Effects of Nitridation Temperature on Characteristics of Gallium Nitride Thin Films Prepared Via Two-Step Method

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Abstract In this research, the growth of GaN thin films on *c*-plane sapphire (0001) substrates via two-step method without the assist of buffer layer and catalysts was demonstrated. First, gallium oxide (Ga₂O₃) thin films were deposited on sapphire substrates by radio frequency magnetron sputtering method. The deposited Ga₂O₃ thin films were then nitridated at various temperatures. In this research, attention is focused on the influence of nitridation temperatures on the structural and optical properties of the synthesized GaN thin films. It is revealed that 950 °C is the optimal nitridation temperature for synthesizing hexagonal wurtzite GaN thin film with preferential (0002) growth direction.

KEY WORDS: Sputtering; Nitridation; Gallium oxide; Gallium nitride

1 Introduction

Since the early 1990s, much effort has been made to prepare a wide band gap gallium nitride (GaN) semiconductor [1]. This is owing to its outstanding fundamental physical and chemical properties, such as direct and wide band gaps of 3.39 eV at room temperature, high breakdown field voltage [2] and high thermal, mechanical and chemical stabilities. These unique properties make GaN a promising material in numerous optoelectronic and electronic applications such as light-emitting diodes, laser diodes, sensors and high-efficiency solar cells, as well as high-speed and high-frequency electronic devices.

Several research groups have recently succeeded in synthesizing GaN thin films on silicon substrates via various methods such as molecular beam epitaxy (MBE),

radio frequency (RF) magnetron sputtering and metalorganic chemical vapor deposition (MOCVD). However, most of the methods used have complicated setups and costly productions. RF magnetron sputtering method is a rather simple and easy method among all of the methods mentioned above, though it is one of the most popular methods for early investigations of GaN thin films [3]. Furthermore, this method is also highly useful in semiconductor technology industry [4]. Until now, only a few reports have appeared on sputtered GaN, including the work of Xie et al. [5], who have shown that nanocrystalline GaN thin films have been prepared using DC magnetron sputtering of Ga target and annealed in nitrogen ambient. Besides, GaN target have been used by Xiao et al. [6] for the growth of polycrystalline GaN thin films on Si (111) substrates. The direct growth of GaN using the GaN target has rarely been used by researchers because of its very high cost compared with a gallium oxide (Ga₂O₃) target. For the above-mentioned reasons, there is a need to search for an alternative target material to be used for the sputtering of GaN thin films. Our motivation is to use the cheap Ga₂O₃ target to overcome the problem.

In this paper, we will report the deposition of GaN thin films on *c*-plane Al₂O₃ (0001) substrates via two-step

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method, in which the Ga₂O₃ thin films will be first deposited on *c*-plane Al₂O₃ (0001) by RF magnetron sputtering method, then the deposited Ga₂O₃ thin films will be transformed into GaN through nitridation process. No additional metal catalyst and buffer layer will be used throughout the processes. In this work, attention will be focused on the influences of the nitridation temperatures to the structural and optical properties of the deposited GaN thin films. Various characterization techniques will be employed including X-ray diffraction (XRD), scanning probe microscope (SPM), field emission scanning electron microscopy (FESEM) and Raman spectroscopy.

2 Experimental

2.1 Preparation of Gallium Oxide Thin Films

The 1 cm × 1 cm *c*-plane Al₂O₃ (0001) substrates were sonically cleaned using acetone and deionized water for 10 min each before the deposition of the Ga₂O₃ thin films. The Ga₂O₃ films were deposited on the *c*-plane Al₂O₃ (0001) substrates using a conventional RF magnetron sputtering technology system. High-purity Ga₂O₃ target and argon gas with purity of 99.99 and 99.999%, respectively, were used. The target-to-substrate distance is around 10 cm. The thin films were grown at RF power of 150 W, and gas pressure was kept constant at 2.2×10^{-2} Pa for 2 h. The thermal annealing process was carried out after the RF sputtering process. The thin films were annealed in a horizontal tube furnace at a temperature of 950 °C for 2 h in N₂ ambient.

2.2 Formation of Gallium Nitride Thin Films

The coated Ga₂O₃ thin films were nitridated in two-zone conventional tube furnaces. The first zone of the tube furnace was ramped up and fixed from room temperature to 1,000 °C. The second zone of the tube furnace, on the other hand, was heated up to the required temperature that ranged from 850 to 1,050 °C. When the furnaces were heated up to the designed temperature, the quartz boat that was filled with the coated Ga₂O₃ thin films was placed at the center of the second zone of tube furnace. The coated Ga₂O₃ thin films were then nitridated under a constant flow of highly pure ammonia (NH₃) gas with a flow rate of 300 mL/min for 1 h at the temperature of 850, 950 and 1,050 °C, respectively. Ammonia reacted with Ga₂O₃ thin films at a high temperature. The reaction could be described by:

After nitridation process, NH₃ was switched off and nitrogen (N₂) gas was flowed in order to flush out the

excess NH₃ inside the tube furnaces. Finally, the thin films were taken out for characterization.

