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Influence of annealing time on microstructure of one-dimensional Ga_2O_3 nanorods

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ABSTRACT

Ga_2O_3 nanorods have been successfully synthesized on Si(1 1 1) substrates by magnetron sputtering through ammoniating Ga_2O_3 thin films catalyzed with Mo. The influence of ammoniating time on microstructure, morphology and optical properties of GaN nanorods was analyzed in detail using the methods of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) spectrum. The results demonstrate that the nanorods are single crystal β-Ga_2O_3 with high-quality crystalline after annealing 20 min and these nanorods have the best crystalline with 200 nm in diameter. The growth direction of β-Ga_2O_3 nanorods is parallel to [$\bar{1}$ 1 0] orientation. The optical properties of nanorods synthesized at 950 °C for 20 min are the best due to strong emission intensity. The luminescence mechanism can be explained by the presence of vacancy.

1. Introduction

Monoclinic gallium oxide (β-Ga_2O_3) is promising as a semiconductor material due to its wide band gap (4.8 eV), which exhibits particular conduction and luminescence properties, thus has potential applications in optoelectronic devices and high-temperature stable gas sensors [1,2]. One-dimensional β-Ga_2O_3 nanostructures have been synthesized by various techniques like laser ablation, carbon-assisted route, arc discharge and so on [3–8]. However, the synthesis of beta-gallium oxide nanostructures using thermal annealing Ga_2O_3/Mo films has not been reported by other group except us [9–12]. In this study, we used a new method to prepare β-Ga_2O_3 nanorods through annealing sputtered Ga_2O_3/Mo films under flowing NH_3 at 950 °C for different annealing times in a quartz tube, and the effect of annealing time on the microstructure, morphology and optical properties is studied in particular as a progress report of the results published previously in the other papers [9–12]. This growth method allows a continuous synthesis and produces a large quantity of single-crystalline β-Ga_2O_3 nanorods with relatively high purity.

2. Experimental procedure

In our research, metallic Mo and Ga_2O_3 were deposited on the polished *n*-type Si(1 1 1) substrates in turn using a JCK-500A magnetron sputtering system (150 W, 13.56 MHz).The targets for depositing Mo films and Ga_2O_3 films were hot-pressed Mo with a purity of 99.9% and sintered Ga_2O_3 with a purity of 99.99%. The sputtering time of Mo and Ga_2O_3 were 5 min and 90 min with the thickness of 300 nm and 500 nm, respectively. The background pressure was about 6.5×10^{-4} Pa and the working gas was argon with purity of 99.999% and the working pressure was 2 Pa. The distance between the target and the substrate was 8 cm. After sputtering, the samples were ammoniated in a NH_3 ambient (with purity of 99.999%) at 950 °C for different times. After ammoniation, the samples were taken out for characterization.

The microstructure, composition, morphology and optical properties of the samples were studied using X-ray diffraction (XRD, Rigaku D/max-rB, Cu K_α, $\lambda = 1.54178$ Å), X-ray photoelectron spectroscope (XPS, Microlab MKII), scanning electron microscope (SEM, Hitachi S-570), high-resolution transmission electron microscope (HRTEM, Philips TECNAI-20), and photoluminescence spectrum (PL, LS50-fluorescence spectrophotometer).

3. Results and discussion

3.1. Microstructure and components analysis

Fig. 1 shows the X-ray diffraction patterns of the samples ammoniating at 950 °C for different times.

As seen in Fig. 1(a)–(d), the samples after ammoniation are β-Ga_2O_3 with lattice constant $a = 12.24$ Å, $b = 3.04$ Å, $c = 5.81$ Å, and $\beta = 103.76°$, which are consistent with the bulk β-Ga_2O_3, as compared with JCPDS card of 41-1103.

