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Preparation and Characterisation of Porous Nanosheets Zinc Oxide Films: Based on Chemical Bath Deposition

[1]Nugroho P. Ariyanto, [1]Huda Abdullah, [1]Sahbuddin Shaari, [2]Syarif Junaidi and [3]Brian Yuliarto

[1]Department of Electric, Electronic and System Eng.,
Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia
[2]Department of Mechanical and Materials Eng., Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia, Malaysia
[3]Department of Physics Engineering, Institut Teknologi Bandung, Indonesia

Abstract: Nanosheet zinc oxide film is prepared through pyrolitic of synthesised zinc carbonate hydroxide by chemical bath deposition (CBD) process. Thermal analysis which is confirmed by crystalline structure analysis reveals that transformation from zinc carbonate hydroxide to zinc oxide can be conducted by calcination at 300°C. Films morphology observed by Scanning Electron Microscopy (SEM) shows nanometer-scale layer thickness of sheets which are separated by micrometer-scale space among them. Further morphology observation by Transmission Electron Microscopy (TEM) reveals a mesoporous structure with random mesopores spread in nanosheet.

Key words: Chemical bath deposition · Thin film · Zinc oxide · Nanosheet · Mesoporous

INTRODUCTION

A film porous structure of semiconductor is barely achieved through simple conventional wet chemistry method, which usually produces dense film. Nevertheless, importances and unique characteristics of porous material have encouraged researches to exploit nanotechnology for designing and fabricating porous structure [1]. Functional device exploits properties of porous structure for various field usage such as ion exchange, separation, catalysis, sensor, biological molecular isolation and purification.

Mesoporous semiconductors offer great interest for their vast ability to adsorb and interact with atoms, ions and molecules on their wide interior surface and in the nanometer pore size. Zinc oxide with high energy band gap of 3.35 eV and large exciton binding energy of 60 meV, which is called as 'future materials', has been utilised in wide range of appliances from sensors to ultra-violet laser diodes and nanotechnology-based device [2]. Moreover, high surface area of porous zinc oxide also has been applied for gas sensor materials [3], biosensor material [4], photocatalysts [5] and photoelectrode of dye-sensitized solar cells [6].

CBD is a well-known process of depositing dense films of metal chalcogenides or metal oxide through heterogeneous nucleation on substrate surface [7]. CBD process apply wet-chemistry method which has simple procedure, low energy demand and cost, also environmental friendly. Moreover, CBD allows formation of very small crystal size under nucleation. Controlling solid kinetic formation in supersaturated solutions is carried on by adjusting the precursor concentration, temperature, pH and selecting proper and adequate quantities of additives [8-10].

This paper covers study about synthesis of zinc oxide thin film based on CBD process which offers simplicity, low cost and low energy demand. Charaterisation of obtained sample covers the crystalline structure and morphology. Possible condition of solution which allows nucleation in CBD process is also discussed.

EXPERIMENTAL DETAIL

Chemical Bath Deposition Process: CBD solution was synthesized by dissolving zinc nitrate hexahydrate (Analytical Reagent grade from Bendosen) and urea

Corresponding Author: Nugroho P. Ariyanto, Department of Electric, Electronic and System Eng.,
Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia

(purum = 99% from Fluka) in deionised water. The concentration of zinc nitrate and urea in solutions were kept around 0.05 M and 1.0 M respectively. Then, a ratio of ammonium ions to zinc ions, $R=\left[\frac{NH_4^+}{Zn^{2+}}\right]$, would be around 40. Adjustment of solutions pH value down to pH 4 was conducted with nitric acid as corresponding acids.

Flourine tin oxide (FTO) coated conducting glass (Solaronix, SA; sheet resistance of 15 Ω/sq) with 2.2 mm thickness was used as substrate. Clean FTO substrates, which were cleaned by ultrasonic cleaning procedure using acetone, isopropanol and methanol sequentially, were immersed in clear CBD solutions and kept at 70°C for 24 h in tube oven. After deposited for 24 h, the films were rinsed in deionised water several times and dried at 60°C for 1 h in air atmosphere. A transformation into zinc oxide was conducted by calcination of the films at 300°C in air atmosphere for 30 minute by heating rate of 20°C/minute.

Characterisation: Thermal analysis using thermogravitmetry analysis (TGA) and differential scanning calorimetry (DSC) were carried by Metler Toledo STGA851 and Metler Toledo DSC 822e, respectively. Crystalline structure of synthesized films was identified by Phillips PW3040 Diffractometer with CuKá radiation. The film morphology was observed by LEO 1455 VP SEM and Phillips HMG 400 TEM.

