

Structural and Optical Property of High Quality GaN Thin Film on Si with ZnO Buffer Layer

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Abstract: A method was applied to improve the crystallization quality of GaN. ZnO thin films were deposited on n-Si (111) at 600°C by pulsed laser deposition (PLD), and GaN thin films were grown on Si or ZnO/Si by R. F. magnetron sputtering system. Several GaN films were prepared with ZnO as buffer layer without annealing, with ZnO as buffer layer annealed at 850°C, 900°C and 950°C and with no buffer layer annealed at 950°C, respectively. The crystallization, optical property and morphology of all GaN films prepared were studied by X-ray diffraction (XRD), Fourier transform infrared spectrophotometer (FTIR), photoluminescence (PL) and scanning electron microscope (SEM). The results show that ZnO buffer layer plays an important role in improving the crystallization quality of GaN.

Keywords: Structure Property, Optical Property, Crystallization, ZnO Buffer Layer, GaN Film

1. Introduction

The third-generation semiconductor material represented by gallium nitride (GaN) is an excellent III-V group elements compound semiconductor material, with a band gap width of 3.4 eV and exciton binding energy of 20 meV at room temperature [1]. Due to the fact that the light transition probability of direct band-gap material has an order of magnitude higher than that of the indirect band-gap material, coupled with its wide gap, GaN is the preferred material for the preparation of blue-green light emitting diode (LED) and laser diode (LD) photoelectric devices [2]. In addition, GaN is very suitable for making high-temperature, high-frequency and high-power electronic devices due to its high saturation velocity of electron drift, small dielectric constant, good thermal conductivity and good thermal stability [3].

Si has many advantages as the substrate of GaN material, such as better crystallinity, large size, low cost, easy processing, good electrical conductivity, thermal conductivity and thermal stability and easy to make integrated circuits. But it is difficult to grow high-quality GaN epitaxial layer on Si substrate since there is a huge lattice mismatch and thermal mismatch between GaN and Si, this will cause cracks in the GaN epitaxial layer

during the cooling process [4]. Because ZnO and GaN have the same lattice hexagonal wurtzite structure and the little lattice mismatch and thermal mismatch, ZnO can be used as a buffer layer for the growth of GaN thin films [5]. In our experiments, high quality ZnO buffer layer was firstly grown on Si substrate at 600°C by pulsed laser deposition, and then GaN was epitaxial grown by magnetron sputtering method and annealed. The results showed that ZnO buffer layer greatly improved the crystallization quality of GaN.

2. Experiment

The deposition of ZnO films was carried out by PLD. The laser device we used is Nd: YAG, with output wavelength of 1064 nm and single-pulse energy of 208 mJ. The laser spot area hitting the target is 0.43 mm², producing energy density of 48 mJ/cm², with frequency of 10 Hz and pulse width of 10 ns. The solid target is sintered with high purity ZnO (99.99%) which deposited on n-Si (111) substrate. The PLD system was vacuumized to 1.2 × 10⁻⁴ Pa, and then was filled with 0.13 Pa high purity oxygen (99.999%). While the substrate temperature was heated to 600°C, the ZnO target was ablated by focused pulse laser beam that passed through the optical window of system chamber. The deposition finished after

15min, after which ZnO/ Si sample was prepared.

GaN thin films were grown by sputtering GaN target with ZnO as buffer layer using JCK-500A RF magnetron sputtering system. The sintered GaN target has a purity of 99.999%. The system vacuum was 3.2×10^{-4} Pa. When the system was working, high-purity argon gas was applied and the partial pressure is 2 Pa. The sputtering power was 150W, and the sputtering time was 90min. Then the samples were annealed in an atmosphere of NH_3 on the quartz boat at the temperature of 850°C, 900°C and 950°C for 15min, respectively. The crystal orientation and quality of GaN/ZnO/Si samples were examined by X-ray diffraction (XRD, Rigaku D/ max-rB $\text{CuK}\alpha$), Fourier infrared absorption spectroscopy (FTIR, Tensor27), photoemission spectroscopy (FLS920) and scanning electron microscope (HITACHI S-570).

