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Influence of annealing temperature of ZnO layer on synthesizing low dimensional GaN nanostructured materials

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Abstract. As-grown ZnO thin films are annealed in O_2 ambient for 15 min at the temperature of 700 °C, 800 °C, 900 °C and 1000 °C, respectively. Then the Ga_2O_3 thin films are deposited on ZnO/Si(111) substrates by sputtering Ga_2O_3 target in a JCK-500A radio frequency magnetron sputtering system. The low dimensional GaN nanostructured materials are obtained on Si substrates by ammoniating the Ga_2O_3/ZnO films at 950 °C for 15 min in a quartz tube. X-ray diffraction (XRD), Scanning electron microscope (SEM), Fourier transform infrared spectrophotometer (FTIR) and photoluminescence (PL) are used to analyze the structure, morphology and optical properties of GaN nanostructured films. The results show that their properties are investigated particularly as a function of annealing temperature of ZnO layer. The mechanism is also briefly discussed.

PACS. 68.55.-a Thin film structure and morphology – 81.05.Dz II-VI semiconductors – 81.15.Cd Deposition by sputtering

1 Introduction

Group III-nitride semiconductors, since they have direct and wide band gaps and high thermal stabilities, are considered to be the basis for optical devices in the blue and ultraviolet (UV) regions of the optical spectrum and for high-temperature, high-power electronic devices [1,2]. GaN is a scientifically intriguing and technologically important material [3,4]. GaN has a direct band gap of 3.4 eV at room temperature and high external photoluminescence quantum efficiency, as well as a high excitonic binding energy of 20 meV [5]. In addition, GaN exhibits high thermal conductivity and little radiation damage, which can be applied to high power and high temperature microelectronic device. However, owing to the large mismatch between the lattice parameters of GaN and Si (16.9%: tensile) and the thermal expansion coefficient ($\alpha_{\mathrm{GaN}} = 5.9 \times 10^{-6}$/K and $\alpha_{\mathrm{Si}} = 3.59 \times 10^{-6}$/K), the direct epitaxial growth of GaN on Si substrate is difficult. Therefore, a buffer layer is used to decrease the differences between both materials. A ZnO thin layer is found to be an effective buffer layer for the growth of GaN films on Si(111) substrates due to the excellent properties [6]. Recently, there have been many reports on the formation of one-dimensional GaN structures using various methods by several groups [7–9].

In this paper, GaN nanostructured materials have been synthesized on Si(111) substrates by ammoniating the Ga_2O_3/ZnO films at the temperature of 950 °C for 15 min. The ZnO layers are firstly grown on Si(111) substrates at room temperature and annealed in O_2 ambient at different temperature. Then a Ga_2O_3 epilayer about 500 nm is deposited on the ZnO buffer layer. The growth of the Ga_2O_3 epilayers and ammoniating temperature are kept under the same condition, but the annealing temperatures of ZnO buffer layers are different for different samples. We also deposit the Ga_2O_3 films directly onto the Si substrates with the same condition. However, no nanostructured films are formed. In this letter, we study the growth of GaN influenced by the annealing temperature of ZnO buffer layers.

2 Experimental details

In our experiment, the GaN nanosized films were prepared by self-assembly of Ga_2O_3 films in their reaction with NH_3 and the process could be fallen into two steps. The first step was that ZnO thin films were firstly deposited on Si(111) substrates by sputtering ZnO target in a JCK-500A radio frequency magnetron sputtering system. Si substrates were ultrasonically cleaned by deionized water, acetone, isopropyl alcohol, and deionized water before the experiment. The sputtering chamber was evacuated by a turbomolecular pump to a base pressure of 4.0×10^{-4} Pa as a background pressure, and then argon gas (99.999%) was introduced into the chamber at a pressure of 2 Pa. When the pressure of the chamber was stabilized, the radio frequency generator was set to 150 W. The target was used as the cathode and the substrates as the anode, respectively. The distance between the target

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and the substrates was 80 mm. Then ZnO films were deposited on Si(111) substrates at room temperature after cleaning of the target with Ar plasma for 5 min, and the sputtering time is 15 min at room temperature. The thickness of ZnO film is about 300 nm. The as-grown ZnO thin films were subsequently annealed in O_2 ambient for 15 min at the temperature of 700 °C, 800 °C, 900 °C and 1000 °C, respectively.