RESULTS AND DISCUSSION

Characterisation of Deposited Films: The experiment attempts to synthesise zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) by supplying carbonate and hydroxides ions owing to decomposition of excessive urea in aqueous zinc solution. In aqueous solution, urea will decompose to be ammonium and carbonate ions. Carbonate ions will partially hydrolyse deionised water to give hydroxide ions and increase pH value of solutions [11]. These anions supply will initiate nucleation on substrate surface as reaction below;

$$\left(NH_2\right)_2CO + 2H_2O \rightarrow NH_4^+ + NCO^-$$
$$NCO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}$$
$$CO_3^{2-} + 2H_2O \rightarrow H_2CO_3 + OH^-$$
$$5Zn^{2+} + 2CO_3^{2-} + 6OH^- \rightarrow Zn_5\left(CO_3\right)_2\left(OH\right)_6$$

The crystal phase and the mode of deposition (via heterogeneous nucleation on the surface or homogeneous nucleation in the bulk of CBD solutions) are influenced by the molar ratio of the ammonium ion to zinc ion and the pH solutions [10]. In pH 9.0-13.0, zinc oxide nucleation is occurred whereas desired zinc carbonate hydroxide is expected to precipitate below pH 9. Adjusting initial pH value of solutions from pH 6.5 to pH 4.0 is an effort to control zinc carbonate hydroxide nucleation and obtain optimum result.

Gradual changes of pH value in heated solutions is monitored and compared to decomposition of urea solutions as illustrated in Fig. 1. In elevated temperature at 70°C, urea solution decomposes almost instantly up to pH 8, followed by gradual changes in beginning hours and finally constant at pH 9. Comparing with CBD solutions, pH will increase instantly to pH 6, followed by gradual increment till pH 8 in first twelve hours and finally constant at pH 8. It is observed there is difference between both plots which is thought as difference of hydroxide ions concentration in solution.

The difference can be considered as hydroxide ions usage in CBD solutions in beginning hours of deposition. This is also thought to be indication of optimum condition of nucleation in CBD process. Observation for deposited sample shows that nucleation has been occurred in first three hours deposition which solution condition is pH 6.3. The nucleation is followed by particle growth which halts at pH 8 when the equilibrium condition is reached.

Crystalline structure which is analysed using JCPDS 19-1458, as illustrated in Fig. 2, shows that zinc carbonate hydroxides structure is obtained. Identified crystalline planes reveals that plane (200), (020), (220) and (021) grow generally with similar peak intensity. Low intensity of (200) plane which is usually dominant is thought that substrate condition affects crystalline growth in nucleation process.

Observation of as-deposited film's surface shows that the film consists of nanosheet structure perpendicularly formed on substrate surface as shown if Fig. 3. The synthesised nanosheet has a wide area and very low thickness below 100 nm which mean free path of each nanosheet is about few micrometers. This morphology of obtained structure can be classified as macroporous structure due to pores spacing among nanosheets.

Transformations to Zinc Oxide Nanosheets: Figure 4 shows thermal analysis of deposited film, using TGA-DSC. Result of the thermal analysis exhibits valuable

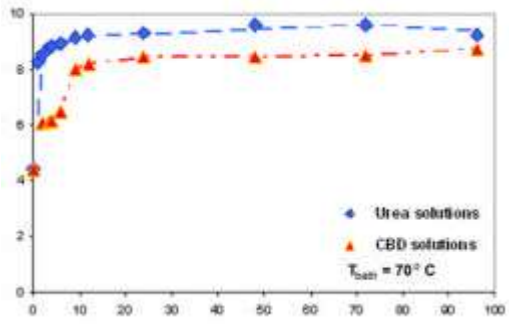

Fig. 1: Time dependence of pH adjusted solutions

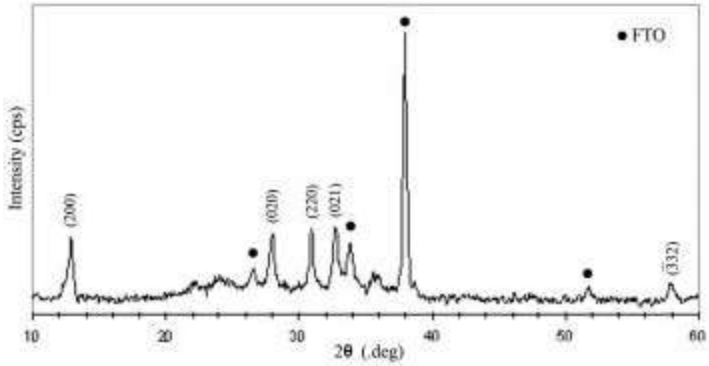

Fig. 2: X-ray diffraction patterns of as-deposited film

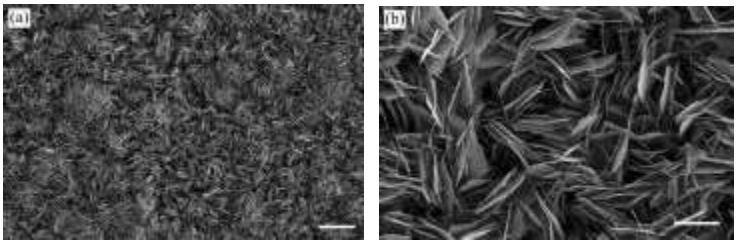

Fig. 3: SEM micrographs of deposited film under (a) low magnification (scale bar is 20 µm) and (b) high magnification (scale bar is 5 µm)

