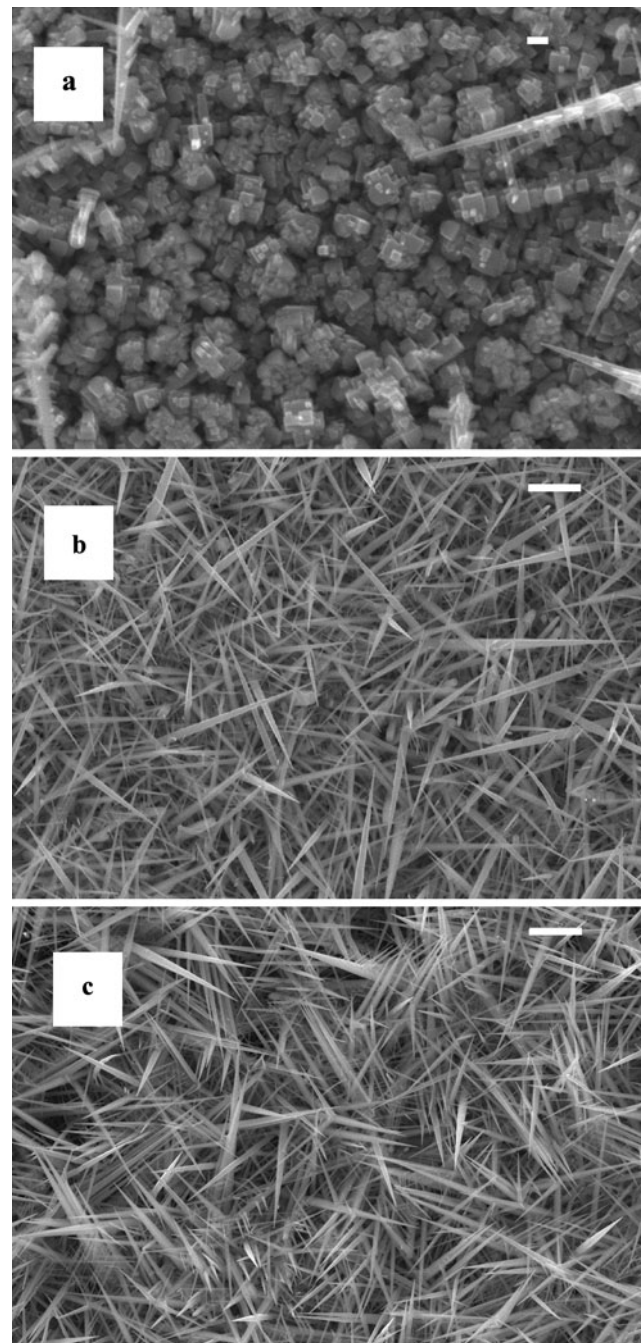


Fig. 6 SEM images of (a) ITO film on Ti foil (scale bar is 100 nm), (b) ITO nanowires on Ti foil (scale bar is 1 μ m), (c) ITO nanowires on ITO film on Ti foil (scale bar is 1 μ m)

are randomly oriented, and their diameter becomes narrower toward the top of the nanorod. Some of the nanorods exhibit a rounded structure on the top, as shown in the TEM image, which exhibits the same lattice spacing as the main body of the nanorod. Thus, self-catalytic VLS growth of the nanorods is possible, but further study is needed to conclusively establish the growth mechanism.

