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Morphology and field emission from ZnO nanowire arrays synthesized at different temperature

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Abstract

Three kinds of ZnO nanowire arrays were fabricated on Au coated (1 1 0)silicon wafer by using of heating the mixture of zinc oxide (ZnO) and graphite powders at various depositing temperature. The synthesized samples were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) analytic technology, respectively. Structural analyses revealed that the morphologies and crystal microstructures of ZnO nanoarrays were related with the substrate temperature. And control to the growth morphologies can be achieved by carefully tuning the depositing temperature. The testing results to different nanowire arrays showed that the properties of field emission follow the Fowler–Nordheim law. The quais-aligned ZnO nanowire array sample synthesized at 750 °C had the lowest turn-on field of 7.4 V/μm, highest β of 1028. This largest emission efficiency is attributed to the clear tip and appropriate coverage density. As well as the nanowires are straight with long length and parallel to each other with good crystal quality. The experimental results could be very useful for field emission materials and other nanoelectronics device applications.

Keywords: ZnO; Nanoarrays; Morphology; Field emission

1. Introduction

Recently, the semiconductor ZnO nanostructures have gained substantial interest in the research community due to its large exciton binding energy (60 meV), high electromechanical coupling constant, good thermal and chemical stability to harsh environment. Therefore, a large number of publications have been reported for the synthesizing of ZnO nanostructures with various shapes (nanowires, nanobelts, nanorings, nanotubes, nanodonuts, nanopropellers, etc.) [1–5]. Among these various ZnO nanostructure, one dimension (1D) ZnO nanowire arrays are considered to be potential application in a wide range of field-emission-base devices such as flat-panel display, parallel-electron-beam microscope, vacuum microwave amplifiers, X-ray source, etc. [6–8]. According to the experimental parameters of carbon nanotubes, which have been proved as promising material for a field emitters, its geometrical morphologies and growth structures are very fatal to its field-emission character [9]. Up to now, the field emission properties of ZnO nanowires with various shapes and growth tendency are still not sufficiently studied. It was necessary to evaluate the field emission characteristic for different ZnO nanowire arrays systematically.

In this paper, three kinds of ZnO nanowire arrays were fabricated by vapor-phase transport method of heating the mixture of zinc oxide and graphite powders at different depositing temperature. The field emission properties of ZnO nanowire arrays with different growth tendency and shape were studied and analyzed. These experimental results are very useful for the application of advanced optoelectronic devices of ZnO nanowire arrays.

2. Experiments

A thin layer (15–20 nm) of gold was deposited on the cleaned n-type (1 1 0) plane silicon wafers by thermal evaporation. ZnO nanowire arrays were grown on Au coated substrates via vapor–liquid–solid (VLS) growth method. The experimental

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system included a horizontal tube furnace (110 cm long), a temperature controller, a quartz reacting tube (6 cm diameter, 120 cm long), a rotary pump system, and a gas control system. The carrier gas entered at the right of end of the quartz tube and was pumped out at the left end by the rotary pump system. The source material was ZnO powder (99.995%) mixed with graphite (99.995%) in molar ratio of 1:1. The mixed powder was ground and located on the alumina boat positioned at the center of the quartz reacting tube. Several Au coated silicon substrates were placed downstream, one behind other, inside the quartz tube. The substrate temperature dropped with the distance of its location from the position of the reactant, and the temperature at central zone was 1150 °C. So the temperature of tube furnace was decreases gradually from left to right, giving different temperature regions (high, medium and low temperature region). In our experimental process, ZnO nanoarrays were synthesized on the Au-coated silicon substrates at 650, 750, and 900 °C temperature zones for 30 min, respectively.

In this process, the quartz tube was evacuated to a base pressure of 200 Pa and then heated at a rate of 20 °C/min from room temperature. Once the central region reached the scheduled temperature, the heating process was turned off and maintained it for 15 min to make the Au coating to form small catalyzing particles. Then the high-purity argon (99.999%) had been introduced as the carrier gases with the flux of 50 ml/min. The quartz tube was maintained its pressure of ∼1000 Pa in the depositing processes. After 30 min, the quartz tube was slowly cooled down to room temperature in the protection of argon. White/grey products were formed on the surface of the Si wafers in different deposited condition.