When the ammoniating time is 20 min, the intensities of diffraction peaks are stronger than that of other peaks, whereas the full-width at half-maximum value (FWHM) is at the minimum, which shows the best crystalline at this experimental condition. The weaker peaks are probably caused by incomplete growth at less time and decomposition or sublimation at more time [13]. And

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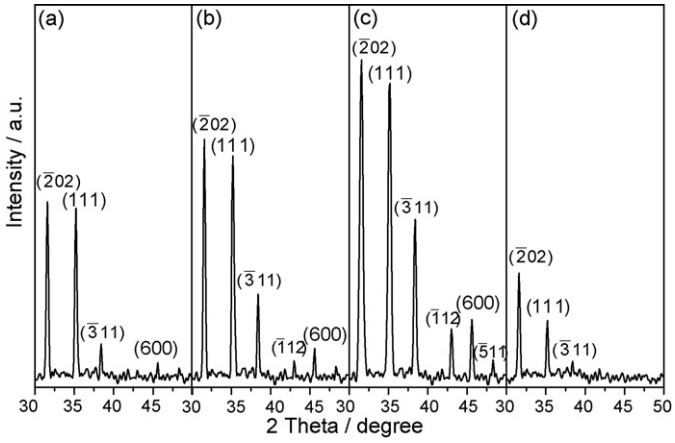

Fig. 1. X-ray diffraction pattern of the samples after ammoniation at 950 °C for different times: (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min.

the peak of GaN does not exist, which proves that the sample is Ga_2O_3 crystal with best purity.

To further analyze the components of the Ga_2O_3, the XPS test was carried out for the sample after ammoniation at 950 °C for 20 min, as shown in Fig. 2.

Fig. 2(a) shows the general scan in the binding energy, ranging from 0 eV to 1100 eV with the main components being Ga, C, and O with XPS peaks at the location of Ga3d (19.9 eV), $Ga3p_{3/2}$ (1117.9 eV), $Ga2p_{1/2}$ (1144.7 eV), and O1s (531.0 eV). The percentage of elements is calculated according to the formula [14] as follows:

$$X(\%) = \frac{A_x/S_x}{\sum_{i=1}^{N}(A_i/S_i)}$$

where A_x (A_i) indicates the peak area of element, x (i); S_x (S_i) is the atomic sensitivity factor of x (i) element; N is the number of the total elements. After calculation, quantification of the peaks shows that the atomic ratio of Ga to O is approximately 2:3.

The strong peak at the site of 189.6 eV is LMM Auger peak of Ga element. The elements of C and O arise from the surface pollution of the sample [15]. As seen in Fig. 2(c), the binding energy of Ga is 19.9 eV, which confirms that the Ga atom exists as an oxide [16]. The binding energy of $Ga2p_{3/2}$ is 1117.9 eV, which is different from that of free-state Ga element [17]. The core level of Ga has a chemical shift from elemental Ga, which arises from the tiny change of the inner electron binding energy, which is caused by different chemical environment of atoms due to the difference between atomic valences. In short, Ga element exists as combined-state, not free-state. Fig. 2(d) shows that the binding energy is 531.0 eV, which is consistent with that of O atom in β-Ga_2O_3 [18]. The result of XPS shows that the component of the samples is Ga_2O_3.

3.2. Surface morphology

Fig. 3 shows the typical SEM images of the samples synthesized at 950 °C for different times.

As shown in Fig. 3(a), there are one-dimensional β-Ga_2O_3 nanorods generated on the substrate surface with rough surface and bad crystalline quality. Whereas after annealing 15 min, the nanorods are smooth with uneven size in diameter. The diameter of nanorods in the sample (b) is almost the same as that of the sample (a). The nanorods become thicker than those shown in samples (a) and (b) with even size of about 200 nm in diameter when annealing time prolongs to 20 min. These nanorods are straight and smooth without any fine particles on their tips, which show that β-Ga_2O_3 nanorods have been obtained with high-quality crystalline. However, when annealing time increases to 25 min, nanorods dis-

