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Influence of Potassium Chloride on the Electrochemical Deposition of ZnO plate films

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Abstract. KCl is usually used as the supporting electrolyte in electrochemical deposition of Zinc oxide materials. Besides the role of supporting electrolyte, it can also influence the morphology of the fabricated materials. In this work, ZnO and zinc hydroxide chloride hydrate ($Zn_5(OH)_8Cl_2 \cdot H_2O$) mixture with platelet-like morphology were electrochemically deposited directly on ITO-coated glass substrates at 65°C. The electrolyte was 0.1M $Zn(NO_3)_2 \cdot 6H_2O$ with KCl concentration varied from 0 to 3.2M. It was found that only ZnO thin film was obtained when the concentration of KCl was below 0.02M. Plates structure appeared as the concentration of KCl increased to 0.04M. Plentiful plates were obtained when the concentration of KCl was 0.05M-0.2M. From the X-ray diffraction, it was confirmed that the plate films was the mixture of ZnO and $Zn_5(OH)_8Cl_2 \cdot H_2O$. The plates showed perfect single crystal structure confirmed by selected area electron diffraction. Zn and $Zn_5(OH)_8Cl_2 \cdot H_2O$ were obtained when the concentration of KCl was above 0.8M.

Introduction

ZnO is one of the few marvelous semiconducting and piezoelectric materials that has various applications, such as nanogenerators [1], rectifying diodes [2], gas sensors [3] and solar cells [4]. So successful synthesis of diverse ZnO nanostructures is of great importantce. Among the research for the fabrication of ZnO mico/nano materials, electrodeposition is a cost-effective way for preparation of large-area thin films on arbitrary substrate shapes, at low-temperature and with precise control of the film thickness. The reaction is usually carried out in aqueous solution containing zinc precursor (zinc chloride or zinc nitrate), and KCl is usually used as supporting electrolyte to ensure good conductivity of the aqueous solution. However, many researchers have found KCl may play additional role in the ZnO electrodeposition.

Xu et al [5] obtained ZnO hexagonal particles electrodeposited from 0.05M $Zn(NO_3)_2$ solution and ZnO platelets by addition of 0.06M KCl. They suggested the preferential adsorption of chloride ions onto (0001) ZnO surfaces as one of the responsible mechanism for the formation of platelet-like ZnO nanocrystals. Chloride adsorption may result in the stabilization of (0001) ZnO surface, therefore, hindering the growth along the corresponding direction (c axis). Recently, Pradhan et al [6] mixed 0.1M KCl with 0.1-0.001M $Zn(NO_3)_2 \cdot 6H_2O$ to fabricate diverse morphology of ZnO nanostructures. They found the concentration of $Zn(NO_3)_2 \cdot 6H_2O$ in electrolyte is important to control the dimensionality of the nanostructures and Cl^- ions also played a capping role under fast hydroxylation kinetics condition. Pradhan's work can be seen as fixing KCl concentration and investigating the influence of Zn^{2+} precursor concentration for the ZnO electrodeposition. Tena-Zaera et al [7] have studied the influence of KCl concentration (from 0.05M to 3.4M, $ZnCl_2$ concentration fixed as 5×10^{-4} M) for the electrochemical deposition of ZnO nanowire Arrays. They found that high KCl (>1M)

enhanced of the longitudinal and lateral growth of ZnO nanowires. So it is interesting to investigate the influence of Cl^- ions for the ZnO electrodeposition at high Zn^{2+} precursor concentration such as 0.1M.

