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Low-temperature Heteroepitaxy of Morphology-controlled ZnO Mirco/Nanorod Arrays on GaN Substrates

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The influence of GaN seed morphology on the growth of ZnO rods by solution-based process is investigated. The orientation, defect density, and crystallinity of ZnO rods are systematically studied in this research. The structural properties of ZnO rods are investigated using field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). With different solution concentration treatments, the scale of ZnO rods is controlled with a wide size range from 130 nm up to 2.5 µm in diameter. Our investigation demonstrates that the morphologies of GaN seeding layers have strong influences on the features of the ZnO rods grown thereon. The low-temperature heteroepitaxy of ZnO mirco/nanoarchitecture arrays on GaN can be very useful for many device applications, especially for light-emitting diodes.

In recent years, one-dimensional (1D) semiconductor materials have drawn a great deal of interest due to their importance in basic scientific researches and potential applications in micro/nanoscale electronic and optoelectronic devices.[1,2] Such perspectives have stimulated a lot of approaches to obtain size-controllable, finely ordered, uniformly aligned, and single crystalline 1D semiconductor materials. ZnO, a wide bandgap (3.37 eV) compound semiconductor with large exciton-binding energy (60 meV) at room temperature, is a suitable material for applications in blue/ultraviolet (UV) optoelectronic devices.[3] Several gas phase methods have been demonstrated to fabricate 1D ZnO nanostructures,[4–8] but these techniques still have some limitations for substrate size and the need for high-temperature operation. Most importantly, it is not easy to well control the morphology and geometry of ZnO rods with gas phase methods. Recently, solution deposition approaches,[9] which are based on wet chemical and bottom-up processes, have been developed to prepare ZnO nanostructures. Such methods are simple, can be carried out at low temperature and are inexpensive. Reports have been made of the growth of ZnO on various substrates, such as Si,[10] indium tin oxide (ITO),[11] sapphire,[12] and GaN.[13] Among these substrates, it is considered that the GaN is the most suitable to be used as a template for the heteroepitaxy of ZnO since these two materials have the same wurtzite crystal structure, low lattice constant misfit (only 1.9%), and similar thermal expansion.

Due to similar crystal properties, ZnO is expected to epitaxially grow on a GaN template. Le et al.[13] have reported on the growth of ZnO nanorods on thin GaN films via aqueous solution method. Uniformly distributed ZnO nanorods with a diameter of 80–120 nm can be fabricated. GaO et al.[14] successfully synthesized ZnO nanorods and nanoflowers on GaN epiwafer. Recently, Cole et al.[15] have reported on the controlled formation of ZnO microcrystal arrays by photolithography. Most researches focused on preparation and properties of ZnO micro/nanostructure. To date, the influence of GaN seed morphology on the growth of ZnO rods has not been reported. In addition, a wide size range of controlled growth of ZnO rods on GaN without the lithography-based technique has not been achieved. Here we report a simple method to achieve feature-controlled ZnO mirco/nanorod arrays via hydrothermal method on GaN substrates. The influence of GaN seed morphology on the growth of ZnO rods by solution-based process was systematically investigated. The size of ZnO mirco/nanorod arrays was controlled over a wide size range from 130 nm up to 2.5 µm in diameter and the crystallinity of ZnO rods grown on different GaN substrates is also discussed in this work.

The fabrication processes are as follows: At first, undoped GaN layers were epitaxially grown on a sapphire substrate by using metal–organic vapor phase epitaxy (MOVPE). Trimethylgallium (TMGa) and ammonia were employed as the reactant sources and hydrogen was the carrier gas. Three different phases of GaN serving as the seeding layers for growing ZnO micro/nanorods were deposited on sapphire substrates. Typical morphologies of GaN grown in different phases are shown in Figure 1. In the phase 1, the deposited GaN initially formed numerous nucleation seeds on sapphire substrates. As the growth temperature and reactant time increased, GaN nucleation seeds were merged into larger islands in the phase 2 and finally formed into thin GaN films in the phase 3. These three different kinds of GaN substrates were then employed as the seeding layers to grow ZnO rods, respectively. The hydrothermal growth of ZnO rods was performed by putting the sample in an aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine (HMT) at 90 °C for 3 h.[9] In order to understand the influence of the solution concentrations on the size of ZnO rods, we prepared two growth solutions with 50 and 100 mM concentrations to make a comparison.

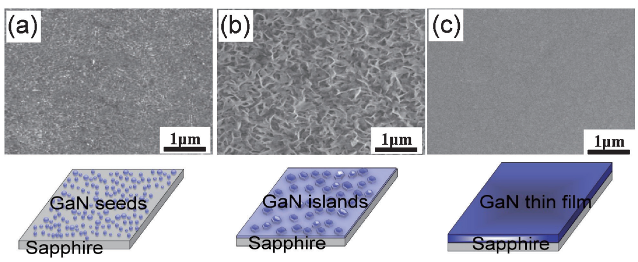

Figure 1. FESEM and schematic images of GaN seeding layers grown on sapphire substrate in different phases. (a) Phase 1, (b) phase 2, and (c) phase 3.