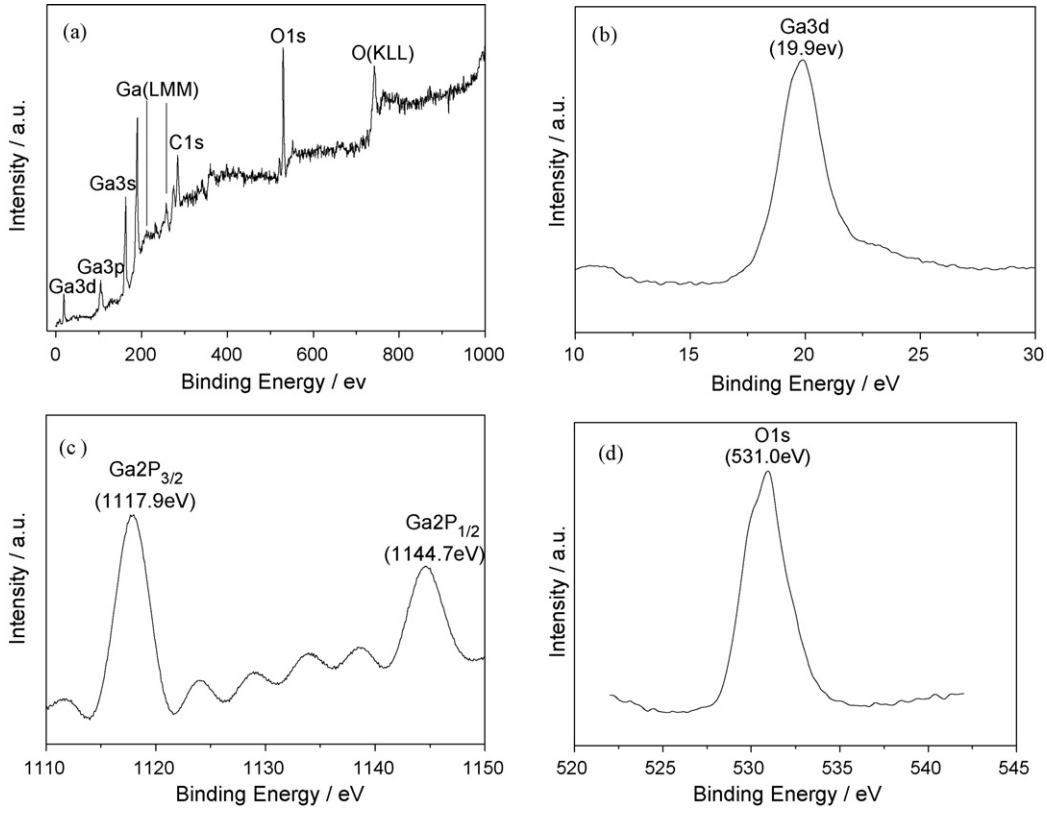

Fig. 2. XPS spectra of the sample after ammoniation at 950 °C for 20 min.

