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Low temperature synthesis of GaN films on ITO substrates by ECR-PEMOCVD

Yue Zhao [a,b], Fuwen Qin [a,b,*], Yizhen Bai [a,b], Zhenhe Ju [c], Yan Zhao [f], Xiaohui Zhang [f], Shuangmei Li [e], Dong Zhang [c], Jiming Bian [a,d], Yang Li [b]

[a] School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China
[b] Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Ministry of Education, Dalian University of Technology, Dalian 116024, China
[c] New Energy Source Research Center of Shenyang Institute of Engineering, Shenyang 110136, China
[d] Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, China
[e] Department of Physics, Shenyang Institute of Engineering, Shenyang 110136, China
[f] Department of Automatic Control Engineering, Shenyang Institute of Engineering, Shenyang 110136, China

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ABSTRACT

GaN films were deposited on indium tin oxide (ITO) coated glass substrates at various deposition temperatures using an electron cyclotron resonance plasma enhanced metal organic chemical vapor deposition (ECR-PEMOCVD). The TMGa and N_2 are applied as precursors of Ga and N, respectively. The crystalline quality and photoluminescence properties of as-grown GaN films are systematically investigated as a function of deposition temperature by means of X-ray diffraction analysis (XRD), reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and room temperature photoluminescence (PL). The results show that the dense and uniformed GaN films with highly c-axis preferred orientation are successfully achieved on ITO glass substrates under optimized deposition temperature of 430 °C, and the room temperature PL spectra of the optimized GaN film show an intense near-band-edge luminescence located at 360 nm. The obtained GaN/ITO/glass structure was especially attractive for transparent optoelectronics applications with inexpensive ITO/glass substrate.

1. Introduction

Gallium nitride (GaN) and related group III–V nitrides have been widely applied in optoelectronic devices such as laser diodes (LDs) [1] and light-emitting diodes (LEDs) [2] due to their appealing physical properties such as direct wide band gap, high saturated electron velocity and high breakdown voltage [3–5]. Although great progress has been made in related area, some difficulties remain challenging and unresolved. For example, an important and key issue with the optoelectronics application of GaN material is the selection of substrates, since the properties of GaN based film and the subsequent device process are highly dependent on the employed substrates. Conventional GaN films are hetero-epitaxially grown on lattice-mismatched sapphire substrates, leading to a high dislocation density and stacking faults in GaN layers. And the poor electrical conductivity of sapphire leads to the current crowding effect, causing the degradation of lifetime and efficiency of the devices. Therefore, conductive SiC seem to be more suitable than insulating sapphires to be used as the substrate for GaN films. However, SiC substrates are expensive and hard to get large area. In contrast, Tin-doped indium oxide (ITO, cubic bixbyite structure, a_{ITO} = 1.0118 nm [6,7]) coated glass substrates have a large area and they are inexpensive. Meanwhile, low electrical resistivity ($<5 \times 10^{-4}$ Ω cm) ITO is an n-type semiconductor with bandgap ~ 3.5–4.3 eV, this value is close to the bandgap of GaN (3.39 eV) [8,9]. It will be imperative for improving the current spread capability of high power GaN devices. In addition, its merits of excellent adherence, hardness, chemical inertness also make ITO glass a good candidate to be used as the substrate for GaN films. It is worthwhile to mention here that there have been several reports on the growth of GaN films and even electroluminescent devices on ITO coated glass substrates, where the polycrystalline GaN films were deposited by RF-PECVD or PECVD [10–13]. Their report further demonstrated that the grown of GaN films on ITO coated glass, acting as current spread layer, would be a feasible solution for high-power semiconductor devices. However, there was little report about the deposition of the GaN films on ITO substrate by low temperature electron cyclotron resonance plasma enhanced metal

* Corresponding author. School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China. Tel.: +86 411 84708380x8304; fax: +86 411 84708389.
E-mail address: qfw@dlut.edu.cn (F. Qin).

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organic chemical vapor deposition (ECR-PEMOCVD) with N_2 as N precursor due to its relatively chemical inertness. Instead, energy-activated gas such as ammonia was commonly used in high temperature MOCVD process. But the high deposition temperature that is necessary for decomposition of ammonia may cause decomposition of the ITO from the substrate. In our previous studies, ECR has been successfully proved to be a feasible method to remarkably activate reactive energy of N_2 and hence GaN film can be grown by ECR-PEMOCVD at an extremely low temperature [14–17].

In this paper, GaN films were deposited on ITO substrates at various deposition temperatures by ECR-PEMOCVD. The results indicated that the dense and uniformed GaN films with highly c-axis preferred orientation are successfully achieved on ITO substrates under optimized deposition temperature of 430 °C, and the room temperature PL measurement of the GaN films show intense near band edge (NBE) emission at 360 nm with a weak yellow luminescence (YL) band.

