Communication

Growth of Crossed ZnO Nanorod Networks Induced by Polar Substrate Surface

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ABSTRACT: We show that by controlling the growth conditions, the crossed networks of ZnO nanorods were grown on an MgO (001) substrate. The [0001] ZnO nanorods grow along the (111) directions of MgO substrate and form aligned arrays. This growth is a result of polar surface induced growth from both the MgO {111} and ZnO ± {0001}. The crossed ZnO nanorod networks are a potential candidate for field emission, optoelectronics, ultrasensitive sensing, catalysts and filtering.

In this communication, we report the growth of crossed nanorod networks of ZnO on MgO. The structure of the crossed ZnO networks is characterized, and its formation process is explained on the basis of polar surfaces for both the substrate and the ZnO. The photoluminescence (PL) spectrum of ZnO nanorod networks exhibits a strong emission peak at 386 nm. The 3D crossed ZnO network reported here could be important for applications in the transistor, optoelectronics, field emission, filtering, catalysis, and gas sensing.

Experimental Section. In the vapor—liquid—solid (VLS) growth, a 2 nm thick Au thin film was deposited onto the (001) MgO substrates at room temperature in an electron beam evaporation system at a pressure of ~5 × 10⁻⁶ Torr. Upon heating, the Au nanoparticles served as the catalyst for the VLS growth. The experimental apparatus includes a horizontal tube furnace, a rotary pump system, and a gas supply system. A mixture of commercial ZnO and graphite powders in a 4:1 Zn:C ratio was placed in an alumina boat, which was heated to a peak temperature of 1100 °C. The MgO substrate was placed at a temperature zone of ~800 °C for collecting ZnO nanostructures. After the tube had been evacuated to a pressure of 1 × 10⁻³ Torr, the samples were heated to 1100 °C at a rate of 5 °C/min and held at 1100 °C for 30–120 min with a mixture of 25 sccm Ar and 5 sccm O₂ flowing through the tube.

After the growth process, the resulting product was collected for phase identification using grazing incidence X-ray diffractometry (XRD) with a fixed incident angle of 0.5°. The substrate-bound nanorods were mechanically scrapped and sonicated in ethanol and deposited on carbon-coated copper grids for transmission electron microscopy (TEM) characterization. Morphological studies of grown ZnO nanostructures have been performed with a JEOL 2010 TEM operating at 200 kV and a JEOL JSM-6500 field emission scanning electron microscopy (SEM). The PL properties of synthesized nanorods were studied at room temperature using a He—Cd laser with a wavelength of 325 nm as the excitation source.

Results and Discussion. For the samples cooled down to room temperature, the structure of the as-grown nanorods was determined by XRD. As shown in Figure 1, all of the diffraction peaks can be ascribed to the hexagonal-structured ZnO with the lattice constants of a = 0.325 nm and c = 0.52 nm, consistent with the standard data file (ICDD-PDF36-1451). No characteristic peaks from other phases were observed.

For the samples heated to 1100 °C and held at 1100 °C for 30 min, self-oriented ZnO nanowires were grown on the Au-deposited (001) MgO substrate, as shown in Figure 2. Figure 2a is a top view SEM image of the ZnO arrays on the MgO substrates. Figure 2b shows a cross-sectional SEM image of the sample with the viewing
The relative crystal orientations are shown in the insets of a and b in Figure 2. It is clear that these ZnO nanorods formed crossed networks. In addition, beltlike ZnO nanostructures were also formed. From the information provided by images a and b in Figure 2, the ZnO nanorods grow along the 〈111〉 direction of the MgO substrate, as shown schematically in Figure 2c. In the present study, there are four directions of the growth for ZnO nanowire on the MgO substrates, which is a result of polar surface induced growth. In contrast, crossed ZnO nanowire networks on m-sapphire substrates were obtained by taking advantage of the good epitaxial interface between the (0001) plane of ZnO and the (1120) plane of the sapphire. TEM has been performed to further characterize the ZnO nanostructures. Figure 3a shows a typical TEM image of the single ZnO nanorod with a sharp tip. The diameter is about 50 nm. The corresponding selected area electron diffraction, as shown in Figure 3(b), confirms that the phase of nanorods is hexagonal wurtzite-structured ZnO. Images c and d in Figure 3 are high-resolution TEM (HRTEM) images from the outlined region indicated in Figure 3a. Images c and d in Figure 3 depicts that ZnO nanorods are single-crystalline and free of defects. The growth direction of ZnO nanorod was determined to be [0001]ZnO.

