Short Communication

Effects of Anions in Electrodeposition Baths on Morphologies of Zinc Oxide Thin Films

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Zinc oxide thin films were prepared in electrodeposition baths with three electrodes. The work electrode is a silicon substrate coated with Pd metal by sensitization and activization process. The work electrode is kept at -1.9 voltage v.s saturated calomel electrode. The electrodeposition baths contain $ZnCl_2$ (4 mM) and KCl (50 mM) as host composition. The K_2SO_4, KNO_3, and CH_3COOK were respectively added into baths for studying the effects of SO_4^{2-}, NO_3^-, and CH_3COO^- anions on the morphologies of zinc oxides. A scanning electron microscope was used to view the morphologies of various zinc oxides. The results showed that the shape of zinc oxide deposited in baths of $ZnCl_2$ (4 mM) + KCl (10~100 mM), and $ZnCl_2$ (4mM) + KCl (50 mM) + KNO_3 (1~50 mM) is hexagonal pillar and when baths are $ZnCl_2$ (4 mM) + KCl (50 mM) with addition of K_2SO_4 and CH_3COOK the zinc oxides became curved sheets and hexagonal plates. A formation mechanism for the zinc oxide with different shapes was also proposed and discussed in this work.

Keywords: zinc oxide; electrodeposition; morphologies; anions.

1. INTRODUCTION

Nano-sized zinc oxides such as nanowires, nanorods, nanosheets, nanobelts, and nanotubes have many important applications such as dye sensitized solar cells, sensors, transducers, and battery [1~4]. Due to the simplicity and low cost the electrodeposition has been quickly studied and developed for nano-sized zinc oxides in the last few years.

The mechanism of zinc oxide thin films prepared by electrodeposition has been studied by Inamdar, A.I et.al.[5], and Yoshida, T. et.al[6]. Mahalingam,T. et.al.[7] have researched the microstructure of electrodeposition zinc oxide thin films. The electrochemical behavior of ZnO thin

films has been investigated by Zhang, lisha et.al.[8]. The ZnO thin porous films have been prepared by cathodic electrodeposition in presence of additives, such as different organic acids (benzoic acid, p-toluenesulfonic acid, benzenetetracarboxylic acid) and a surfactant (sodium laurglsulfate) by Michaelis, E. et.al.[9]. Inamdar, A.I et.al.[10] have studied the effect of bath temperature on the electrodeposition ZnO and Otani, Shiji et.al.[11] have also studied the effect of bath temperature on the electrodeposition mechanism of ZnO. The nanocrystalline ZnO thin films have been formed by novel double pulse single step electrodeposition [12].

To the best of our knowledge, there are few researches concerning with the effect of anions in the electrodeposition baths on the morphologies of zinc oxides. In this work, the K_2SO_4, KNO_3, and CH_3COOK were respectively added into electrodeposition baths containing $ZnCl_2$ and KCl as host composition to study the effects of SO_4^{2-}, NO_3^-, and CH_3COO^- anions on the morphologies of zinc oxides. A formation mechanism for the zinc oxide with different shapes was also proposed and discussed.

2. EXPERIMENTAL

The zinc oxide thin films were prepared in electrodeposition baths in which a silicon substrate coated with Pd metal is taken as the work electrode. A Pt plate is taken as the counter electrode, and a saturated calomel electrode (SCE) is taken as the reference electrode. Before silicon substrate was coated with Pd metal, it was pre-treated [13]. A process containing seven times of sensitization in $SnCl_2$ + HCl solution and activization in $PdCl_2$ + HCl solution [13] was used for Pd coating with enough thickness.

The operation condition and composition of electrodeposition baths for zinc oxide thin films were listed in table 1. The electric voltage of work electrode is kept at -1.9 voltage v.s SCE. The pH value of electrodeposition baths was adjusted by dilute HCl and NaOH solution. The electrodeposition baths contain $ZnCl_2$ (4 mM) and KCl (50 mM) as host composition. The K_2SO_4, KNO_3, and CH_3COOK were respectively added into electrodeposition baths for studying the effects of SO_4^{2-}, NO_3^-, and CH_3COO^- anions on the morphologies of zinc oxide thin films. The values in the table 1 are determined from the results of previous experiments, which could prepare zinc oxide thin films with a suitable growth rate is about 70 nm/min.

