Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Preparation of GaN films on glass substrates by middle frequency magnetron sputtering

C.W. Zou^{a,b}, H.J. Wang^a, M.L. Yin^a, M. Li^a, C.S. Liu^a, L.P. Guo^a, D.J. Fu^{a,*}, T.W. Kang^b

^a Accelerator Laboratory, Department of Physics and Key Laboratory of Acoustic Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, China ^b Quantum Functional Semiconductor Research Center, Dongguk University, Seoul 100-715, Republic of Korea

ARTICLE INFO

Article history: Received 13 May 2008 Received in revised form 17 September 2008 Accepted 7 October 2008 Communicated by M. Schieber Available online 29 October 2008

PACS: 78.55.Cr 78.30.Fs 78.66.Fd 78.67.Bf

Keywords:

A1. Surface structure

- A3. Physical vapor deposition processes
- B1. Gallium compounds

B2. Semiconducting III-V materials

1. Introduction

Considerable efforts have been devoted to GaN recently for its application potential in electronic and optoelectronic devices such as electron field emitter and light-emitting diodes (LED) in the blue, violet, and near-ultraviolet spectral ranges [1–3]. Traditional growth methods for GaN films such as metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and hydride vapor phase epitaxy (HVPE) are always at high temperatures ranging from 800 to 1000 °C. However, for large-area, lowcost fabrication of LED, thin-film transistor displays and solar cells that utilize glass substrate, it is necessary to deposit GaN films at low temperature. Recently, single-crystalline GaN films with full-width at half-maximum (FWHM) of 77 arcmin for the (002) rocking curve have been successfully grown at relatively low substrate temperature by radio frequency (RF) reactive magnetron sputtering [4], which brought considerable interest to the preparation of GaN films using the sputtering technique. Middle frequency (MF) reactive magnetron sputtering is a technique that

E-mail address: djfu@whu.edu.cn (D.J. Fu).

ABSTRACT

GaN films were deposited on glass substrates by the middle frequency magnetron sputtering method at low substrates temperatures. X-ray diffraction (XRD) intensity and full-width at half-maximum (FWHM) values of the films were strongly influenced by the composition of $(Ar+N_2)$ mixture gas and the negative bias voltages. Optical band gaps deduced from absorption plots show a decrease trend with increasing bias voltages. The unintentionally doped films deposited under optimal conditions were normally n type with a typical carrier concentration of $1.92 \times 10^{17}/\text{cm}^3$ and Hall mobility of $49 \text{ cm}^2/\text{V}$ s. Two photoluminescence emission peaks appear at 3.30 and 3.36 eV at temperatures below 100 K, and the origin of these two peaks can be attributed to excitons bound to structural defects.

© 2008 Published by Elsevier B.V.

霐

CRYSTAL GROWTH

effectively eliminates poisoning of targets and therefore it is possible to produce films with a very high growth rate.

In this study, we report initial work on the deposition of GaN films on glass substrates using a modified MF magnetron sputtering system and especially the influence of deposition parameters on the structure, absorption, electric and optical properties of the resulting films.

2. Experimental details

GaN films were deposited using a modified MF magnetron sputtering system operated at 40 kHz and the experimental details have been described in Refs. [5,6]. Pure Ga (99.99%) was put into the twin magnetron targets, which were 3 mm in depth and back-cooled by refrigerated water maintained at a temperature of 5 °C. Soda-lime silicate glass substrates were ultrasonically cleaned in acetone, ethanol and rinsed in de-ionized water before being mounted onto the substrate holder. The sputtering gas was a mixture of N₂ (99.999%) and Ar (99.999%). The substrate was glow discharge cleaned for 10 min in Ar atmosphere at 4 Pa. Deposition parameters of the typical conditions are summarized in Table 1. The Ar ratio or negative bias was varied at a time during



^{*}Corresponding author. Tel./fax: +862768753587.

Table 1

Typical deposition parameters for GaN films.

| Base pressure 5×10^{-3} P.MF power1600 WTarget-substrate distance10 cmTotal gas pressure0.6 PaBias voltages -50 VAr ratio50%Substrate temperature ~ 80 °CDeposition time60 minFilm thickness ~ 3 µm | Parameters | Values |
|--|---|--|
| | Base pressure MF power Target-substrate distance Total gas pressure Bias voltages Ar ratio Substrate temperature Deposition time Film thickness | $\begin{array}{c} 5\times 10^{-3}P,\\ 1600W\\ 10cm\\ 0.6Pa\\ -50V\\ 50\%\\ \sim 80^\circ C\\ 60min\\ \sim 3\mu m\end{array}$ |

deposition, and then the changes in the properties of the films were measured.

