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Synthesis of GaN by electrochemical method at low temperature

S. El-Safty[1], *Y. Hayashi*[2,*]

[1]National Institute for Materials Science (NIMS), Research Center for Functional Materials, 1-2-1 Sengen, Tsukuba-shi, Ibaraki-ken, 305-0047, Japan
[2]Graduate School of Natural Science and Technology, Okayama University, Okayama, 700-8530, Japan
*) Email: hayashiyy@okayama-u.ac.jp

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The growth of GaN thin films using this technique is still a challenge. According to our knowledge, up to now there are limited theoretical and experimental studies on ECD of GaN [7,8]. In our previous work we presented a synthesis of GaN thin film using a simple and low-cost ECD on n-Si (1 1 1) substrates and for the first time below room temperature at 20 °C using different current densities and constant deposition duration. In order to have a deeper insight on the growth mechanism of GaN films by ECD, study on the effects of deposition time is desirable.

Keywords: GaN; Electrochemical; Temperature.

1. Introduction

Gallium nitride is a direct wide band gap semiconductor (3.39 eV) at room temperature, which has a wide use in optical devices operating at blue and ultraviolet wavelengths and at high temperature [1]. In the last few decades, many efforts have been made to grow GaN thin films by various growth techniques, including metalorganic chemical vapor deposition (MOCVD) [2], reactive molecular beam epitaxy (MBE) [3], hydride vapor phase epitaxy

(HVPE) [4] and reactive sputtering [5]. However, these are very expensive techniques, which add a very high cost to the products made from such material. The search for cost effective technique therefore has begun and seems to have found hopes in chemical related technique, namely electrochemical deposition (ECD). Among the above mentioned methods, (ECD) has many advantages such as the follows: the thickness and surface morphology can be controlled by growth parameters, the deposition rate is relatively high, the experimental setup is of low cost and low temperature, environmentally friendly and the ease of impurity doping [6]. However, the growth of GaN thin films using this technique is still a challenge. According to our knowledge, up to now there are limited theoretical and experimental studies on ECD of GaN [7,8]. In our previous work we presented a synthesis of GaN thin film using a simple and low-cost ECD on n-Si (1 1 1) substrates and for the first time below room temperature at 20 1C using different current densities and constant deposition duration [7]. In order to have a deeper insight on the growth mechanism of GaN films by ECD, study on the effects of deposition time is desirable.

In this paper, we report the synthesis of GaN thin films using a simple one-step ECD on n-Si (1 1 1) substrates for different durations, and the effects of deposition duration on the quality and on the properties of GaN thin film are studied. Structural and optical properties are investigated by scanning electron microscopy (SEM), EDX, X-ray diffraction (XRD), Raman scattering and photoluminescence (PL) spectroscopy.

2. Experimental

GaN thin films were prepared by electrochemical technique in one step using an aqueous solution consisting of a mixture of gallium nitrate ($Ga(NO_3)_3$) with ammonium nitrate (NH_4NO_3) in the ratio of (1:1) in deionized water kept at atmospheric pressure, and at 20 1C since Ga metals melts at 29 1C [7,8]. N-type Si (1 1 1) was used as a substrate. Before deposition, Si (1 1 1) was cut into 1 cm x 1 cm substrates. The substrates were cleaned first with 50:10:10 $H_2O/NH_4OH/H_2O_2$ for 10 min, second with 1:50 $HF:H_2O$ for 10 min and third with 60:10:10 $H_2O/HCl/H_2O_2$ at 80 1C for 10 min to remove the surface oxides. Between the cleaning steps, we rinsed the substrates in deionized water. A simple homemade Teflon cell with two electrodes was used. A gallium plate with (99.999%) purity was used as an anode and n-Si (1 1 1) as a cathode. The distance between anode and cathode was about 0.5 cm. In the electrochemical deposition process, we used constant current density J ¼ 2.5 mA/cm^2 (supplied by a Keithley 220 programmable current source) for different duration times: t ¼ 6, 12, 24 and 48 h.

The deposited films underwent a series of material characterization techniques, namely scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), Raman scattering and photoluminescence (PL) spectroscopy performed at room temperature. Finally, the film thickness was measured using an optical reflectometer (Filmetrics F20).

3. Results and discussion

Fig. 1 shows the scanning electron micrographs of the morphology of GaN films deposited on Si (1 1 1) substrates using ECD. The films were deposited for different durations: 6, 12, 24 and 48 h, keeping the current density 2.5 mA/cm^2 (corresponding to the applied potential voltage of 15 V) constant. The SEM images show different surface morphologies of the grown structures on Si substrate according to the deposition durations. For the 6 h duration (Fig. 1a), GaN thin film started depositing with some spaces on the Si substrates and with thickness about 100 nm. For the 12 h duration (Fig. 1b), network of nanoflakes was formed. The flakes were a mixture of large and small sizes from a micron to 100 nm and with film thickness of about 180 nm. On the other hand, for the film deposited for 24 h duration (Fig. 1c), the nanoflakes became compact with three- dimensional sponge-like structures and the film thickness increased to 260 nm. Lastly, for the longest duration of 48 h (Fig. 1d), the nanostructure became uniform, compact, crystal- lized, symmetry cell-like and the film thickness increased to 270 nm. One could observe that the deposition duration has a significant effect on the morphology, the shape, the thickness and

