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# Broadband anti-reflection and enhanced field emission from catalyst-free grown small-sized ITO nanowires at a low temperature

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**Abstract**

Small-sized indium tin oxide (ITO) nanowires were fabricated using the electron beam evaporation (EBE) technique at low temperature (~150 °C) without adding any catalyst. The ITO nanowires have a typical diameter of around 10 nm and a length of more than 100 nm, with body-centered cubic crystal structures that grow along the ⟨1 0 0⟩ directions, as revealed by transmission electron microscopy. The growth mechanism of the branched ITO nanowires was found to be a vapor–solid process. The nanowire films show a broadband anti-reflection property due to the graded refraction index from the film surface to the substrate. Enhanced field emission properties with a low turn-on electric field and a high field enhancement factor were also observed in the ITO nanowires.


*Keywords:* ITO; Nanostructure; e-Beam evaporation; Field emission; Anti-reflection

## 1. Introduction

One-dimensional (1-D) metal–oxide nanostructures are currently the subject of much interest both for their novel structures and physical properties and for their potential applications in nanoelectronics and nanophotonics [1–3]. Many kinds of 1-D oxide, such as ZnO and $SnO_2$, have been fabricated and studied. As one of the most important and widely used materials, tin-doped indium oxide (ITO) has been applied in various devices, such as light-emitting devices, sensors and solar cells [4–7]. It has been reported that 1-D ITO nanostructures can be prepared by many kinds of techniques. For example, by using a carbothermal evaporation method, Chiquito et al. [8] were able to obtain ITO 1-D nanobelts with a thickness of around 60 nm and a length of several microns at a temperature of 1150 °C through the vapor–solid (VS) process, and novel electrical transport properties were found. Wan et al. [9] used the Au-catalyzed vapor–liquid–solid (VLS) route to obtain ITO nanowires in a pulsed laser deposition system. Because the Au catalyst was used, the preparation temperature could be decreased greatly to 600 °C. The nanowires had a diameter of <200 nm and a length of about 2.5 μm. Good field emission behavior was observed in the nanowires due to the high aspect ratio and the highly aligned geometry. More recently, O'Dwyerl et al. [10] reported the fabrication of ITO nanowires at 500–600 °C by using a molecular beam evaporation method through the VLS route. In–Sn droplets were used as the catalyst in the deposition process, and the ITO nanowires had diameters of 8–20 nm and lengths of 40–500 nm, which were used as the transparent conduction electrode in the electroluminescence devices to enhance the emission efficiency [10].

The conventional thermal evaporation and condensation process usually requires a high temperature (~1000 °C). Catalyzed growth, on the other hand, can be performed at a temperature of ~500–600 °C. However, the use of the catalyst may cause contamination by extra elements, which may cause a deterioration in the properties of the applications [1]. As a result, the fabrication of ITO nanostructures at low temperature with low cost and enhanced properties is currently a very attractive goal. Moreover, the formation

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of ultrathin 1-D nanowires (<10 nm) is also of interest as decreasing the diameter will increase the surface area and colloidal stability, which can have repercussions on applications [11]. Here, we report the growth of single-crystal ITO nanowires over a large area using a low-temperature process (∼150 °C) in an e-beam evaporation system without adding any catalyst. The approach used in the present work has the advantage of low cost, high uniformity and good reproducibility. The diameter of the ITO nanowire is around 10 nm and the length is longer than 100 nm. Moreover, enhanced field emission and broadband anti-reflection characteristics were observed in the ITO nanowires, which indicates the potential application of these films in future optoelectronic devices.

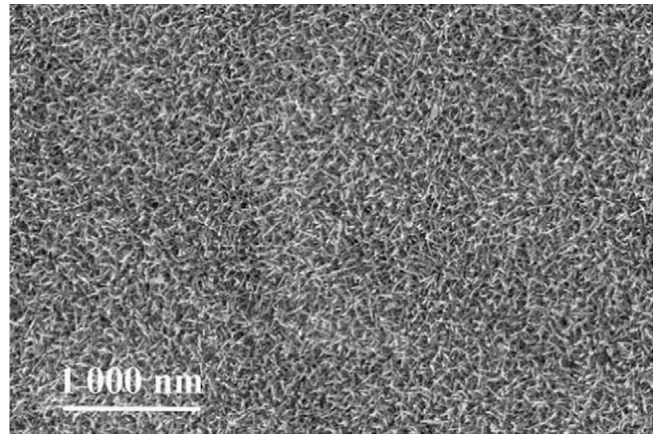


Fig. 1. FESEM image of the ITO nanowires.