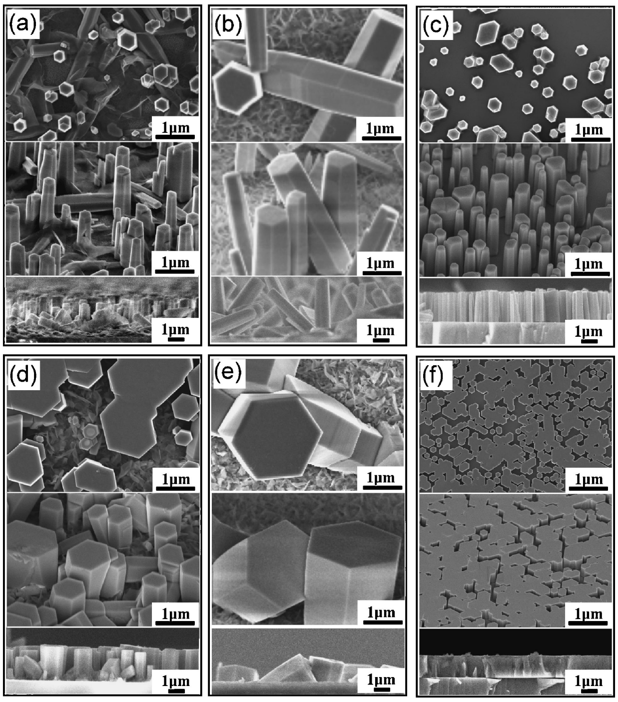

Figure 2. FESEM images of ZnO micro/nanorods grown on different phases of GaN seeding layers with different solution concentrations for 3 h: (a) phase 1 with 50 mM, (b) phase 2 with 50 mM, (c) phase 3 with 50 mM, (d) phase 1 with 100 mM, (e) phase 2 with 100 mM, and (f) phase 3 with 100 mM.

The general morphologies of as-synthesized ZnO micro/nanorods on GaN substrates were examined by FESEM (Elionix, ERA 8800). Figure 2 shows the plan view, cross-sectional view, and tilt-angle view of FESEM images of ZnO micro/nanorods grown on different GaN seeding layers with different solution concentrations, all were grown for 3 h. We can clearly observe the morphology and density of ZnO rods from these images. The plan view images all show that the ZnO micro/nanorods grown at 90 °C are consistent with the typical growth habit of ZnO crystals, hexagonal surfaces bounded with the six crystallographic planes. The typical average diameters of ZnO micro/nanorods, as shown in Figures 2a to 2f, were measured to be about 380 nm, 1.4 μm, 300 nm, 1.4 μm, 2.5 μm, and 800 nm, respectively. The average lengths of ZnO micro/nanorods were measured to be 2, 6, 1.5, 1.5, 4, and 0.9 μm, respectively. These images show that as the concentration of solution increased, the diameters of ZnO micro/nanorods all increased and the lengths of ZnO micro/nanorods all decreased correspondingly. The concentration dependence on the formation of ZnO rods on Si substrates has been reported by Vayssieres.[9] However, there is no report on concentration and the seed morphology dependence on GaN substrates. We can also observe that the orientation of ZnO rods grown with the phase 2 of GaN seeding layers is far different from the phase 1 and phase 3. The reason is that the morphology of GaN islands is too rough to grow well-aligned ZnO rods.

The full-range XRD spectra of the ZnO micro/nanorods all exhibited two peaks at 34.4 and 72.5°, corresponding to the ZnO(0002) plane and ZnO(0004) plane, respectively. The full width at half maximum (FWHM) value in XRD rocking curve

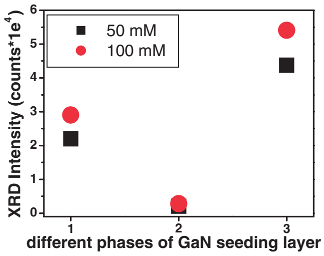

Figure 3. The intensities of XRD versus different phases of GaN seeding layers.

data at 34.4° with these six samples were all examined to be 0.2°. The peak intensities at 34.4° of samples grown with different solution concentrations and various phases of GaN seeding layers are plotted in Figure 3. The peak intensities of samples grown with 100 mM concentration are all more intense than those with 50 mM concentration. In the phase 3, the grown ZnO rods show preferred orientation along the *c* axis, and the (0002) peak intensities are more intense than phase 1 and phase 2. This implies its perfect *c* axis orientation, and this result is in accordance with its FESEM images in Figures 2c and 2f.

In summary, the influence of the GaN seed morphology and the solution concentrations on the geometry of ZnO rods via hydrothermal method are investigated. The dimension of ZnO micro/nanorods grown on the GaN can be controlled from 130 nm to 2.5 μm in diameter. The results show that GaN seeding morphology critically affects the formation and crystallinity of ZnO rods. This controlled growth of ZnO rods on GaN is beneficial to the design of electronic and optoelectronic devices.

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