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Synthesis, characterization and field emission properties of tin oxide nanowires

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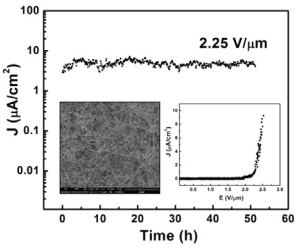
HIGHLIGHTS

- SnO_2 nanowires (NWs) are grown by chemical vapor deposition of Sn and C mixture.
- Electron microscopy studies reveal towards high aspect ratio of SnO_2 NWs.
- NWs exhibit low turn-on and threshold fields of 1.75 and 2.48 V/μm, respectively.
- Importantly, SnO_2 NWs exhibit emission stability over a period of more than 50 h.

GRAPHICAL ABSTRACT



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ABSTRACT

Tin oxide (SnO_2) nanowires are synthesized by Au catalyzed chemical vapor deposition of Sn and C mixture at 900 °C by employing a continuous flow of Ar: O_2 (10:1) for an hour. X-ray diffraction and Raman spectroscopy studies indicate that the as-grown SnO_2 nanowires are crystalline in nature with tetragonal rutile phase. Electron microscopy studies reveal towards high aspect ratio of nanowires. The field emission studies show that SnO_2 nanowires grown on Si substrate exhibit low turn-on field of 1.75 V/μm (at 0.1 μA/cm^2) and long-term emission stability over a period of more than 50 h with a current density of 4 μA/cm^2 at a constant electric field of 2.25 V/μm. Hardly any considerable degradation in the emission current is noticed even after 50 h which may be attributed to the high crystallinity of SnO_2 nanowires.

1. Introduction

One dimensional nanostructures such as nanotubes, nanowires, etc. have been advocated as potential materials to be employed as efficient and reliable electron field emitters. It is due to the fact that possible enhancement of applied electric field at nanometer–sized tips can result in high emission current densities (of the order few mA/cm^2) at relatively low applied fields (of the order of few V/μm) [1–4]. Electric field driven electron emitters are much needed as alternative electron sources as they can replace thermionic electron emitters in devices such as microwave amplifiers, parallel electron beam microscopes, X-ray tubes for designing them in more efficient and portable form. Among various 1D nanostructured materials, metal oxide nanowires [such as zinc oxide nanowires, tin oxide (SnO_2) nanowires etc.], in particular have great potential as field emitters because of their high thermal stability, high melting points and intrinsic stability in harsh environments. It is to be noted that the work function is an important parameter for choosing a

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material for its possible use in the field emission devices.

SnO_2 is an important transparent conducting oxide having a direct bandgap of 3.6 eV which has been widely studied as gas sensing material [5–10]. However, its potential as a field emitter is not well studied even though the work function of SnO_2 (4.7 eV) is comparatively lower than the other nanostructured field emitters such as CNTs (5.0 eV) and zinc oxide nanostructures (5.3 eV) [11]. Crystalline SnO_2 nanostructures can serve as high brightness electron sources due to the strong field enhancement at their nanometer scale emission tips. Variety of nanostructures of SnO_2 such as nanowires, nanobelts, nanorods etc. have been synthesized till now by different approaches [11–23]. Chemical vapor deposition (CVD) is the most common and widely used method of synthesizing highly crystalline nanostructures of SnO_2. Most often Au nanoparticles are used as catalyst for the growth of SnO_2 nanowires. Recently, a few groups have reported the field emission of CVD grown SnO_2 nanowires [11,14]. However, the number of reports on the field emission of SnO_2 is less compared to other 1D nanostructures such as CNTs and ZnO; hence detailed studies are required for the possible improvements in the field emission of SnO_2 nanostructures. Most of the studies on the field emission of SnO_2 nanostructures with different morphologies address the improvement of emission turn-on and threshold fields to obtain high current densities at lower applied voltages. But the stability of field emitter over a period of time is one of the most important parameters, which is hardly addressed. In this report, we have presented an experimental study of field emission properties of SnO_2 nanowires grown by CVD. The nanowires show excellent stability for a period of more than 50 h which is the highest among so far reported values.

2. Experimental

SnO_2 nanowires were grown on Au (2 nm) coated Si substrate by vapor phase deposition of Sn powder (99.99% pure) and graphite powder (200 mesh), mixed at a ratio of 1:1 by weight. The source powder (1.0 g) was kept in an alumina boat and was placed at the central zone inside one inch diameter quartz tube, where the temperature gradient is the minimum. Au coated Si substrate was placed quite close to the source (~1 cm). Thereafter, the quartz tube was placed inside a horizontal tube furnace, and vacuum seals are firmly tightened to prevent any unwanted O_2 leaking from the ambient. The system was then pumped down to rotary vacuum by using a rotary pump. Prior to the temperature ramping, the quartz reactor tube was flushed with Ar gas for 15 min and then the furnace temperature was ramped to 900 °C, and was maintained at the same temperature for 60 min with a continuous flow of Ar (20 sccm) and O_2 (2 sccm) mixture. Afterwards the furnace was allowed to cool naturally to room temperature and the Si substrate with SnO_2 nanowires was collected.