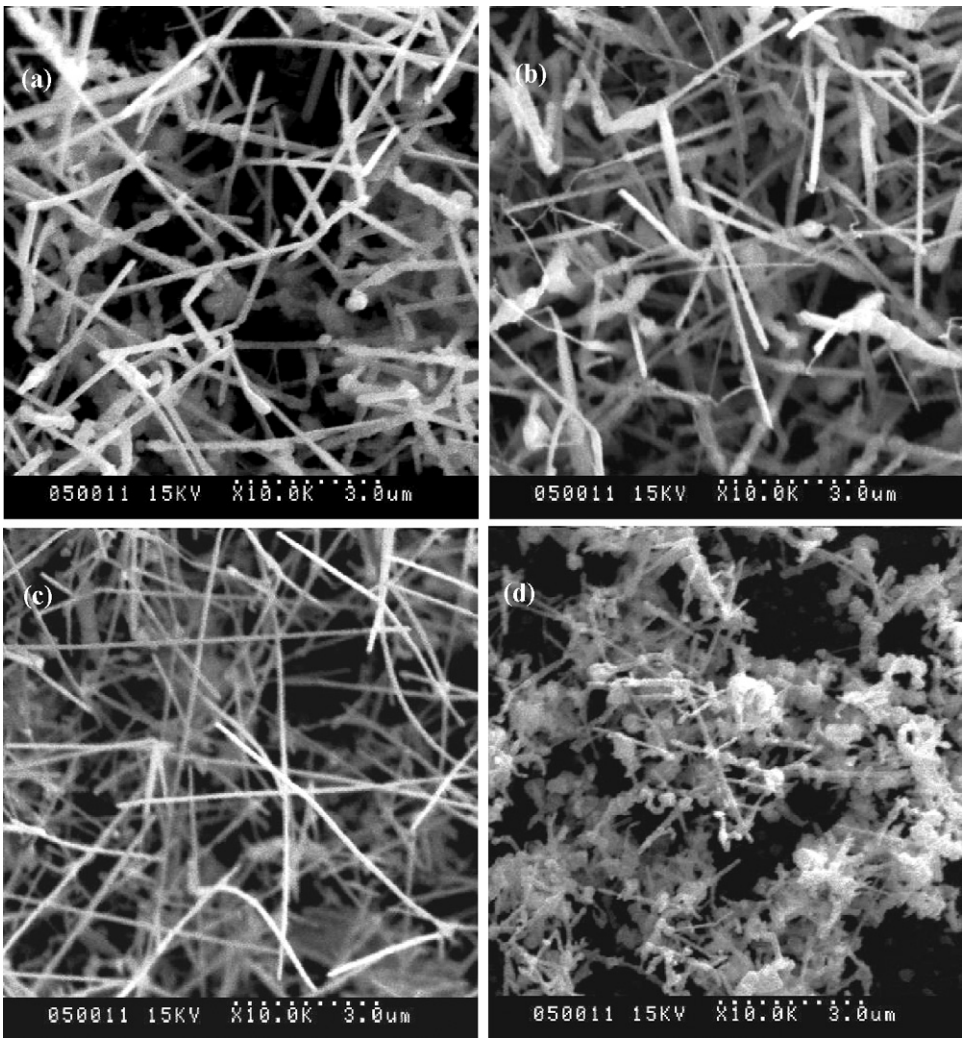

Fig. 3. SEM images of the samples after annealing at 950 °C for different times: (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min.

appear, cluster-like structures exist on the sample surface, which ascribes to recrystallination of the grains.

Fig. 4 shows the TEM, SAED and HRTEM images of an individual nanorod after ammoniating at 950 °C for 20 min.

Fig. 4(a) shows that the nanorod is straight and smooth with size of 200 nm in diameter, without fine particles on its tip, which shows the growth mechanism does not comply with vapor–liquid–soild (VLS) process [19]. As seen from Fig. 4(b), HRTEM lattice image of

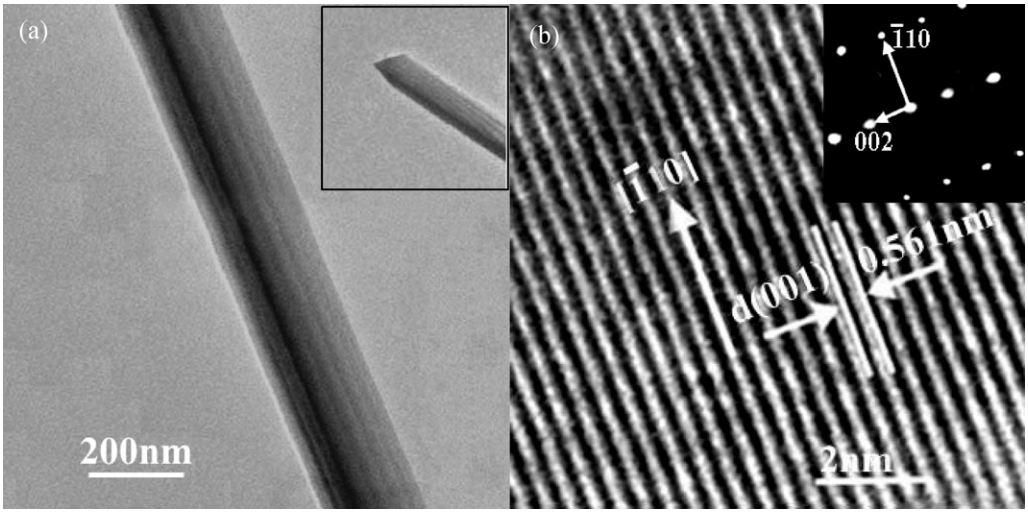

Fig. 4. TEM (a), HRTEM (b), and SAED (the inset) images of an individual nanorod fabricated at 950 °C for 20 min.

