Zn-Al Layered Double Hydroxide Thin Film Fabricated by the Sputtering Method and Aqueous Solution Treatment

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Abstract: Zn-Al layered double hydroxides (LDHs) were synthesized herein via a simple process. First, Al-doped ZnO film was deposited onto a glass substrate using the facing target sputtering system. Successful synthesis of the Zn–Al LDH was achieved via a treatment process using an aqueous solution which contains NO$_3^−$ anions. X-ray diffraction analysis confirmed that it was consistent with the previous Zn–Al LDH synthesis experiment data, and the calculated d-value was 9.1 Å. Scanning electron microscopy observations revealed that the as-synthesized sample had a plate-like structure.

Keywords: Zn–Al; layer double hydroxide; sputter; solution process

1. Introduction

Layered double hydroxides (LDHs) comprise anions that are interchangeable with different metal cations of M$^{2+}$/M$^{3+}$ with an octahedral brucite structure [1]. As shown in Figure 1, LDH exhibits strong binding in the XY plane, and the anions inserted between floors are easily exchanged owing to weak binding forces between layers [2]. Using these characteristics, LDH is being studied not only as an anionic exchange agent, catalyst, photocatalyst, and for hydrogen production and CO$_2$ capture, but also for resistive random access memory (ReRAM) applications [3–8].

![Figure 1. Structure of layered double hydroxides.](image-url)
When applied to the field of photocatalysts, the wide absorbance of Zn–Al LDH can be expected to increase the efficiency of light energy. It was expected to improve the photocatalytic properties when synthesizing Zn–Al LDH.

For the synthesis of LDH, the coprecipitation method and hydrothermal method have mainly been used [10,11]. However, these are complex processes that can enable fabrication of only powder samples. Moreover, conventional synthesis methods are sensitive to solution conditions such as pH and temperature during the reaction process, and their shapes and crystallographic properties are easily altered. Therefore, a simpler and more effective process for the synthesis of LDH is required.

In order to apply it to more diverse fields such as photocatalyst in actual applications, LDH other than the powder type is required. Therefore, research on thin film (TF)-LDH grown on a substrate using metal substrate has been actively conducted [12,13]. However, it is difficult to control the band gap of LDH when using a metal substrate. Therefore, we focused on the previous metal oxide-based LDH synthesis study [14] and we aim to fabricate LDH containing a host layer, which corresponds to Al doped ZnO (AZO). If a host layer of AZO is present, the organic decomposition reaction occurs via [76,337]

The substrate was washed with a mixture of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30%, Wako, Japan), ammonia solution (NH\textsubscript{3}, 28%, Wako), and DI water, followed by washing with an ultrasonic cleaner. Subsequently, ultrasonic cleaning with acetone and ethanol distilled water was performed, and the washed substrate was dried using nitrogen gas. Table 1 summarizes the sputtering conditions.
Additionally, LDH can be synthesized with a small amount of Al\(_3\) ions, process, conditions such as molar concentration (0.2, 0.3, 0.4, 0.5 M) and solution temperature (60, 70, 80 °C) were varied; the samples were heated for 30 min and dried using nitrogen gas, and variations in their properties were evaluated.

Table 1. Sputtering conditions.

| Parameters       | Conditions                                      |
|------------------|-------------------------------------------------|
| Target           | Al doped ZnO, 4 inch (Zn: 98 wt.%, Al\(_2\)O\(_3\): 2 wt.%) |
| Substrate        | Glass                                            |
| Working pressure | 2 mTorr                                          |
| Gas flow         | Ar, 10 sccm, O\(_2\), 0.8 sccm                  |
| Input power      | 500 W (DC)                                      |
| Thickness        | 100 nm                                           |

After AZO thin film deposition, a solution containing NO\(_3^-\) anions was prepared to synthesize Zn–Al LDH with anions inserted between the host layers. Zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\) 6H\(_2\)O, 95%, DUKSAN) was added to DI water. The chemical composition of the actual synthesized LDH is different from the ratio of the actual deposited AZO film. Based on a general equation, LDH is formed. Additionally, LDH can be synthesized with a small amount of Al\(^{3+}\) ions [19,20]. During the treatment process, conditions such as molar concentration (0.2, 0.3, 0.4, 0.5 M) and solution temperature (60, 70, 80, 90 °C) were varied; the samples were heated for 30 min and dried using nitrogen gas, and variations in their properties were evaluated.

X-ray diffraction (XRD, MPA–2000, Rigaku, Japan, Step—0.05 [degree], Speed—5 [degree/min]) was used to evaluate the crystallographic properties, including basal spacing and crystallinity. The surface morphologies of the samples were observed via scanning electron microscopy (SEM, S-4700, Hitachi, Japan). Ultraviolet-visible spectroscopy (Lambda 750 UV-vis-NIR, Perkin Elmer, Waltham, MA, USA) and Fourier-transform infrared spectroscopy (FT-IR with Raman/NIR, FEI Company, Hillsboro, OR, USA) were used to investigate the optical properties.

3. Results

Figure 3 shows the XRD patterns of AZO thin films and the samples treated with an aqueous solution with different molar concentrations. In the case of the AZO thin films, the (002) peak was observed at 34.5° (JCPDS 36-1451); however, all the samples treated with the solution with different molar concentrations exhibited the (003) peak at approximately 10°. The samples treated at 0.2 M still showed the (002) peak, which disappeared from the other samples. This result means that the high molar concentration of the NO\(_3^-\) solution promoted a reaction with the AZO thin film owing to the increase in the number of NO\(_3^-\) ions, leading to the reduction in the (002) peak of the host layer. Even if the reaction time and solution temperature were the same, a high molar concentration did not result in a peak in the host layer being exhibited. It was assumed that obtaining the LDH peak whilst maintaining the peak in the host layer is a better characteristic.