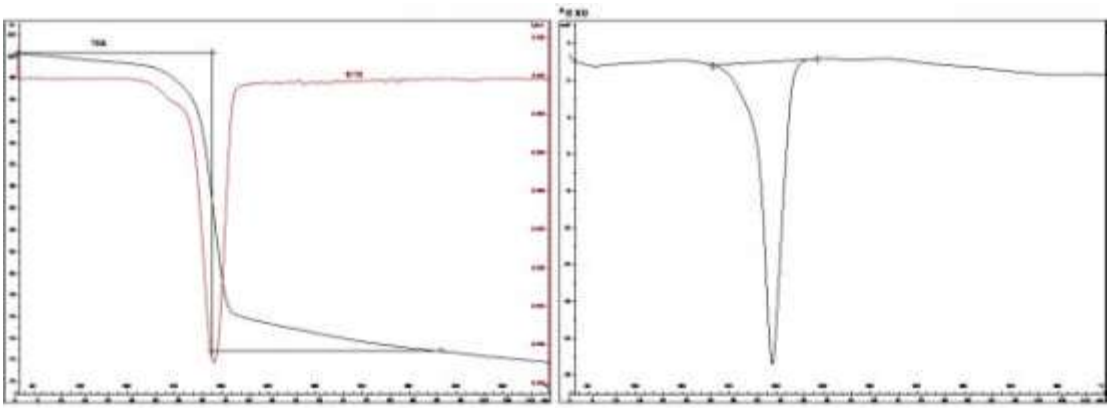

Fig. 4: (a) TGA-DTG graph and (b) DSC graph of as-deposited film.

