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Hexagonal GaN nanostructure via electrochemical etching

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Gallium nitride GaN thin films were deposited on Si (111) substrates using electrochemical deposition technique at 20 °C. SEM images and EDX results indicated that the growth of GaN films varies with the current density. XRD and Raman analyses showed the presence of hexagonal wurtzite and cubic zinc blende GaN phases with the crystallite size around 18–19 nm. Photoluminescence spectrum showed that the energy gaps of h-GaN/Si (111) and c-GaN/Si (111) were near 3.39 eV and 3.2 eV respectively at 300 K. Raman spectrum indicated the presence of mixed phonon modes of hexagonal and cubic GaN.

Keywords: Hexagonal; Nanostructure; Etching.

1. INTRODUCTION

GaN has received much attention because of its wide direct band gap 3.4 eV [1], and its promising potential for semiconductor optical and electronic devices, which are suitable for high temperature, high power, and high frequency applications. Typical techniques of GaN layer growth include metalorganic chemical vapor deposition (MOCVD) [2], reactive molecular beam epitaxy (MBE) [3], hydride vapor phase epitaxy (HVPE) [4] and reactive sputtering [5]. There is large number of reports on synthesis of GaN powders by chemical reaction [6,7], but synthesis of GaN thin films is still a challenge. Among these techniques,

the advantages of the electrochemical deposition (ECD) in comparison with other methods are as follows: the thickness and surface morphology can be controlled by growth parameters, the deposition rate is relatively high, the experimental setup is low-cost, low temperature process, and ease of impurity doping [8].

The use of ECD technique was limited due to complexities in the process and the stringent material property requirements for device applications, hence very limited number of reports. Roy and Pal [9] reported the ECD of GaN films using a constant current density and potential above room temperature on Si (100) substrate. In this paper, we presented for the first time, a synthesis of GaN thin films by ECD on n-Si (111) at 20 °C with different current densities.

2. RESULTS AND DISCUSSION

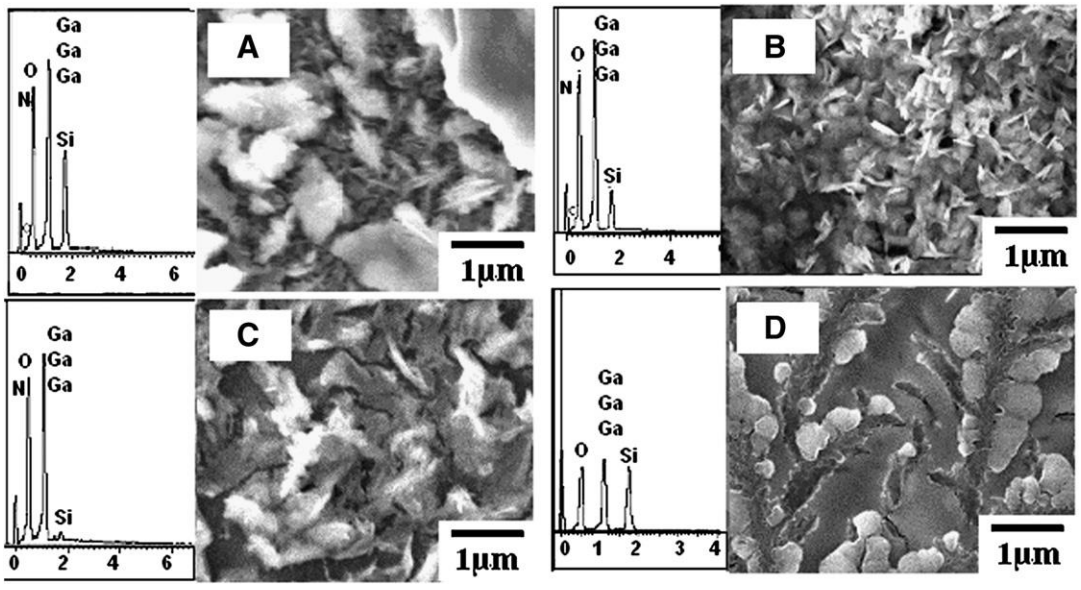

Figure 1 EDX and SEM spectrum of GaN/Si (111) deposited by different current densities, (A) 1.5, (B) 2.5, (C) 3.5 and (D) 4.5 mA/cm^2.