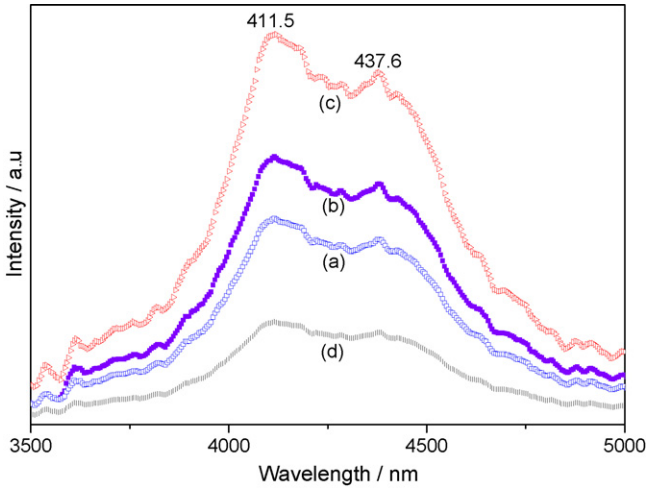

Fig. 5. Photoluminescence spectra of the samples after ammoniation at 950 °C for different times: (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min.

straight β-Ga_2O_3 nanorods, the well-spaced lattice fringe in the image indicate the single crystal structure of Ga_2O_3 nanorods with high-quality crystalline but with less dislocations and defects. The crystal plane spacing of nanorods is about 0.561 nm, which is similar to that of (0 0 1) crystal plane spacing (0.565 nm) of β-Ga_2O_3 single crystal [15]. The growth direction of this nanorod is parallel to [$\bar{1}$ 1 0] orientation. Diffraction spots from SAED (the inset in Fig. 4(b)) are regular, which shows β-Ga_2O_3 nanorod is monocrystal with high-quality crystalline.

3.3. Optical properties

Fig. 5 is the photoluminescence spectra of the samples ammoniating at 950 °C for different times, detected with He–Cd laser used as the excitation source (of wavelength 325 nm) at room temperature.

Fig. 5 shows there are two strong emission peaks centered at 411.5 nm and 437.6 nm. The peak at 437.6 nm corresponds to that of bulk Ga_2O_3, as compared with 435 nm reported by reference [20], which proves that the products are single crystal Ga_2O_3 phases and are the same as the results of XRD. β-Ga_2O_3 nanorods are fabricated in reducing atmosphere and annealing at high temperature, and these experimental conditions contribute to the generation of O vacancies (V_O) and Ga vacancies (V_{Ga}). Therefore, the luminescence mechanism can be explained by the presence of vacancies.

Binet and Gourier [20] thought that there could bring forth a vacancy for the accepter of Ga vacancy after excited, and an electron could form from the donor of O vacancy. The electron of donor and vacancy of accepter can combine and generate a blue photons. Blue shift is discerned for the peak at 411.5 nm, which ascribes to quantum confinement effects [21]. It can also be seen that the two emission peak sites do not change, only their strength changes obviously, with the increase in the ammoniating time. The intensity of emission peaks is the strongest after ammoniating 20 min, which states that Ga_2O_3 nanorods have the best optical properties.

4. Conclusion

β-Ga_2O_3 GaN nanorods of single crystal with high-quality crystalline and the size of 200 nm in diameter have been successfully synthesized on Si(1 1 1) substrates by magnetron sputtering through ammoniating Ga_2O_3/Mo thin films. Nanorods can be affected by the ammoniating times significantly, and the β-Ga_2O_3 nanorods are the best in crystallinity after ammoniating 20 min. The growth direction of this nanorod is parallel to [$\bar{1}$ 1 0] orientation. Ga_2O_3 nanorods have excellent optical properties and the intensities of emission peaks reach their best after ammoniated 20 min, which states that the optical properties of Ga_2O_3 nanorods depend on the ammoniating time significantly.

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