2.3 Characterization of Thin Films

A variety of methods was applied to characterize the structural and optical properties of the thin films. High-resolution XRD (PANalytical X'Pert Pro MRD) system with a CuK_{α1} radiation source ($\lambda = 0.15406$ nm) was used to identify the crystalline structures and properties of the deposited thin films. All the XRD measurements were taken under 2θ - ω scan mode. A scanning probe microscope (SPM-9600, Shimadzu) was used to investigate the surface morphologies and the surface roughness of the deposited thin films. A field emission scanning electron microscope (FESEM, NOVA NANOSEM 450) was used to examine the morphology and microstructures of the as-synthesized thin films. The optical quality of GaN thin films was studied using Raman spectroscopy (Horiba Jobin-Yvon HR800UV). An argon ion laser (514.5 nm) with 20 mW was used as an excitation source for Raman measurements. The thickness of the GaN thin films nitridated at 850, 950 and 1,050 °C was measured using the Filmetrics model F 20, which was 0.49, 0.48 and 0.37 μm, respectively.

3 Results and Discussion

3.1 Analysis of Structural Properties

3.1.1 XRD Study

Figure 1 shows the XRD patterns of GaN thin films nitridated after flowing NH₃ for 1 h at temperatures ranging from 850 to 1,050 °C. As observed in Fig. 1, the diffraction peaks correspond to the wurtzite GaN (JCPDS File No. 05-0792) and the Ga₂O₃ (JCPDS Card No. 41-1103). The GaN thin film nitridated at temperature 850 °C resulted in a broad preference plane GaN (0002) peak and exhibits a Ga₂O₃ peak at around $2\theta = 41.59^\circ$ in the XRD spectrum. The presence of the Ga₂O₃ peak was due to the fact that Ga₂O₃ does not have enough energy to fully convert into GaN during the nitridation process at 850 °C [7]. Ga₂O₃ has been partially converted into GaN at this nitridation temperature. As the nitridation temperature increases to 950 °C, three dominant diffraction peaks can be observed at $2\theta = 32.44^\circ$, $2\theta = 34.61^\circ$ and $2\theta = 36.83^\circ$, which are the characteristics of the GaN (10 $\bar{1}$ 0), GaN (0002) and GaN (10 $\bar{1}$ 1) peaks, respectively. All the diffraction peaks were ascribed to the formation of wurtzite structure GaN. No Ga₂O₃ peak was detected in the XRD spectrum. The reason lies in that the grains in the film obtained enough

Fig. 1 XRD patterns of the GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates and nitridated at 850, 950, 1,050 °C

energy during nitridation and have high mobility on the substrate surface to take up low-energy lattice points and form high-orientation film, so the crystallization of the film improves [8]. However, the preference plane GaN (0002) peak decreased drastically and became broadening in intensity at 1,050 °C. This phenomenon was caused by the thermal decomposition or sublimation of the GaN thin film [9]. Thus, all the synthesized GaN materials were evaporated and deposited on the walls of the quartz tube. Furthermore, this process led to the degradation of the crystal quality of the GaN thin film.

Further investigation on crystallinity was conducted. When grain size is small, the average crystallite size of the deposited GaN thin films was estimated using the Scherrer's formula [10]:

$$\tau = \frac{k\lambda}{\beta \cos \theta}, \quad (2)$$

where τ is the crystallite size of GaN, K is a shape factor with value of 0.9, λ is the wavelength of the incident beam (0.15406 nm for the $\text{CuK}_{\alpha 1}$ radiation), β is the full-width at half-maximum (FWHM) of the most intense diffracted peak (in radians), and θ is the Bragg's angle of the diffracted peak. The crystallite size for each GaN thin films is listed in Table 1. As the nitridation temperature increases from 850 to 950 °C, the crystallite size of the GaN thin film increased. However, the crystallite size decreases when the thin film was nitridated at 1,050 °C. It can be explained by the work from Lee *et al.* [11], who stated that larger grain size manifested enhancement in crystallinity.

As we know, the FWHM of the preference plane GaN (0002) peaks in the XRD patterns mainly reveals the crystal quality of the film [8]. Thus, further analysis has

been carried out. The FWHM of the GaN (0002) diffraction peaks nitridated at different temperatures are shown in Table 1. As the nitridation temperature increases from 850 to 950 °C, the FWHM of the GaN (0002) diffraction peak decreased, which means that the quality of the GaN thin films has been improved. Comparing the GaN (0002) diffraction peaks of the thin films nitridated at 950 and 1,050 °C, we found that the FWHM of the thin film nitridated at 950 °C was smaller than that nitridated at 1,050 °C, while its intensity was also greater than the intensity of the thin film nitridated at 1,050 °C. All these results indicate that the quality of the GaN thin films was improved at nitridation temperature of 950 °C. In a nutshell, 950 °C was the best nitridation temperature for GaN thin films to obtain good crystalline quality.

