

Self-supported $Zn_5(CO_3)_2(OH)_6$ film formation at air-liquid interface

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Self-supported zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) film was fabricated using an air-liquid interface. ZnO film was firstly prepared from an aqueous solution containing zinc nitrate hexahydrate and ethylenediamine at 60 °C for 6 h and 25 °C for 42 h. ZnO was dissolved gradually as the solution temperature decreased. $Zn_5(CO_3)_2(OH)_6$ was then crystallized by ion supply from the solution to form a film at the air-liquid interface for 1 month. The resultant film was a single phase of $Zn_5(CO_3)_2(OH)_6$ and an assembly of thin sheets. The film had different morphologies on the air side and on the liquid side, reflecting the direction of crystal growth of thin sheets. The air-liquid interface provided a novel reaction field for crystal growth.

Key words: $Zn_5(CO_3)_2(OH)_6$, self-supported film, air-liquid interface, morphology control, ZnO

1. INTRODUCTION

ZnO is an attractive oxide for dye-sensitized solar cells[1-3], gas sensors[4, 5], varistors[6], piezoelectric devices[7], electroacoustic transducers[8], vacuum fluorescent displays[9], field emission displays[10, 11], electroluminescent displays[12], UV light-emitting diodes, laser diodes[13-15], and displays[16, 17].

Although ZnO films have usually been prepared on substrates[18-33], self-supported crystalline ZnO film has a wide range of applications such as windows of optical devices or low-value-added products, and it can also be pasted onto a desired substrate such as low heat-resistant polymer film, glass, metal or paper.

As a precursor of ZnO[34], zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) has attracted much attention. The morphology of ZnO can be controlled by the crystal growth of $Zn_5(CO_3)_2(OH)_6$ [34], and controlling the morphology of ZnO and $Zn_5(CO_3)_2(OH)_6$ films is very important for the development of ZnO-based devices[35].

We recently reported a self-supported ZnO film formed at the air-liquid interface[36]. The film was crystallized from a solution containing zinc nitrate hexahydrate and ethylenediamine at 60 °C for 6 h and 25 °C for 42 h. The ZnO film was an assembly of nano-sheets having high c-axis orientation. The liquid-side surface of the film has many ultra-fine spaces surrounded by nano-sheets and has high specific surface area, whereas the air-side surface is flat, reflecting the flatness of the air-liquid interface.

The self-supported ZnO film is gradually dissolved by nitric acid in the zinc nitrate hexahydrate solution as the solution temperature decreases. $Zn_5(CO_3)_2(OH)_6$ crystallizes at the air-liquid interface of the solution at 25 °C for 1 month. In this study we investigated the formation of a self-supported $Zn_5(CO_3)_2(OH)_6$ film, and compared the crystal growth and morphology of self-supported

$Zn_5(CO_3)_2(OH)_6$ films with those of ZnO films.

2. EXPERIMENTAL

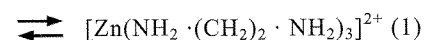
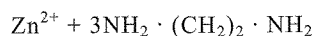
Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, > 99.0%, MW 297.49, Kanto Chemical Co., Inc.) and ethylenediamine ($H_2NCH_2CH_2NH_2$, > 99.0%, MW 60.10, Kanto Chemical Co., Inc.) were used as received. Zinc nitrate hexahydrate (15 mM) was dissolved in distilled water at 60 °C and ethylenediamine (15 mM) was added to the solution to induce the formation of ZnO. The solution was kept at 60 °C using a water bath for 6 h with no stirring. The solution was then left to cool for 1 month in the bath. Polyethylene terephthalate (PET) film, glass (S-1225, Matsunami Glass Ind., Ltd.) and an Si wafer (p-type Si [100], NK Platz Co., Ltd.) were used as substrates.

Morphology of the films was observed by a field emission scanning electron microscope (FE-SEM; JSM-6335F, JEOL Ltd.). Crystal phase was evaluated by an X-ray diffractometer (XRD; RINT-2100V, Rigaku) with CuK α radiation (40 kV, 40 mA). Glass was used as a substrate for XRD evaluation. The diffraction pattern was identified using JCPDS data No. 19-1458.

3. RESULTS AND DISCUSSION

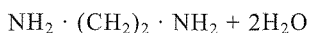
3.1 Self-supported ZnO film[36]

The solution became clouded shortly after the addition of ethylenediamine by the homogeneous nucleation and growth of ZnO particles. Ethylenediamine plays an essential role in the formation of crystalline ZnO. Zinc-ethylenediamine complex forms in the solution as follows[37]:

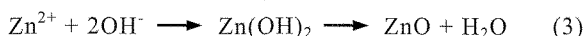


The chemical equilibrium in eq. 1 moves to the left and the zinc-ethylenediamine complex decomposes, causing the concentration of Zn^{2+} to increase at elevated temperature.