The as-grown nanowires were characterized by using Quanta 200 scanning electron microscope (SEM), and Technai T20 transmission electron microscope (TEM). Raman characterization of the nanowires was done by using HORIBA JOBINYVON LAB RAM HR spectrometer with Ar ion laser (525 nm). X-ray diffraction (XRD) spectrum is collected by using Philips X-ray diffractometer with Cu K_α radiation as X-ray source. Field emission measurement was carried out by using a simple two-electrode (i.e. diode) configuration using cathode (sample) and parallel anode plate (copper) in a vacuum chamber maintained at a pressure of 4×10^{-6} mbar at room temperature. Distance between cathode and anode was adjusted to 200 μm. Keithley 2410 source meter is used for obtaining the field emission characteristics.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of as-synthesized SnO_2 nanowires on Si substrate. The occurrence of strong diffraction peaks corresponding to various planes indicates high degree of crystallinity of SnO_2 nanowires. The peaks in the XRD pattern are identified as originating from the reflections of (110), (101), (200), (211) planes of tetragonal rutile phase of SnO_2 (identified with JCPDS card no. 41-1445) with lattice constants a = b = 4.7382 Å and c = 3.1871 Å. Fig. 1(b) depicts the Raman spectrum of SnO_2 nanowires. The peaks obtained at 476, 633 and 775 cm^{-1} in Raman spectra are consistent with E_g (translational), A_{1g} (symmetric stretching of Sn–O bond) and B_{2g} (asymmetric stretching) vibrational modes of SnO_2 respectively, indicating that the as-grown SnO_2 nanowires belong to tetragonal rutile structure. An additional peak at 696 cm^{-1} corresponds to IR-active A_{2u} LO (longitudinal optical phonon) mode of SnO_2 [24].

Fig. 2(a) depicts the SEM micrograph of thick mat of nanowire sample at low magnification revealing that the length of the nanowires is around ~50 μm. It can also be noticed from shown micrographs that the surface coverage of nanowires over the Si substrate is high. SEM micrographs shown in Fig. 2 (b), (c) & (d) reveal the nanowires have catalytic Au nanoparticles at the tips. The presence of Au nanoparticles at the tips of the SnO_2 nanowires suggests the vapor-liquid-solid (VLS) mechanism of nanowire growth. TEM micrographs, shown in Fig. 3(a), indicate that the

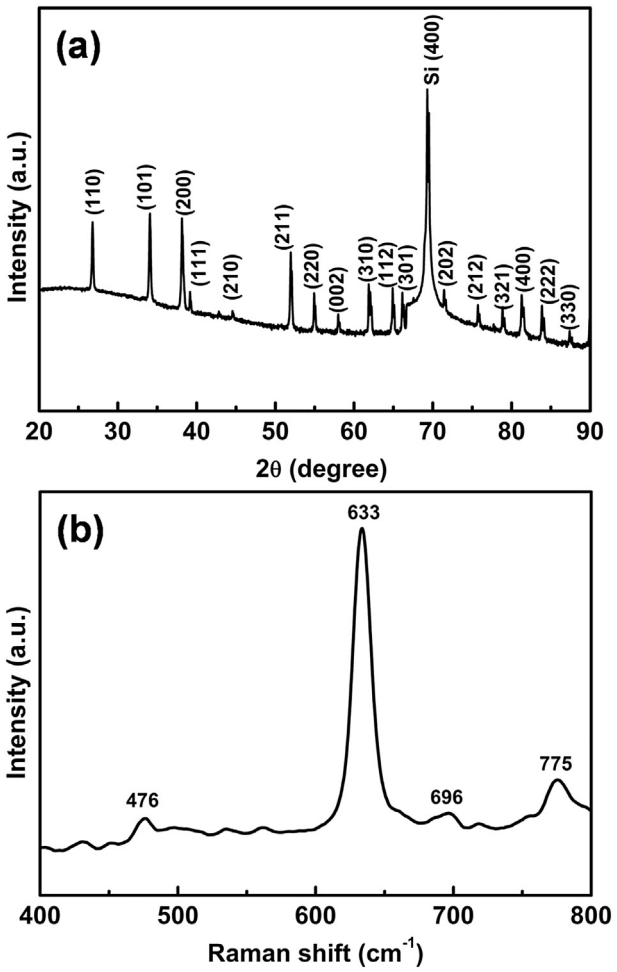

Fig. 1. (a) XRD pattern of as-prepared SnO_2 nanowires on Si substrate, (b) Raman spectrum of as-prepared SnO_2 nanowires.