The crystal structure of the deposited GaN film was characterized by X-ray diffraction (XRD) with Cu Ka radiation $(\lambda = 0.15406 \text{ nm})$. The elemental composition was determined using an energy dispersive spectroscopy (EDS) system [EDAX genesis 7000] operated at 12 kV. The surface morphologies and chemical bonding properties were investigated by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. The microstructure measurements were carried out on a JEM-2010FEF (UHR) transmission electron microscope (TEM) operated at 200 kV. The absorption plot was obtained by a UV-vis-NIR spectrophotometer (VARIAN CARY 5000). Temperature dependence photoluminescence (PL) emissions were investigated with a 325 nm line of He-Cd laser as an excitation source, using a 1 m grating monochromater and a phase-sensitive detection. PL measurements were conducted in a closed-cycle He cryostat at temperatures from 10 to 300K and the excitation power was set at about 30 mW on the front surfaces of the specimen.

3. Results and discussion

Fig. 1 shows the XRD patterns of GaN films deposited on glass substrates under various Ar ratios. All the films exhibit a preferred orientation in the crystal plane of (002). The peak intensity of (002) reaches a maximum value when the Ar ratio is 50 at%. Then the intensity decreases with further increase of Ar ratio. The FWHM values of the (002) peaks for films deposited at Ar ratios of 0, 20, 30, 50 and 70 at% are 483, 351, 280, 380 and 596 arcsec, respectively. The crystallite sizes are calculated from (002) diffraction using the Scherrer formula assuming the shape factor of 1 [7] and were found to range from 15 to 20 nm. In magnetron sputtering, the target is primarily sputtered by Ar rather than by N₂ [8]. Higher Ar ratio makes the deposited films excess in Ga and deficient in N. On the other hand, lower Ar ratio leads to a reduction in the Ar⁺ density in the plasma and a corresponding decrease in Ar⁺ bombardment on both the Ga target and the growing film surface, which results in the formation of GaN film with lower density. Therefore, an optimal Ar ratio exists, e.g., 30-50 at%, in the present experiment. From the density functional theory calculation, it has been found that the Ga is very mobile at the wurtzite (001) surface while the diffusion of N is slow by orders of magnitude [9,10]. Excess N content in the films significantly increases the Ga diffusion barrier and the surface diffusion length of Ga. Therefore, the structure evolution is correlated to the Ga/N ratio. It is then controlled by the Ar/N₂ flow ratio. Ar pressure has been found to be an important parameter that affects the properties of III-nitrides. For example, Lee et al. [11] have studied RBS and XRD of sputter-deposited AlN and found Ar pressure has evident influence on the residual stress



Fig. 1. X-ray diffraction patterns of GaN films deposited on glass substrates under various Ar ratios.



Fig. 2. X-ray diffraction patterns of GaN films deposited on glass substrates under various negative bias voltages.

and interplanar spacing of the films. In GaN and InN, Ar partial pressure was found to influence the elemental composition, structure and optical properties deposited by magnetron sputtering [12,13].

Fig. 2 shows the XRD patterns of GaN films deposited on glass substrates under various bias voltages. The peak intensity of (002) reaches a maximum value when the bias voltage is -250 V. Then the intensity decreases with further increase of bias voltage to -300 V. FWHM values of the (002) peaks for films deposited at bias voltages of 0, -50, -150, -250 and -300 V are 479, 380, 411, 408 and 325 arcsec, respectively. The electric field between the targets and substrates will be strengthened by the increase in bias voltage. Therefore, the sputtered atoms with higher kinetic energies could migrate more easily on the growing surface and reach the positions of potential minima before being covered by the subsequent arriving atoms. So, the increase of diffraction intensities and decrease of FWHM can be attributed to the improvement of the crystalline quality. This phenomenon can be certificated by the AFM images shown in Fig. 3; it is found that increasing substrate bias voltages affected its microstructure to



Fig. 3. AFM images of GaN films deposited on glass substrates under various negative bias voltages.



Fig. 4. EDS (a) and XPS (b) spectrum of GaN films deposited on glass substrates under typical conditions.

become larger in grain size and more random-oriented in the crystallographic direction.