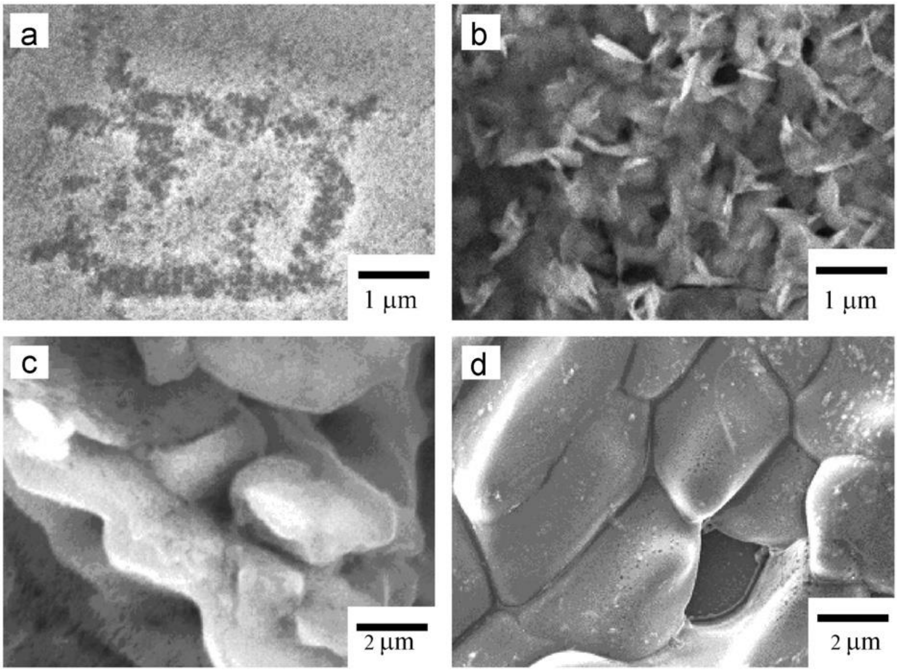

Figure 1 Scanning electron microscopy images of the four GaN films deposited for different durations: (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h.

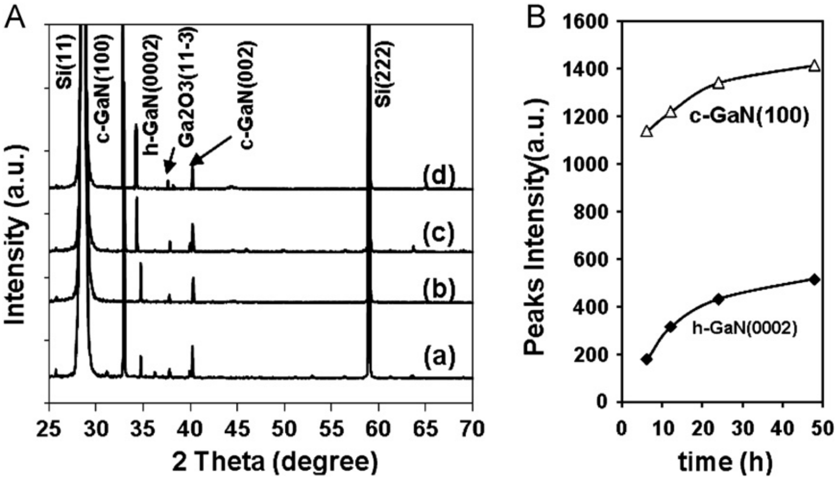

Figure 2 (A) XRD of the four GaN films deposited for different durations: (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h and (B) peak intensity of h-GaN and c-GaN versus deposition time.

When gallium nitrate and ammonium nitrate dissolve in water, the possible reactions that take place in the cell under the applied electric field can be written as [7,8] peak intensity of h-GaN and c-GaN versus deposition time Fig. 2B). The XRD spectrum indicates two peaks: one at 2y ¼ 32.91 and the other at 2y ¼ 40.11 for c-GaN corresponding to reflections from (1 0 0) and (0 0 2) planes, respectively. One peak could be observed at 2y ¼ 34.51 for h-GaN corresponding to reflection from (0 0 0 2) planes. A peak with a weak intensity of b-Ga_2O_3 could be observed at 2y ¼ 37.81 corresponding to reflection plane (1 1 –3) [9]. There are two other strong peaks at lattice constants have been determined for the four samples. The average size of h-GaN crystals, D, can be calculated from the well known Scherrer formula D ¼ kl/(b cos y) where k is a constant equals to 0.9, l is the incident X-ray wavelength and b is the FWHM; these values are in good agreement with reported values [10]. It summarizes the variation of the lattice constants and crystallite size with deposition time. The constants a and c saturated for duration longer than 24 h; meanwhile the crystallite size D increases almost linearly with deposition time. It shows the variation of the film thickness with deposition time and the variation of the lattice parameters a and c with film thickness. It is clear that as the deposition time increases the film thickness increases, while at high deposition time the thickness tends to saturate.

The in-plane (along a-axis) and out of plane (along c-axis) strains, e_a and e_c, , have been calculated from the two relations e_a ¼ Da/a_0 and e_c ¼ Dc/c_0 [11], respectively, where Da and Dc are defined as the deviation of the calculated lattice parameters a and c from the corresponding unstrained values.

4. CONCLUSIONS

The lattice constants and the average size of GaN crystals were seen to be increased with deposition duration. The XRD, PL and Raman spectra confirmed the presence of mixed phases of h-GaN and c-GaN in the films and all known peaks have been assigned. The in-plane strain (e_a) and the out of plane strain (e_c) indicated that the strain caused by the substrate was tensile in all samples except for the 6 h sample (compressive strain), and this strain decreased with deposition durations. PL spectrum indicated that the h-GaN band gap intensity increased with deposition time. The work showed that it is possible to use this cost effective technique to grow strain free (stable) GaN films on Si substrate suitable for light emission and photodetection.

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