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Physics Letters A 370 (2007) 345–350
PHYSICS LETTERS A
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Field emission characteristics of ZnO nanoneedle array cell under ultraviolet irradiation

Woong Lee [a], Min-Chang Jeong [b], Min Jun Kim [c], Jae-Min Myoung [b,*]

[a] School of Nano & Advanced Materials Engineering, Changwon National University, 9 Sarim-Dong, Changwon, Gyoungnam 641-773, Republic of Korea
[b] Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-Dong, Seoul 120-749, Republic of Korea
[c] Department of Mechanical Engineering & Mechanics, Drexel University, 3141 Chestnut St, Philadelphia, PA 19104-2875, USA

Received 25 April 2007; accepted 22 May 2007
Available online 7 June 2007
Communicated by V.M. Agranovich

Abstract

Field emission (FE) behaviours of ZnO nanoneedle array under ultraviolet (UV) irradiation have been investigated. UV irradiation noticeably stabilized the FE behaviours. Modifications in the tunnelling barrier height and effective aspect ratio due to the oxygen-related surface species, which can be desorbed by UV irradiation, are supposed to be responsible for these observations.

PACS: 61.46.-w; 79.70.+q; 81.05.Dz; 85.45.Db

Keywords: II–VI compound semiconductor; ZnO nanoneedle; Field emission

1. Introduction

One-dimensional (1D) nanostructures such as carbon nanotubes (CNTs) and semiconductor nanowires are regarded as promising candidates for building blocks or basic units of various electronic and photonic devices due to their unique and novel physical and chemical properties. One of the potential application fields of such 1D nanostructures is the field emission (FE) device for display devices. For FE applications, a great deal of research has been concentrated on CNTs to exploit their superior electrical properties and inherent geometric advantage, high aspect ratio [1–7]. In addition to CNTs, 1D ZnO nanostructures have attracted attention recently since they have environmental stability, high melting point, negative electron affinity and good mechanical properties in addition to high aspect ratios and unique controllable apex structures. Intensive work on the field emission of ZnO nanowires has thus been carried out and there are ample observations that ZnO nanowires have promising FE characteristics comparable to or superior to those of CNTs [8–15].

In order for the 1D nanostructures to be used as the building blocks of FE devices, some requirements should be fulfilled. Previous experimental studies suggested that 1D nanostructures with small diameters and high aspect ratios should form arrays with good vertical alignments on the substrate (electrode) to achieve desirable FE characteristics [9,10,12,16]. In addition, sharp tips tended to show better FE performances [14,17]. In this regard, recent advances in fabrication techniques have enabled production of 1D ZnO nanostructures with high crystalline and optical qualities via relatively simple routes such as thermal evaporation employing chemical vapour transport and condensation (CVTC) process [18]. Another important factor influencing the FE behaviour is the surface states. Experimental observations on both CNTs and ZnO nanostructures suggested that the presence of surface adsorbates or imperfections could modify the energy band structure through the formation of surface states to control the FE properties. Regarding the role of surface structures including the adsorbates, scare works are available [11,13] and therefore, more investigation would be necessary.

* Corresponding author. Tel.: +82 2 2123 2843; fax: +82 2 365 2680.
E-mail address: jmmyoung@yonsei.ac.kr (J.-M. Myoung).

0375-9601/$ – see front matter
doi:10.1016/j.physleta.2007.05.106

In order to obtain an array of 1D ZnO nanostructure fulfilling the morphological requirements, one may employ catalyst-free metal-organic chemical vapour deposition (MOCVD) and use substrates providing a good epitaxial interface with the $(000\bar{1})$ plane of the wurtzite ZnO. Through this method, it is possible to form vertically aligned array of 1D ZnO nanostructures with sharp tips [19]. However, for FE applications, there is a technical difficulty. The only practical substrate providing good epitaxial interface with the $(000\bar{1})$ plane of the wurtzite ZnO is *c*-plane sapphire, which is electrically insulating [20]. On the other hand, use of metallic or Si substrates to incorporate an electric conduction path to the ZnO nanostructures could result in somewhat poor alignments and/or blunt tips due to catalytic reaction of the metals with ZnO [21]. One possible way of obtaining good vertical alignments of ZnO nanowires on these substrates is the incorporation of a ZnO buffer layer. It is expected that by forming an Al-doped ZnO buffer layer, which exhibit *n*-type conductivity, provision of seed for good vertical alignment and conduction path can be achieved simultaneously.

In the current study, field emission characteristics of ZnO nanoneedles grown by catalyst-free MOCVD are investigated from the viewpoint of the good vertical alignment and the role of oxygen-related surface species. An array of ZnO nanoneedles was formed on Si (001) substrate deposited with ZnO/Pt buffer electrode first. Field emission characteristics were then measured on test FE cells with and without ultra violet (UV) irradiation, which has been shown to modify surface states in the previous work by the current authors [22].

