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Structural characterization and optoelectronic properties of GaN thin films on Si(111) substrates using pulsed laser deposition assisted by gas discharge

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ABSTRACT GaN films have been grown on Si(111) substrates with a thin AlN buffer layer using pulsed laser deposition (PLD) assisted by gas discharge. The crystalline quality, surface morphology and optoelectronic properties of the deposited films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), photoluminescence (PL) spectroscopy, and room-temperature Van der Pauw–Hall measurements. The influence of the deposition temperature in the range 637–1037 K on the crystallinity of GaN films, the laser incident energy in the range 150–250 mJ/pulse on the surface morphology and the optoelectronic properties were systematically studied. The XRD analysis shows that the crystalline quality of the GaN films improves with increasing deposition temperature to 937 K, but further increase of the deposition temperature to 1037 K leads to the degradation of the crystalline quality. AFM results show that the surface roughness of the GaN films can be decreased with increasing laser incident energy to 220 mJ/pulse. Further increase of the laser incident energy to 250 mJ/pulse leads to an increase in the surface roughness. The optoelectronic properties of GaN films were also improved by increasing the laser incident energy to 220 mJ/pulse. GaN films which have a n-type carrier concentration of 1.26×10^{17} cm^{-3} and a mobility of 158.1 cm^2/Vs can be deposited at a substrate temperature of 937 K, a deposition pressure of 20 Pa and a laser incident energy of 220 mJ/pulse. Their room-temperature PL spectra exhibit a strong band-edge emission at 365 nm.

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1 Introduction

Semiconductor nitrides such as aluminum nitride (AlN) and gallium nitride (GaN) can be considered as very promising materials for their potential use in optoelectronic devices and high-frequency/power/temperature electronic devices [1–3]. The Si technique is a mature semiconductor technique. The growth of group-III nitride on Si substrates will open a new possibility in the field of optoelectronics devices. Si substrate has many good advantages such as low cost, high thermal conductivity and large diameter of available wafers; thus it can be considered as a very attractive substrate for the growth of GaN films [4, 5]. However, the large lattice and thermal mismatches between GaN and Si substrate can lead to the formation of a high defect density in the GaN films deposited, which deteriorates the optoelectronic properties of the GaN thin films [6]. Several attempts to improve the GaN film quality by using a buffer layer between GaN and the Si substrate have been reported [7].

A few techniques have been used to grow GaN thin films, such as molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE) techniques [8–10]. Compared to these techniques, PLD is considered as a novel growth method for thin films. PLD has many features; for example, the laser ablation of a target can create a highly energetic growth precursor, thus leading to the formation of non-equilibrium growth conditions, so that high-quality films can be obtained at a fairly low substrate temperature. Furthermore, PLD can be performed in a background gas or in conjunction with a source of reactive species, and offers more flexibility than other conventional techniques [11]. Ohta et al. have recently studied the heterointerfaces between GaN films and AlN films grown by PLD [12]. Mah et al. have investigated the properties of GaN thin films grown with PLD [13]. Basillais et al. have studied the reactive laser ablation process assisted by a radio frequency discharge device that was used to grow AlN and GaN thin films [14]. Alessio reported that the laser incident energy and the substrate temperature were the most crucial processing parameters for the formation of high-quality crystalline thin films [15]. This paper shows a study of the GaN film deposition and the characterization of GaN thin films at different substrate temperatures and different laser incident energies, via a novel technique using PLD assisted by gas discharge technique.

2 Experimental

Figure 1 shows a schematic diagram of the experimental set-up. Depositions were carried out in a stainless steel vacuum chamber evacuated by a turbomolecular pump to a base pressure of $10^{-5} \sim 10^{-6}$ Pa. A KrF excimer laser beam (wavelength 240 nm, repetition rate 5 Hz) was fo-

