Effect of Heat Treatment of Al Substrate on GaN Film Electrodeposited in Aqueous Solution

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1. Introduction

Gallium nitride (GaN) is one of the most promising III-V semiconductor materials that use nitrogen as a group V element [1] [2] [3] [4] [5]. In particular, GaN has been recognized to be the most important material for blue and ultraviolet optoelectronic devices and has recently attracted considerable attention after the...
successful fabrication of high-efficiency blue light-emitting diodes [6] [7] [8] [9].

During the last two decades, numerous studies have been conducted on GaN semiconductors, and several reports have been published on the synthesis technology of these semiconductors [10]-[19]. Various dry plating methods, such as metal-organic chemical vapor deposition (MOCVD) [20] [21], molecular beam epitaxy (MBE) [22] [23] [24], thermal ammoniation [25], physical vapor deposition [26], and chemical vapor deposition [27] [28] [29], have been adopted and used in many researches. However, the high cost of these equipments is one of the major challenges to be overcome for commercialization and widespread application. Moreover, the use of high-temperature systems and ultra-pure gases for GaN fabrication entails considerable complexity and additional manufacturing cost [30].

Therefore, the electrodeposition has recently been proposed as one of low temperature and low-cost synthesis methods of semiconductor materials, and has been studied by some researchers as an alternative for GaN synthesis. Several reports have also confirmed the possibility of GaN synthesis by electrodeposition [31]-[37]. Most low-temperature GaN syntheses have been conducted on silicon (Si) substrate because of their high quality, large size, and low cost. However, Si and deposited metal usually exhibit a weak interaction that leads to three-dimensional island-like growth or Volmer-Weber mechanism [38] [39]. This is because the rate of electrochemical reaction on Si is slower than on metals [40].

The substrate effect of various aluminum compounds, such as aluminum nitride (AlN) [41] [42], aluminum gallium nitride (AlGaN) [43] [44] and aluminum oxide (γ-Al₂O₃) [45], which can improve the crystallinity of GaN, has been studied and reported by many researchers [46] [47]. High-quality GaN have been grown on Al-based intermediate layers. It can be considered that Al plays an important role in GaN growth. In particular, it can be expected to be more suitable as substrate material for fabrication of GaN film in wet processes since Al has better conductivity than Si.

Therefore, the synthesis of GaN film was performed on Al substrate in this study. In addition, the effect of heat treatment of Al substrate on the GaN formation was investigated.

2. Experimental Details
2.1. Materials and Reagents

For electrodeposition, a commercial Al plate (99.9% purity) and Pt coil (99.99% purity) are purchased and used as working and counter electrodes, respectively. Gallium nitrate hydrate (Ga(NO₃)₃·xH₂O, ≥99.9%, Sigma Aldrich) and ammonium nitrate (NH₄NO₃, ≥98%, Sigma Aldrich) are used as sources of Ga and N, respectively. Boric acid (H₃BO₃, ≥99.5%, Sigma Aldrich) is purchased and employed to prepare the electroplating electrolyte as a surfactant and a buffer. Concentrated nitric acid (HNO₃, 70.0%, Nacalai Tesque) is used to adjust the pH
level of each solution. Deionized water with a resistivity of 18.2 MΩ·cm is used in all the experiments.

2.2. Electrode Preparation

The working electrodes are 1.0 × 1.0 cm² Al plates with a 99.9% purity, and a Pt coil is used as counter electrode. An Ag|AgCl|sat’d–KCl electrode is employed as reference electrode. The Al substrates are prepared by polishing using emery paper to a grade of 2000. They are ultrasonically cleaned with ethanol for 10 min, followed by deionized water for another 10 min. The Pt coil is immersed in hydrochloric acid (HCl, 35%, Nacalai Tesque) to clean the surface and is thereafter washed with distilled water. Finally, all electrodes are washed with distilled water and dried under atmospheric conditions. Prior to electrodeposition, the Al plate is covered with a Nitoflon adhesive tape (Nitto Denko) to yield an electrode area of 0.5 × 0.5 cm².