Experimental

The electrchemical deposition experiments were carried out in a two electrode system glass cell immersed in a water bath held at 65°C. The anode was graphite plate (1cm of width and 2.5cm of length). ITO glass substrates (0.8cm of width and 2.5cm of length) were used as the working electrode. The immerged length of both electrodes into aqueous solutions is about 1cm. ITO glass substrates were washed in acetone and cleaned ultrasonically in acetone and then rinsed with deionized water again before used as the working electrode. The electrolyte were 0.1M $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution mixed with 0M-3.2M KCl. The current between the two electrodes was 5mA supplied by an electrochemical workstation (Princeton Applied Reasearch,V^3-400). The reaction times is fixed as 4min. After deposition, the freshly electrodeposited films were thoroughly washed by deionized water and dried naturely in air at room temperature.
These deposits were characterized by a Hatachi S4300 scanning electron microscope (SEM) at an accelerating voltage of 10 kV, transmission electron microscopy (TEM, JEOL 2100 at accelerating voltage of 200kV) and selected area electron diffraction (SAED) pattern, X-Ray diffractometry (XRD) was performed with a Rigaku RAD-C using Cu Ka radiation by the 2h/h scanning mode.

Results and discussion

Fig. 1 shows the SEM images of the obtained thin films electrochemically grown on ITO-coated glass substrates with different concentrations of KCl. The concentration of $Zn(NO_3)_2 \cdot 6H_2O$ is fixed at 0.1M. Fig. 1(a) shows there was only a thin film composed of particles with diameter of 0.2-1μm obtained when there was no Cl^- ion in the aqueous solutions. As 0.02M KCl was introduced to the solutions, a similar thin film was obtained (Fig. 1(b)).

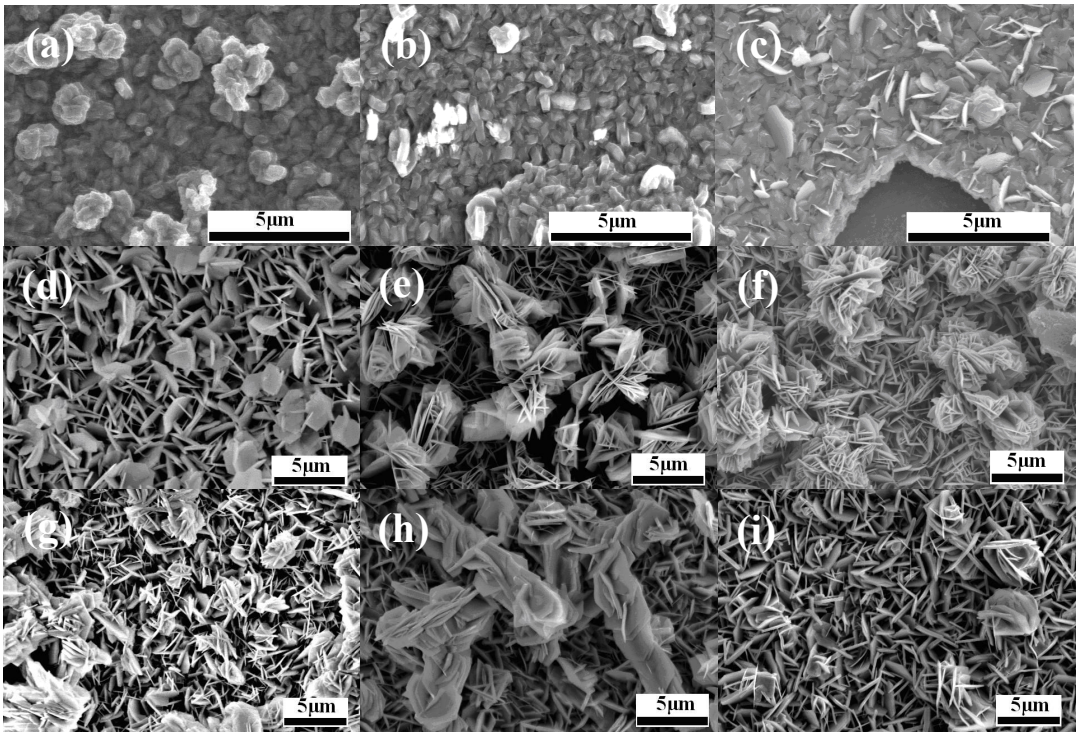

Fig. 1 SEM images of the samples abtained as the concentration of KCl was (a) 0M, (b) 0.02M, (c) 0.04M, (d) 0.05M, (e) 0.1M, (f) 0. 2M, (g) 0.4M, (h) 0.8M, (i) 3.2M KCl respectively.

