電析形態に及ぼす重力レベル効果

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Gravitational Effects on Electrochemically Evolved Morphology

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ABSTRACT: Electrochemical Processing is essentially influenced by the mass transfer rate governed by natural convection accompanying the electrode reactions. JAMIC facility provided good opportunities to understand the effect of gravitational level to the initial state of non-equilibrium electrochemical processing including single metal electrodeposition and water electrolysis. Now, the non-equilibrium electrochemical processing of alloy or semiconductor nanowire arrays are focused Free standing ZnO nanowire array has been successfully synthesized on ITO/FTO substrate by template-free method in $Zn(NO_3)_2$ aqueous solutions in the terrestrial experiment. Two types of electrode configurations were employed: (a) a horizontal cathode surface facing downward over an anode (C/A) and (b) an anode over a cathode (A/C). More uniform nanowires are synthesized in C/A configuration than in A/C. The coupling phenomena between multi-component diffusion process around nanowire and the shape evolution must be clarified.

Introduction

The electrochemical deposition of ZnO films in $Zn(NO_3)_2$ or $ZnCl_2$ aqueous solution have been reported by Izaki et al. and Lincot et al.. Oxygen source is supplied from NO_3^- species in the former case, while the dissolved oxygen gas in the latter. Electrochemical processing of semiconductor nanowire array is attractive. The measurements of PL spectra for ZnO film are the most popular subjects. ZnO nanowire array is electrodeposited in $Zn(NO_3)_2$ aqueous solution containing $LiNO_3$. The electrodeposited ZnO nanowire is irradiated by He-Cd laser.

Experimental

ZnO were electrodeposited onto transparent conductive glass substrates (FTO/ITO coated glass, 2 Ω/□, Fujikura Co. Ltd.) at 343K. Ag/AgCl electrode was used as RE. The amount of electricity is restricted with the coulomb meter. The electrode assembly was composed of a short rectangular channel (10 mm x 10 mm x 30 mm, Teflon) with two open ends and immersed in a 50 ml electrolytic bath. The counter electrode was pure zinc sheet (Nilaco Corp.). Effective surface of both electrodes were 10 × 10 mm. They were embedded in either side of channel walls.

Photoluminescence spectra from deposited ZnO were measured using a low-power, unfocused 325 nm line of a He–Cd laser as the excitation source.

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Results and discussion

Effect of Zn^{2+} Concentration

ZnO nanowire array was electrodeposited in aqueous electrolyte solution containing 0.1 M $LiNO_3$ and 0.5 ~ 10 mM $Zn(NO_3)_2$. PL spectra of ZnO nanowire were measured at room temperature. In the lower Zn^{2+} concentration region less than 2mM, two peaks are observed. One is strong narrow peak around 380 nm in UV band, while the other is a weak broad green-yellow band (visible emission) around 570 nm.

The UV emission band is due to a near band-band-edge (NBE) transition of wide band gap of ZnO, namely the recombination of free exitons through an exiton-exiton collision process. The green-yellow emission is attributed to the radial recombination of a photogenerated hole with an electron that belongs to singly ionized oxygen vacancy in the surface and sub-surface lattice of materials.

In the higher Zn^{2+} concentration region of 5mM, the UV peak shifted to the higher energy and the intensity became weaker. P. Yang et al. believe the intensity of green band is size-dependent such that the intensity increase as the wire diameter decreases. ZnO nanowire array is not uniformly elecrodeposited on the substrate. Thus, the full-width at half-maximum (FWHM) of the UV peak, and the ratio of the UV and yellow-green emission intensities (I_{UV}/I_{GY}) are measured in order to extract the effect of Zn^{2+} concentration to the PL characteristics. The nanowires synthesized in solution containing 1 mM Zn^{2+} show the largest UV to visible intensity ratio (I_{UV}/I_{GY}=21.2) and the smallest FWHM (154 meV). It indicates that the highest crystalline ZnO is deposited in this electrolyte composition.

Gravitational Field Effect

ZnO nanowire is electrodeposited in 1 mM $Zn(NO_3)_2$ - 0.1 M $LiNO_3$ solution in two different electrode configurations: (1) a horizontally installed cathode facing downward over an anode (C/A) and (2) an anode over a cathode (A/C). In the C/A configuration, less concentrated and lighter electrolyte solution stays adjacent to the downward cathode surface and the gradient of electrolyte density profile is parallel to the gravitational field. No natural convection is principally expected under such a configuration. It may simulate quasi μ-g environment.