2.3. Heat Treatment of Al Substrates

The influence of electrode conditions, such as the composition and crystallinity of various electrodes, on material synthesis has been widely investigated [48]. Here, the Al substrates are prepared to examine the influence of Al oxide layer on the synthesis of GaN film by electrodeposition. Since Al can form gamma phase alumina at 500°C or higher, heat treatment was performed at 200°C and 500°C for 1 h. The Al substrates, referred to as Al200HT and Al500HT, are heat-treated at 200°C and 500°C for 1 h, respectively, in an atmospheric electric furnace according to the commercial Al plate used. The oxide formation and crystallinity of each Al substrate are characterized by SEM and XRD.

2.4. Electrodeposition Process

All the electrochemical depositions are performed using a potentiostat (Hokuto Denko, HA3003A) in a three-electrode cell configuration at atmospheric pressure and temperature of 25°C. As shown by the E-pH diagram of Ga in Figure 1(a) [49], gallium ion (Ga³⁺) exists in the form of passivated gallium oxide (Ga₂O₃) or gallium hydroxide (Ga(OH)₃) in a solution with a pH level of 3 or more. Thus, all electrochemical experiments are performed from acidic solutions at pH 1.5. The electrodeposition is conducted in acidic solutions composed of 0.1 M of Ga(NO₃)₃, 2.5 M of NH₄NO₃, and 0.6 M of H₃BO₃. To prevent the abrupt change in the pH level of the solution by hydrogen ion (H⁺) depletion near the electrode surface during the electrodeposition process, H₃BO₃ is used as buffer. The electrodepositions are attempted using the galvanostatic method at a current density of 3.5 mA·cm⁻² for 3 h. In our previous study, the best results were obtained at this current density [50]. The working and counter electrodes are separated by a distance of approximately 1.0 cm, and the electrolyte is vigorously stirred during the electrodeposition process. After deposition, the specimens are immediately rinsed thoroughly with distilled water.
Figure 1. Potential vs. pH equilibrium diagrams of (a) gallium and (b) nitrogen in aqueous solution at 25°C [modified from ref. 49 and 50, respectively].

2.5. Characterization and Tests

The cyclic voltammetry experiments are performed to confirm the electrochemical behavior of each ion on the Al surface. The current response is recorded against the applied voltage (V vs. Ag/AgCl), which is scanned in a triangular waveform.

The surface morphology is characterized with scanning electron microscopy (SEM, Hitachi, S-4800), and the chemical composition is analyzed by energy dispersive X-ray spectroscopy (EDX, HORIBA, EMAX ENERGY, EX-350). The SEM measurement is performed at 10 kV, and the EDX analysis is conducted at an acceleration voltage of 12 kV and current of 10 μA. The crystalline quality and the lattice parameter of the samples are characterized by X-ray diffraction (XRD, Rigaku, Ultima IV) with a Cu–Kα1 radiation source (λ = 1.541 Å). To examine the chemical bonding states, X-ray photoelectron spectroscopy (XPS) measurements are performed with a PerkinElmer PH1 ESCA system. Monochromatic Mg–Kα ionizing radiation (1254 eV) is used with the X-ray source operating at 300 W (15 kV and 20 mA). Raman measurements are performed using
Horiba Jobin Yvon HR system, and an argon ion laser (514.5 nm) is utilized as an excitation source. The Raman scattering experiment is implemented in the $z$ ($x$, unpolarized) $z$ scattering configuration. The resolution of this system is 1 cm$^{-1}$, and the integral time is 3000 ms.

3. Results and Discussion

3.1. Electrochemical Behavior of Gallium and Nitrogen Ions

The CV experiments are performed for aqueous solutions containing several chemicals to examine the electrochemical behavior of ions. The pH level of all solutions is adjusted by HNO$_3$. Table 1 lists the conditions of solutions used in the CV experiment. The CVs are recorded at a scan rate of 20 mV·s$^{-1}$ between −2.0 and 2.0 V vs. Ag/AgCl, start from rest potential to negative direction and repeated 5 cycles.