**Table 1.** Operation condition and composition of electrodeposition baths for zinc oxide thin films.

Operation condition	Voltage	Temperature	Time	pH	
	-1.9 V v.s SCE	80℃	30 min	.5~8	
Composition (mM)	$ZnCl_2$	KCl	K_2SO_4	KNO_3	CH_3COOK
	4	10~100	1~50	1~50	1~50

After the zinc oxide thin films were prepared in various electrodeposition baths they were characterized by a scanning electron microscope (SEM JEOL Ltd. JSM-T330A) for studying the effects of anions in electrodepostion baths on morphologies of zinc oxide thin films.

3. RESULTS AND DISCUSSION

(a)   Effect of Cl^- anion

The zinc oxides deposited in baths of $ZnCl_2$ (4mM) + KCl (10~100 mM) were shown in Fig.1, (A) (for 50 mM KCl), and (B) (for 100 mM KCl). All zinc oxides have a structure of hexagonal pillar. The average sizes (diameter) of zinc oxide nanorod were measured to be 150 and 250 nm in 50 mM KCl sample and in 100 mM KCl sample, respectively. The results show that the diameter of zinc oxide nanorod increases with increasing the concentration of KCl. When KCl increase form 50 mM to 100 mM in solution, more Cl^- ions would be adsorbed preferentially on the positive polar face of the (0001) surface. This accelerates the radial growth and limits the axis growth along the C-axis [14]. The zinc oxide nanorod remains hexagonal pillar in different concentration of KCl solution. Therefore, the concentration of Cl^-, 10~100mM, has almost no effect on the morphologies of zinc oxides.
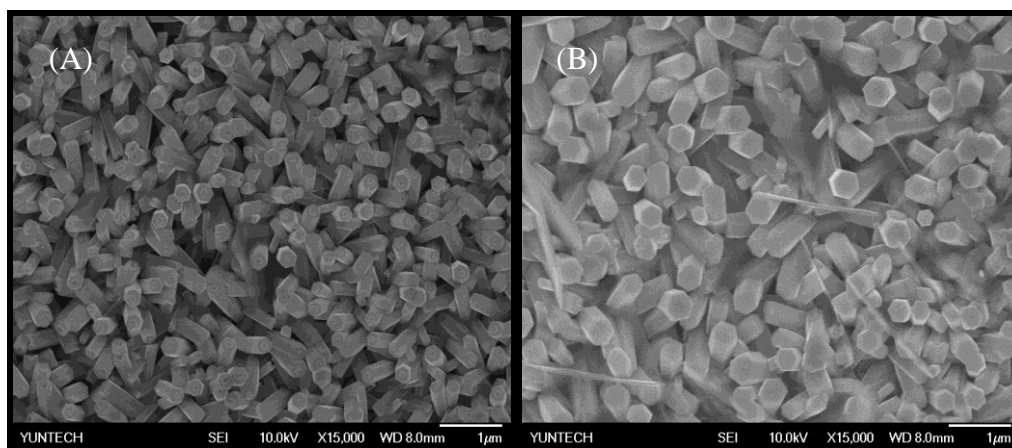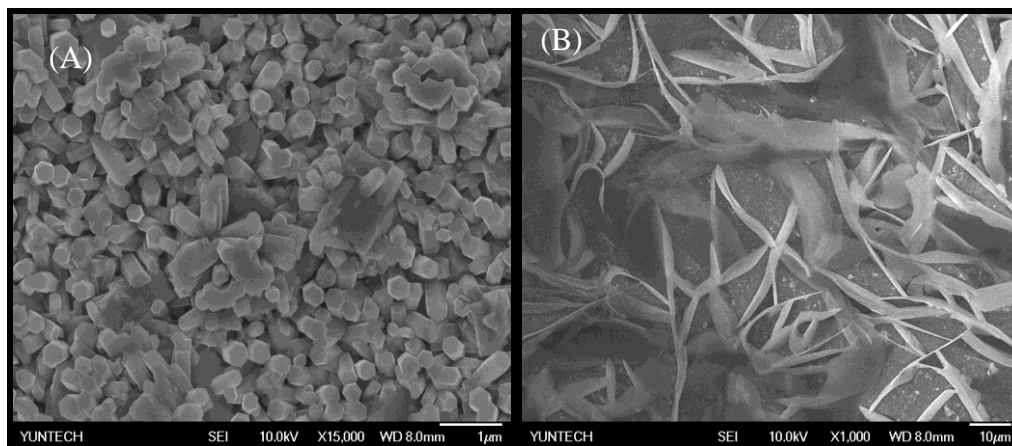