Fig. 1 shows the room temperature PL spectra for $Zn(NO_3)_2$ = 1 mM. The intensity of UV peaks and I_{UV}/I_{GY} is higher and FWHM is smaller in C/A configuration. Furthermore, PL characteristics are measured at randomly selected locations in the deposited array sample. Fig. 1 clearly demonstrates more uniform film is obtained in C/A configuration; the natural convection is induced in A/C configuration. The fluctuating concentration of chemical species may disturb the crystallization process of ZnO nanowire array.

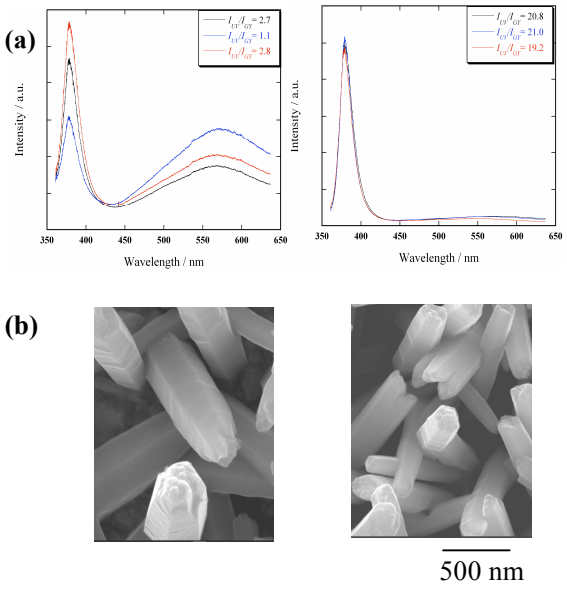

Figure 1. (a)PL spectra from ZnO electrodeposited in aqueous solution. (b) SEM images of deposited nanowire. (left) A/C, (right) C/A

The ultraviolet and visible photoluminescence (PL) of as grown nanowire arrays deposited in 1 mM $Zn(NO_3)_2$ – 0.1 M $LiNO_3$ solution was measured in the

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temperature range 17 K ≤ T ≤ 300 K. As the temperature decreases, two peaks significantly grow with freezing-out of phonons and quenching of nonradiative recombination processes. A 61 meV blue shift of the band-edge emission over this temperature range is caused by the thermal contraction of the lattice and changing electron–phonon interactions. The orange peak (~600 nm) appears as the temperature decrease. Finally it surpasses the intensity of UV peak. A simple thermal activation model can express temperature dependence of the orange PL intensity,

$I = I_0/(1+ A \exp(E_A/k_B T))$.

where I is measured PL intensity, I_0 and A are constants, E_A is activation energy, k_B is Boltzmann constant, and T is temperature.

By fitting the experimental data, we obtain an activation energy E_A=73 meV for the non-radiative mechanisms responsible for quenching the orange luminescence. P. Yang et al. reported the yellow-orange emission for ZnO nanowire deposited by the hydrothermal process. Their activation energy is 71 meV. It is comparable to the energy reported in a previous study of single-crystal and powder samples. The orange emission is less commonly reported. Its origin, although not fully understood, may be caused by the interstitial oxygen ions (O_i^-). Orange PL has been seen in ZnO grown electrochemically, hydrothermally, and pulsed laser deposition and spray pyrolysis. The strong orange PL and complete absence of green emission from the nanowire arrays grown by aqueous solution processing presented in this work is consistent with the above assignments. Regardless of the exact origin of the orange emission, the large ratio of orange PL intensity to band-edge PL intensity indicates that the density of atomic defects in as-grown nanowires is rather high.

ZnO *Deposition Mechanism*

Multi-component diffusion process among Zn^{2+}, NO_3^-, OH^- and H_2O species must be precisely understood to tailor ZnO nanowire array at 343K. The key parameter is how to define the surface pH value at the cathode and how to nucleate and grow ZnO dendrite precursor to result in ZnO nanowire. It must be understood how the stoichiometry and/or crystallinity of ZnO nanowire is controlled.. The optical properties in $Zn(NO_3)_2$-KOH solution have not been reported, but many papers are available on $CuSO_4$ system since Ibl & Muller.

