Journal of Alloys and Compounds 690 (2017) 304–314

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Controllable preparation of 1-D and dendritic ZnO nanowires and their large area field-emission properties

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ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form
3 August 2016
Accepted 14 August 2016
Available online 17 August 2016

Keywords:
ZnO nanowires
Ion bombardment
Stress
Growth mechanism
Field emission arrays

ABSTRACT

Large-scale one-dimensional (1-D) and dendritic ZnO nanowires were synthesized on Si substrates using a catalyst-free thermal oxidation technique. By adjusting the stress of the starting Zn thin film for the growth using an Ar ion bombardment process, controllable syntheses of samples composed of only one or a mixture of these two morphologies were achieved. Different nucleation mechanisms were proposed by detailed observations of nucleation and growth process of 1-D and dendritic ZnO nanowires. The strain-induced mass diffusion model and self-catalytic gas-liquid-solid model were used to explain the growth of 1-D and dendritic ZnO nanowires, respectively. In addition, the field-emission characteristics of ZnO nanowires were measured, which showed that dendritic ZnO nanowires have stable emission current.

1. Introduction

Because of their excellent physical and chemical properties, ZnO nanostructures have been explored for applications such as ultraviolet light sources, field effect transistors, solar cells, gas sensors, piezoelectric nanogenerators, and cold cathode electron sources [1–6]. Among them, large-aspect ratio ZnO nanostructures, such as ZnO nanowires and nanotips, show promising application for large-area field emitter arrays (FEAs) because of their excellent field-emission performances [6–11]. Applications of ZnO nanowires as FEAs for flat panel displays, X-ray sources, and parallel electron beam exposure have been reported [12–14]. However, controlling the morphology of ZnO nanostructures in a large area is still a major issue that needs to be addressed before their practical application.

To realize large-area FEAs, ZnO nanostructures should be prepared on a large area, for which glass substrates are usually preferred. Therefore, the preparation temperature of ZnO nanostructures must be less than the softening point of glass. At present, the vapor transport (VT) [15], chemical vapor deposition (CVD) [16], aqueous solution [17], and thermal oxidation techniques [18] are the main methods for preparing ZnO nanostructures. In general, the ZnO nanostructures prepared by VT or CVD have good crystallization; however, high temperature is needed, which increases the difficulty of integrating ZnO nanowires into the device structure. As for aqueous solutions, the preparation temperature is low and it has the advantages of simplicity, low cost, and good morphology. However, materials prepared in aqueous solutions have poor adhesive force and electrical contact performance with the substrate. Also, the samples are easily polluted by impurities introduced in solution. In addition, catalysts are used in some fabrication methods for ZnO nanowires [19], which not only increases the process complexity, but also introduces some unwanted impurities in the ZnO nanostructures. In contrast, the catalyst-free thermal oxidation method has the advantages of simple preparation, low cost, good crystallization, and low preparation temperature, which leads to its preponderance in the field of large-area cold cathode electron sources.

It is well known that the morphology of ZnO nanostructures has a great influence on the field-emission performance, according to the field emission theory [20]. The ZnO nanostructures applied to field emission should be robust, uniform, and have a large field enhancement factor. In this case, we think that dendritic ZnO nanowires could have better field-emission performance than 1-D ZnO nanowires. On the one hand, the dendritic ZnO nanowires may

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http://dx.doi.org/10.1016/j.jallcom.2016.08.123
0925-8388/

have larger field emission enhancement factor and more field-emission tips, resulting in larger field-emission current. On the other hand, the robust dendritic ZnO nanowires can operate under a large current and the "head-shaking" effect [21] could be reduced so that the field emission current is more stable. Though large-scale quasi-one-dimensional ZnO nanowires have been prepared using the thermal oxidation method successfully [22], controllable large-scale preparation of dendritic ZnO nanowires by thermal oxidation technology has not been realized. It has been reported that dendritic ZnO nanostructures can be grown from a single Zn particle [23]. However, the preparation technology for large-area and uniform dendritic ZnO nanowires still needs to be explored.

Undoubtedly, the realization of controllable large-area ZnO nanostructures depends on an accurate growth mechanism for ZnO nanostructures. To date, several growth mechanisms have been proposed for ZnO nanostructures prepared by the thermal oxidation technique, including the stress model [24], self-catalytic model [25], ion-diffusion model [26] and vapor-solid model [27]. Even though the growth of ZnO nanowires is influenced by many environmental factors, those growth mechanisms all suggest that the morphologies of ZnO nanostructures depend on the initial states of Zn seeds. In addition, metal oxidation theories, such as the Pilling–Bedworth rate formula [28] and Mott model [29], are used to describe the oxidation behaviors. For example, Kirkham M. et al., proposed that because of the different thermal expansion coefficients of ZnO layers and Zn layers in the process of thermal oxidation, larger thermal stress was generated in the internal region of the film, causing cracks in the ZnO layer and leading to the growth of ZnO nanobelts by the reaction of Zn sources and air at the crack positions [30]. From this perspective, the difference in membrane stress would cause different oxidation behaviors, including the nucleation position and transport mechanism, leading to different morphologies for ZnO nanostructures. Therefore, it is necessary to study the relationship between thin film stress and thermal oxidation behavior quantitatively, which still has not been explored clearly.