2. Experimental details

Test FE cells were prepared by combining the ZnO nanoneedle array, transparent conductive oxide (TCO) electrodes and ceramic ball spacers. Initially, Pt conductive layer was deposited to the thickness of 500 Å on a Si (001) substrate by DC magnetron sputtering with the sputtering power of 20 W at room temperature. To facilitate the formation of ZnO nanoneedles in the form of a vertically grown array while providing a conduction path to them, an Al-doped ZnO buffer layer was subsequently deposited on the Pt conductive layer to the thickness of 150 nm by RF magnetron sputtering. Sputtering was carried out using an Al-doped ZnO target (3 wt% Al) with the sputtering power of 150 W in Ar atmosphere at 673 K. On this layer-structured ZnO/Pt/Si substrate, an array of ZnO nanoneedles was formed by catalyst-free MOCVD at 883 K. Diethylzinc (DEZn) was used as the Zn precursor and high-purity (5N) O_2 gas was used as the oxidiser. Ceramic ball spacers were then placed on the ZnO nanoneedle array before finishing the assembly of the test FE cell by covering the structure with ITO-coated glass (ITO coating by sol-gel technique on Corning 1373 glass) to provide the anode. The spacing between the nanoneedle cathode and the anode was about 500 μm. Morphology of the ZnO nanoneedle array and the shapes of individual nanoneedles were observed in scanning electron microscopy (SEM). Crystallinity of the nanoneedles was evaluated by X-ray diffraction (XRD) in θ–2θ scan mode and high-resolution transmission electron microscopy (HRTEM). Current density-applied field

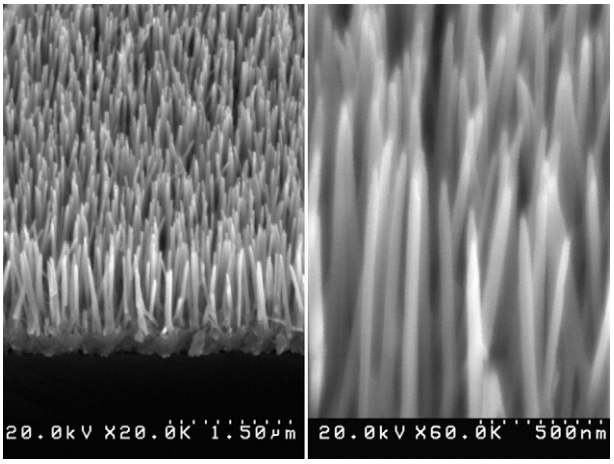

Fig. 1. SEM micrograph showing the morphology of the ZnO nanoneedle array formed on the layered ZnO buffer/Pt/Si substrate by catalyst free MOCVD.

(J–E) characteristics of the test FE cell were measured in a vacuum (1.3×10^{-4} Pa) using a Keithley 485 picoammeter. The role of the oxygen-related surface species was investigated by measuring the J–E characteristics with and without UV irradiations. A Xe arc lamp with a monochromator was used as a UV source which gave the UV wavelength of 350 nm and the power intensity of 1 mW cm^{-2}.

3. Results and discussion

ZnO nanoneedles on the Al-doped ZnO buffer layer formed a dense array with their growth directions normal to the substrate surface as shown in the SEM image of Fig. 1. The typical length and diameter of the nanoneedles were approximately 1.6 μm and 40 nm, respectively yielding an aspect ratio of about 40. In Fig. 1, it is seen that the nanoneedles have good vertical alignments comparable to the ZnO nanowire arrays formed on *c*-plane sapphire substrates [19]. Since the measured electrical resistivity of the Al-doped ZnO buffer layer was about 6×10^{-3} Ω cm, it is expected that the buffer layer itself can function as a suitable electrode to provide an electron conduction path to the nanoneedle emitters as well. Thus, use of a ZnO buffer layer would be an effective way of forming a vertical array of 1D ZnO nanostructures on substrates that have no epitaxial relation with the $(000\bar{1})$ plane of wurtzite ZnO while incorporating a seamless electrode to the 1D nanostructure emitters. In the detailed view of the nanoneedles shown in right side of Fig. 1, it can be seen that ZnO nanoneedles have sharp tips, which are the characteristic of the catalyst-free growth.

Uniformity in the alignments with respect to the surface normal is further confirmed from the XRD spectra shown in Fig. 2. The peaks in the XRD spectra in Fig. 2 correspond to ZnO (0002), ZnO $(10\bar{1}1)$, ZnO $(10\bar{1}2)$, ZnO $(10\bar{1}3)$, Si (004) and ZnO (0004), respectively, from the left to right. Among the ZnO-related peaks, the (0002) peak at $2\theta = 34.47°$ is the most prominent while the relative intensities of the $(10\bar{1}l)$ peaks are very low (less than about 1% with respect to the (0002) peak) indicating that the ZnO nanowires were grown with *c*-axis ori-