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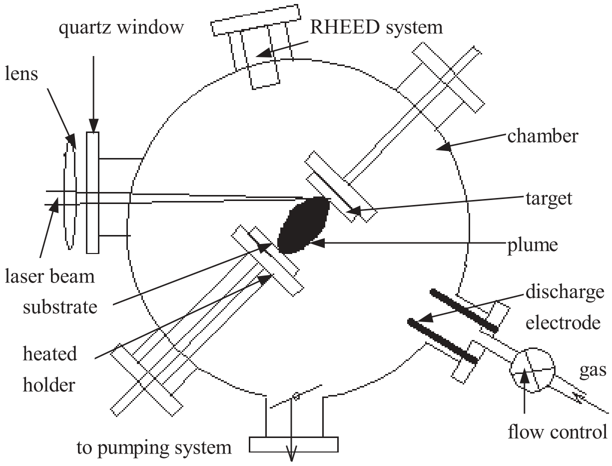

FIGURE 1 Schematic diagram of the experimental set-up

cused by a lens on a rotating Al target (99.999%) or GaN (99.999%) target, and the GaN target was prepared by pressing and sintering 99.999%-pure polycrystalline GaN powder in N_2 (99.999%) at 630 °C. The rotating heating stage of the substrate was located 3–6 cm away from the targets. The GaN layer and the AlN buffer layer were prepared in the same system. High-purity nitrogen gas (99.999% purity) was used as a reactive gas. During the deposition, the N_2 partial pressure was maintained at 20 Pa by adjusting the flow rate of the N_2 gas. In order to promote a chemical reaction of the plasma plume particles with N_2, a pair of direct current discharge electrodes was installed in the deposition chamber near to the nozzle of the N_2 gas. The optimum discharge voltage was 750 V, and a purple-red glow was observed in the space of the gas discharge, which indicated that atomic nitrogen and N_2^+ ions were being produced in the deposition chamber. The atomic nitrogen and N_2^+ ion bombardment could increase the N incorporation probability [16, 17]. An AlN buffer layer was deposited on Si(111) substrate to improve the lattice mismatch of the GaN layer with Si(111) substrate. It is important to point out the different ways of growing the GaN films, which were deposited at different process parameters. The GaN films were deposited by a two-step method. In the first step, the AlN buffer layers were deposited at 637 K depositing temperature for 20 min. In the second step, the GaN film layers were deposited for 30 min. In order to study the effect of the substrate temperature, the laser incident energy was kept at 220 mJ/pulse. The deposition temperature of GaN films was varied in the range 637–1037 K. In order to study the effect of the laser incident energy, the deposition temperature of the GaN films was kept at 937 K. The laser incident energy was varied in the range 150–250 mJ/pulse.

In order to examine the crystalline quality of the GaN films, a high-resolution X-ray diffraction (XRD) with a Cu K_α radiation source was used to characterize the phases in the GaN films. The surface morphologies of the GaN films were studied using atomic force microscopy (AFM, Seiko, Instruments, SPA-400). The electrical properties of the GaN thin films were determined by Van der Pauw–Hall measurements at room temperature (307 K). The PL measurements were performed at room temperature (307 K), using a He–Cd laser emitting at 325 nm to study the optical properties of the GaN thin films. The luminescence signals were detected by the same PL system.

3 Results and discussion

3.1 *The effect of the deposition temperature*

Figure 2a–d shows the XRD measurement results of the different GaN films formed at deposition temperatures of 637, 837, 937 and 1037 K, respectively. As shown in Fig. 2a–d, the GaN films grown on Si(111) substrate with AlN buffer layers exhibit three obvious XRD peaks in the diffraction patterns. The XRD peaks which are located at $2\theta = 28.58°$, $34.56°$ and $58.64°$ are attributed to Si(111), GaN(0002) and AlN(11$\underline{2}$0), respectively. In addition, there is one broad and weak peak appearing between 2θ of 42° and 48°, and no well-defined diffraction peaks of crystalline phases are present; this can be attributed to the AlN buffer layers. The AlN buffer layer formed contains a mixture of crystalline and amorphous phases. It has a low crystallinity, which may be due to the low deposition temperature (637 K). The XRD results show that GaN layers have a wurtzite structure. As shown in Fig. 2a–c, the intensity of the GaN(0002) peaks becomes stronger with increasing deposition temperature. This is an indication that the crystalline quality of GaN films improves with increasing the deposition temperature to 937 K. Normally, the high substrate temperature enhances the mobility of surface atoms, and increases the formation of the thermodynamically stable GaN(0002) phase. When the deposition temperature is further increased to 1037 K, (the XRD pattern of the GaN film is shown in Fig. 2d), the intensity of