disappeared and the film is dominated by Ga_2O_3. The Si peak intensity gets smaller with increasing current density, suggesting an increasing film thickness except for Fig. 1D where Si peak strongly emerged. This could be that the lifted off thin films have gaps allowing the EDX signal to reach the Si substrate. The possible reactions of gallium nitrate and ammonium nitrate melt in water are [9] dominates and blocks the current and causing the deposition process to stop at 4.5 mA/cm^2. Fig. 2 shows a typical XRD pattern of GaN/Si (111) by ECD technique at different current densities. The XRD spectrum (Fig. 2A) revealed two peaks; $2\theta =$ 32.9° and $2\theta = 40.1°$ for c-GaN due to reflections from (100) and (002) planes respectively. Both peaks showed increasing intensity with increasing current density. The strong peak at $2\theta = 28.4°$ is due to Si (111). Peaks noticeable from sample c, namely at $2\theta = 34.5°$ and $2\theta =$ 36.1° and $2\theta = 37.6°$. The first two peaks are for h-GaN, due to reflections. The positive ions of Ga^{+3} and NH^{+1} were concentrated on the surface of the cathode (Si substrate), upon which combination will form clusters of critical sizes of GaN, leading to the growth of continuous thin films. From SEM and EDX analyses, when the current density increases from 1.5 to 3.5 mA/cm^2 the rate of deposition of GaN and Ga_2O_3 increases. Beyond 3.5 mA/cm^2, the deposition rate of Ga_2O_3 from (0002) and (1-101) planes respectively and the last peak is for β-Ga_2O_3, due to reflection plane (11-3). A strong peak at $2\theta = 58.9°$ (Fig. 2B) for h-GaN is due to reflection from (110) plane [10].A strong peak at $2\theta = 58.8°$ is due to Si (222). Thus, our deposited films contain both the hexagonal and cubic phases of GaN. From the XRD data, the determined lattice constants are a =3.35 Å, and c = 5.159 Å for hexagonal, which are in good agreement with reported values [11]. The average size of h-GaN crystals, D calculated from the well known Scherrer formula is between 18 and 19 nm.

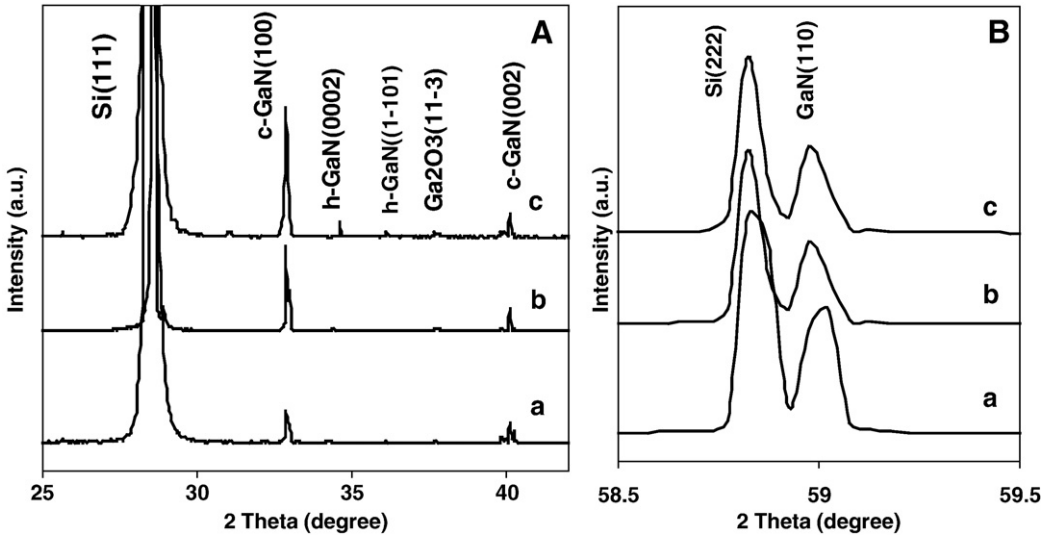

Figure 2 XRD of deposited GaN/Si (111) for 12 h using different current densities of 1.5, 2.5 and 3.5 mA/cm^2 indicated by a, b and c respectively, A) for the range of 2θ =25–45° and B) for the range of 2θ =58.5—59.5°.