3. Results and Discussions

3.1. XRD

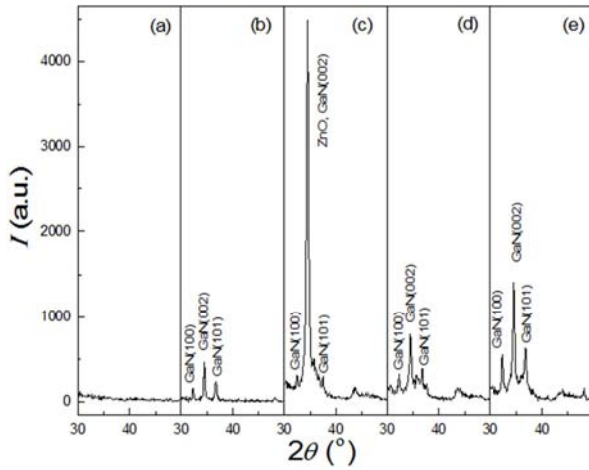


Figure 1. X-ray diffraction patterns of as-deposited GaN with ZnO buffer layer (a), GaN with no buffer layer at 950°C (b), GaN with ZnO buffer layer annealed at 850°C (c), 900°C (d) and 950°C (e).

Figure 1 shows the X-ray diffraction patterns of GaN thin films under various condition. It can be seen from Figure 1(a) that GaN thin films sputtered with ZnO as buffer layer are still in an amorphous state when they are not annealed. In Figure 1(c), (d) and (e), the diffraction peaks at $2\theta = 32.1^\circ$, 34.4° , and 36.6° correspond to the lattice plane of GaN (100), (002), and (101) respectively, indicating that GaN thin films are hexagonal wurtzite structures with lattice constants $a=0.318\text{nm}$ and $c=0.518\text{nm}$. The diffraction peak of GaN (002) has the maximum intensity, indicating that GaN grows along the c axis which is a preferred orientation. It has been reported that ZnO starts to volatilize when it is annealed in NH_3 at the temperature of more than 650°C [6], and would disappear at the temperature of 900°C [7]. If the annealing temperature does not exceed 900°C, the ZnO buffer layer will not evaporate completely. Therefore, the (002) peak in Figure 1(c) can be ascribed to the superposition of the (002) planes of ZnO and GaN which have the similar lattice structure. Figure 1(d) and (e) show that GaN has the best crystallization quality at the annealing temperature

of 950°C when all of the ZnO has volatilized, which means that the GaN grain size increases [8]. Compared with Figure 1(b), Figure 1(e) shows that ZnO buffer layer can improve the crystallization quality of GaN. This is because ZnO buffer layer effectively alleviates lattice mismatch and thermal mismatch, decreases internal stress and reduces dislocation density.

3.2. FTIR

As shown in Figure 2, there are two main absorption peaks within the range of $450 \sim 750 \text{ cm}^{-1}$. The peak near 560cm^{-1} is the characteristic peak which corresponds to stretching vibration of Ga-N bond in hexagonal GaN [9, 10]. The peak near 603cm^{-1} is caused by the vibrational absorption of substituted carbon in the silicon lattice [11]. The carbon is impurities in the Si substrate. It can be seen that the absorption peak of the Ga-N bond becomes stronger and stronger with the increase of annealing temperature. The peak is the strongest when the annealing temperature is 950°C, showing that the crystallization quality of GaN is the best at the annealing temperature. On the other hand, it also indicates that the strong peak (002) in Figure 1(c) is not generated by GaN alone. The absorption peak of Ga-N bond has a red shift with the increase of annealing temperature. This is due to the increase of the grain size, the decrease of surface tension and elongation of Ga-N bond length, which lead to the decreases of intrinsic vibration frequency of Ga-N bond.

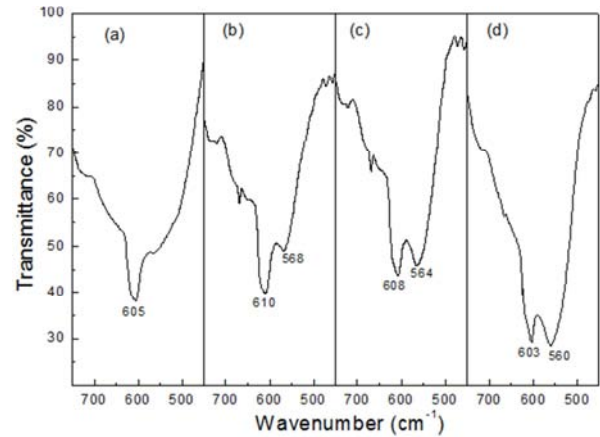


Figure 2. FTIR spectra of unannealed GaN with ZnO buffer layer (a), ammoniated at 850°C (b), 900°C (c) and 950°C (d).

3.3. PL

Figure 3 is the photoluminescence spectrum (PL) of the sample excited by Xe lamp ($\lambda = 280\text{nm}$) at room temperature. It can be seen that there are a strong Photoluminescence peak at 367nm and two relatively weak ones at 416 and 437nm. The luminous peak at 367nm (3.39eV) corresponds to the intrinsic excitation of GaN at room temperature [12]. The luminescence peak at 437nm (2.84eV) is caused by the radiative transition from the conduction band to the deep acceptor level [13]. However, the luminescence peak at 416nm (2.99eV) is a relatively rare purple peak, which may be related to the Zn atoms diffused into the GaN lattice, and its detailed luminescence mechanism needs to be further studied. With the increase of annealing temperature, the positions of the three

luminescent peaks did not change, but the luminous intensity increased obviously. This is because atoms will be rearranged to reduce the interface energy at a high annealing temperature [14]. Thus grains with good crystallinity will be formed in GaN films, which affect the luminous characteristics of the films.