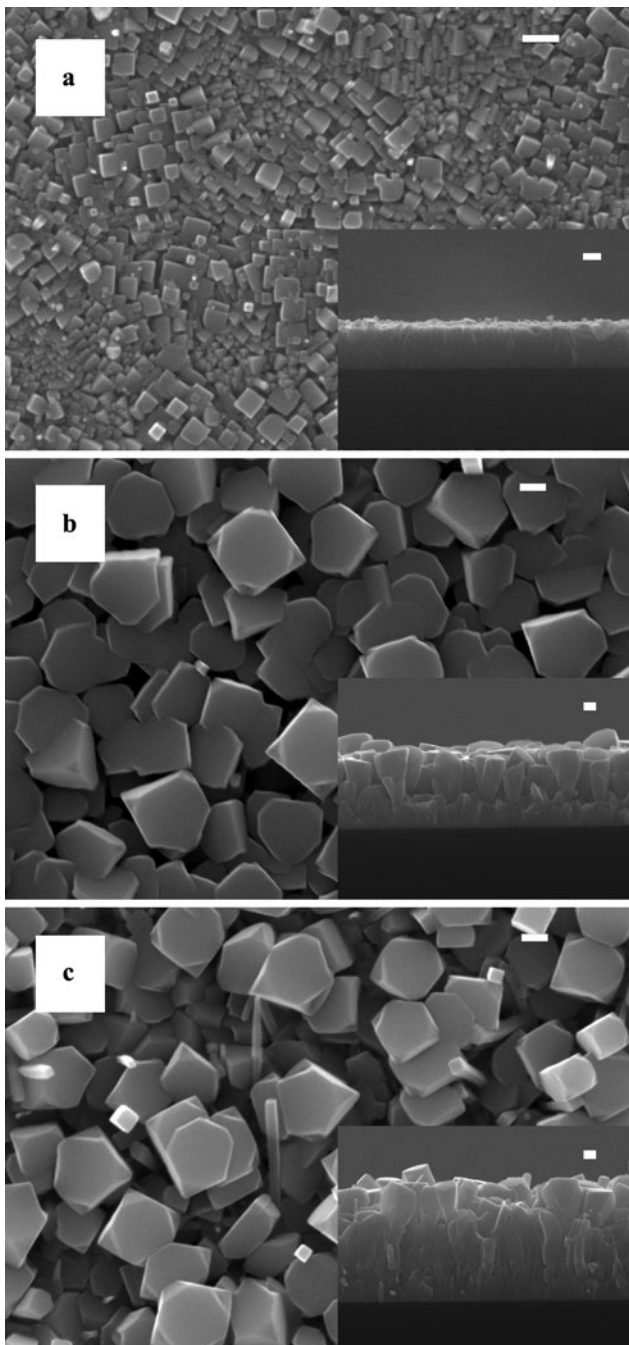


Fig. 7 SEM images of (a) ITO film on Si, (b) ITO nanorods on Si, (c) ITO nanorods on ITO film on Si. The scale bars are 100 nm. The insets show the corresponding side view SEM images

We have also explored the possibilities of ITO nanowire growth on other substrates, with and without ITO film. In case of Ti foil, ITO film consists of small square grains, as shown in Fig. 6. Nanowires are grown both on bare Ti foil and on ITO/Ti foil substrates. Compared to nanowires grown on glass and ITO/glass, the tips of the nanowires on Ti exhibit more significant narrowing toward the tip of the nanowire. Also, branched structures appear to be more com-

mon on ITO/Ti substrate compared to Ti substrate. On the other hand, morphologies on Si (100) substrate are different, as shown in Fig. 7. The ITO film also consists of square grains, but it is less rough compared to the film on Ti foil. However, on both Si and ITO/Si, instead of long nanowires, short rods with large diameters are formed. This is likely due to differences in nucleation rates and surface migration rates on different substrates (due to different substrate material and different roughness).

4 Conclusions

To summarize, ITO nanowires with length in the range 3–5 μm and diameter 50–100 nm were grown on different substrates (glass, ITO/glass, Ti foil, ITO/Ti foil), using a simple and fast method (dc sputtering, deposition time of 20 min). The nanowires were likely formed by a self-catalyzed VLS growth mechanism, with oxygen-deficient environment and rapid growth rate facilitating nanowire formation and growth. The nanowires exhibited excellent electrical properties, with the sheet resistance of nanowires grown on ITO film of 8 Ω/sq .

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