The second step was that Ga_2O_3 thin films were deposited on ZnO/Si(111) substrates by sputtering Ga_2O_3 target in a JCK-500A radio frequency magnetron sputtering system. The different sputtering condition was as follows: a base pressure was 3.0×10^{-4} Pa; the work pressure of Ar gas (99.999%) was 2 Pa; the radio frequency generator was set to be 150 W and the frequency was 13.56 MHz; the sputtering time of Ga_2O_3 film was 90 min with the thickness of about 500 nm. Subsequently, the quartz boat with the samples was placed into the constant temperature region for ammoniating. Above all, the flowing N_2 was introduced into the tube to flush out of the residual air for 5 min, and then ammonia was flowed into the tube with a flow rate of 500 mL/min for 15 min at 950 °C while N_2 was switched off. After ammoniated, the samples were cooled down to room temperature in the N_2 ambient.

A Rigaku D/max-rB X-ray diffractometer (XRD) with Cu K_a-line, a Hitachi S-570 scanning electron microscope (SEM), Tensor 27 Fourier transform infrared (FTIR) system and LS50-B fluorescence spectrophotometer were employed to examine the structure, surface morphology and photoluminescence properties of the GaN nanostructured materials.

3 Results and discussion

3.1 XRD analysis

XRD patterns of GaN nanostructured films are taken to examine the crystal structure. Figure 1 shows the typical XRD patterns of GaN nanostructured films with the ZnO layers annealed in oxygen ambient at different temperatures: (a) unannealed, (b) 800 °C, (c) 900 °C, (d) 1000 °C. Three peaks of (100), (002) and (101) of GaN films are located at 32.36°, 34.54° and 36.78°, demonstrating that the GaN nanostructured films possess a hexagonal wurtzite structure (a = 0.318 nm and c = 0.518 nm) and have a preferred (002) orientation [10]. This c-axis orientation is believed to result from the lowest surface energy of the (002) basal plane in GaN, leading to a preferred growth in the [002] direction. As the annealing temperature of ZnO layer increases up to 1000 °C, the diffraction intensity of GaN is increased significantly, compared with the GaN of the unannealing ZnO layer, indicating that the crystal quality of GaN is improved by high temperature annealing treatment of ZnO layers. However, as the annealing temperature of ZnO layers increase, the intensity of c-axis preferred (002) orientation of GaN nanostructured films become weaker as shown in the above patterns (at 800 °C, the diffraction intensity of GaN is the strongest), demonstrating that a further increase in the temperature up to 1000 °C leads to the decrease of crystal quality of ZnO because ZnO is thermodynamically unstable with in an oxygen-free ambient leading to its evaporative dissociation into Zn and O_2 [11].

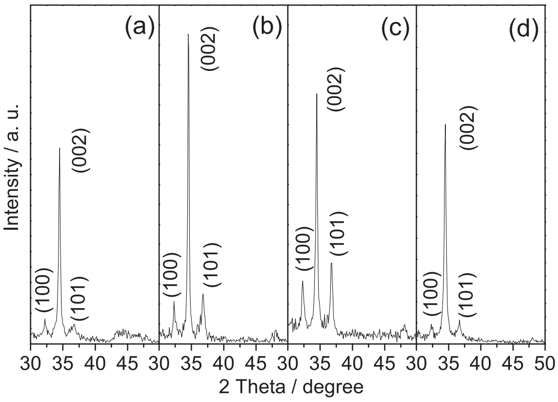

Fig. 1. XRD patterns of GaN nanostructured films with the ZnO layers annealed in oxygen ambient at different temperatures: (a) unannealed, (b) 800 °C, (c) 900 °C, (d) 1000 °C.

3.2 SEM analysis

The morphologies of the samples are characterized by SEM at room temperature. From Figure 2a, a small quantity of nanorods is found on the surface. Besides the rods, there are also a large scale of crystal grains on the surface, which have not formed into the rod and agglomerate into micrograins. Figure 2b shows the typical SEM image of the high-yield GaN nanowires, exhibiting that the GaN nanowires cross each other and are randomly distributed on the whole surface. These nanowires have a straight and smooth curved structure with diameters in the range of 60–160 nm and lengths of several tens of micrometers, indicating a high aspect ratio. As illustrated in Figure 2c, low quality GaN nanorods and agglomeration-like micrograins arbitrarily disperse on the whole surface. The GaN nanowires have extremely rough sidewalls, probably with a high density of defects resulting from Zn diffused in GaN in the ammoniating process, shown in Figure 2d. From SEM analysis, we can conclude that the low dimensional GaN nanostructured material is better with the ZnO layer annealed at 800 °C in oxygen ambient.