3.1.2 SPM Study

Figure 2 shows the SPM images of the GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates under different nitridation temperatures. These images were obtained in the non-contacting mode taken over a scale of $1 \mu\text{m} \times 1 \mu\text{m}$ scans. The images show that the GaN thin films have a three-dimensional island-like morphology. The average grain size of GaN thin films was found rather uniform for all the GaN thin films. The root-mean-square roughness value (R_{rms}) of the surface of the GaN thin films is summarized in Table 1. The rms value of roughness can be estimated using the following equation [12]:

$$R_{\text{rms}} = \left(\frac{\sum_{i=1}^N (Z_i - Z_{\text{ave}})^2}{N} \right)^{1/2}, \quad (3)$$

where Z_i is the value of Z at the i th pointing, Z_{ave} is the average of the Z value, and N is the number of points. Based on the rms roughness values, it was found that the effect of nitridation temperature on the surface morphology of GaN thin films is very obvious. When the nitridation temperature increases from 850 to 950 °C, the R_{rms} value decreases, which demonstrates an improved film quality. However, the rms roughness value increased when the nitridation temperature was increased from 950 to 1,050 °C. Lee *et al.* [11] indicated that at high temperatures, more energy should be available for the atoms to diffuse and occupy the correct site in the crystal lattice and that grains with lower surface energy will also grow larger at high temperatures. However, we found that there was an upper limit for the nitridation temperature. When the nitridation temperature is too high, the amorphous nitridated layer will be partially crystallized, which will result in the formation of high density of surface protrusions [13]. As a consequence, the surface morphology of the GaN thin film will become rough again. It is concluded from SPM

Table 1 The 2θ and FWHM values of GaN (0002) peak, crystallite size and R_{rms} of GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates and nitridated at different temperatures

Temperature (°C)	2θ (°)	FWHM (°)	Crystallite size (nm)	R_{rms} (nm)
850	34.55	0.26	31.99	1.47
950	34.61	0.22	37.81	0.99
1,050	34.56	0.53	15.70	1.14

Fig. 2 SPM surface morphologies and roughness analysis ($1\ \mu\text{m} \times 1\ \mu\text{m}$ scans) of GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates and nitridated at different temperatures: **a** 850 °C; **b** 950 °C; **c** 1,050 °C

results that 950 °C is the optimal nitridation temperature at which a smooth surface morphology with a minimum rms value of 0.99 μm could be got for the deposited GaN thin film.

3.1.3 FESEM Study

Figure 3 is the surface morphology of the GaN thin film deposited on *c*-plane Al_2O_3 (0001) substrates under different nitridation temperatures. From the plane-view FESEM images, it is clearly exhibited that all the deposited GaN thin films have smooth and uniform surface morphologies.

3.2 Analysis of Optical Properties

3.2.1 Raman Study

Figure 4 displays the room temperature Raman spectra of GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates nitridated at various temperatures from 850 to 1,050 °C. The Raman scattering experiment was carried out in the z (x , unpolarized) $\hat{z}$ scattering configuration, where z and $\hat{z}$ are the directions of incident and scattered light [14]. In this configuration, the allowed zone-center

phonon modes of wurtzite GaN were $E_2(\text{Low})$, $E_2(\text{High})$ and $A_1(\text{LO})$ [15]. $E_2(\text{High})$ mode is atomic oscillation in the *c*-plane, whereas $A_1(\text{LO})$ mode is atomic oscillation along *c*-axis of the wurtzite unit cell [16]. $E_2(\text{Low})$ mode is given atomic displacements perpendicular to the *c*-axis [17]. Three dominant peaks situated at 422, 567 and 728 cm^{-1} were clearly observed in the Raman spectra, which represents the phonon vibration frequencies of the Al (g) mode of Al_2O_3 , $E_2(\text{High})$ and $A_1(\text{LO})$ modes of the hexagonal wurtzite GaN, respectively. For the GaN thin film nitridated at 850 °C, the three dominant peaks in Raman spectrum show only broad and wide peaks. When the nitridation temperature increases to 950 °C, the intensity of three dominant peaks obviously increases and becomes sharper. According to the results reported by Man et al. [8], the $E_2(\text{High})$ mode of the wurtzite GaN is attributed to the deformation potential scattering and its intensity can be correlated to the quality of the crystal. Thus, this result indicates that the crystal quality of GaN thin film was improved. Further increment in the nitridation temperature, however, decreased the intensity of the $E_2(\text{High})$ peak (as well as other peaks). Subsequently, it is concluded that 950 °C is the best nitridation temperature for the crystallization of GaN thin films, which is in consistent with that of XRD.

Fig. 3 FESEM images of GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates and nitridated at different temperatures: **a** 850 °C; **b** 950 °C; **c** 1,050 °C

Fig. 4 Raman spectra of GaN thin films deposited on *c*-plane Al_2O_3 (0001) substrates and nitridated at 850, 950, and 1,050 °C

4 Conclusions

GaN thin films were successfully synthesized on the *c*-plane sapphire substrate using RF sputtering method in combination with the subsequent nitridation at various temperatures. The structural and optical properties of GaN thin films were highly dependent on the nitridation temperature. It is revealed that 950 °C is the optimal nitridation temperature for synthesizing a uniform, smooth GaN thin film. The present work is very important in providing a new framework for researchers involved in the nitridation process for the development of GaN thin film.

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