OH^- concentration increases by the hydrolysis of ethylenediamine as follows:



ZnO and $Zn(OH)_2$ are thus formed in the aqueous solution as follows:



ZnO particles were gradually deposited and covered the bottom of the vessel, and the solution became light white after 1 h and clear after 6 h. The supersaturation degree of the solution was high at the initial stage of the reaction for the first 1 h and decreased as the color of the solution changed.

White films were formed at the air-liquid interface and they grew into large films. The films had sufficiently high strength to be self-supporting. Additionally, a film was pasted onto a desired substrate such a PET film, Si wafer, glass plate or paper, and the pasted ZnO film was then dried to bond it to the substrate. X-ray diffraction pattern showed the film was a single phase of ZnO with high c-axis orientation. The film was an assembly of thin sheets and its morphology was evaluated in detail as described in our previous work[36].

3.2 Self-supported $Zn_5(CO_3)_2(OH)_6$ film

The solution was further kept at 25 °C for 1 month. The film formed at the air-liquid interface had sufficiently high strength to be self-supporting. It was pasted onto a glass substrate for XRD and FE-SEM evaluation. X-ray diffraction peaks were observed at $2\theta = 13.0^\circ, 24.1^\circ, 27.9^\circ, 30.9^\circ, 32.7^\circ, 35.6^\circ, 38.6^\circ, 47.0^\circ, 47.2^\circ$ and 54.3° (Fig. 1). They were assigned to 200, -310, 020, 220, 021, 510, -420, 222, 330 and 800 diffraction peaks of zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$ [38]) (JCPDS No. 19-1458). Crystallite size was estimated from the peak at $2\theta = 13.0^\circ$ to be 18 nm. A broad diffraction peak from the glass substrate was observed at about $2\theta = 25^\circ$.

ZnO was crystallized at 60 °C for 6 h. ZnO would be gradually etched and dissolved by nitric acid[39-41] as the solution temperature decreased. $Zn_5(CO_3)_2(OH)_6$ was then

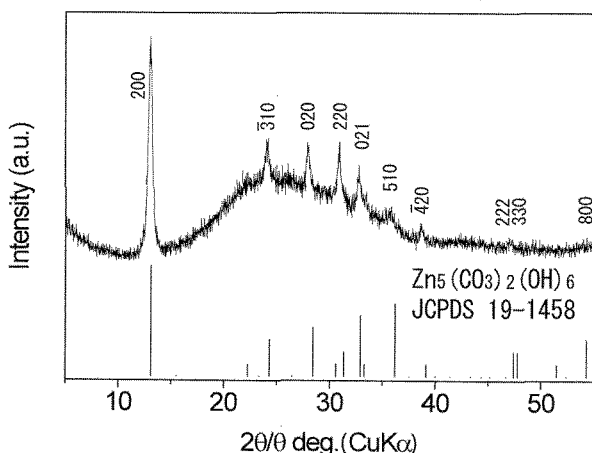


Fig. 1. XRD diffraction pattern of self-supported $Zn_5(CO_3)_2(OH)_6$ film.

crystallized using Zn ions which were supplied by the dissolution of crystalline ZnO .

Morphology of the film was further evaluated by FE-SEM. The air side of the film was smooth all over the surface, reflecting the flatness of the air-liquid interface (Fig. 2a, b). The flatness would contribute to the strong strength with which the pasted film adhered to the substrates. The film was an assembly of thin sheets which were connected with each other. The nano-sheets had a thickness of 5 nm – 20 nm and were 100 nm – 500 nm in size (Fig. 2c). The surface thus had many pores surrounded by thin sheets.