Figure 1. Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(10~100mM), (A) for 50mM KCl and (B) for 100mM KCl.
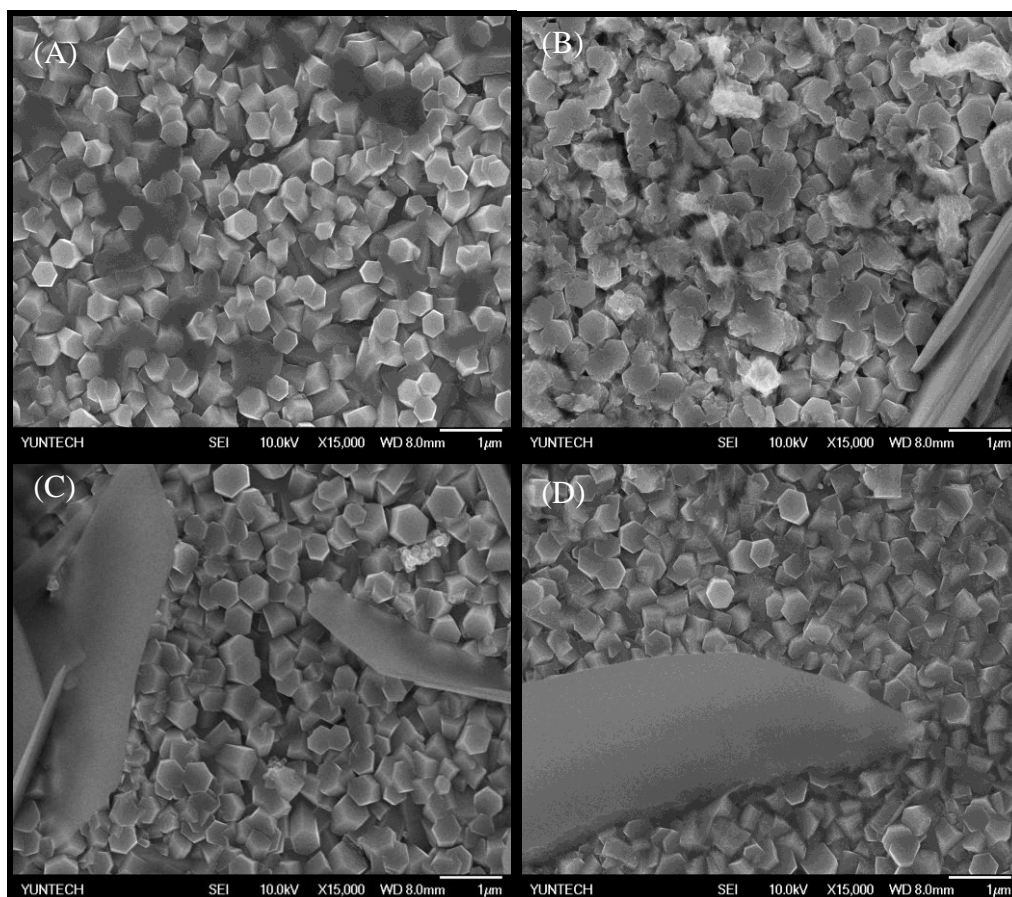
(b)   Effect of SO_4^{2-} anion

Fig. 2 showed the zinc oxide deposited in baths of $ZnCl_2$ (4 mM) + KCl (50 mM) + K_2SO_4 (0.1 and 10 mM). The shape of zinc oxide in Fig. 2(A) is hexagonal pillar and the shape of zinc oxide in Fig.2(B) is curved sheet. To gain further insight into the growth processes of ZnO sheets, the morphologies with different concentration of K_2SO_4 (0.15-0.5 mM) was recorded. Fig. 3 shows the morphologies of the zinc oxide deposited obtained from the baths of $ZnCl_2$ (4 mM) + KCl (50 mM) containing different concentrations of K_2SO_4. In the Fig. 3, when the concentration of K_2SO_4 is larger than 0.2 mM, there are zinc oxides with a shape of curved sheet appeared among those with a shape of hexagonal pillar, and the amount of zinc oxides with curved sheet shape increases with the increase of K_2SO_4 concentration. Typically, the ZnO particles prefer to grow along C-axis. ZnO growth was