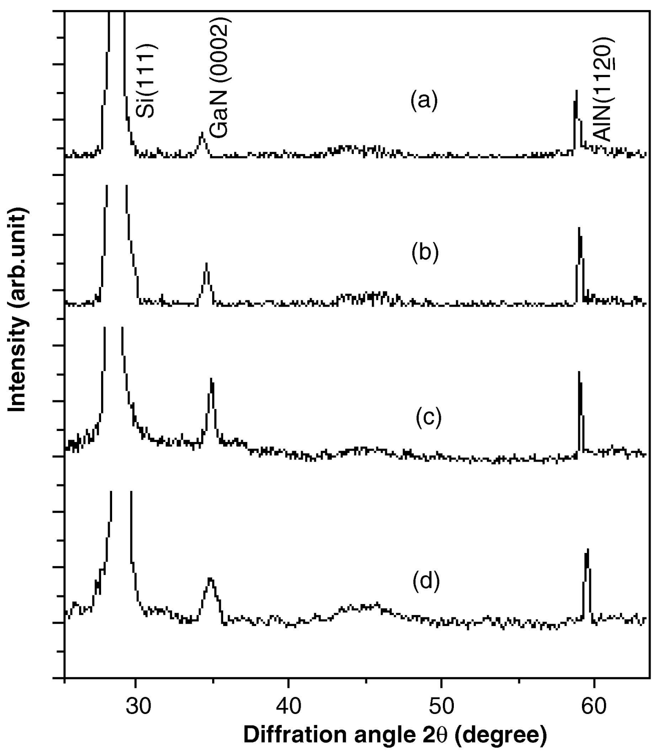

FIGURE 2 The XRD measurement results of the GaN films formed at deposition temperatures of 637 K (a), 837 K (b), 937 K (c) and 1037 K (d)

the GaN(0002) peak becomes weak and the full width at half maximum becomes broad, which indicates that the crystalline quality of the GaN film is degraded. The GaN film becomes thermodynamically unstable, so that there is no longer growth at this too-high substrate temperature; it can be inferred that a high substrate temperature may lead to re-evaporation of the adatoms from the film surface [2].

4 The effect of the laser incident energy

The surface morphology of the GaN films is strongly dependent on the laser incident energy. The surface morphology and topography were investigated through AFM measurements. All the images were obtained in tapping mode with standard Si tips of radius 10 nm. The images were post-processed using a quadratic plane fit in both directions and, in some cases, a zero-order line-by-line flattening routine. All the GaN film layers were deposited at the same temperature (937 K), the same pressure (20 Pa) and a laser incident energy of 150, 180, 220 and 250 mJ/pulse. The AFM images are shown in Fig. 3a–d. The most obvious features in Fig. 3a, b and d are the appearance of small grains and large particles. As laser incident energy increases to 220 mJ/pulse, a decrease in the fraction of the large particles and an increase in the fraction of the small grains can be seen, and uniform-size grains can be observed. Upon further increase of laser incident energy to 250 mJ/pulse, the larger particles can be observed again. A possible explanation for this is that increasing laser incident energy will lead to an increase in the ion densities and ion kinetic energy in the plasma. When they arrive at the surface of the substrate, the kinetic energy can be transformed into the energy of mobility and diffusion. Lowering the laser incident energy for the deposition may reduce the mobility and the diffusion of the growing films, which leads to the formation of small-sized grains. A few large particles flying from the target surface to the substrate can survive. This is because there is not enough energy for the large particles to be mobile and diffuse, which leads to the formation of large particles. When the laser incident energy is too high, the GaN films overgrow and the GaN grains become coarser and agglomerated. In addition, too high laser incident energy ablates the target; a few more large particles can be produced. The larger particles remain for reasons of incomplete mobility and diffusion. Therefore, larger particles can be observed in Fig. 3d. The root-mean-square roughness of the samples of GaN films that are shown in the images of Fig. 3a–d was measured by AFM over $1.5 \times 1.5\,\mu m^2$ scanning ranges. The surface root-mean square roughness values for these samples were determined to be 22.3, 8.9, 3.3 and 4.9 nm, respectively. The surface roughness is related to the substrate surface adatom mobility and diffusion. It is obvious that the surface roughness of GaN films decreases with increasing laser incident energy to 220 mJ/pulse, and increases with further increase of laser incident energy to 250 mJ/pulse.

