Gravitational Effect on Electrochemical Processing of ZnO Thin Film

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Abstract
ZnO films were potentiostatically electrodeposited in 0.1 M Zn(NO₃)₂ aqueous solution on to ITO/FTO substrate. Two types of electrode configurations were employed in order to discuss quantitatively the effect of gravitational strength on nucleation and growth of ZnO in detail: (a) a horizontal cathode surface facing downward over an anode (C/A) and (b) an anode over a cathode (A/C). Current transients were generally derived into four stages: the increased measured current quickly drops in the first stages, records a minimum current in the 2nd and then starts to increase in the 3rd followed by the 4th. The measured transient in the 4th stage is surely influenced by gravitational field vector: it slightly declines in C/A while continues to increase with time in A/C. SEM pictures show that the A/C configuration introduces more number of nuclei than the case of C/A configuration. The present research is provided for the preliminary terrestrial experiment before the electrochemical processing in microgravity environment.

1. Introduction
The electrical, optical and acoustic characteristics of zinc oxide have been considerably interested in microelectronics industry. It is widely applied to chemical sensor, liquid crystal display, and dyestabilized solar cell. Izaki and Omi reported ZnO electrodeposition from an aqueous solution containing nitrate ions [1]. Since then, many papers have been reported annually [2-5]. The creation of unique physical properties by introducing another degree of freedom to the heterogeneous reaction field is key issue of these works.

By the way, a number of studies to grow perfect crystals or to produce composite materials with a homogeneous matrix or a tailored structure have been conducted in space environment. These experiments have focused mainly on physical aspects of crystal growth. The opportunity to study corresponding electrochemical processing aspects has been quite limited, except for highly advanced separation techniques using electrophoresis cell in biochemistry.

Traditionally the industrial electrochemical science and technology made a great progress through ancestor’s endless efforts in the industrial plants; for example, process productivity has been greatly improved by better understanding of natural convection phenomena [6-12]. Ionic mass-transfer rates are enhanced by natural convection, while the local electrolyte composition is partly stratified in industrial electrolytic cells. Electrolyte circulation is thus a key technology in industrial operation in copper refining process. The morphological variation of deposits under different electrolytic condition has been received with the great technological and academic interests.

Kyoto university research group has successively studied the gravitational effects on metal electrodeposition. It has been clarified that nucleation density, grain size, and morphology are greatly influenced by the gravitational level as long as Cu and Ag electrodeposition in aqueous solution concerns [13, 14] The present purpose is to understand the coupling phenomena between the mass transfer rate and the shape evolution in electrochemical processing of ZnO and to explore the possibility to control the surface morphology and microstructure by the gravitational level.

Two different electrode configurations were employed to electrodeposited ZnO film: (a) a horizontal cathode surface facing downward over an anode (C/A) and (b) an anode over cathode (A/C). Benard type natural convection is inevitably induced in the A/C, while no macroscopic natural convection is expected in the C/A configurations. The C/A configuration therefore simulates the ionic mass transfer rate under microgravity.

2. Experimental
Electrochemical experiments are carried out with a conventional three-electrode system as illustrated in Figure 1. The electrode assembly is composed of a short rectangular channel (10 mm x 10 mm x 30 mm, Teflon) with two open ends. The assembly was immersed in a 50 ml electrolytic bath. The working electrode is conductive glass substrates (FTO/ITO coated glass, 2 Ω/□, Fujikura Co. Ltd.). Pure zinc
Zinc ions precipitate with the hydroxyl anions and are spontaneously dehydrated into ZnO.

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (2) \]

The overall expression of the reaction therefore is,

\[ \text{Zn}^{2+} + \text{NO}_3^- + 2e^- \rightarrow \text{ZnO} + \text{NO}_2^- \quad (3) \]

Figure 2 shows the current density transients at various electrode potentials. Below 900 mV, the characteristic behavior of the current transient categorized into four stages is observed. The 1st stage is defined by a rapid decrease of current within the duration period of a few second. The 2nd stage corresponds to the bottom of current ravine. A steep increase of current is introduced in the 3rd stage. This increase is subsequently followed by a slower curve. The 4th stage is defined to start at the time when the gradient of the transient current significantly changes.