The particles were of average diameter about 0.25μm which is smaller than that in Fig. 1(a). A few thin plates with thickness about 50nm and hexagonal shape began to grow from the thin film as the concentration of KCl increased to 0.04M (Fig. 1(c)). Plentiful plates with thickness 50-250nm and average size of 2μm started to appear when the concentration of KCl increased to 0.05M (Fig. 1(d)). Some thin and whole hexagonal plates were grown above the plate films.

Fig. 1(e), (f), (g) show the morphology of electrodeposited plate films with KCl concentration of 0.1M, 0.2M and 0.4M respectively. These plates with thickness about 50-200nm and average size of 2.3μm were densely grown and uniformly distributed over all area of the substrate surface. The morphology of these plate films were similar to that reported by Pradhan et al [6], but there were many flower-like architecture composed of plates appeared above the thin films. The most dense and fruitful plates appeared as KCl was 0.2M. There are many 2D ordered superstructures (composed of plates) grown from the plate films as KCl was 0.8M. As KCl concentration increased to 3.2M, the fabricated plates became uniform and more thicker than before.

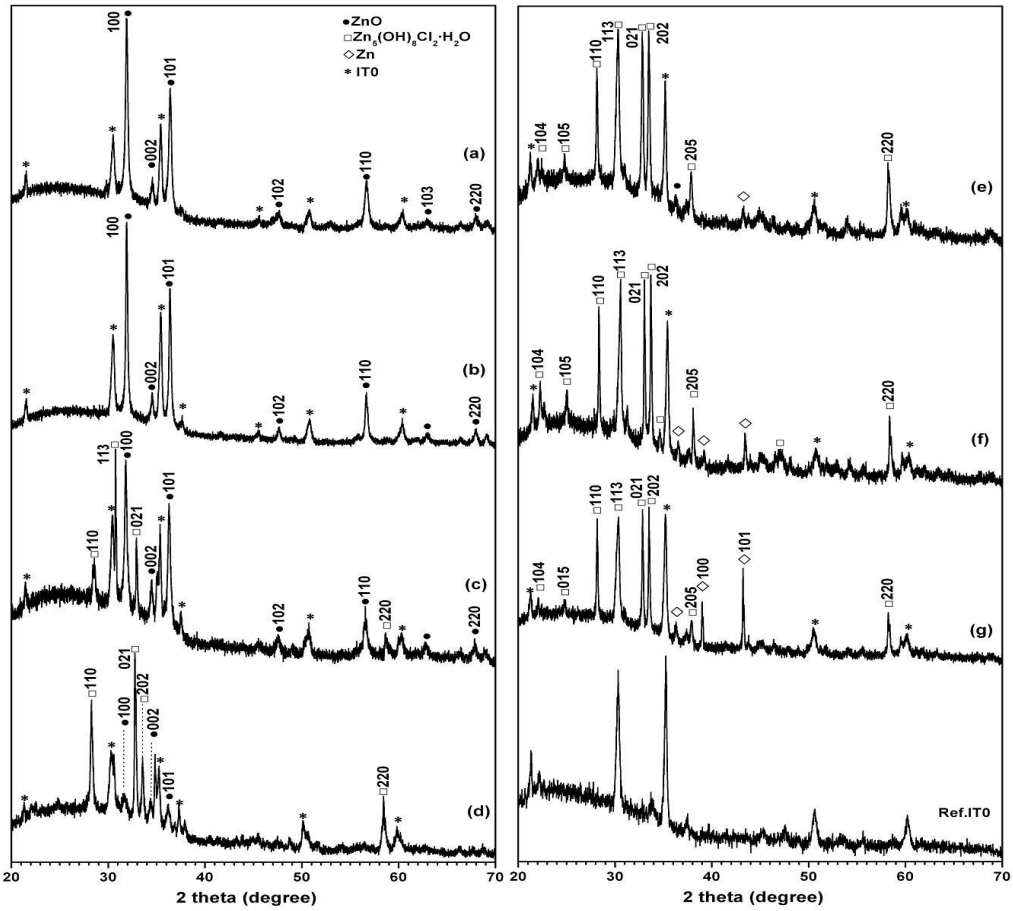

Fig. 2 XRD patterns of samples prepared by the aqueous solution containing 0.1M $Zn(NO_3)_2 \cdot 6H_2O$ and (a) 0M, (b) 0.02M, (c) 0.05M, (d) 0.2M, (e) 0. 4M, (f) 0.8M, (g) 3.2M KCl.

Fig. 2 shows the XRD patterns of the thin films electrodeposited on ITO-glass substrates at diffrent KCl concentration. The XRD spectrum of pure ITO-glass was given as reference. From Fig. 2(a), (b), It indicates that the particles product is wurtzite (hexagonal) ZnO structure (JCPDS card 76-704) as KCl concentration below 0.02M. There are no additional features appeared except ITO spectrum. The values of a=3.24, c=5.29 can be calculated. From Fig. 2(c)-(e), we can see that the XRD patterns have regular change when KCl concentration varied from 0.05M to 0.2M. ZnO