



Growth and optical band gap of CdAl-layered double hydroxide thin structures on rigid substrate



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ABSTRACT

We report the optical and chemical properties of a CdAl-layered double hydroxide (LDH) grown by a low-temperature hydrothermal method on rigid substrates. Structural and chemical investigations showed that the CdAl-LDH structures were formed as the source concentration was increased up to 45 mM. Mixed phases of CdO, Cd(OH)₂, and CdAl-LDH structures were formed when the source concentration was less than 30 mM. X-ray photoelectron spectroscopy indicated that the Cd and Al metal ions were present in the LDHs as divalent and trivalent ionic states, respectively. Optical investigations by UV–vis spectroscopy indicated that the CdAl-LDH had a direct band gap structure with an energy band gap of 3.01 eV.

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1. Introduction

Layered double hydroxides (LDHs), which are also known as hydrotalcite-like nano-materials, have recently received much attention due to the wide variety of possible applications originating from their catalytic activity, unique anion exchange capacity, and large surface area [1,2]. Exfoliating LDHs into single-layer nanosheets have studied to maximize the utility of a high specific surface area [3]. And electrochemical properties that the easy tunability of cations in their host layers and exchangeability of anions without altering the structure have been studied in the last decades [4]. Importantly, LDH structures possess environmental friendly advantages for feasible processes to obtain cost-effective and non-toxic compositions. Because of these properties, LDHs have potential value in diverse areas, such as luminescence sources, photocatalysts, sensors, electrode materials of supercapacitors and biological nano-carriers [5,6].

LDH structures consist of positively charged stacked brucite-type M(OH)₂ lamella layers with M²⁺ and M³⁺, which are balanced by an interlayer of anions. They have a general formula of [M_{1-x}M_x²⁺(OH)₂]^{x+} [A_{x/n}ⁿ⁻·yH₂O]^{x-} (M²⁺ = Ca²⁺, Zn²⁺, Mg²⁺ and Ni²⁺, M³⁺ = Al³⁺, Cr³⁺, Ga³⁺; Aⁿ⁻ = CO₃²⁻, Cl⁻, NO₃⁻, CH₃COO⁻) [7]. One of the most promising advantages of LDHs is the great number

of possible compositions and metal-anion combinations. Each composition and combination has diverse structural, chemical, electric, and photoelectric properties [8–11]. In particular, MgAl-LDH and ZnAl-LDH have a large electron energy band gap in the UV region along with many potential applications, and they have been investigated widely [12–14].

In addition to these material combinations, if it is possible to fabricate Cd-alloy-based LDH structures, band gap engineering with a three-material system would be feasible because the addition of Cd to the material can reduce the electron band gap energy [15]. However, the fabrication of Cd-related LDH structures and their properties have not been reported previously. In this study, we fabricated LDH structures containing Cd as a divalent metal ion on a rigid substrate for the first time. The CdAl-LDH structures were grown on Si and glass substrates via a simple hydrothermal method. Unlike traditional hydrothermal growth, only a single salt is dissolved in the solution to provide the divalent metal ion, Cd²⁺, while the trivalent metal ion, Al³⁺, is provided by an Al thin film that has been deposited beforehand by a thermal evaporation method. We studied the structural and chemical properties of the CdAl-LDHs and report their optical band gap of them for the first time.

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2. Experimental details

2.1. Experimental

Fig. 1 shows a schematic of the fabrication process. The CdAl-LDH structures were obtained via low-temperature hydrothermal growth on both Si (100) and glass substrates with size of $1.5 \times 1.5 \text{ cm}^2$ square. The CdAl-LDHs were grown uniformly over the whole substrates. The CdAl-LDHs were grown uniformly whole over the substrates. We mainly used the Si as a rigid substrate to investigate the morphological, structural, and chemical properties except the optical properties of the CdAl-LDHs. To measure the transmittance of the LDHs, we used transparent glass substrate. The LDHs on both substrates were grown by using the same conditions and showed no significant differences because already-deposited Al thin film acted as a seed layer. The substrates were first cleaned with acetone, methanol, and deionized (DI) water in an ultrasonic bath for 5 min each before the deposition process. A 20-nm-thick Al seed layer was deposited by a thermal evaporation method.

The CdAl-LDH layers were grown by dipping the Al-coated substrates into mixed solutions of cadmium nitrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98.0% purity, KANTO Chemical] and hexamethylenetetramine [(HMTA; $\text{C}_6\text{H}_{12}\text{N}_4$), Sigma-Aldrich Company] dissolved in DI water. The molar contents of the cadmium nitrate and HMTA sources were varied from 10 to 20, 30, 45, and 60 mM, respectively. Before dipping the substrates, the solution was maintained for 30 min at 95°C to completely dissolve the sources. The substrates were then dipped into middle of the solution and maintained by using Teflon Jig at the same temperature for 2 h. After the reaction, the samples were cleaned in an ultrasonic bath for 5 min, rinsed with flowing DI water for 5 min to remove the homogeneously formed residues in the solutions and dried using N_2 gas.