Figure 2 shows the CV results of 5th cycle. In order to easily compare each cathodic curve, the expanded graphs in the range of −2.0 to 0 V is displayed in the graph below. In the solution at pH 1.5 containing only HNO$_3$ shown in graph (a), a slight reduction current is observed starting from approximately −0.6 V, and then a small curve appears at ca. −1.0 V. From the HNO$_3$ solution, the first curve seems to correspond to hydrogen evolution reaction (HER), and second curve can be regarded as the reduction of nitrate (NO$_3^-$) ion. As confirmed from E–pH diagram of nitrogen (N) in Figure 1(b) [51], NO$_3^-$ ion can be reduced through the following cathodic reactions.

\[
\begin{align*}
\text{NO}_3^- + 2\text{H}^+ + 2e^- & \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \\
\text{NO}_2^- + 8\text{H}^+ + 6e^- & \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}
\end{align*}
\]

Although the reduction potential of NO$_3^-$ ion is very positive than HER, it can be seen that the NO$_3^-$ ion does not reduce easily before HER. And if the reaction continues, N species ion may change to most stable ammonium (NH$_4^+$) ion.

In the graph of Figure 2(b) obtained from the solution containing NH$_4$NO$_3$, cathodic curves starts at −0.7 and shows two peaks at −1.3 and −1.7 V. Additional curve compared to the graph obtained in the only HNO$_3$ solution can be expected to the reaction to other nitrogen species by the influence of ammonium.
Figure 2. Comparison of CVs from (a)-(e) aqueous solutions in Table 1. The CVs are recorded at a scan rate of 20 mV s\(^{-1}\) between −2.0 and 2.0 V, start from rest potential to negative direction and repeated 5 cycles. The graph below shows the cathodic current curves corresponding to a potential region of −2 to 0 V.

The electrochemical reactions of NO\(^3\)\(^-\) is known to be complex \[52\]. However, a previous report on the electrodeposited Cr in the solution containing nitrogen element by N. Ryan et al. found that NO\(^3\)\(^-\) ion forms adsorbed nitrogen (N\(_{\text{ads}}\)) in aqueous solutions during the electrodeposition process \[53\]. In particular, the large amount of NH\(_4\)\(^+\) ion present in this solution may accelerate the formation of N\(_{\text{ads}}\), through a comproportionation reaction with NO\(^2\)\(^-\) ion, as follows:

\[
\text{NO}^3^- + \text{NH}_4^+ \rightarrow \text{N}_{\text{ads}} + 2\text{H}_2\text{O} \tag{3}
\]

In a solution containing 0.1 M Ga(NO\(_3\))\(_3\) (graph (c)), the current flow starts at −0.8 V, and a current hill appears at −1.1 V. This start point is close to the potential corresponds to reduction from Ga\(^{3+}\) to solid gallium (Ga) in Figure 1(a),
and a current hill can be considered as a result of the consumption of Ga$^{3+}$ at the electrode surface. Therefore, the precipitation of Ga may occur on the Al electrode.

$$\text{Ga}^{3+} + 3\text{e}^- \rightarrow \text{Ga}_{\text{ads}}$$ (4)

It is generally known that hydrogen discharge is preferred for Ga deposition, thus the reduction reaction of Ga$^{3+}$ can therefore occur after the HER on the cathode surface [54]. The curve appearing at $-1.7$ V thereafter corresponds to the reduction reaction of NO$_3^-$ of Equation (1) and Equation (2). That is, even if Ga is adsorbed on the Al substrate, the reduction reaction of NO$_3^-$ ion can occur, and it can be expected that the reaction of NO$_3^-$ ion occurs at a more negative potential under the influence of the adsorbed gallium (Ga$_{\text{ads}}$).

In the graph (d) obtained from a solution containing Ga$^{3+}$, NO$_3^-$ and NH$_4^+$ ions, three clearly separated cathodic peaks appear. After the large current peak corresponding to the precipitation of Ga$_{\text{ads}}$, $i_{\text{Ga}_{\text{ads}}}$, a distinct reduction peak is found at the potential region corresponding to the formation of N$_{\text{ads}}$, $i_{\text{N}_{\text{ads}}}$, confirmed from graph (b). In addition, the increased and separated current peak with the addition of Ga$^{3+}$ ion indicates the formation of new phase precipitates on the Al substrate. During the reactions of Equations (3) and (4) on the Al surface, N$_{\text{ads}}$ can be combined with Ga$_{\text{ads}}$ and finally forms clusters to form GaN layer.