To understand the growth orientation of the [0001] ZnO nanorods on the (001) MgO substrate, we start from the structure of ZnO. ZnO has the hexagonal structure with \( a = 0.325 \) and \( c = 0.52 \) nm. ZnO can be simply viewed as composed of alternative layered \( \text{Zn}^{2+} \) and \( \text{O}^{2-} \) ions planes parallel to the basal plane. The (001) and (001) surfaces of ZnO are terminated with \( \text{Zn}^{2+} \) and \( \text{O}^{2-} \) ions, respectively, which are known as the polar surfaces. MgO has the NaCl cubic structure with lattice parameter of \( a = 0.421 \) nm. The \( \text{Mg}^{2+} \) and \( \text{O}^{2-} \) ions are distributed alternatively in parallel to the {111} plane, thus, the {111} polar surfaces of MgO, respectively. (b) [0001] projection of ZnO structure and (c) [111] projection of MgO structure.

To understand the growth orientation of the [0001] ZnO nanorods on the (001) MgO substrate, we start from the structure of ZnO. ZnO has the hexagonal structure with \( a = 0.325 \) and \( c = 0.52 \) nm. ZnO can be simply viewed as composed of alternative layered \( \text{Zn}^{2+} \) and \( \text{O}^{2-} \) ions planes parallel to the basal plane. The (001) and (001) surfaces of ZnO are terminated with \( \text{Zn}^{2+} \) and \( \text{O}^{2-} \) ions, respectively, which are known as the polar surfaces. MgO has the NaCl cubic structure with lattice parameter of \( a = 0.421 \) nm. The \( \text{Mg}^{2+} \) and \( \text{O}^{2-} \) ions are distributed alternatively in parallel to the {111} plane, thus, the {111} polar surface can be terminated either with \( \text{Mg}^{2+} \) or \( \text{O}^{2-} \) ions. The structure model of growth of [0001] ZnO nanorods along the (111) \(_{\text{MgO}} \) direction is shown in Figure 4a. The structure models of the ZnO along [0001] direction and MgO along [111] direction are illustrated in Figure 4. The (001) surface of MgO, however, is a nonpolar surface, thus a direct
stacking of [0001] ZnO nanorod along [001]MgO is restricted by the crystal symmetry, lattice mismatch as well as the surface charge. On the other hand, the [001]MgO surface may be rough as a result of polishing, and it can exhibit tiny {111} type facets. Because of the polar charges on both MgO {111} and ZnO (0001), a direct facing of ZnO (0001) and MgO {111} as a result of polar surface induced growth from both the MgO and ZnO planes have 6-fold symmetry. The lattice mismatch between the two prominent planes {110}MgO to {211}ZnO is as high as 10.4%. This lattice mismatch is large enough to prevent the growth of large-size epitaxial films, but facilitate the formation of small size nuclei of ZnO leading eventually to the growth of nanorods.

From the symmetry point of view, both (0001)ZnO and (111)MgO planes have 6-fold symmetry. The lattice mismatch between the two prominent planes [110]MgO to [211]ZnO is as high as 10.4%. This lattice mismatch is large enough to prevent the growth of large-size epitaxial films, but facilitate the formation of small size nuclei of ZnO leading eventually to the growth of nanorods. Figure 5 shows a room-temperature PL spectrum of the crossed ZnO nanorod networks. There is a strong emission peak at 383 nm, corresponding to the near band edge emission of ZnO material. Encouraged by the recent demonstration of ultrasensitive and highly selective gas sensors using three-dimensional tungsten oxide nanowire networks, a study on the gas sensing capability may yield very positive results. Furthermore, field emission, optoelectronic, and filtering performances of 3D crossed ZnO nanorod network should be explored since it appears as a promising material for such applications because of its unique nanostructure.

**Conclusion.** In summary, we show that by controlling the growth conditions, the crossed networks of ZnO nanorods were grown on an MgO (001) substrate. The [0001] ZnO nanorods grow along (111) directions of MgO and form ordered arrays. This growth is a result of polar surface induced growth from both the MgO [111] and ZnO ± (0001).

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**References**