different when K_2SO_4 was added into the bath. The SO_4^{-2} interacts with ZnO positive site and suppressed ZnO growth along C-axis [15].
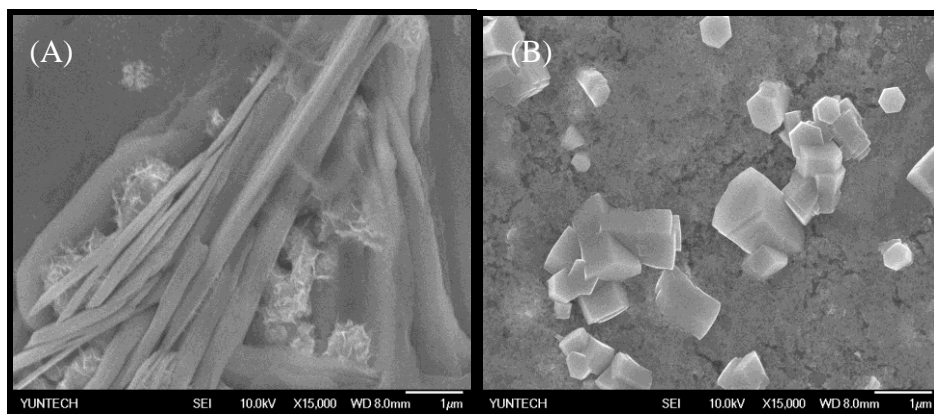

Figure 2. Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(50mM) + K_2SO_4(0.1 and 10mM), (A) for 0.1mM K_2SO_4 and (B) for 10mM K_2SO_4.

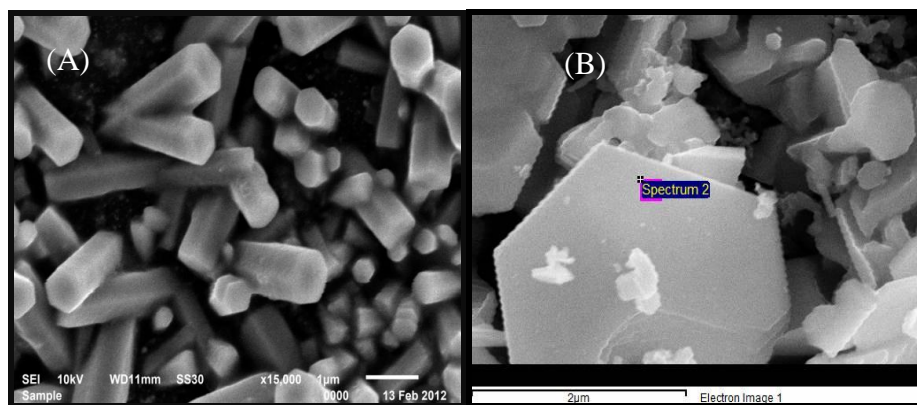**Figure 3.** Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(50mM) + K_2SO_4(0.15~0.5mM), (A) for 0.15mM K_2SO_4, (B) for 0.2mM K_2SO_4, (C) for 0.4mM K_2SO_4, and (D) for 0.5mM K_2SO_4.

(c) Effect of pH

The morphologies of zinc oxide deposited in baths of $ZnCl_2$ (4 mM) + KCl (50 mM) + K_2SO_4 (0.5 mM) with pH 4.5~8.0 were shown in Fig.4, (A) for pH 4.5 and (B) for pH 7.0. Most zinc oxides in Fig. 4(A) have a shape of curved sheet and all zinc oxide in Fig. 4(B) have a shape of hexagonal pillar. When pH≤6 the zinc oxides with curved sheet shape begin to appear among those with hexagonal pillar shape, and the amount of zinc oxides with curved sheet shape increases with the decrease of pH value.

Figure 4. Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(50mM) + K_2SO_4(0.5mM), (A) for pH 4.5 and (B) for pH 7.0.