## 2. Experiments

ITO nanowires were prepared in a conventional e-beam evaporation system with the accelerating voltage of the e-beam set at 6 keV. Before the evaporation process, the chamber was pumped down to a base pressure of $<10^{-4}$ Pa. The substrate temperature was 150 °C and ITO ceramic pellets with an In/Sn molar ratio of 85/15 were used to grow ITO nanowires without introducing any extra atmosphere. The growth of the flat ITO films was performed at <150 °C with an In/Sn molar ratio of 95/5 and an oxygen pressure of $2.7 \times 10^{-2}$ Pa. In order to improve the film's uniformity, the sample holder was rotated at a speed of 30 rpm. Si wafer and aluminum foil were used as substrates. It is worth pointing out that neither catalyst nor template was used during the preparation process.

The microstructure of the ITO nanowires was characterized by field emission scanning electron microscopy (FESEM; LEO 1530VP, Zeiss) and field emission transmission electron microscopy (TEM; TECNAI F20, FEI). The composition of the nanostructures was determined using the electron energy dispersion spectra (EDS) in the TEM system, which worked under the scanning transmission electron microscopy mode. The optical transmission and reflection were measured using a Shimadzu UV-3600 spectrometer. The transmission spectra ($T$) were obtained under normal incidence geometry and the reflection spectra ($R$) were obtained under 5° mirror reflection geometry, using an aluminum mirror with a smooth reflection dependence in the measured wavelength region as the reference. The field emission measurement was performed in a vacuum chamber at room temperature, with the pressure at less than $1 \times 10^{-4}$ Pa. The emitting area was 7 mm × 7 mm and the cathode–anode distance was about 280 μm. During the measurements, the applied voltage was ramped up and down for several cycles until the stable field emission behavior was obtained.

## 3. Results and discussion

Fig. 1 shows a typical FESEM image of synthesized ITO nanowires. As seen in the figures, the ITO nanowires have good uniformity in a large area with high density. The ITO nanowires have an average diameter in the sub-10 nm range, with a length larger than 100 nm. The morphologies and structures were further investigated by planar and side-view TEM images, as shown in Fig. 2a and b, respectively. It can also be seen from the TEM images that the diameter of the ITO nanowires is quite uniform. The ITO nanowires are seen to be straight, and some of them have branches. The branches have grown perpendicular to the truck along all four possible directions, and adjacent branches are perpendicular to each other. This structure is illustrated in the inset of Fig. 2b. It is also noted that the ITO nanowires have the

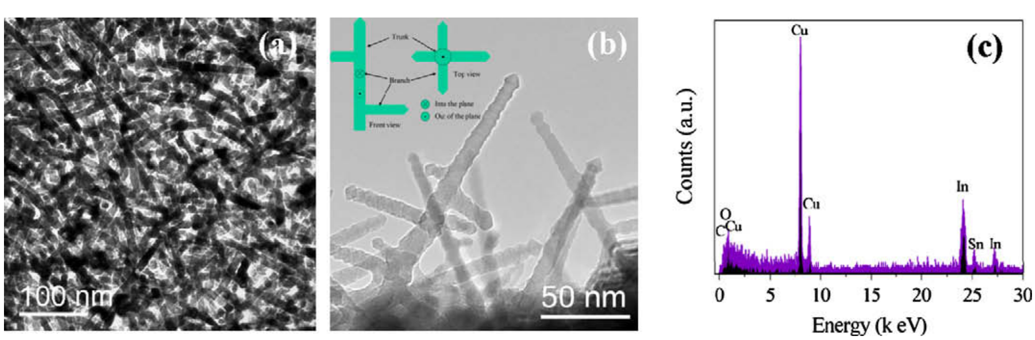


Fig. 2. (a) Planar view and (b) side view of the TEM image of the ITO nanowires; (c) the EDS spectrum of the ITO nanowires. The inset in (b) is a schematic figure showing the orientation of the branches grown on the nanowire trunks.