$$\text{Ga}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{GaN}$$ (5)

Clusters of critical sizes are formed, subsequently leading to the growth of continuous films. These Ga-N bonds cause Ga and N to have electronic states of trivalent Ga cations (Ga$^{3+}$) and trivalent N anions (N$^{3-}$), respectively, resulting in secondary growth of GaN with Ga$^{3+}$ and NH$_4^+$ ions in the solution.

$$\text{Ga}^{3+} + \text{NH}_4^+ + 4\text{e}^- \rightarrow \text{GaN} + 2\text{H}_2$$ (6)

$$\text{Ga}^{3+} + \text{N}^{3-} \rightarrow \text{GaN}$$ (7)

The third current may be considered to correspond to the reduction of H$^+$ ion caused by the consumption of NH$_4^+$ ion, $i_{\text{H}^+}^\circ$.

When H$_3$BO$_3$ is added (graph (e)), the current density decreases, and the amount of hydrogen gas bubbles generated on the Al surface is reduced, and also the bubble size becomes smaller. Boric acid thus acts as a surface agent and may be expected to function as a buffer to retard the generation rate of hydrogen ion (H$^+$) as well as prevent hydrogen adsorption, which can interfere with the permeation of N source ion on the Al surface [54].

### 3.2. Heat Treatment of Al Substrates

**Figure 3** shows the XRD spectra of Al samples heat-treated at different temperatures. Four main diffraction peaks are observed at 2$\theta$ values of 38.5, 44.8, 65.1, and 78.3 degrees, corresponding to the reflections of Al (111), Al (200), Al (220), and Al (311) in the Al plate (Figure 3(a)). In the XRD results of heat-treated Al samples (Figure 3(b) and Figure 3(c)), the diffraction patterns indicate the existence of gibbsite (Al(OH)$_3$) and gamma ($\gamma$) phase of alumina (Al$_2$O$_3$) on the Al
Figure 3. XRD spectra of Al plates heat-treated at different temperature; (a) Free; (b) 200˚C for 1 h; (c) 500˚C for 1 h.

surface. In the Al200HT sample, a peak corresponding to Al(OH)$_3$ and very small peaks due to γ-Al$_2$O$_3$ are detected at 2θ = 24.3 and 29.6 degrees, respectively. The peaks caused by the reflection of γ-Al$_2$O$_3$ are strongly observed at 2θ = 29.6, 39.8, and 47.7 degrees, and the small peaks due to the reflection of α-Al$_2$O$_3$ are observed at 2θ = 26.8, 35.6, 48.6, and 50.3 degrees for the Al500HT sample. The XRD pattern also confirms that no additional contamination exists on the Al samples.

Figure 4 shows SEM images of three Al sample surfaces. On the surface of the Al plate before heat treatment, oxide-form particles do not appear, but large plate-like particles are observed on the Al200HT sample. In the Al500HT sample, it is found that the spherical particles with an average diameter of 1.2 µm, which are generally observed from γ-Al$_2$O$_3$ are distributed.

3.3. Electrodeposition and Characterization

The electrodeposition of GaN film in an aqueous solution is attempted on Al substrates, and their morphology and composition are characterized by SEM and EDX. Figure 5 shows the SEM images of GaN films deposited with a current density of −3.5 mA cm$^{-2}$ for 3 h in the solution corresponds to Table 1(e). And the corresponding EDX analysis data are summarized in Table 2. The films obtained from Table 1(c) solution without NH$_4^+$ ion, N was not detected, and more than 40 mol% O was detected in the films electrodeposited from Table 1(d) solution via EDX. Therefore, this paper describes the films electrodeposited from Table 1(e) solution.
Figure 4. SEM images of the surface of Al samples heat-treated at different temperature; (a) Free; (b) 200˚C for 1 h; (c) 500˚C for 1 h.