(d) Effect of CH_3COO^- anion
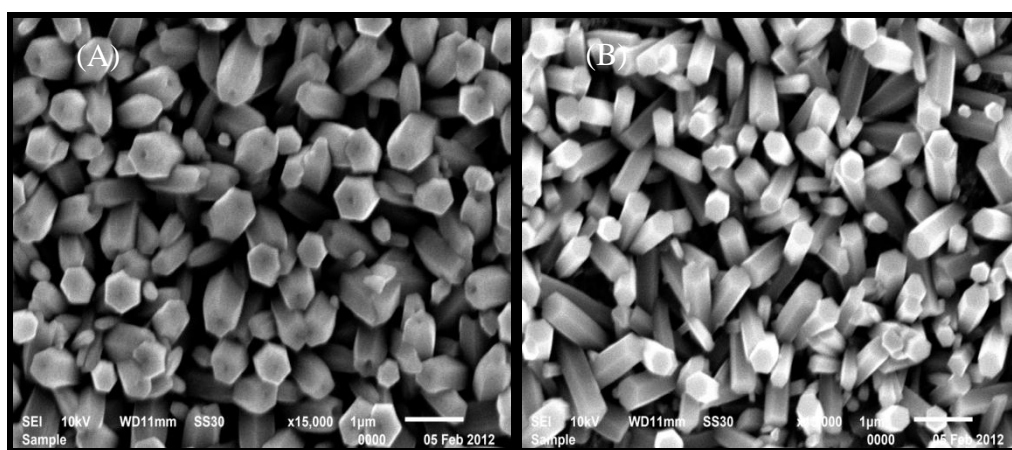

Figure 5. Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(50mM) + CH_3COOK (1~50mM), (A) for 1mM CH_3COOK and (B) for 15mM CH_3COOK.

Fig. 5, (A) for 1 mM CH_3COOK and (B) for 15 mM CH_3COOK, showed the morphologies of zinc oxides deposited in baths of $ZnCl_2$ (4 mM) + KCl (50 mM) + CH_3COOK (0.1~50 mM). All zinc oxides in Fig. 5(A) have a shape of hexagonal pillar. As shown in Fig. 5(B), some of zinc oxides have a shape of hexagonal plate and most of zinc oxides are irregular in shape. When the concentration of CH_3COOK is larger than 3 mM the zinc oxides with hexagonal plate or irregular shape begin to appear

among those with hexagonal pillar shape, and the amount of zinc oxides with irregular shape increases with the increase of CH_3COOK concentration. This revealed that the CH_3COO^- adsorb on ZnO (0001) plane and suppressed ZnO growth along C-axis.

(e)   Effect of NO_3^- anion

The morphologies of zinc oxides deposited in baths of $ZnCl_2$ (4 mM) + KCl (50 mM) + KNO_3 (0.1~50 mM) were shown in Fig.6, (A) for 10 mM KNO_3 and (B) for 50 mM KNO_3. It can be seen that the KNO_3 has no effect on the morphologies of zinc oxides, which are still hexagonal pillar. Chandera also show that ZnO nanorods can be grown by electrodeposition from aqueous solution of Zinc Nitrate and Hexamethylenetetramine (HMT) [16].

Figure 6. Surface morphologies of zinc oxide thin films deposited in baths of $ZnCl_2$(4mM) + KCl(50mM) + KNO_3 (1~50mM), (A) for 10mM KNO_3 and (B) for 50mM KNO_3.

(f)   Formation mechanism of zinc oxides with different shapes.

A well known formation mechanism process of zinc oxide[6] is：

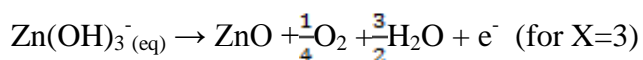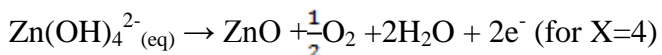$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$
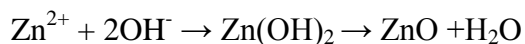
Because the zinc oxides in this work were formed on anode which has an electric attraction to the atom group with negative charges and an electric repelling to the atom group with position charges, a more detailed formation mechanism process for zinc oxide could be suggested as follows：

① $Zn(OH)_X^{2-X}$ complexes with negative charges formed in solution.
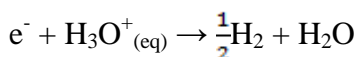
$$Zn^{2+} + X(OH)^- \rightarrow Zn(OH)_X^{2-X}{}_{(eq)} \ (X \geq 3)$$
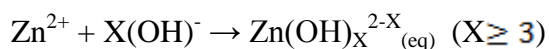
② $Zn(OH)_X^{2-X}{}_{(eq)}$ was oxidized on anode surface (anodic reaction).

$$Zn(OH)_3^-{}_{(eq)} \rightarrow ZnO + \frac{1}{4}O_2 + \frac{3}{2}H_2O + e^- \ (for \ X=3)$$

$$Zn(OH)_4{}^{2-}{}_{(eq)} \rightarrow ZnO + \frac{1}{2}O_2 + 2H_2O + 2e^- \text{ (for X=4)}$$

③ $H_3O^+{}_{(eq)}$ was reduced on cathode surface (cathodic reaction)

$$e^- + H_3O^+{}_{(eq)} \rightarrow \frac{1}{2}H_2 + H_2O$$

In anodic reaction, $Zn(OH)_X{}^{2-X}{}_{(eq)}$ ($X \geq 3$) is more preferable than Zn^{2+}, $Zn(OH)^+{}_{(eq)}$, and $Zn(OH)_2$ for the formation of ZnO. Because $Zn(OH)_2$ has no electric charge, it can't be electrically attracted to anode. The Zn^{2+} and $Zn(OH)^+{}_{(eq)}$ have positive charges, so they would be electrically repelled by anode electrode.