![Figure 3](image-url)  
**Figure 3.** X-ray diffraction (XRD) patterns of AZO thin film and Zn-Al LDH with different molar concentrations.
The basal spacing (d-value) was also calculated and Table 2 shows the d-value for each sample synthesized at different molar concentrations. However, it was observed that the d-value did not change for all the samples synthesized at different molar concentrations [20]. The d-value of the (003) peak in LDH is an important factor that shows the change in intercalated material between layers. From the XRD results, we confirmed the presence of the (003) peak and the LDH synthesis by obtaining the interplanar spacing between layers. It was also confirmed that the AZO thin film prepared by sputtering was formed to Zn–Al LDH through solution treatment.

Table 2. d-values of each sample calculated by the XRD result.

| Sample       | 2 Theta(degree) | d-Value(Å) |
|--------------|-----------------|------------|
| AZO (002)    | 34.5            | 2.598      |
| 0.2 M, 80 °C | 9.692           | 9.121      |
| 0.3 M, 80 °C | 9.703           | 9.110      |
| 0.4 M, 80 °C | 9.685           | 9.127      |
| 0.5 M, 80 °C | 9.734           | 9.081      |

In this study, we attempted to synthesize LDH containing the host layer (002) peak of AZO which has the ZnO photocatalytic reaction. Therefore, considering the XRD results, 0.2 M was considered as the optimal molar concentration for LDH synthesis owing to the presence of the peak of the host layer. Thus, the experiment was conducted to determine the change according to the heating temperature at molar concentration of 0.2 M.

Figure 4a indicates the XRD patterns of all the samples synthesized at 0.2 M for 30 min at different heating temperatures. The sample synthesized at 60 °C exhibited (003) and (006) peaks at approximately 10° and 19°, respectively. The AZO (002) peak (34.5°) of the host layer was also observed. On the other hand, the sample synthesized at 70 °C or more did not show a clear peak at approximately 19°. The sample synthesized at above 90 °C was assumed to reduce the (002) peak of the host layer by promoting the reaction at a high solution temperature. The presence of (006) peaks shows that growth is better in the (001) direction, and that crystallographic properties are better than when only (003) peaks are present. In addition, it was confirmed through the d-value of the (003) peak that the material inserted between layers was NO$_3^-$ in all the samples synthesized at 0.2 M.

Table 3 shows the d-value for each sample synthesized at different heating temperatures. Even when the heating temperature increased from 60 °C to 90 °C, no significant change was observed.
Table 3. Distance calculated by XRD result.

| Sample     | 2 Theta(degree) | d-Value(Å) |
|------------|----------------|------------|
| 0.2 M, 60 °C | 9.636          | 9.174      |
| 0.2 M, 70 °C | 9.632          | 9.177      |
| 0.2 M, 80 °C | 9.692          | 9.121      |
| 0.2 M, 90 °C | 9.727          | 9.088      |

Figure 4b shows that AZO thin films generally exhibit dense surfaces [21], but show a rough surface structure after aqueous solution treatment. The solution-treated samples shows the plate-like structural characteristic of LDH, and we confirmed the formation of hexagonally-shaped plate-like particles of LDH at 100 k magnification [22].

In Figure 5a, the UV-vis measurements show that the samples synthesized at 0.2 M and 60 °C for 30 min did not differ significantly from the AZO thin film, but the samples synthesized at temperatures above 70 °C exhibited higher transmittance than the AZO thin film. LDH was synthesized using AZO thin film with an aqueous solution treatment; hence, the thickness of thin film was reduced. The thickness of the thin film was reduced via LDH synthesis, and the decrease in absorbance in the relationship of $A = -\log T$ was attributed to the increase in transmittance (Beer–Lambert law). Therefore, the reduced thickness of the thin film resulted in the decrease in the optical path length, which led to a decrease in absorbance.

![Figure 5](image_url)

**Figure 5.** (a) Transmittance of all the samples, inset is optical bandgap energies; (b) Fourier-transform infrared spectroscopy (FT-IR) spectra of all the samples.
In the case of the optical band gap energy ($E_g$), conventional ZnO is approximately 3.4 eV [23], but that of the synthesized AZO thin film was 4.18 eV. This can be explained by the Burstein–Moss effect, according to which free electrons grown by Al-doping raise the Fermi level by filling the conduction band. At this time, the carrier concentration and energy band gap increased, and the wavelength band shifted to that of the blue wavelength, resulting in a blue shift [24]. LDH values ranged between 4.21 and 4.23 eV, and showed no significant trends regarding molarity or temperature.

Figure 5b shows the FT-IR spectra of the samples. We performed FT-IR measurements to determine whether the intercalation ions were NO$_3^-$ ions. The results showed that all the samples, except the AZO thin film, exhibited a NO$_3^-$ peak near 1385 cm$^{-1}$. This result is in agreement with the reference data, and we confirmed that the synthesized LDH contains NO$_3^-$ bonds [25].

4. Conclusions

Zn–Al LDH was synthesized and all the samples were confirmed to exhibit a (003) peak. It was determined that 0.2 M was the optimum molar concentration with the host layer peak and LDH peak. The characteristics of the synthesized LDH were confirmed by changing the heating temperature at 0.2 M and, as a result, the (006) peak was observed at 60 °C and the LDH synthesized at 60, 70, and 80 °C still exhibited the host layer peak. All the samples exhibited high transmittance and FT-IR measurements confirmed that the synthesized LDH contained an NO$_3^-$ bond found at approximately 1385 cm$^{-1}$.

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