In the present work, the adhesive forces between the Zn film and substrate were changed, causing different stresses during the thermal oxidation process, and large-area ZnO nanowires with different morphologies were prepared successfully. Under the different membrane stresses, the detailed thermal oxidation behaviors and morphologies of ZnO nanowires were explored in depth, and we put forward a unified growth mechanism. In addition, arrays of patterned ZnO nanowires with controllable morphologies were demonstrated, showing good field-emission performance. This study has important guiding significance for the preparation of large-area ZnO nanostructures using thermal oxidation and their application in cold cathode electron source devices.

2. Experimental

2.1. Preparation of materials

ZnO nanowires were grown by a thermal oxidation technique. First, 1 cm × 1 cm n-type Si (100) substrates were cleaned by ultrasonication in acetone, followed by alcohol and deionized water for 30 min each. Then, the Si substrates were bombarded in situ for 1 h by Ar ions generated by a Huffman ion source in a vacuum. The pressure during the bombardment was approximately 5×10^{-2} Pa. The flow of Ar gas was 6 sccm, the anode voltage was 215 V, and the ion beam was 50 mA. Afterwards, 1.3-μm-thick Zn films were deposited on silicon substrates by electron beam evaporation with a deposition rate of 0.6 nm/s. Last, the samples were placed into a horizontal quartz tube furnace in air and the temperature was raised from room temperature to 773 K (which took 192 min) and was maintained for 3 h. When the furnace was cooled to room temperature, the ZnO nanowires had been prepared successfully. To investigate the growth process of ZnO nanowires, nine identical samples were prepared together, and one each was removed during growth at the time of 142 (375 °C), 152 (400 °C), 162 (425 °C), 172 (450 °C), 182 (475 °C), 192 (500 °C), 222 (500 °C), 252 (500 °C) and 372 (500 °C) min. Furthermore, arrays of patterned ZnO nanowires were achieved on indium tin oxide (ITO)-coated glass substrates using the abovementioned conditions. The ITO layer was 500 nm, and the Zn film patterns were prepared using a lift-off method.

2.2. Characterization methods

The morphologies of the deposited Zn film and grown ZnO nanowires were viewed using a scanning electron microscope (SEM; SUPRA™ 60). High-resolution lattice images of the samples and selected area electron diffraction (SAED) patterns were obtained on a high-resolution transmission electron microscope (HRTEM; FEI Titan G2 300 KV). Before and after the ion bombardment, the roughness and elemental composition of the Si substrate's surface were analyzed using an atomic force microscope (NT-MDT NTEGRA Spectra) and X-ray photoelectron spectroscopy (Thermo Fisher Scientific ESCALAB 250). The stress of the Zn film and ZnO thin film were measured using a level gauge. A 4-in wafer was applied for stress measurement, and the measuring length was 9 cm, with the wafer center as the midpoint.

The field-emission characteristics of ZnO nanowires grown on Si substrates were measured in a vacuum chamber using an anode probe technique. A circular metal rod with a diameter of 2 mm was used as the anode, and the gap between two electrodes was 260 μm. For the ZnO nanowires grown on the ITO substrate, the field-emission characteristics were measured by the anode screen technique with a gap between two electrodes of 500 μm. The voltage between the two electrodes was adjusted from 0 to 10 kV, and the field-emission current was recorded automatically by a computer that was connected to the voltage source and current meter. The pressure in the vacuum chamber was kept at approximately 1×10^{-5} Pa for all of the measurements.

3. Results and discussion

3.1. Morphologies of deposited Zn film and ZnO nanowires

Fig. 1(a) shows representative SEM images of the Zn thin film deposited by electron beam evaporation. The Zn film is composed of uniform Zn particles stacked with a certain gradient. The distribution density of Zn particles is approximately 1.25×10^9 cm^{-2}. The single Zn particle shown in the inset of Fig. 1(a) has a hexagonal structure and a smooth top plane, with an average diameter of 350 nm. As can be seen from the inset of Fig. 1(a), the Zn particles had some hexagonal cracks, demonstrating that the Zn particles were formed by self-assembly. According to the cross-section SEM view shown in Fig. 1(b), the Zn film was composed of hexagonal prisms, with the diameter increasing from bottom to top gradually, and the hexagonal prism was layered (as shown in the inset of Fig. 1(b)). Some small, unshaped Zn particles that formed at the interface of the Zn film and Si substrate could increase their adhesion. The upright grain boundary between the hexagonal prisms is indicated in Fig. 1(b); this is beneficial for the transport of Zn^{2+}. It is notable that the morphologies of Zn films were similar, regardless of whether the Si substrate was bombarded by Ar ions.

Fig. 1(c) shows the typical morphology of ZnO nanowires grown on the Si substrate exposed to ion bombardment. The distribution density of ZnO nanowires is ~5×10^8 cm^{-2}. The amplified SEM