A stable phase for zinc oxide (ZnO) is wurtzite which belongs to hexagonal crystal system. When the growth rate of (0001) phase is larger than that of $\{01\bar{1}0\}$ planes, the zinc oxide would become hexagonal pillar, and when the growth rate of (0001) plane is smaller than that of $\{01\bar{1}0\}$ planes the zinc oxides would become hexagonal plates, as shown in Fig.7 (A) and (B).
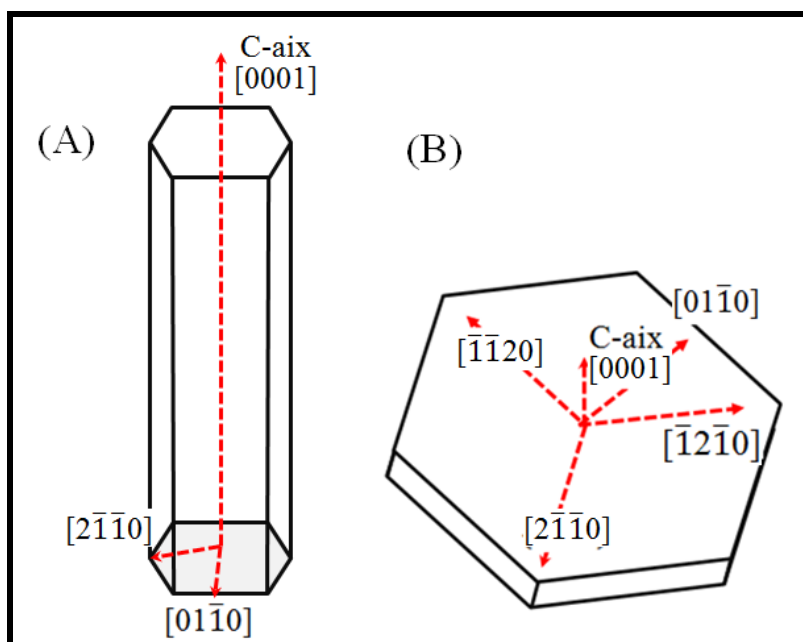
Figure 7. Schematic views of hexagonal pillar (A) and hexagonal plate (B) of zinc oxides.

From the results of (a)~(e), it can be seen that the zinc oxides became a shape of sheet and hexagonal plate under the action of $SO_4{}^{2-}$ and CH_3COO^- anions, respectively. This phenomena can be ascribed to the electrochemical absorption of $SO_4{}^{2-}$ and CH_3COO^- on (0001) plane more easily than on $\{01\bar{1}0\}$ planes. Therefore, the growth rate of (0001) plane is smaller than that of $\{01\bar{1}0\}$ planes due to the presence of $SO_4{}^{2-}$ and CH_3COO^- anions on (0001) plane, which would hinder the growth of zinc oxides. Under the similar reasons, the zinc oxides became a shape of hexagonal pillar under the action of NO_3^- and Cl^- anions, respectively, due to the electrochemical absorption of NO_3^- and Cl^- on $\{01\bar{1}0\}$ planes more easily than on (0001) plane.

4. CONCLUSION

The shape of zinc oxides deposited in baths of $ZnCl_2$ (4 mM) + KCl (10~100mM) , and $ZnCl_2$ (4 mM) + KCl (50 mM) + KNO_3 (0.1~50 mM) is hexagonal pillar due to the electrochemical absorption of NO_3^- and Cl^- on $\{01\bar{1}0\}$ planes more easily than on (0001) plane. The shape of zinc oxides deposited in baths of $ZnCl_2$ (4 mM) + KCl (50 mM) with addition of K_2SO_4 and CH_3COOK became sheet and hexagonal plates due the electrochemical absorption of SO_4^{2-} and CH_3COO^- on (0001) plane more easily than on $\{01\bar{1}0\}$ planes.

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