3.3 FTIR analysis

Figure 3 shows the FTIR spectrum of the GaN nanowires ammoniated at 950 °C with ZnO layer annealed at 800 °C. Four prominent absorption bands are observed at 559.2 cm^{-1}, 605.5 cm^{-1}, 1108.9 cm^{-1} and 1227.9 cm^{-1}. The absorption band at 559.2 cm^{-1} corresponds to Ga-N stretching vibration in hexagonal-type GaN crystal [12]. The absorption band at 605.5 cm^{-1} is associated with the local vibration of substitutional carbon in the Si crystal

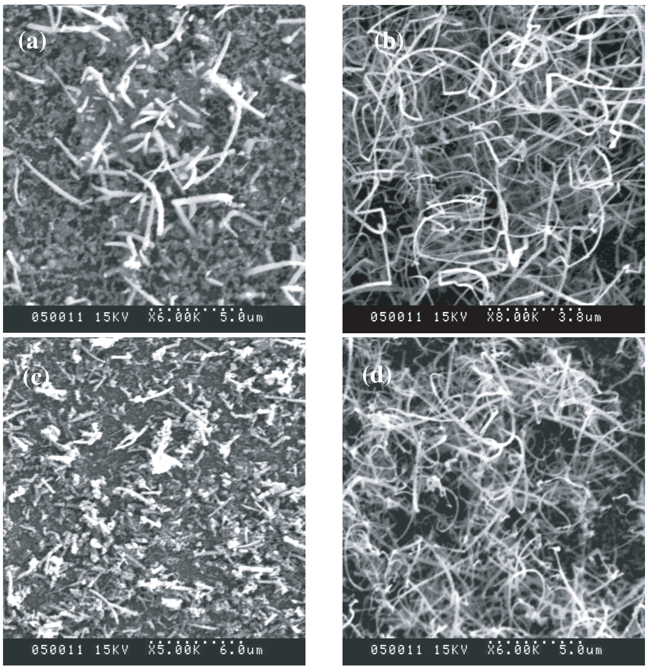

Fig. 2. SEM images of the GaN nanostructured films with the ZnO layer annealed in oxygen ambient at different temperatures: (a) unannealed, (b) 800 °C, (c) 900 °C, (d) 1000 °C.

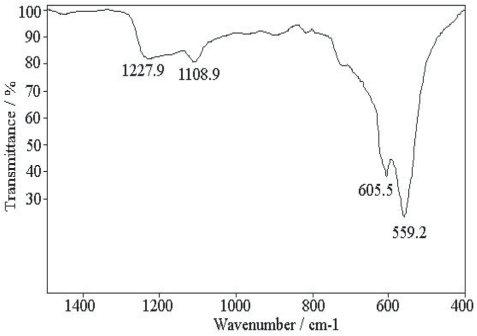

Fig. 3. FTIR spectrum of the GaN nanowires ammoniated at 950 °C with ZnO layer annealed at 800 °C.

lattice [13]. According to the literature [14], the band at 1108.9 cm^{-1} and 1227.9 cm^{-1} is related to Si-O-Si asymmetric stretching vibration mode, which ascribes to extremely thin oxide layer on the Si surface. There is no Zn-O absorption band in Figure 3 [15], which reveals that hexagonal ZnO doesn't exist and volatilized completely during high-temperature ammoniating process. Also, there is no Ga_2O_3 absorption band [16], proving that the Ga_2O_3 film reacts with NH_3 completely. The FTIR spectrum further confirms that the GaN is obtained under this condition. We also examine other samples, whose results are similar.

3.4 PL analysis

For the optical property, the measurement of PL spectrum was performed by LS50-B fluorescence spectrophotometer with a Xe lamp as the excitation source (wavelength was 298 nm) at room temperature. Figure 4 shows the PL spectrum of as-grown GaN nanomaterials ammoniated at 950 °C. Band-edge emission is observed in these nanorods samples located at 375.9 nm [17]. Because the as-grown GaN nanorods and nanowires are too large for quantum confinement effects, and even the diameter of the thinnest nanowire is much larger than the Bohr exciton radius (11 nm) of GaN [18], the UV light emission has no blue shift from the band-gap emission compared with bulk GaN [19]. Because GaN films are formed with ZnO buffer layers, Zn may diffused in GaN in the process of the ammoniation [20]. So the emission peak at 436.8 nm may correspond to the transition of Zn impurity energy level. It may be also ascribed to the electron transition from the deep acceptor level, resulting from C impurity taking place of N atoms, to the conductor band [21]. Another peak at 472.3 nm may be ascribed to existence of defects or surface states [22–24], which is attributed to the rearrangement of GaN and ammoniation process. It has been reported that the PL emission characteristics of GaN are strongly dependent on the crystal quality. The GaN with unannealing ZnO layer shows a fairly weak PL peak. As the annealing temperature of ZnO film increases up to 1000 °C, the PL intensity of GaN with ZnO film annealed at 800 °C is the highest. A further increase in the temperature up to 1000 °C leads to the decrease of the PL intensity of GaN nanoatructured films. This PL behavior indicates that the crystal quality of GaN is greatly dependent on the annealing temperature of ZnO films, which is consistent with the result of XRD.