Figure 5. SEM images of the films deposited at 3.5 mA·cm⁻² for 3 h on (a) Al plate; (b) Al200HT; (c) Al500HT. And the enlarged images are shown on the right.
Table 2. EDX results of the films deposited on Al substrates at −3.5 mA cm\(^{-2}\) for 3 h.

| Element | Al plate | Al200HT | Al500HT |
|---------|----------|----------|----------|
|         | mass%    | mol%     | mass%    | mol%     |
| Ga      | 68.48    | 35.02    | 69.17    | 33.99    | 36.73    | 14.28    |
| N       | 14.87    | 37.85    | 13.60    | 33.27    | 14.67    | 28.40    |
| O       | 5.64     | 12.58    | 12.47    | 26.70    | 20.88    | 20.88    |
| Al      | 11.01    | 14.55    | 4.76     | 6.05     | 36.27    | 36.44    |

As shown in Figure 5, the film formed on the Al plate exhibit an island-like morphology. And the island-like particles are connected and grow in the form of a thick plate for the film deposited on Al200HT (Figure 5(b)). In the film deposited on Al500HT, a cauliflower-like structure, which was found in the γ-Al\(_2\)O\(_3\) or β-Ga\(_2\)O\(_3\) samples, is further formed [55] [56].

The EDX results summarized in Table 2 clearly reveal that more than 35 mol\% of N and Ga are present with O in the GaN film grown on the Al substrate. This indicates that the GaN compound film is formed according to Equation (6). The mapping micrographs of Figure 6 clearly reveal the presence of Ga and N on the Al substrate. These elements are uniformly dispersed in the deposited films. Similarly, the N content is more than 28 mol\% at any given position in the films that form on Al200HT and Al500HT. On the other hand, oxygen increases by more than 20 mol\%, which can be attributed to γ-Al\(_2\)O\(_3\). The mapping results in Figure 6 also show that the films containing a large amount of N are formed on the Al substrates, and Ga, N and O coexist.

Figure 7 shows the XRD spectra of GaN films that are prepared by electrodeposition. Two peaks that correspond to the reflection of h-GaN are observed at 2θ = 32.7˚ and 36.8˚; these peaks are caused by reflections from the (1 \( \overline{1} \) 00) and (1 0 \( \overline{1} \) 1) planes for the film deposited on the Al plate, respectively [57] [58]. In contrast, a strong peak corresponding to the reflection of (0002) plane is detected at 2θ = 34.4˚ in the diffraction result for the film deposited on Al200HT (Figure 7(b)). In the film formed on Al500HT (Figure 7(c)), the peaks caused by the reflection of h-GaN at the three aforementioned positions are detected, and the peak corresponding to the reflection of the h-GaN (1 \( \overline{1} \) 00 ) plane appears to be the strongest. The strong peaks at 2θ = 38.1˚ and 2θ = 45.4˚ are caused by reflections from Al (111) and (200), respectively, and a peak at 2θ = 29.3˚ is caused by the reflection of γ-Al\(_2\)O\(_3\). The weak intensity peaks corresponding to Ga and β-Ga\(_2\)O\(_3\) are also confirmed. Based on the XRD measurement of all samples, it can be observed that the h-GaN film is formed under the experimental conditions used in this study.

The surface of the as-deposited material is characterized by XPS studies. Figure 8 shows the evolution of XPS spectra of Ga 3\( d\) and N 1\( s\) on the surface of the films. All spectra are deconvoluted using a Gaussian-Lorentzian function with background subtraction. Three main peaks are detected in the spectra of Ga 3\( d\) at 18.1, 22.4, and 26.4 eV corresponding to Ga, GaN, and Ga\(_2\)O\(_3\), respectively, as
Figure 6. SEM micrographs along with elemental mapping via EDX for Ga, O, N and Al for the surface of films deposited on (a) Al plate; (b) Al200HT; (c) Al500HT.

Figure 7. XRD spectra of the films deposited at 3.5 mA·cm⁻² for 3 h on (a) Al plate; (b) Al200HT; (c) Al500HT.
Figure 8. XPS spectra of Ga 3d photoelectron peak of GaN films deposited on (a) Al plate; (b) Al200HT; (c) Al500HT, and the graphs on the right side show N 1s photoelectron peak for the same samples; (d)-(f). (a)-(c) Ga 3d; (d)-(f) N 1s.

shown in Figures 8(a)-(c) [59]. These peaks are higher than those observed in GaN (Ga 3d at 19.6 eV), but three separated peaks corresponding to each chemical bonding are clearly observed [60] [61]. The binding energy of N 1s at 399.7 eV clearly shows the presence of nitride (N³⁻) (Figures 8(e)-(f)), and peaks corresponding to N-O bonds appear at a binding energy of 408.6 eV [62]. In the deposited film on the Al plate without Al₂O₃ layer (Figure 8(d)), only peaks corresponding to N-Ga-O bonds appear, and there are no peaks corresponding to Ga-N bonds. Despite the inclusion of H₃BO₃ in the electrodeposition solution, there is no detected peak caused by boron in all samples.