The room-temperature PL spectra of the GaN films deposited at a laser incident energy of (a) 150; (b) 180; (c) 220 and (d) 250 mJ/pulse are shown in Fig. 4. The PL spectra of the GaN films deposited at a laser incident energy of 150 and 250 mJ/pulse are mainly composed of a band-edge emission peak and a weak yellow band-emission peak. The yellow luminescence is related to defect levels [18], which need to be reduced as much as possible. The weak yellow band-emission peak is due to the defects caused by too low or too high laser incident energy. The PL spectra for the films deposited at a laser incident energy of 180 and 220 mJ/pulse are shown in Fig. 4b and c. The yellow band-emission peak is not present, there is a strong band-edge emission and its

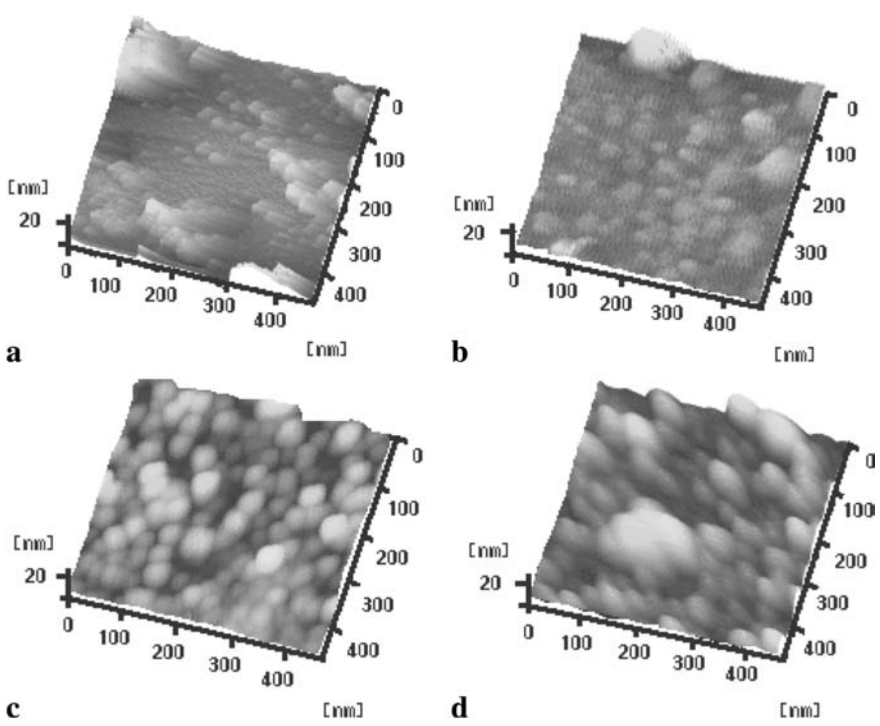

FIGURE 3 The surface three-dimensional topography of the GaN films deposited at a laser incident energy of 150 mJ/pulse (**a**), 180 mJ/pulse (**b**), 220 mJ/pulse (**c**) and 250 mJ/pulse (**d**)