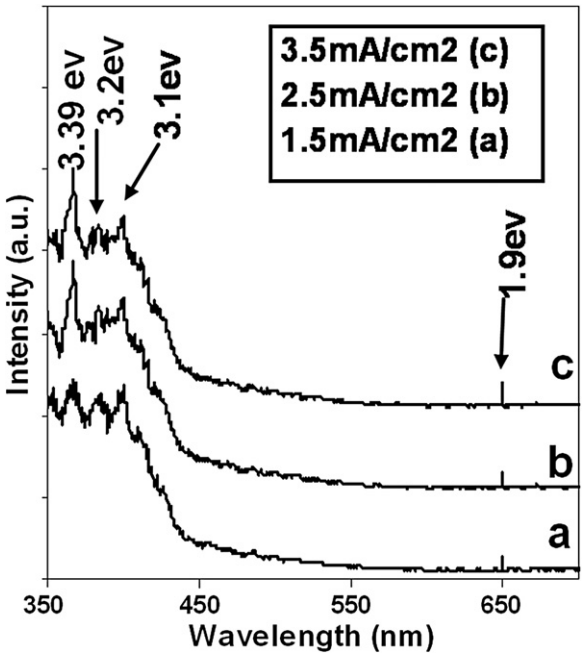

Figure 3 PL spectra of deposited GaN/Si (111) for 12 h using different current densities; (a) 1.5, (b) 2.5, and (c) 3.5 mA/cm^2.

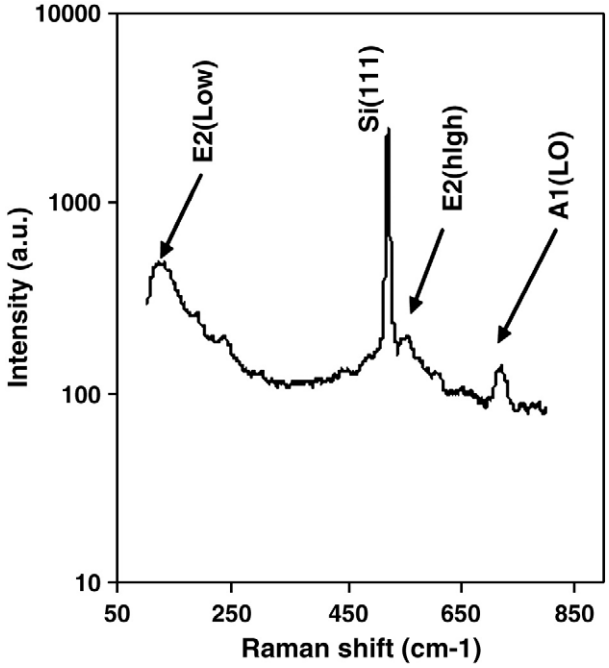

Figure 4 Raman spectra of GaN/Si (111) for 12 h using current density of 2.5 mA/cm^2.

Fig. 3 shows the PL spectrum of GaN/Si (111) showing four peaksat 3.39, 3.2, 3.1 and 1.9 eV. The peak positions at 3.39 and 3.2 eV are due to the band gap for h-GaN and c-GaN respectively, and these values are in good agreement with other reported work [12]. The third peak centered at 3.1 eV, may be due to the donor acceptor (DA) transition [13]. The last at

1.9 eV has low intensity and may be due to the deep level states related to gallium or nitrogen vacancy [14]. The increasing of the 3.39 and 1.9 eV peaks intensity with current density indicates the increased rate of the deposition of hexagonal GaN. Increasing the current from 1.5 mA/cm^2 to 2.5 mA/cm^2 seems to increase the peak 3.39 eV, but showing a saturation of h-GaN deposition at current density beyond. There was no observable change for peak 3.2 eV for all samples, implying no significant dependency of c-GaN formation on the deposition current. Increasing the current from 1.5 mA/cm^2 to 2.5 mA/cm^2 seems to reduce the eV peak, and increasing the current further has almost no change on the peak intensity. Finally, 1.9 eV peak shows increasing intensity with increasing deposition current, suggesting the increment of deep level states due to gallium or nitrogen vacancy.

A Raman spectrum of GaN/Si (111) for current density of 2.5 mA/cm^2 is shown in Fig. 4, representing the spectrum for all samples since no significant difference found between samples. A strong band at 522.04 cm^{-1} is from the Si (111) substrate, and a small band at 250 cm^{-1}, may be due to the acoustic phonons of Si. Three Raman active optical phonons are assigned to GaN, one for c-GaN at 733 cm^{-1} due to A_1 (LO) modes, and two modes for h-GaN at 140 cm^{-1} and 566 cm^{-1} due to E_2 (low) and E_2 (high) respectively [15].

3. CONCLUSIONS

The GaN thin films have been successfully grown on Si (111) using ECD technique. The surface morphology shows a network of nanoflake structures with varying sizes. The GaN films contained mixed phases of h-GaN and c-GaN with grain size in the range of 18–19 nm as well as Ga_2O_3. The GaN and Ga_2O_3 contents increased with increasing deposition current from 1.5 mA/cm^2 to 3.5 mA/cm^2. At 4.5 mA/cm^2 the Ga_2O_3 dominated and the deposition process stopped. The PL and Raman spectra confirmed the presence of mixed phases in the GaN thin films and all-important peaks have been assigned.

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