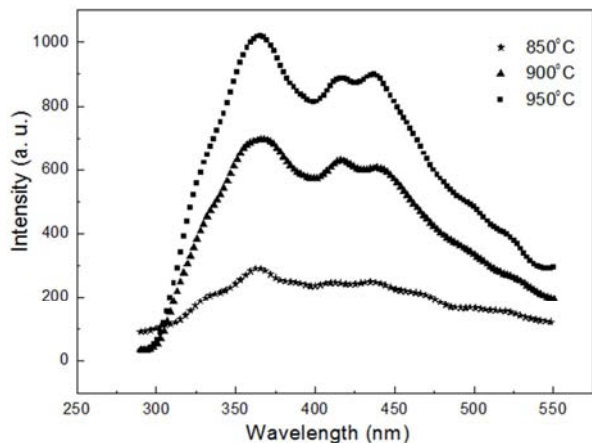


Figure 3. PL spectra of GaN with ZnO buffer layer ammoniated at 850°C, 900°C and 950°C.

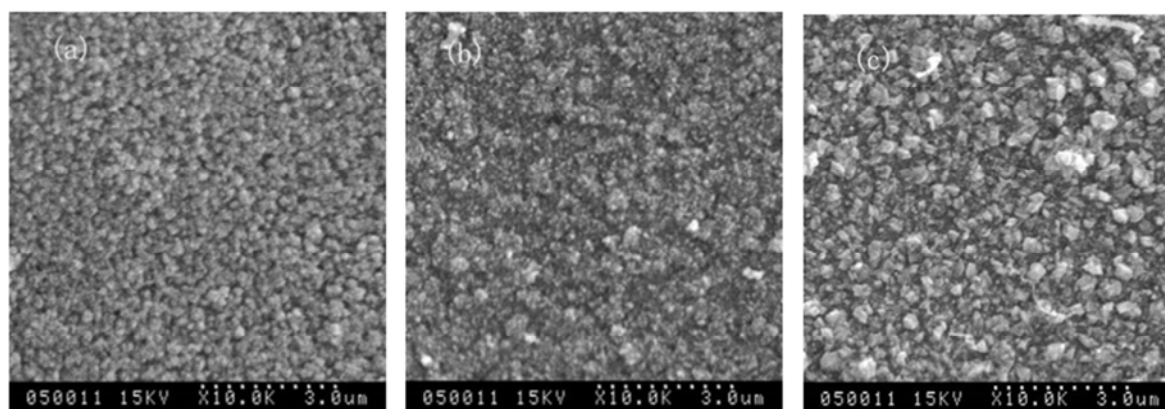


Figure 4. SEM images of GaN with ZnO buffer layer annealed at 850 °C (a), 900°C (b) and 950°C (c).

4. Conclusion

In summary, GaN thin films with good crystallization were successfully prepared on ZnO/ Si substrates by RF magnetron sputtering at the annealing temperature of 950°C, which have hexagonal wurtzite and prefer orientation of c axis. XRD patterns, FTIR spectra, PL spectra and SEM images showed that GaN films prepared with ZnO as buffer layer possess much better crystallization than those without buffer layer at the same annealing temperature of 950°C. The results show that ZnO buffer layer greatly improves the crystalline quality of GaN film because ZnO and GaN have the same lattice structure with similar lattice parameters.

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3.4. SEM

Figure 4 shows the SEM images of GaN thin films with magnification of 10K, in which the surfaces of the samples are smooth and the structures are dense. There are many GaN grains on the surface of the film which sizes are relatively uniform. It is because the adsorbed atoms on the surface of GaN film can get enough energy to move to the lowest energy point at a high temperature, thus leading to a film with uniform grain size and dense structure on the macro level [15]. Figure 4(a) shows that the grain size is about 260nm at the annealing temperature of 850°C. Figure 4(b) and (c) show that grain size increases with the increase of the annealing temperature. The grains are in the process of agglomeration at the annealing temperature of 900°C, so their grain boundary is fuzzy. When the annealing temperature reaches 950°C, the grain boundary is clear and the grain size is about 500nm. It is shown that Si-based GaN films prepared with ZnO as buffer layers have a fine crystallization quality at the annealing temperature of 950°C.

(ZR2015FQ004).

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