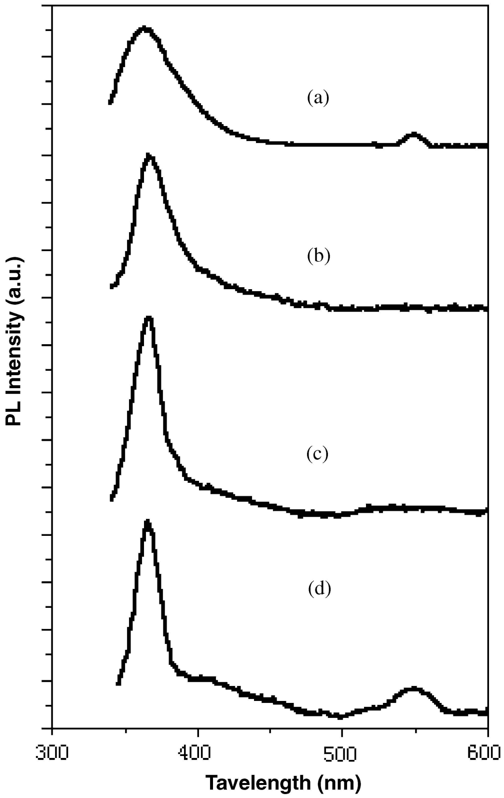

FIGURE 4 Room temperature PL spectra of the GaN films deposited at a laser incident energy of 150 mJ/pulse (**a**), 180 mJ/pulse (**b**), 220 mJ/pulse (**c**) and 250 mJ/pulse (**d**)

intensity increases with increasing laser incident energy to 220 mJ/pulse. As shown in Fig. 4c, the edge-emission peak for GaN films around 365 nm is strongest in Fig. 4a–d, which suggests a low defect density and high optical quality of the GaN film. It is consistent with the AFM measurement results.

The Hall measurements of the electrical properties of the GaN thin films deposited at a laser incident energy of 150, 180, 220 and 250 mJ/pulse are shown in Table 1. It is found that the resistivities of the GaN films deposited at a laser incident energy of 150 and 250 mJ/pulse are bigger than those at 180 and 220 mJ/pulse, and the resistivity of the GaN film deposited at a laser incident energy of 220 mJ/pulse is the lowest. The Hall electrical mobility of the GaN films deposited at a laser incident energy of 150 and 250 mJ/pulse is lower than that for 180 and 220 mJ/pulse. The PL spectra of the GaN films have suggested that the defect density of the GaN film is bigger in the GaN films deposited at 150 and 250 mJ/pulse than at 180 and 220 mJ/pulse. Film resistivity is mainly correlated to defect density [19]. The defect density is related to film crystalline quality. That is why the GaN films that were deposited at a deposition temperature of 937 K, a deposition pressure of 20 Pa and laser incident energy of 220 mJ/pulse had better crystalline quality. In addition, the electron mobility decreases with increasing resistivity; this effect is caused by the increase in the conductive paths of the electrons. Therefore, the GaN films deposited at a laser incident energy of 220 mJ/pulse have good electrical properties. GaN films which have a n-type carrier concentration of 1.26×10^{17} cm^{-3} and a mobility of 158.1 cm^2/Vs can be deposited at a substrate temperature of 937 K, a deposition pressure of 20 Pa and a laser incident energy of 220 mJ/pulse, and their room-temperature PL spectra exhibit a strong band-edge emission at 365 nm. The optoelectronic properties are approximately consistent with those reported in the literature [20].

Laser incident energy (mJ/pulse)	Growth rate (nm/s)	Carrier type	Carrier concentration (cm^{-3})	Mobility (cm^2/Vs)	Resistivity (Ω cm)
150	3.85	N	1.4×10^{16}	9.8	45.6
180	4.22	N	1.1×10^{17}	115.1	0.53
220	4.51	N	1.26×10^{17}	158.1	0.31
250	4.62	N	5.5×10^{17}	11.9	9.2

TABLE 1 The growth rate and the room-temperature electrical properties of GaN films deposited at a temperature of 937 K, a pressure of 20 Pa and a laser incident energy of 150 mJ/pulse, 180 mJ/pulse, 220 mJ/pulse and 250 mJ/pulse, respectively

5 Conclusions

A study was carried out to investigate the structural and optoelectronic properties of GaN thin films deposited on Si(111) substrates using PLD assisted by gas discharge. We have demonstrated that the structure, surface morphology and optoelectronic properties of the films are strongly dependent on the substrate temperature and the laser incident energy. GaN films deposited at a substrate temperature of 937 K and at a laser incident energy of 220 mJ/pulse have better structure and better optoelectronic properties.

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