Fig. 4a shows the EDS image of GaN films deposited on glass substrates under typical conditions. The concentrations of Ga and N are 47 and 53 at%, respectively. Fig. 4b shows a general scan of the same GaN film, which records the core-level peaks at Ga 3d (19.8 eV), Ga 3p (106.7 eV), Ga 3s (161.7 eV), Ga LMM (190.3 eV), N 1s (396.8 eV) and O 1s (533 eV). The binding energy of N 1s and Ga 3d are in good agreement with the published values of compound GaN [14]. The core-level values of Ga were found to have a positive shift with respect to elemental Ga, indicating the nitridation of Ga and the absence of elemental Ga. The O contaminations may come from oxidation in the deposition process and air exposure after withdrawal of the samples from the chamber. Because of the limitation of EDS for light elements, the exact concentration of N and O by Rutherford backscattering spectroscopy (RBS) is under way.

At room temperature (RT), a Hall effect measurement was performed on the GaN films grown under typical conditions. The unintentionally doped films deposited under optimal conditions were normally n type with a typical carrier concentration of 1.92×10^{17} /cm³ and Hall mobility of 49 cm²/V s. This high carrier

concentration is associated with the native defects in the film and the impurities of silicon and oxygen incorporation as detected by XPS. However, RT electron mobility of 380 cm²/Vs has been obtained by the rf-plasma-assisted MBE method [15]. More detailed investigation is going on for exploiting the electric properties of GaN films.

Fig. 5 shows TEM (a) and high-resolution TEM (HRTEM) (b) images of GaN films deposited on glass substrates under typical conditions. GaN films are composed of nanocrystalline particles (black area) with sizes of \sim 20 nm embedded in polycrystalline matrix, which was clearly distinguished from each other by select area electron diffraction (SAED) pattern shown in the inset of Fig. 5a: the concentric rings consist of bright spots, which confirm orientation along a particular direction and these spots can be assigned to be diffraction from the (002) plane of wurtzite GaN and support the results obtained by XRD.

Optical absorption spectra of the GaN film deposited under various negative voltages have been recorded over the range 300–900 nm, and the square of absorption coefficient (α^2) as a function of energy ($h\nu$) is shown in Fig. 6a. Optical band gaps were estimated by extrapolating linear fits to plots of α^2 versus the photon energy $h\gamma$ at the band edge [16]. The crystalline band gaps



Fig. 5. TEM (a) and HRTEM (b) images of GaN films deposited on glass substrates under typical conditions. SAED pattern is shown in the inset of (a).



Fig. 6. α^2 versus photon energy plot (a) and temperature dependence PL spectrum (b) of GaN films deposited on glass substrates.

show a decrease trend with increasing bias voltage from 3.3 eV without bias to 3.1 eV at a substrate bias of -300 V. The optical absorption at energies below the band gap may arise out of defects and disorder produced during films' deposition. When at higher bias voltages, ion bombardment or re-sputtering-induced lattice damage creates defect energy levels below the conduction band and hence the band gap decreases. Similar results have been reported for N⁺ ion implantation on n-GaN [17]. Another reason for the decreasing of band gap may due to the excess Ga in the films reacting with the N₂ [18].

Fig. 6(b) shows the temperature dependence PL spectrum of GaN films deposited under typical conditions. Two emission peaks appear at 3.30 and 3.36 eV at temperatures below 100 K while the band gap emissions almost disappear at RT. RT PL emission with an FWHM of 6 nm and an electron mobility of 380 cm²/V s has been obtained by the rf-plasma-assisted MBE method [15]. In contrast to polycrystalline GaN films consisting of singlecrystalline GaN nanolines with blueshift in the optical band gap relative to bulk GaN [19], we can see a redshift of PL peaks compared to a strain-free 400 µm-thick freestanding GaN [20]. The reason may be as follows: in their case, the diameter of GaN nanocrystalline is less than the exciton Bohr radius for GaN (11 nm). So, both the optical excitation recombination that took place in the nanometer grain and the energy gap of the grain are enlarged due to quantum confinement. However, in our case, the nanocrystalline size is larger (18-20 nm). Similar results have been obtained for polycrystalline GaN films produced by RF magnetron sputtering and the peaks were attributed to defectlevel transitions [21]. Therefore, the origin of these two peaks may come from excitons bound to structural defects as a result of the big thermal expansion coefficient mismatch between the GaN film and the amorphous glass substrate [22]. Tampo et al. [23] observed that the PL excitation spectrum of GaN grown on a quartz glass substrate was essentially the same as that on a sapphire substrate, except for having a lower energy band tail [24]. Then, another possibility for the origin of these two peaks is that they are located at the lower energy tail due to the polycrystalline structure of GaN.

