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Enhanced field emission from ZnO nanowire arrays utilizing MgO buffer between seed layer and silicon substrate

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ABSTRACT

Field emitters based on ZnO nanowires and other nanomaterials are promising high-brightness electron sources for field emission display, microscopy and other applications. The performance of a ZnO nanowire field emitter is linked to the quality, conductivity and alignment of the nanowires on a substrate, therefore requiring ways to improve these parameters. Here, ZnO nanowire arrays were grown on ZnO seed layer on silicon substrate with MgO buffer between the seed layer and Si. The turn-on field and enhancement factor of these nanowire arrays are 3.79 V/μm and 3754, respectively. These properties are improved greatly compared to those of ZnO nanowire arrays grown on ZnO seed layer without MgO buffer, which are 5.06 V/μm and 1697, respectively. The enhanced field emission properties can be attributed to better electron transport in seed layer, and better nanowire alignment because of MgO buffer.

1. Introduction

Zinc oxide (ZnO) has attracted a great deal of attention in recent years as a wide band gap (3.37 eV) semiconducting, piezoelectric, and photoconducting material [1–3]. It is promising for exciton-based applications because of its high exciton binding energy of 60 meV. ZnO nanostructures have also been studied extensively for their great potential in applications in optoelectronic devices [4], field effect transistors [5], waveguides [6], photocatalysis [7], sensors [8], surface acoustic solar cells [9], and field emitters [10]. Among various ZnO nanostructures, vertical one-dimensional (1D) ZnO nanostructures such as nanowire, nanorod and nanotip arrays are expected to act as functional building blocks for future electronics including nanogenerator, field emitter and other nanoscale systems [11]. Take nanogenerator as an example, growth of orientation-, position-, and size-controlled nanowire arrays is the key for raising the output voltage and power [12]. Meanwhile, the alignment is an important factor for field emission (FE) properties [13]. All kinds of fabrication methods such as vapor transfer process [14], metal organic chemical vapor deposition [15], thermal evaporation [16] and hydrothermal synthesis [17] have been utilized to prepare 1D ZnO nanostructures.

Silicon and sapphire wafers are widely utilized as substrates to fabricate ZnO based devices. Compared with sapphire wafers, silicon wafers have advantages such as lower cost and resistivity. ZnO nanowire arrays on Si wafer have not reached satisfactory quality because of the large stress as well as their chemical dissimilarities [18,19]. Metal catalysts such as Au have been used to assist and control ZnO growth on Si substrates [20]. However, after this vapor-liquid-solid (VLS) process, the residual catalysts may be a source of contamination that will influence the purity of ZnO nanowire arrays. On the other hand, the vapor-solid (VS) route appears to be more versatile because it is not confined by the catalyst nanoparticles. It was reported that a thin film of ZnO seed layer was utilized as the nucleation template to grow well aligned high-quality ZnO nanowires by vs methods [21]. However, there is still a large strain at the interface of the ZnO seed layer and Si substrate due to their large lattice mismatch. The lattice mismatch could have a detrimental impact on the crystallinity of ZnO seed layer, which degrades the electron transport, and in turn, affects the FE properties of field emitters and electrical properties of other ZnO based devices such as solar cells, photodetectors and light emitting diodes [3]. Epitaxial synthesis of 1D ZnO nanowire arrays on ZnO substrates would provide a high-quality interface, which is favorable for electrical

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properties. However, single-crystal ZnO wafers are not cost effective for the moment.

Meanwhile, buffer layers including amorphous and crystalline ones are widely used in the field of 2D heteroepitaxial film growth on various substrates to improve the active film quality [22,23]. One of the popular buffer layers for ZnO epitaxy is MgO [22–24]. MgO is thermodynamically stable, and also has low dielectric constant. Both lattice mismatches between MgO and ZnO and between MgO and silicon are lower than that between ZnO and silicon [25]. High-quality ZnO thin films have been grown on Si (100) substrates by utilizing MgO as buffer layers [25,26]. However, the effect of MgO buffer layer between the ZnO seed layer and Si substrate on the growth of ZnO nanowire arrays on top and the FE properties of the nanowire arrays has not been reported yet. In this paper, we report better field emission properties from ZnO nanowire arrays grown on ZnO seed layer on Si with a MgO layer as the buffer than that without MgO buffer. The reasons of the improvement of FE properties are discussed.

2. Experimental details

2.1. Synthesis of ZnO nanowire arrays

ZnO nanowire arrays were synthesized by chemical vapor deposition (CVD) on ZnO thin film seed layers. ZnO seed layers with and without MgO buffer were grown on pre-cleaned p^+-Si (100) substrates in a radio frequency plasma-assisted SVTA molecular beam epitaxy system [27]. Zn and Mg sources were provided by regular Knudsen-cells filled with elemental Zn (6N) and Mg (6N), respectively. O source was provided by a radio frequency plasma source sustained with O_2 (6N) gas. A mass flow controller was used to precisely tune the O_2 flow rate. MgO thin film was grown on Si substrate at 350 °C with 455 °C Mg cell temperature, 5.0 sccm (standard cubic centimeter per minute) O_2 gas flow rate, and 400 W oxygen plasma power, followed by a ZnO buffer layer growth at 350 °C, for 1 min to improve subsequent ZnO seed layer quality. The ZnO layers were grown on MgO buffer layer or directly on Si substrate at 550 °C, with Zn cell temperature of 345 °C, O_2 gas flow rate of 5.0 sccm, and oxygen plasma power of 400 W. The thickness of the seed layers is around 140 nm. Then the two ZnO seed layer substrates with and without MgO buffer were transferred to a CVD quartz tube furnace. Analytical grade zinc powder (purity 99.99%) was employed as Zn source. The source material was placed in a quartz boat located in the center of the tube. The substrates were placed downstream of the carrier gas flow. The quartz tube was purged with 500 sccm of argon and 0.8 sccm of oxygen during the entire furnace process of nanowire growth. The pumping speed of a mechanical pump was regulated to maintain the pressure inside the quartz tube at the lowest level during the evaporation. Then the furnace temperature was raised to 700 °C at a rate of 10 °C/min. After growth for 30 min, the furnace was cooled naturally down to room temperature.

