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Optical properties of nanocrystalline GaN films prepared by DC magnetron sputtering

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Nanocrystalline GaN films with different crystallite size were prepared by direct current (DC) magnetron sputtering technique under different substrate temperature. The sizes of nanocrystals derived from grazing-incidence X-ray diffraction (GIXRD) peaks were 4 nm and 7 nm for films grown at 770 K and 870 K, respectively. The Raman peak centered at 657 cm^{-1} might be primarily attributed to a V_N-related band in the nanocrystalline GaN. The similar broad near-band-edge emission peak about 356 nm characterized by photoluminescence (PL) was observed and no yellow luminescence can be found.

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1. Introduction

GaN has become one of the most important semiconductor materials for optoelectronic applications such as light-emitting diodes (LEDs), laser diodes (LDs) and detectors [1]. In recent years, synthesis of GaN in nanocrystalline have attracted the attention of the scientists because of the new exotic properties of GaN in nanocrystalline form such as a shift of luminescence to large energies, transparent in the visible range and n-type semiconductor [2-5]. Survey of literature indicates that sputtering technique does not encourage grain growth and are conductive to the formation of nanocrystalline materials [6-8]. However, there are not very many studies reported on the optical properties of nanocrystalline GaN films prepared by sputtering technique up to now. The optical properties of the nanocrystalline GaN films should pave the way for more detailed studies and promote novel and intriguing functional applications. In this paper, the optical properties of GaN nanocrystalline films grown on silicon substrates by DC magnetron sputtering technique were investigated. The results are discussed in comparison with earlier findings.

2. Experimental details

GaN thin films were grown on p-type Si (111)-oriented wafers by DC magnetron sputtering of Ga target (99.999%) in pure

nitrogen atmosphere (99.999%). Prior to the introduction of nitrogen, a base pressure of about 2.0×10^{-3} Pa was attained using a turbo-molecular pump. The substrate temperate during the film growth was measured using a copper constantan thermocouple, and was changed between 615 K and 870 K. The nitrogen gas flow rate was set up at 40 SCCM and the gas pressure was maintained at 5.0 Pa. The deposition time was 1 hour.

The structure characteristics of the deposited GaN films were determined by GIXRD using a Philips X'Pert diffractometer with Cu $K\alpha1$ radiation (λ=1.54056 Å). Raman spectroscopy was performed on a Jobin-Yvon LabRam HR80 spectrometer with a 532 nm line of torus 50 mW diode-pumped solid-state laser at room temperature. PL spectra were recorded at room temperature using a spectrophotometer (SHI-MADZU RF-540) with a He-Cd laser, whose wavelength and power were 325 nm (3.81 eV) and 19 mW.

3. Results and discussion

Fig. 1 shows the GIXRD traces for the sputter-deposited GaN films with nearly equal film thickness (~0.2 μm) on Si (111) substrates at temperature ranging from 615 K to 870 K. The GaN nanocrystalline films deposited here exhibited the presence of predominant phase. These peaks correspond to (100), (002), (102), (110) and (202) of h-GaN phase. The peak at 2θ=44.4° was caused by the XRD instrument. It may be noted here that the diffraction peaks are broadened indicating that the GaN nanocrystal sizes are very small. The sizes of nanocrystals derived from GIXRD peaks by using Scherrer's formula were 4 nm and 7 nm for the film grown at 770 K and 870 K, respectively. The size of the film deposited at 615 K can not derive because of no apparent GaN crystalline peaks. The crystallite size is so small that the quantum confinement effects (quantum dots) can be observed. It will be discussed later in this study.

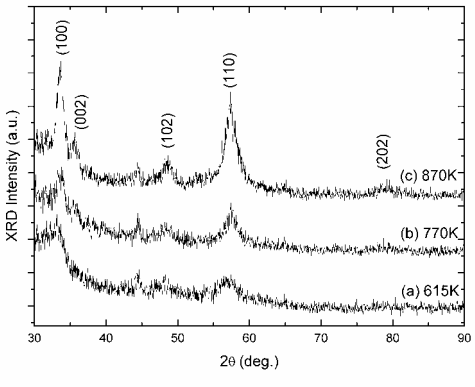

Fig. 1. X-ray traces spectra of the GaN films on Si (111) substrates at substrate temperature: (a) 615 K, (b) 770 K, (c) 870 K.

Figs. 2(a)-2(c) show the Raman spectra of the films prepared 615 K, 770 K and 870 K in the range between 100 and 900 cm^{-1} with a break region from 500 to 555 cm^{-1}. In order to identify the peaks from substrate and GaN films, a bare Si substrate was also characterized by Raman study (see Fig. 2 (d)). In particular the first order Si line at 520 cm^{-1} was stronger than the sample signal by typically two orders of magnitude.

Considering the reported experimental and calculated frequencies of phonons at Γ point in the Brillouin zone of GaN crystal [9]. Only the 143 cm^{-1}, 570 cm^{-1} and 750 cm^{-1} peaks, which in any case are a strong in GaN, can be assigned to the E2 (low and high) and A1(LO) mode. Nearly all of the other peaks are not at all from the film, rather they are the second-order features from the Si substrate. In brief the shoulder at 220 cm^{-1}, the peak at 305 cm^{-1}, the 437 cm^{-1} feature, the pair at about 625 cm^{-1} and the peak at 825 cm^{-1} are all found with exactly these relative intensities in Si second order.