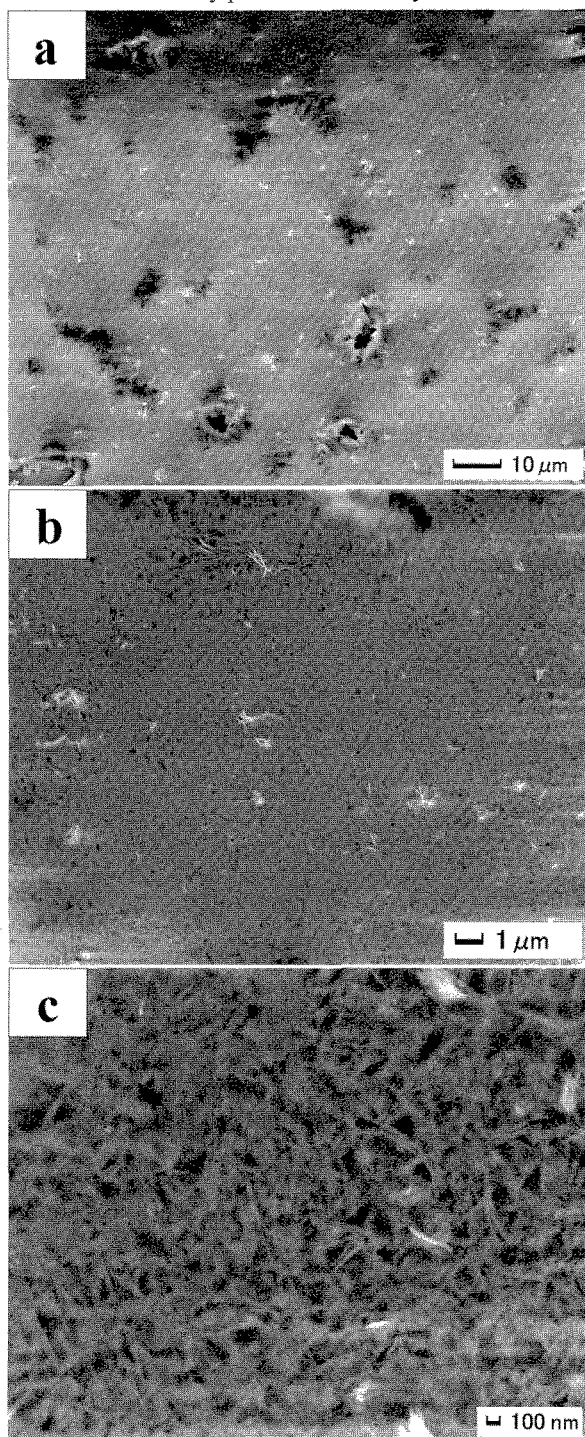


Fig. 2. SEM micrograph of (a) air-side of $Zn_5(CO_3)_2(OH)_6$ film and (b, c) magnified area of (a).

On the other hand, the liquid side had a rough surface as shown in Figs. 3a, b. Additionally, flower-like particles constructed of thin sheets were adhered on the liquid surface. The sheets had a thickness of 5 nm – 30 nm and were 500 nm – 3 μm in size (Figs. 3b, c), and were larger than those observed on the air side. This would be because the growth face was the liquid side of the film and the sheets grew downward by the supply of ions from the solution. The liquid surface had a large roughness due to the assembly of large thin sheets.