The parabolic flight opportunity has been given to CNRS-Kyoto University team on the gravitational effects on the secondary battery reversibility including advanced Li battery for EV. It is inherently relating the shape evolution phenomena during the electrochemical reactions. We have experiences on the drop tower, but no parabolic flight experiment.

First of all, it is decided to preliminarily in-situ measure the refractive index profile around growing Cu dendrite in $CuSO_4$ solution during the parabolic flight. The electrolytic cell powered by the potentiostadt or galvanostadt must be reasonably designed in order not to have any leakage of aqueous electrolyte solution for the crew safety. Moreover, the conventional electrolytic power system with large sized transducer must work properly. Because the transducer utilizes air cooling system, its function is not always guaranteed under microgravity environment. These aspects must be examined during the parabolic flight, before the electrolytic experiments are engaged.

The experimental data are now under characterization in CNRS. It seems to have normal operation of electrolytic power sources even during the parabolic flight microgravity duration period over 22seconds. However, a small amount of electrolytic current recorded under potentiostatic electrolysis might be seriously disturbed by the circuit noise. Moreover, a slight oxidation or corrosion phenomena of cathode

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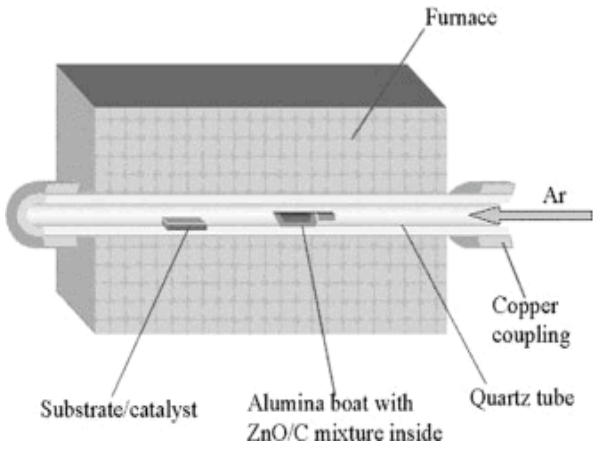
substrate immersed in electrolyte over 12 hours before the electrolytic experiment introduce additional resistance in the circuit. More precise control of dissolved oxygen gas in aqueous electrolyte solution may be indispensable. Shielding operation with Al foil around the electrolytic circuit may improve the measurement precision. Next opportunity may be utilized to confirm these experimental efforts.

Another materials processing of ZnO nanowire array may be challenged independently from the electrochemical processing. ZnO reduction process was analyzed in Kyoto University 20 years ago. At that time, bright ZnO microcrystal formation was confirmed near the exhausting gas port of reactor. The reoxidation reaction in the lower temperature zone must result in the formation of ZnO microcrystalline, as the thermodynamic calculation result suggests. When an appropriate substrate is placed in the temperature gradient furnace, ZnO nanowire array should be expected. P. Yang. et al.[i] used the VLS method proposed by Wagner and Ellis to grow ZnO nanowires on gold films in the presence of a ZnO and graphite and Ar. Higher temperature processing is more favorable to accelerate the surface diffusion of atoms to result in better crystallinity. Figure 2 illustrates the apparatus they used to synthesize ZnO nanowires. A similar furnace design is proposed to test our hypothesis about the expected difference in the electrical and optical properties of ZnO nanowires grown by an aqueous electrochemical technique.

Future Projects on Electrochemical Processing

Energy conversion and storage technology must be key issue in the future research targets on in-situ resources utilization. Materials processing of energy conversion and storage devices like Li negative electrode is very challenging. Dendritic growth must be suppressed during rapid charging & discharging operation. Phenomenological researches



have been conducted in PC or ionic liquid. URFC is another target. Wettability phenomena around the three phase interface must be understood. Microgravity environment surely provides an ideal experimental opportunity to clarify such a fundamental physicochemical hydrodynamic behavior.

Molten salt electrolysis must play the major role in future energy technology in space. Metal extraction behavior must be understood as well as oxygen gas evolution relating to in-situ resources utilization.

Conclusion

ZnO nanowire array was electrodeposited in aqueous solution containing various Zn^{2+} concentrations under quasi μ-g environment of C/A configuration. Parabolic flight experiments are scheduled in Air Bus A300.

Acknowledgement

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[1] Yang, P. et al. *Adv. Funct. Mater.*, 12, 323-330, 2002

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