2.2. Characterizations and measurements of the obtained nanoarrays

The crystal structure and chemical nature of ZnO nanowire arrays were analyzed using X-ray diffractometry (XRD) (parallel lights) with Cu K-alpha radiation (=1.54187 Å) operating at 40 kV and 20 mA. The morphology of the samples was obtained utilizing a field emission scanning electron microscope (FESEM). The interface is characterized by atomic resolution scanning transmission electron microscopy (STEM) and the elemental map is characterized by STEM electron energy loss spectroscopy (EELS). The FE properties were measured in vacuum at a pressure of 5×10^{-6} Pa, a distance of 300 μm, and a temperature of about 300 K.

3. Results and discussion

3.1. Crystallinity and surface morphology

Fig. 1(a) and (b) show SEM images of the surface morphology of ZnO seed layers with and without MgO buffer, respectively. The scale bars are 200 nm. The grains of ZnO seed layer with MgO buffer are more regular than that without MgO buffer. When nanowire arrays are grown on ZnO seed layer with MgO buffer (denoted as nanowire arrays with MgO buffer), they are relatively more vertically aligned than those grown on ZnO seed layer without MgO buffer layer (denoted as nanowire arrays without MgO layer), as shown in the top-view (Fig. 1(c) for nanowire arrays with MgO layer and Fig. 1(d) for nanowire arrays without MgO layer) and side-view (Fig. 1(e) for nanowire arrays with MgO layer and Fig. 1(f) for nanowire arrays without MgO layer) SEM images, respectively. The inset of Fig. 1(c) shows a high-magnification image of a single nanowire, indicating that the nanowires are c-oriented. The scale bars are 500 nm. The diameter and length of the nanowires are about 35 nm, 4.3 μm, respectively.

Fig. 2 shows XRD patterns of the two ZnO nanowire array samples. Both nanowire arrays exhibit the preferred orientation of (001), which is consistent with the theory that ZnO is usually grown with c-axis preferred orientation under typical growth conditions because of the lowest surface energy of the (001) basal plane in ZnO [28]. The degree of the orientation can be illustrated by the relative texture coefficient [29], which is given by

$$TC_{002} = \frac{I_{002}/I^0_{002}}{I_{002}/I^0_{002} + I_{103}/I^0_{103}}$$

where TC_{002} is the relative texture coefficient of diffraction peaks (002) over (103), I_{002} and I_{103} are the measured diffraction peak intensities due to (002) and (103) planes, respectively, $I^0{}_{002}$ and $I^0{}_{103}$ are the corresponding values of standard PDF card measured from randomly oriented powder samples. For materials with random crystallographic orientations, e.g. powders, the texture coefficient is 0.5. For nanowire arrays with MgO layer, the calculated TC_{002} is 1, which means the nanowire arrays with MgO layer are totally c-oriented. The lattice constant is c = 5.205 Å. For nanowire arrays without MgO layer, the calculated TC_{002} is 0.756, which means the directions of the nanowires are relatively diverse. The lattice parameters are a = 3.252 Å, c = 5.205 Å. Both patterns are in good agreement with the standard values (JCPDS card No. 36-1451: a = 3.2498 Å c = 5.2066 Å). These results reveal that the synthesized ZnO nanowires have good crystalline wurtzite structure.

3.2. Characterizations of substrates

The STEM annular bright field (ABF) and the elemental map of the selected area by STEM EELS spectrum images for the interface of LT-ZnO/MgO/Si are shown in Fig. 3. Fig. 3(a) is the STEM annular bright field image. Fig. 3(b)–(e) are elemental maps of (b) O, (c) Zn, (d) Mg, and (e) Si. Fig. 3 shows that the middle layer between Si substrate and LT-ZnO layer is amorphous MgO.

Since crystal quality of ZnO seed layer can affect the electron transport, and in turn, FE properties [3], XRD was utilized to estimate effect of amorphous MgO layer on the crystal quality of the seed layers. As can be seen from the XRD spectra in Fig. 4, both ZnO seed layers have wurtzite crystalline structure. For ZnO seed layer with MgO buffer, only (002) peak appears, indicating that it is highly c-oriented. Meanwhile, XRD pattern of ZnO seed layer without MgO buffer shows multiple peaks, indicating that it is lowly c-oriented. The lattice constants of ZnO seed layers with and without MgO buffer are c = 5.2093 Å, and a = 3.2543 Å, c = 5.2123 Å, respectively,