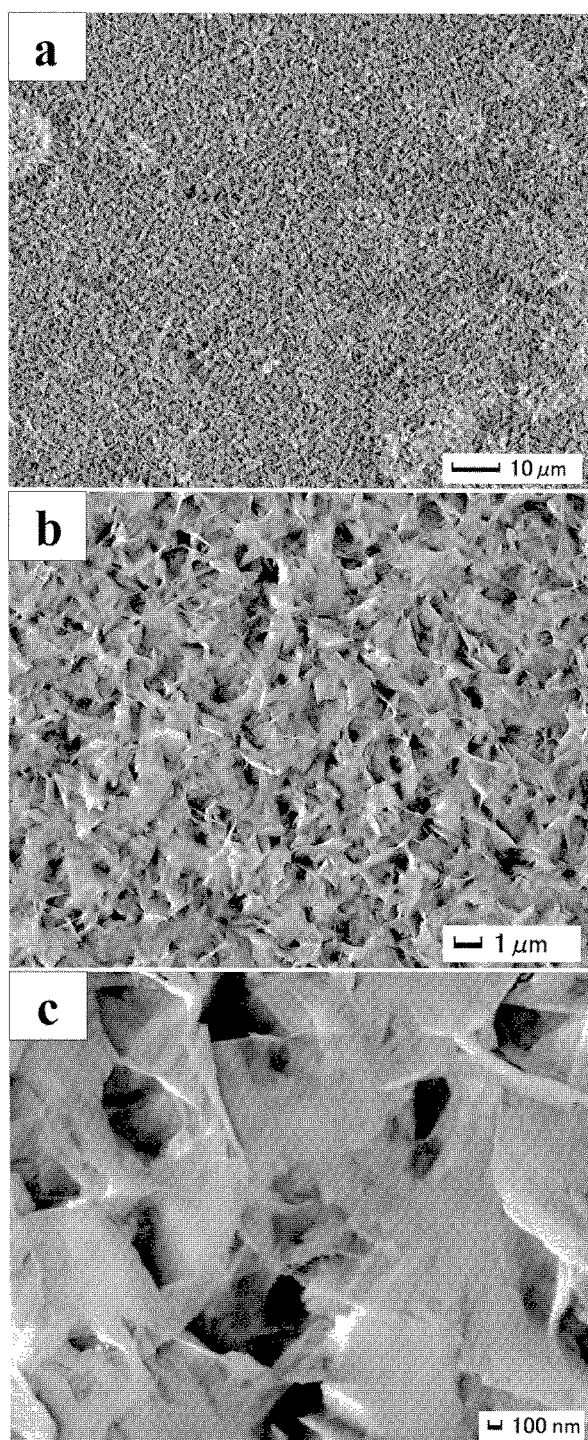


Fig. 3. SEM micrograph of (a) liquid-side of $Zn_5(CO_3)_2(OH)_6$ film and (b, c) magnified area of (a).

The film had a smooth surface on the air side and a rough surface on the liquid side. This characteristic is similar to that of ZnO film fabricated for 48 h. Flatness of the air-liquid interface was effectively used to create a smooth surface on the air side of the film. Additionally, both of the films were constructed of thin sheets and the sheets grew downward (Figs. 4a, b). The sheets on the liquid side were thus larger than those on the air side or inside of the films. The rough surface of the liquid side depended on the crystal growth in the solution. An air-liquid interface has two different chemical fields: an air side and a liquid side. Both of the conditions were optimized for the development of self-supported films. A smooth surface constructed of a dense assembly of sheets and a rough surface constructed of large sheets were attained in the same film by using the air-liquid interface.

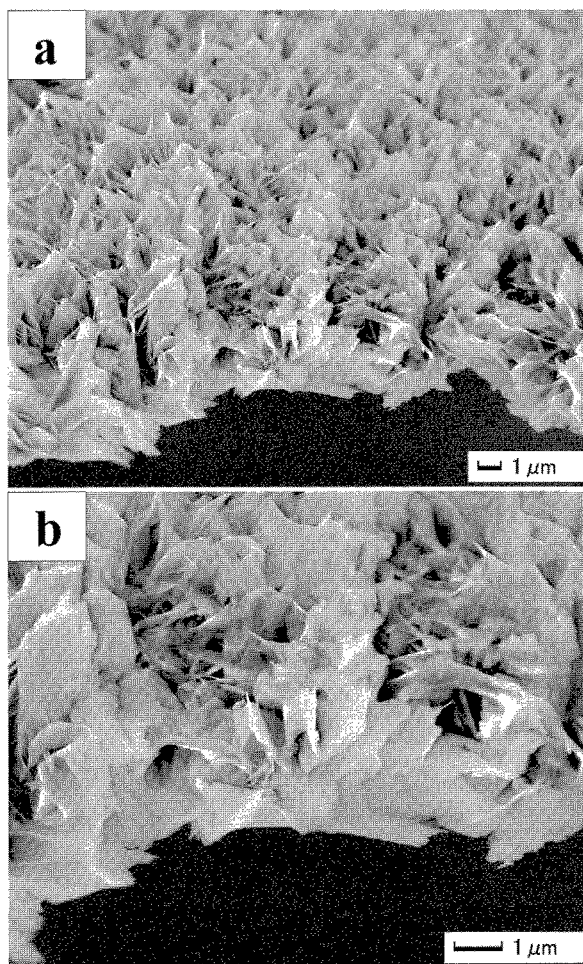


Fig. 4. SEM micrograph of (a) edge face profile of air side of $Zn_5(CO_3)_2(OH)_6$ film and (b) magnified area of (a).

4. CONCLUSION

Self-supported $Zn_5(CO_3)_2(OH)_6$ film was fabricated using the air-liquid interface. ZnO film was firstly prepared from a solution containing zinc nitrate hexahydrate and ethylenediamine at 60 °C. ZnO was gradually dissolved as the solution temperature decreased. $Zn_5(CO_3)_2(OH)_6$ was then crystallized to form self-supported films for 1 month. The film had sufficiently high strength to maintain a self-supporting structure and could be pasted onto desired

substrates. The air side of the film had a smooth surface, whereas the liquid side had a rough surface. The film was an assembly of thin sheets which were larger on the liquid side than on the air side. The film had different morphologies on the two sides due to the use of the air-liquid interface. Thus, the air-liquid interface has interesting potential as a reaction field for crystallization and unidirectional material processing.

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