2. Experiments

GaN films were deposited on ITO substrates using an ECR-PEMOCVD. Trimethyl gallium (TMGa) and N_2 were utilized as the precursors of Ga and N, respectively. Hydrogen (H_2) was used as carrier gas. The temperature of the TMGa was kept at −14.1 °C using thermostat. The N_2 reactivity can be remarkably enhanced by ECR process, i.e., there are much more particles of reactive nitrogen over the substrate as a result of ECR enhancement, which was necessary for the formation of GaN films under the low temperature. The ITO coated glasses with the size of 1.50 × 1.50 cm^2 and thickness of 200 nm were used as substrates. Prior to the growth, the substrates were ultrasonically cleaned in acetone, ethanol and deionized water sequentially each for 10 min, and blow-dried by N_2 in order to obtain a clear surface. Afterward the substrates were loaded into the growth chamber. The growth process was initialed by the growth of a GaN buffer layer deposited at 50 °C on ITO substrates for 30 min with fixed nitrogen flow of 80 sccm and TMGa flow of 0.5 sccm. This buffer layer was designed to alleviate the lattice mismatch between the substrate and epitaxial layer, which could lower the threading dislocations density in the upper GaN layers. And this thin layer also can be used for supplying nucleation centers with the same crystallographic orientation as the substrates [18–20]. Then the substrate temperature was raised for the growth of GaN layer. During the growth processing, the flowrates of N_2 and TMGa were set to be 100 sccm and 1.5 sccm, respectively. The growth process was lasted for 180 min, and the power of microwave generator was maintained at 650 W during the whole growth process. To investigate the effect of deposition temperature on the properties of the GaN films, a series of substrate temperatures between 330 °C and 530 °C were used. After deposition, the substrate temperature was cooled slowly to room temperature. The films thickness was measured by surface profiler. The thickness of the as-grown GaN films deposited at 330 °C, 380 °C, 430 °C, 480 °C, 530 °C were measured to be 431 nm, 529 nm, 560 nm, 587 nm, 459 nm, respectively.

The crystalline characteristics of the GaN films were investigated by X-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED). The morphologies of the GaN films were observed by atomic force microscopy (AFM). Photoluminescence (PL) measurement with excitation-source of a 280 nm by Xe arc lamp was carried out at room temperature to study the optical properties of the GaN films.

3. Results and discussion

3.1. XRD measurement

The XRD curves of the GaN films deposited on ITO substrates at different temperatures (330 °C ~ 530 °C) are shown in Fig. 1. All

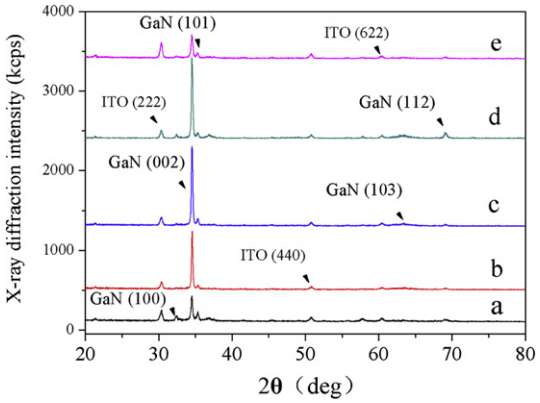

Fig. 1. XRD patterns of the GaN films deposited on ITO substrates at different temperatures of 330 °C (a), 380 °C (b), 430 °C (c), 480 °C (d), and 530 °C (e), respectively.

XRD patterns are dominated by an intense peak located at $2\theta = 34.56°$ which could be identified as the (002) diffraction of wurtzite GaN. It indicates a strong c-axis orientation of the films. Some peaks with relatively lower intensities at $2\theta = 32.43°$, 36.85°, 63.48° and 69.03° correspond to diffractions from (100), (101), (103) and (112) planes of GaN. The rest weak peaks at 30.42°, 50.83° and 60.39° are the informations from the ITO substrates. For further evaluation of the crystalline quality of the films, the (002) diffraction peak position, full width at half maximum (FWHM) of GaN (002) diffraction peak, the c axis lattice parameter and grain size calculated from XRD data are listed in Table 1. Obviously, the FWHM value of GaN (002) peak exhibits a downward trend and then edges up. The films deposited on ITO substrate at 430 °C showed the narrowest FWHM of 0.20°, and the c axis lattice parameter under this condition is 0.5186 nm which is close to the value of bulk GaN (0.51855 nm). Such narrow FWHM and the c constant match indicated the high crystalline quality of the films deposited at 430 °C. For the films grown at higher and lower temperatures, the crystalline quality deteriorates. It can be explain as follows: when the films were deposited at lower temperature (330 °C), the lower energy and the poor mobility of reactive species may lead to small grain size and high defect density, which deteriorates the crystalline quality of the films. However, when further increased deposition temperature to 530 °C, the thermal mismatch between the films and the substrates results in higher dislocation density in the films, leading to the poor crystal quality.

3.2. RHEED measurement

In Fig. 2(a), the fuzzy ring-like pattern of buffer layer implies polycrystalline GaN deposition without any preferred orientation. This thin layer serves as a template for the GaN epitaxial layers. Fig. 2(b)–(f) show the RHEED images of the films deposited on ITO substrates at different temperatures. It is obvious that the faint and continual ring-like patterns gradually change into broken, clear and bright patterns as the deposition temperature increasing to 430 °C.

Table 1
(002) diffraction peak position, FWHM, c axis lattice parameter and grain size of the films.

Sample	Depositing temperature (°C)	2θ (°)	FWHM (°)	C_0 (nm)	Grain size (nm)
a	330	34.52	0.24	0.5192	35
b	380	34.56	0.21	0.5189	39
c	430	34.56	0.20	0.5186	41
d	480	34.57	0.22	0.5187	37
e	530	34.53	0.27	0.5190	30