Figure 9 shows the Raman spectrum of films deposited on Al substrates. Three Raman active optical phonon modes corresponding to h-GaN have been observed from GaN film deposited on the Al plate. One mode is at 144 cm⁻¹ because of E₂ (LO), and two bands are at 518 and 718 cm⁻¹ of modes A₁ (TO) and E₁ (LO), respectively [63]. In the film formed on Al200HT, the band that corresponds to A₁ (TO) is intensified, and the signal at 570 cm⁻¹ that corresponds to E₁ (TO) is also detected. In contrast, weak bands are detected from the film deposited on Al500HT because of the influence of a thick oxide layer. As can be observed from Figure 9(b) and Figure 9(c), strong bands corresponding to...
Al$_2$O$_3$ are also detected in the films deposited on heat-treated Al substrates. The small bands that appear at 359 and 427 cm$^{-1}$ may be caused by the acoustic phonons of Al$_2$O$_3$.

### 3.4. Effect of Heat Treatment of Al on GaN Formation

The effects of the Al substrate on GaN formation by electrodeposition are considered. It is confirmed that Al(OH)$_3$ and γ-Al$_2$O$_3$ are detected on the heat-treated Al samples. The SEM photographs of GaN films on the aforementioned Al substrates show that the film formed on Al200HT substrate has the densest structure. It can be considered that the slight increase in surface energy and oxide formation by heat treatment make it easy to generate the Ga-N combining reaction. However, the formation of a thick γ-Al$_2$O$_3$ layer does not make to improve the crystallinity of the GaN film and causes Ga-O-Al bonding. The XRD results shown in Figure 7 reveal that there is a difference in the orientation of the GaN film formed on the three Al substrates. In other words, it can be seen that the growth of GaN film is affected by the properties of the surface condition and Al$_2$O$_3$ layer.

![Figure 9](image.jpg)

**Figure 9.** Raman spectroscopy of GaN films deposited at 3.5 mA for 3 h on (a) Al plate; (b) Al200HT; (c) Al500HT.
4. Conclusions

The GaN films are synthesized on Al substrates heat-treated different temperatures by electrodeposition under ambient temperatures. The CV analysis reveals that starting from a potential value that approaches the Ga reduction potential, $\text{NO}_3^-$ ion could be combined by adsorbing Ga and O during the deposition process, resulting in the formation of GaN films.

The GaN films are prepared by applying a current density of $-3.5 \text{ mA} \cdot \text{cm}^{-2}$ for 3 h on Al substrates heat-treated at different temperatures. The deposited GaN films contain a mixture of h-GaN and $\text{Ga}_2\text{O}_3$ phases. The GaN film formed on the Al substrate is found to grow in a different structure depending on the substrate composition. Through EDX analysis, it is confirmed that Ga, N, and O are uniformly distributed in the film. Raman analysis, XRD, and XPS are also revealed the presence of h-GaN. The GaN film grown on Al200HT having a very thin Al oxide exhibits the property closest to that of the single crystal h-GaN. The grown GaN films exhibit different growth characteristics depending on the composition and surface energies of Al substrates.

The GaN films produced in this work contain a considerable amount of O and exhibit insufficient crystallinity compared to single-crystal GaN. After the formation of GaN, additional processing, such as annealing at a high temperature in the presence of ammonia, may be required, because the addition of O to the GaN film may cause lattice deformation or diminish material properties. Nevertheless, the possibility of synthesizing GaN on Al substrate using a low-cost temperature method that can replace the current expensive process has been confirmed. The fact that GaN films can be formed on metals other than semiconductors will have many advantages for various potential applications.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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