The morphology of the synthesized products was examined by a JSM-5600LV scanning electron microscope (SEM) as the samples were glued to a metallic support and sputtered with ∼15 nm of Au thin film prior to imaging (JSM-5600 electron microscope). Conventional TEM analysis and high-resolution transmission electron microscope (HRTEM) were both performed on a JEOL-2010 microscope at 10–200 kV. At this analytic process, the growth layers of synthesized ZnO nanowire arrays were removed from the silicon wafer and ultrasonically dispersed in ethanol for 20 min. Then a few drops of the mixed liquid were dropped onto the copper grid to characterize the microstructure and orientation of individual ZnO nanowires with the TEM. And the X-ray diffraction (XRD) measurement was carried out to examine the crystal structure of the nanowires. The spectrum of the samples was obtained by using Rigaku D/MAX PSPC MDG 2000X-ray diffractometer with Cu Kα1 radiation.

Field-emission properties of the samples were carried out inside a vacuum chamber, which was pumped down to about 3.1×10^{-5} Pa at room temperature. The tests were measured using a sample diode configuration. The cathode was the as-grown ZnO nanoarrays and the n-type Si substrate was used as a cathode-conducting layer. The anode was polished pure copper sheet. The gap between cathode and anode was controlled by the thickness of a mica spacer containing a circular hole in the center. The diameter of the circular hole was 3 mm. Voltages up to 2.0 kV were applied to the anode and the emission current (I) was detected with a micro amperometer. The testing electric field (E) was estimated by dividing the applied voltage (V) by the anode–cathode distance (V/d). The emission current density (J) was calculated from the obtained emission current and the area of the rounded hole in the mica. The emission current–voltage characteristics were analyzed by using the Fowler–Nordheim (FN) equation [10].

3. Results and discussion

Fig. 1a appears the typical SEM image of Au catalyzing particles on the surface of silicon wafer, which forming from the Au thin coating when the substrate temperature was elevated and maintained at about 750 °C for 15 min. The diameter of Au catalyzing particles was about 50–150 nm, the distribution is very uniform and few Au agglomerate particle can be observed. This result is helpful for the growth of 1D ZnO nanowires uniformly. Of course, under other two temperature conditions, the SEM images also showed the similar diameter and distribution to Au catalyzing particles on the silicon surface.

In our experiment, 1D ZnO nanowire arrays had been successfully achieved on the Si substrates via vapor–liquid–solid (VLS) growth mechanism. All the growth morphologies of ZnO nanowire arrays are shown in Fig. 1b–d, which are, respectively, the top and side views of the deposited ZnO nanowires. The results indicated that ZnO nanowire arrays grow easily on Au-coated substrates. From these SEM and high-magnification TEM images of synthesized ZnO nanowire arrays deposited at different three temperature conditions, it can be seen that three kinds of growth morphologies were observed. Fig. 1b shows SEM image of the nanowires synthesized at 650 °C for 30 min. The straight 1D ZnO nanowires are uniformly grown over the entire surface of silicon substrate. These nanowires have perfect orientation perpendicular to the substrate and constitute vertically aligned ZnO nanowire arrays. The inset TEM image in Fig. 1b more confirms that the individual nanowire synthesized at 650 °C is well oriented and its microstructure is very uniformity. But some clusters are still observed on the substrate surface and nanowire roots, with a diameter range from several nano-meter to micron scale. These clusters may be composed of Au and ZnO agglomerate particles. From Fig. 1c at 750 °C condition, quasi-aligned nanowire arrays were fabricated. Most of the nanowires are straight with good crystal quality and parallel to each other, a small part of them are curly and intersectant. And the inset HRTEM image in Fig. 1c gives the HRTEM image of synthesized individual ZnO nanowire at this condition. The clear fringes of ZnO(0 0 2) planes indicated by this image reveal that the microstructure is single crystalline. The lattice spacing of adjacent plane alone the growth direction is 0.52 nm, it corresponds to the distance of (0 0 2) crystal plane. This fact suggests that the nanowires grew in the (0 0 2) crystallographic direction; and from SEM image in Fig. 1d, the synthesized ZnO nanoarrays are only consisted of the curling and twisting nanowires at 900 °C condition. All the curling and twisting nanowires have not clear growth direction, and many growth disfigurements and complicated structures were formed. Meanwhile, the nanowires have similar diameters of 50–250 nm in same depositing time in three testing condition. As the increasing of