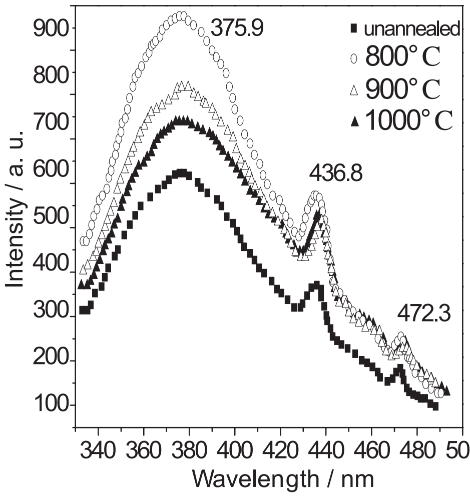

Fig. 4. PL spectrum of as-grown GaN nanorods ammoniated at 950 °C.

3.5 Discussion about growth process

According to the above analysis, as for growth mechanism of the effect of ZnO buffer layers on the following growth of GaN films, we might briefly explain as follows:

On one hand, ZnO films are annealed in oxygen ambient at different temperature. The results of ZnO buffer layers after high temperature annealing at different temperatures, such as AFM and X-ray diffraction are published on the journal of EPJ-Applied Physics [25]. A better crystal structure and more relaxed ZnO films are achieved, which conduces to the subsequent growth of Ga_2O_3 films. It could improve nucleation by lowering the surface energy and providing an improved lattice match in the growth of Ga_2O_3 films. The ZnO films would volatilize during the ammoniating process [26]. ZnO films reacted with NH_3 to produce Zn, NO_2 (or NO), and water vapor in the interface between ZnO layer and Ga_2O_3 layer. Zn sublimed at the high temperature and was brought away by NH_3 gas to the inner wall in the downstream of the tube [27]. Despite the volatilization of ZnO, it is unavoidable to form some defects and dislocations, and self-organized nanometer-sized holes were formed, which can subsequently be used as a mask or growth sites to fabricate the nanowires or act as potential nucleation sites for the GaN nanostructures.

On the other hand, it is well-known that when the ammoniating temperature is above 850 °C, NH_3 decomposes stepwise to NH_2, NH, H_2 and N [28]. The Ga_2O_3 particles should be reduced to gaseous Ga_2O by H_2 and then the reaction of Ga_2O with ammonia result in formation of GaN crystal nuclei at the above-mentioned sites. All the reactions can be expressed as:

$$\begin{aligned} NH_3(g) &\rightarrow N_2(g) + H_2(g) \\ Ga_2O_3(s) + 2H_2(g) &\rightarrow Ga_2O(g) + 2H_2O(g) \\ Ga_2O(g) + 2NH_3(g) &\rightarrow 2GaN(s) + 2H_2(g) + H_2O(g). \end{aligned}$$

Then the very small GaN granules grow up with the progress of the ammoniating process and accordingly lay the foundations for the growth of nanostructured GaN. These GaN molecules continuously come out and agglomerate into micrograins. Under the above condition, the nanostructured GaN surfaces are synthesized. When the growth direction of the micrograins orientate in the same direction, the single GaN nanowires are formed. We also deposit the Ga_2O_3 film directly onto the Si substrates with the same condition but no nanorods are formed. However, the further function of the ZnO buffer layer in the growth of GaN nanorods and more details are under study.

4 Conclusion

The low dimensional GaN nanostructured materials have been obtained on Si(111) substrates by ammoniating the Ga_2O_3/ZnO films at the temperature of 950 °C for 15 min in a quartz tube. The as-prepared products are studied by XRD, SEM, FTIR and PL. The results show that their properties are investigated particularly as a function of annealing temperature of ZnO layer. The postannealing ZnO films also have a great impact on the growth of GaN nanosize materials. The optimally annealing temperature of ZnO layer is 800 °C for the growth of GaN nanowires. Finally, the growth mechanism of the effect of ZnO buffer layers on the following growth of GaN films is also discussed.

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