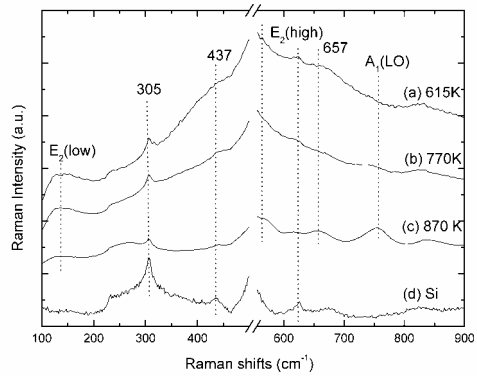

Fig. 2. Raman spectra of the GaN films grown at different substrate temperature: 615 K (a), 770K (b), 870K (c), and Si (d) in the range between 100 and 900 cm^{-1} with a break region from 500 to 555 cm^{-1}.

Note that peak around 657 cm^{-1} which have almost disappeared in Fig. 2(a), but are enhanced in intensity in Fig. 2(c). Previously a band with frequency range from 637 to 657 cm^{-1} was generally assigned to a defect-related band or an overtone of the acoustic phonon. In our experiment, V_N easily comes into being because the probability of nitrogen evaporation increases with increasing the substrate temperature [10]. Therefore the peak might be primarily attributed to a V_N-related band in the naocrystalline GaN.

Fig. 3 shows the PL spectra of the GaN films prepared at 615 K, 770 K, and 870K. The data in this figure were taken at a variety of different experimental conditions; consequently the magnitude of the intensities cannot be compared. However, the dependence of the intensity on the growth temperature shows some interesting phenomena. Two peaks are clearly observed in each film. The similar broad emission peak about at 356 nm was observeds and no yellow luminescence can be found in three films. The resulting films exhibit a blueshift in the optical band gap relative to bulk GaN (E_g=3.4eV, 365 nm). This large blueshift could be attributed to the strong quantum confinement effect in small nanocrystals as the exciton Bohr radius for GaN is reported to be 11 nm [11].

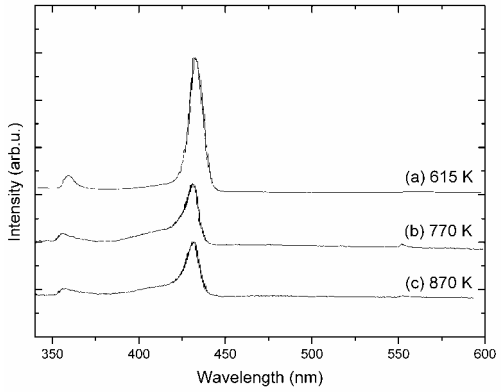

Fig. 3. Room-temperature Photoluminescence spectrum of the GaN films grown at different substrate temperature: 615K (a), 770K (b), 870K (c).

In addition, another very sharp emission peak in the blue region of the spectrum can be observed, which centered at 431 nm. It may be observed that a very weak shift of the BL peak position with varied temperature. The most valid model of this blue emission is the model of radiative recombination by transitions from the shallow donors or conduction band to a relatively deep acceptor [12]. Various proposals have been made as to the nature of the defect responsible for the blue luminescence (BL) band in undoped GaN. Generally the BL band was attributed to V_{Ga}-related complex. Investigations of cathodoluminescence spectra, electro- and photoconductivity of nanocrystalline GaN thin films by

Bondar show that intrinsic defects are primarily responsible for the BL band [13]. Shim has reported that the a-GaN films that consists of nanocrystallites embedded in an amorphous matrix exhibit blue-light emission at ~2.8 eV when the films were nearly stoichiometric [14]. In our experiment, V_{Ga} easily formed at the low temperature because that N source is rich. The characteristics of relatively strong blue luminescence of the film deposited at 615 K are attributed to the formation of the clean band gap where N vacancies are not prevalent at that temperature. With increasing the substrate temperature, the probability of nitrogen evaporation increases. V_N easily comes into being as a result of that. So the intensity of BL peak increased for films with decreasing the temperature. This is agreement with the Raman spectra: V_N prefers to form at higher temperature. Therefore the BL band might be attributed to a V_{Ga}-related complex or an amorphous GaN matrix.

4. Conclusion

In summary, nanocrystalline GaN films with different crystallite size were deposited by DC magnetron sputtering technique under different substrate temperature. The sizes of nanocrystals derived from XRD peaks by using Scherrer's formula were 4 nm and 7 nm for films grown at 700 K and 870 K, respectively. With increasing the substrate temperature, V_N easily comes into being. Therefore the Raman peak centered at 657 cm^{-1} band might be primarily attributed to a V_N-related band in the naocrystalline GaN. The similar broad emission peak about 356 nm characterized by photoluminescence were observed and no yellow luminescence can be found in three films. The large blue shift compared to the bulk band gap could be attributed to the strong quantum confinement effect in small nanocrystals.

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