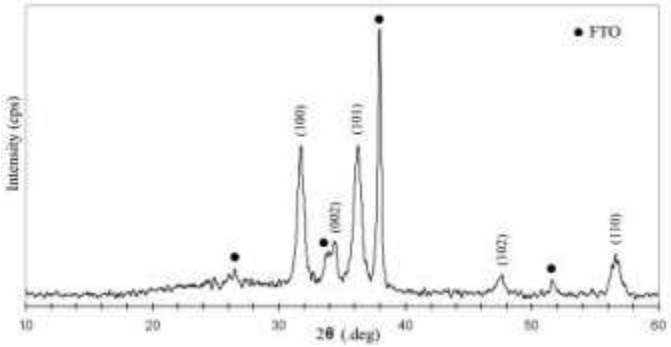

Fig. 5: X-ray diffraction patterns of calcined sample after calcinations

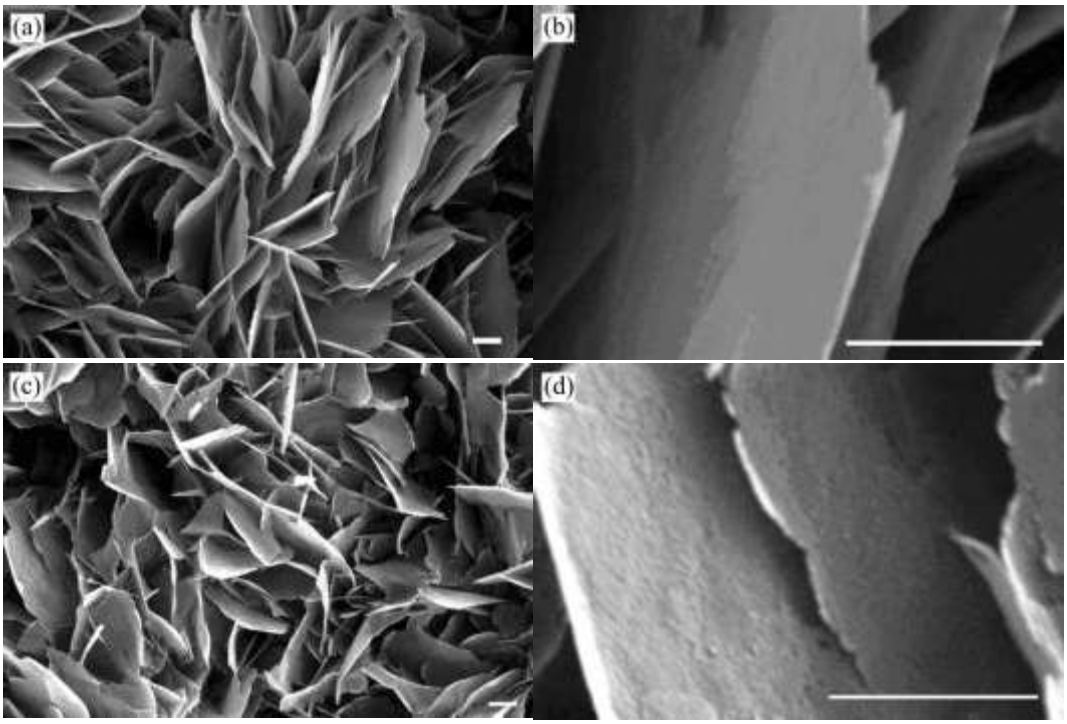

Fig. 6: SEM micrographs of (a,b) as-deposited films and (c,d) calcined films (scale bar is 1 μm).

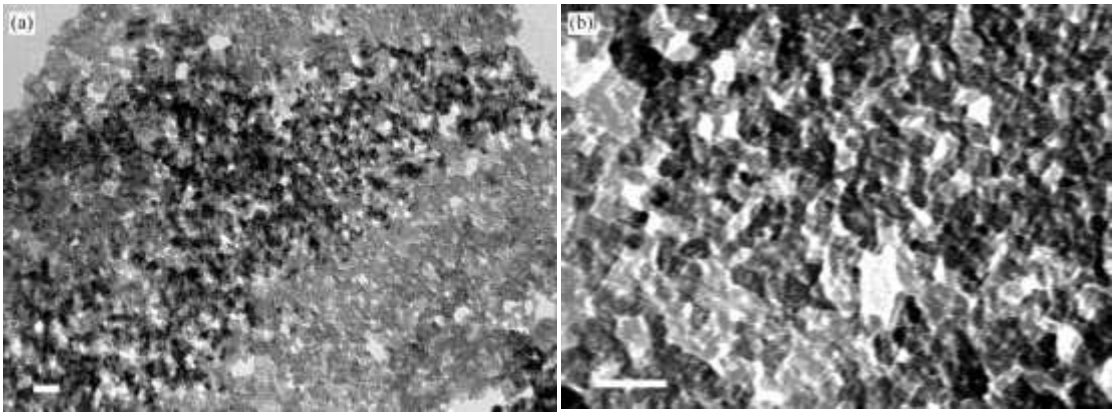

Fig. 7: TEM micrographs of ZnO nanosheet under (a) low magnification and (b) high magnification (scale bar is 50 nm)

information of decomposition and crystallization of samples when temperature increases. It is thought that decomposition of zinc carbonate hydroxide to zinc oxide starts at 170°C and completely finishes at 265°C as shown in Fig. 4. It is also observed peak of decomposition is around 244°C. Overall, there is weight loss of 27% after decomposition reaction, more than calculated weight loss which gives 25.8% weight loss. Instead, DSC graph reveals an endothermic peak when decomposition occurred. The peak is considered as a crystallization which is confirmed by crystalline structure analysis of calcined film.

Figure 5 shows x-ray diffraction (XRD) pattern of calcined sample which is obtained by calcination at 300°C for 30 minutes of 24 h-deposited film. It is found that XRD pattern of calcined sample indicates transformation to zinc oxide has been occurred on calcination. Refering to JCPDS 36-1451, obtained zinc oxide has two dominant planes with similar intensity. Scherrer equation for (100) and (101) plane, it is calculated that crystal size of (100) and (101) plane are 14 nm and 12.6 nm respectively.

Observation of calcined films morphology using SEM micrographs exhibits that structural deformation does not occur after calcinations as shown in Fig. 6. Macroporous structure is kept without significant deformation of nanosheet morphology. The rough nanosheet surface of calcined film indicates an effect of sintering which nanoparticles of deposited sample aggregate under calcinations.

Further observation by TEM reveals that nanosheet consists of nanoparticles in various size 10 – 20 nm with random morphology. Interconnection of nanoparticles is also observed as effect of sintering by calcinations process. Aggregation of particles builds larger particles which consequently create larger pores with 50 nm of approximate pore size. High magnification shows very small pores of 10 -20 nm, considered as mesopores, as some of nanoparticles do not aggregate under calcination.

CONCLUSION

Based on obtained results, nanosheet formation synthesized by CBD is considered consisting of nanoparticles with 20 nm approximate particle size. It can be concluded that CBD process drives nanoparticles nucleation and lead particle growth forms nanosheet morphology through anion supply. Condition of solution allows synthesis of zinc carbonate hydroxide which is converted to be zinc oxide through low temperature calcinations. Morphology observation reveals macroporous film, made up by nanoparticles which form mesoporous structure inside. The mesoporous structure has been moderately deteriorated by particle aggregation as calcination is conducted.

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