4. Conclusions

GaN films were deposited by MF magnetron sputtering on glass substrates. XRD intensity and FWHM of the films depend strongly on bias voltage and Ar ratios. Optical absorption at energies below the band gap arises out of defects and disorder produced during films' deposition. The PL emission can be attributed to the exciton bound to structural defects. The MF magnetron sputtering makes possible the deposition of GaN films on glass substrates at relatively low temperatures.

Acknowledgments

This work was supported by the national Natural Science Foundation of China under contract nos. 10435060 and 10675095 and by the Korea Science and Engineering Foundation through QSRC at Dongguk University.

References

1358.

92 (2002) 976.

- [12] T. Matruyama, H. Miyake, J. Vac. Sci. Technol. A 24 (2006) 1096.
- [13] Q.L. Liu, Y. Bando, J.Q. Hu, J. Crystal Growth 306 (2007) 288.
- [14] J.S. Peak, K.K. Kim, J.M. Lee, D.J. Kim, M.S. Yi, D.Y. Noh, H.G. Kim, S.J. Park, J. Crystal Growth 200 (1999) 55.
- [15] C.F. Zhu, W.K. Fong, B.H. Leung, C. Surya, Appl. Phys. A 72 (2001) 495.
- [16] E.C.K. Davies, S.R.P. Silva, J.M. Shannon, Diam. Relat. Mater. 12 (2003) 1417.
- [17] K. Santhakumar, K.G.M. Nair, R. Kesavamoorthy, V. Ravichandran, Nucl. Instrum. Methods B 212 (2003) 381.
- [18] E.C. Knox-Davies, J.M. Shannon, S.R.P. Silva, J. Appl. Phys. 99 (2006) 073503.
 [19] Y.G. Yang, H.L. Ma, C.S. Xue, X.T. Hao, H.Z. Zhuang, J. Ma, Physica B 325 (2003)
- Growth 237 (2002) 1079. [19] Y.G. [19] Y.G. [19] M.L. Yin, C.W. Zou, M. Li, C.S. Liu, L.P. Guo, D.J. Fu, Nucl. Instrum. Methods B
- 262 (2007) 189.

[1] E. Nogales, I. Joachimsthaler, R. Heiderhoff, J. Piqueras, L.J. Balk, J. Appl. Phys.

[2] F. Ye, E.Q. Xie, X.J. Pan, H. Li, H.G. Duan, C.W. Jia, J. Vac. Sci. Technol B 24 (2006)

[3] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita,

[4] Q.X. Guo, A. Okada, H. Kidera, T. Tanaka, M. Nishio, H. Ogawa, J. Crystal

H. Kiyoku, Y. Sugimoto, Jpn. J. Appl. Phys. 35 (1996) L74.

- [6] C.W. Zou, M.L. Yin, M. Li, L.P. Guo, D.J. Fu, Appl. Surf. Sci. 253 (2007) 9077.
- [7] S. Christiansen, M. Albrecht, H.P. Strunk, S. Veprek, J. Vac. Sci. Technol. B 16 (1) (1998) 19.
- [8] E. Lakshmi, B. Mathur, A.B. Bhattacharya, V.P. Bhargava, Thin Solid Films 74 (1980) 77.
- [9] E. Calleja, M.A. Sanchez-Garcia, F.J. Sanchez, F. Calle, F.B. Naranjo, E. Munoz, U. Jahn, K. Ploog, Phys. Rev. B 62 (2000) 16826.
- [10] T. Zywietz, J. Neugebauer, M. Scheffler, Appl. Phys. Lett. 73 (1998) 487.
- [11] S.H. Lee, K.H. Yoon, D.S. Cheong, J.K. Lee, Thin Solid Films 435 (2003) 193.
- [20] S. Tripathy, L.S. Wang, S.J. Chua, Appl. Surf. Sci. 253 (2006) 236.
 [21] Gi Sinha, K. Adhikary, S. Chaudhuri, Appl. Surf. Sci. (2008)10.1016/ j.apsusc.2008.02.033.
- [22] S. Fischer, G. Steude, D.M. Hofmann, F. Kurth, F. Anders, M. Topf, B.K. Meyer, F. Bertram, M. Schmidt, J. Christen, L. Eckey, J. Holst, A. Hoffmann, B. Mensching, B. Rauschenbach, J. Crystal Growth 189 (1998) 556.
- [23] H. Tampo, H. Asahi, Y. Imanishi, M. Hiroki, K. Ohnishi, K. Yamada, K. Asami, S. Gonda, J. Crystal Growth 227 (2001) 442.
- [24] K. Iwata, H. Asahi, K. Asami, A. Ishida, R. Kuroiwa, H. Tampo, S. Gonda, J. Crystal Growth 189 (1998) 218.