2.2. Characterizations

The structural properties of the CdAl-LDHs grown on Si substrate with various sources concentrations were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) and X-ray diffraction (XRD, Rigaku D-max-2200-pc). The chemical properties were investigated using an energy dispersive X-ray spectroscopy (EDS) attached to the FE-SEM and an X-ray photoelectron spectroscopy (XPS, Vg Multilab2000). The optical properties of the CdAl-LDHs grown on Glass substrate were characterized by UV–vis spectroscopy (UV–Vis, Agilent Cary 100).

3. Results and discussion

Fig. 2 (a)–(e) show the surface morphologies of the CdAl-LDHs with various source concentrations. When the source concentration was lower than 30 mM, less lamellar sheet-like structures were found, but three-dimensional particles and small one-dimensional nanowire (NW)-like structures formed on the surfaces, as shown in Fig. 2 (a)–(c). The lamellar sheet structures are regarded as CdAl-LDH structures, and the particles (CdO) and NW structures are $\text{Cd}(\text{OH})_2$ compounds [13,14]. These will be discussed further based on structural and chemical investigations later. As the source concentration increased further to 45 mM, the CdAl-LDHs became denser and the CdO and $\text{Cd}(\text{OH})_2$ structures gradually disappeared, as shown in Fig. 2(d). Uniform CdAl-LDH structures predominantly formed all over the surface as the source concentration increased up to 60 mM. Closely packed CdAl-LDH structures were formed when the source concentration was larger than 45 mM. Fig. 2 (f) shows the EDS pattern obtained in a selected area for the CdAl-LDHs with a source concentration of 60 mM. Only Cd, Al, and O were found in the EDS results, which indicate that there were no impurities in the structures. The C and Pt peaks in the EDS spectra are attributed from the carbon tapes and intentionally deposited conducting thin films, respectively.

Fig. 3 shows the XRD patterns of the CdAl-LDH with increasing source concentration, which were used to investigate the evolution of the crystal structure. A diffraction peak near $2\theta = 30.4^\circ$ was found for the samples with source concentrations less than 30 mM. This peak corresponds to the (100) plane of the $\text{Cd}(\text{OH})_2$ structures (JCPDS card No. 31-0228) [14]. The diffraction peaks between 10° and 12° are assumed to correspond to the (003) plane of the LDH structures (JCPDS Card No. 48-1023 for ZnAl-LDHs), and the diffraction peak at 23.4° corresponds to the (006) plane of the LDH structures [12]. Thus, mixed phases of the CdAl-LDH, CdO and $\text{Cd}(\text{OH})_2$ structures were found when the source concentration was less than 45 mM. As the source concentration was increased further up to 45 mM, the $\text{Cd}(\text{OH})_2$ phases disappeared and only CdAl-LDH phases were found, as shown in Fig. 3. This coincides with the surface morphologies investigated by FE-SEM. The (003) planes of the LDH structures show three different peaks at 10.32° , 10.9° , and 11.54° . The inter-plane spacings estimated by Bragg's law ($2d \sin\theta = n\lambda$) were 8.54, 8.11, and 7.65 Å, respectively. These are attributed to the LDH structures having various interplanar spacing because of the formation of different stoichiometric proportions of Cd and Al ions, such as Cd-rich or Cd-deficient regions formed by a spinodal decomposition. Generally, alloys with two elements that have a large difference in atomic size form specific phases by

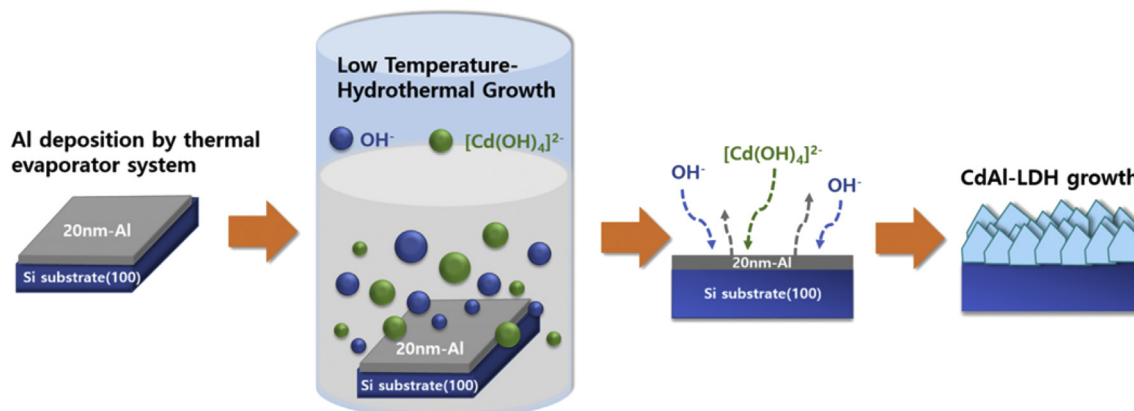


Fig. 1. Schematic of the growth procedure for CdAl-LDH nanostructures by hydrothermal growth.

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