In C/A configuration, the 2nd period is shorter and the current recovery in 3rd stage is steeper than in A/C configuration. The current in the 4th stage starts to gradually decrease in C/A, while it still continues to slightly increase with time in A/C. These
results show that the gravitational level makes a difference even in the early stage of electrodeposition of ZnO.

Figure 3 shows the surface morphological variations of ZnO film electrodeposited at -900 mV as a function of passage of charge. (a), (b), and (c) are corresponding to the images of deposits in the 2nd, 3rd, and 4th stage respectively. Deposits are elongated shape in the 2nd stage, and a larger number of deposits are observed in A/C configuration. In the 3rd stage, the deposits grow up to roundish grains. The sizes evaluated from the number of particle in SEM photographs are approximately 0.7 μm in diameter in both configurations. It is seen that particle size distribution has a rather significant size variance. It indicates that the kinetics of the initial stages of the electrochemical formation of ZnO can be described by a model including progressive nucleation and kinetically controlled 3D growth. The variance evaluated from the pictures seems to be larger in A/C configuration than that of in C/A configuration. Moreover, precipitated particle number is more than in C/A configuration.

The difference between the deposits prepared in two electrode configurations suggests that the surface morphology may be significantly influenced by the gravitational level in early stage of deposition. In the 4th stage, the film is composed of many aggregates of hexagonal column. Apparent morphological difference between both configurations has not been found.

\[
\text{Zn}^{2+} + 1/2\text{O}_2 + 2e^- \rightarrow \text{ZnO} \quad (4)
\]

The nitrate system has the redox potential of +0.5 V, significantly lower than that with oxygen (+0.93 V), but still efficient for ZnO formation to become possible. Moreover the reaction (4) in the oxygen reduction route inevitably involves the bubbling oxygen gas operation. It may not be suitable for experiment in microgravity environment.

D.C. Look reported that ZnO is much more resistant to radiation damage than other common semiconductor materials, such as Si, GaAs, CdS, and even Ge. He concluded that ZnO is useful for space application [17]. These results may be promise to explore a new system of electrochemical processing of ZnO with nitrate reduction route in microgravity environment in order to apply it in space applications or space industry.

4.2 Comparison with previous work on metal electrodeposition

We have successively studied the gravitational field effects on the initial stage of electrodeposition of metals using the drop tower shaft and centrifuge facility. Larger Cu grains were precipitated in C/A than in A/C under 1-G experiment. Much larger grains were, surprisingly, precipitated under μ-G in the drop tower than C/A in 1-G. This gravitational effect was clearly observed even in the samples electrodeposited only for 2s. From the high gravitational field experiment realized inside the centrifuge facility, the nucleus number density is increases and finally saturated as the gravitational field is raised.

Figure 4 is cited from Morisue’s paper [14]. Cu electrodeposition on TiN substrate is characterized an instantaneous nucleation mode. The figure shows a series of current transients during after the electro potential measured with a conventional Cu wire reference electrode is varied from -0.3 V to -0.7 V. Each transient curve characterized by a rapid decrease of current over the initial 0.5-2 s (Stage A). The instantaneous current variation in the very initial period of Stage A should correspond to the phenomena from charging up the double layer to transit or shift to the ionic mass transfer controlling regime. No apparent different of current is observed between the two configurations of C/A and A/C in Stage A. This is followed by the appearance of current density.
recovery with an extreme value around 2-20 s (Stage B). The extreme value with convey curvature is recorded for a longer duration in A/C than in C/A. No extreme value appears at -0.3 V for either electrolytic cell configuration till 40 s. The apparent overpotential of -0.3 V may be too low for the ionic mass transfer resistance to control the electrodeposition process. The current transient curve recorded at less than -0.5 V apparently starts to fluctuate after 10-20 s starting the electrolysis in the A/C configuration (Stage C).

Benard type natural convection should be inevitably induced with time progression in the C/A configuration under normal gravity. The fluctuating characteristics in Stage C must be related directly to Benard type convection. Thus, the surface concentration of Cu^2+ ions is maintained higher in A/C than in C/A configuration, at least 10 s after starting the electrolysis which corresponds to Stage C.