intensity becomes slight and $Zn_5(OH)_8Cl_2 \cdot H_2O$ (JCPDS card number 07-155) spectrum increase more and more. Pradhan et al [6] also found slight $Zn_5(OH)_8Cl_2 \bullet H_2O$ spectrum as KCl was 0.1M. The obtained films are all $Zn_5(OH)_8Cl_2 \bullet H_2O$ when the concentration of KCl was 0.4M. The XRD patterns in Fig.2 (f), (g) indicate that the products are the mixture of $Zn_5(OH)_8Cl_2 \cdot H_2O$ and Zn (JCPDS card 87-173) at high

KCl concentration (0.8M, 3.2M respectively). The obtained $Zn_5(OH)_8Cl_2 \cdot H_2O$ can be used as the precursor to fabracate other morphology ZnO structures [8,9].

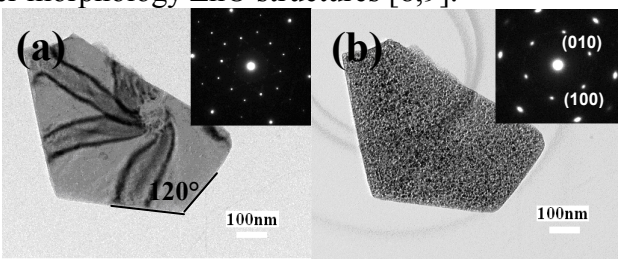

Fig. 3 TEM image a plate (a) before and (b) after electron beam irradiation. Inset shows the corresponding SAED pattern.

Fig. 3(a) shows the TEM image of an single plate peeled off from the substrate obtained by electrodeposition in 0.1M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1M KCl aqueous solutions. The smooth plate can be seen as part of a whole hexagon plate and with diameter of 0.8μm which corresponds well with the SEM observations. The corresponding SAED patterns of the plate reveal its perfect single crystal with hexagonal structure. However, the individual plate is not stable under electron beam irradiation, it changes into porous structure (in Fig. 3(b)) after several minutes. The corresponding SAED patterns also change slightly and can be indexed as hexagonal wurtzite structure of ZnO. We also found the plates can change to porous plates by annealling in air, which is consistent with Zhong's work [9].

Summary

We have investigate systematically the influence of Cl^- ions on the ZnO electrodeposition at 0.1M Zn^{2+} precursor. ZnO, $Zn_5(OH)_8Cl_2 \cdot H_2O$ and Zn can be obtained by electrochemical deposition at certain Cl^- ions concentration. The reslult is meaningful and interesting, the detailed formation mechanism is under investigation.

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