![Current transients for the deposition of copper in (top) the C/A configuration and (bottom) the A/C configuration. The potential was stopped from the open-circuit potential to (a) -0.7, (b) -0.6, (c) -0.5, (d) -0.4, and (e) -0.3 V](image)

**Figure 5** shows that SEM images of copper precipitates electrodeposited on a TiN substrate. The images in the upper row correspond to the precipitates in the C/A configuration and those in the lower to those in the A/C configuration. The nuclei number densities are in the range of 10^7 to 10^10 cm^-2. A clear dependence of the number density on the electrode overpotential was recognized as expected; the nuclei density increases with increase with increasing in overpotential. Moreover, nuclei number density in A/C configuration is higher than in C/A.

The ionic mass transfer rate of Cu^2+ ion should inevitably participate in the nucleation related phenomena, because it is easily influenced by the gravitational strength. Bernard type natural convection should be induced with time progressed in a cavity in the A/C configuration under normal gravity. Thus the surface concentration of Cu^2+ ion can be higher than that in C/A configuration. If the nuclei number density is determined by the surface concentration of Cu^2+ ion at the substrate, the present result can be acceptable for dependence of nuclei density on the gravitational strength.

The reason why was a higher nuclei density is obtained in the potentiostatic electrodeposition of Cu onto TiN substrate in the C/A configuration than the A/C configuration is still questionable. When Cu is electrodeposited on TaN substrate, a progressive nucleation mode has been observed as described elsewhere. Consider such a circumstance. It is natural to accept the experimental result to obtain higher nucleation number caused by hinder surface concentration. Even if the instantaneous nucleation mode is accepted, the duration period of stage A covers 0.5 to 2 s.

When the rate controlling step of electrodeposition process shifts from the surface reaction to the ionic mass transfer step, a micro fluctuation of electrolyte maintained in 1-G environment may more significantly enhance the ionic mass transfer rate than expected from the pure diffusion field. This speculation may be solution to accommodate the effect of gravitational level on the initial stage of electrodeposition on TiN substrate. The terminology of instantaneous is not rigorously
defined. It is a relative concept to be compared with the progressive nucleation mode.

In the present work, $\mathrm{Zn}^{2+}$ transfer rate should be considerably enhanced by the induction of Bernard type natural convection in A/C electrode configuration. Thus, it should introduce higher $\mathrm{Zn}^{2+}$ concentration near the electrode surface in A/C configuration. It may result in the higher nucleus number density as in the case of copper nucleation on TaN. The continuous increase of current density (4th stage) in A/C configuration may be explained by the enhanced mass transfer of ion near the cathode surface. However, a shorter induction time and steeper increase in the 2nd and 3rd stage cannot be similarly explained.

The surface concentration of $\mathrm{OH}^-$ ion may also participate to the nucleation phenomena in electrochemical processing of ZnO as seen from Eq. (3). If the nuclei number density is determined by the surface concentration of $\mathrm{Zn}^{2+}$ ion and $\mathrm{OH}^-$ ion at the substrate, the surface $\mathrm{OH}^-$ concentration is also the key issue to govern the precipitation of ZnO. The thermodynamic analysis at higher temperature at 343 K is necessary to discuss the nucleation phenomena. The present system is rather complicated and more detailed discussion including both $\mathrm{Zn}^{2+}$ and $\mathrm{OH}^-$ concentration must be necessary. However, a significant morphological variation is expected due to the difference of gravitational level. Thus, the experiment in microgravity environment is now planned to make further discussions.

5. Conclusion

ZnO is electrochemically deposited on ITO/FTO substrate. Two kind of electrolytic cell configuration of cathode over anode and anode over cathode were employed. ZnO nucleation rate is influenced by the gravitational field vector; nucleation phenomena are accelerated in A/C configuration. The nucleus number density and variance of particle size was higher in A/C configuration than C/A configuration. The experiments under $\mu$-G field environment should be further required to provide better physical properties for the application of optoelectronic devices.

References


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