

電析 ZnO ナノワイヤー配列の光学特性に及ぼす重力レベルの影響

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Gravitational Level Effects on Optical Properties of Electrodeposited ZnO Nanowire Arrays

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ABSTRACT: Two types of electrode configurations were employed in order to quantitatively examine the effect of gravitational strength on electrodeposited ZnO nanowire array: (a) a horizontal cathode surface facing downward over an anode (C/A) and (b) an anode over a cathode (A/C). The former configuration may simulate a quasi-microgravity environment, because macroscopic natural convection is not induced. Free standing ZnO nanowire array was successfully electrodeposited on ITO/FTO substrate by template-free method in $Zn(NO_3)_2$ aqueous solutions. PL of ZnO nanowire array was measured. Nanowire arrays with more uniform distribution of PL characteristics are synthesized in C/A configuration than in A/C. Seeding ZnO nanoparticles on ITO/FTO substrate can control the diameter as well as the orientation. Drop tower experiments are now planned.

Introduction

ZnO is a unique material exhibiting a large band-gap (3.30 eV at room temperature) and diverse nanostructures. This oxide is a versatile smart material that can be applicable to catalysts, sensors, piezoelectric transducers, transparent conductors and surface acoustic wave devices owing to its asymmetric atomic structure. ZnO structure can be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions stacked along the c-axis. It is considered that the oppositely charged ions produce positively charged Zn(0001) and negatively charged O(0001) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. It is well known that the free-exciton binding energy corresponds to 60 meV, which in principle allows the exciton luminescence at short wavelengths dominant at room temperature. This, in turn, offers the prospective blue or UV lasers with low thresholds.

In general, the materials processing of ZnO films has been engaged by pulsed laser deposition, sputtering, gas phase deposition, metal organic chemical vapor deposition (CVD), molecular beam epitaxy and spray pyrolysis. Solution processings such as sol-gel synthesis, chemical solution deposition, hydrothermal synthesis, anodic oxidation and electrodepositon have also been reported relating to the development of dye-sensitized solar cell. It is noteworthy to describe that 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.

The measurements of PL spectra for ZnO film are popular subjects. However only few measurements

have been performed on electrodeposited ZnO. In the present study, 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. A strong UV exciton emission is confirmed at room temperature.

Experimental

ZnO were electrodeposited onto transparent conductive glass substrates (FTO/ITO coated glass, 2 Ω/ □ , Fujikura Co. Ltd.). Before starting the electrodeposition, the substrates were ultrasonically cleaned sequentially in acetone, ethanol and deionized water for 15 min, respectively.

Electrochemical experiments were carried out with a conventional three-electrode system. Ag/AgCl was used as a reference electrode. 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 the assembly was immersed in a 50 ml electrolytic bath. The counter electrode was a sheet of pure zinc (Nilaco Corp.). Effective surface of both electrodes were 10 × 10 mm. They were embedded in either side of channel walls. The solution temperature was maintained at 343 K.

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

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 $Zn(NO_3)_2$. Figure 1 shows SEM images of electrodeposited ZnO in various electrolyte compositions. When the Zn^{2+} concentration is more than 2 mM, the shape of deposit is like an aggregate of grains. Wire-like shaped deposits are observed and its diameter became smaller as the Zn^{2+} concentration decreased (below 2 mM). Moreover, its surface morphology became smoother as Zn^{2+} concentration decreased. The number density of nanowires is the highest when the Zn^{2+} concentration is 1 mM. The surface morphology of ZnO is significantly influenced by Zn^{2+} concentration.

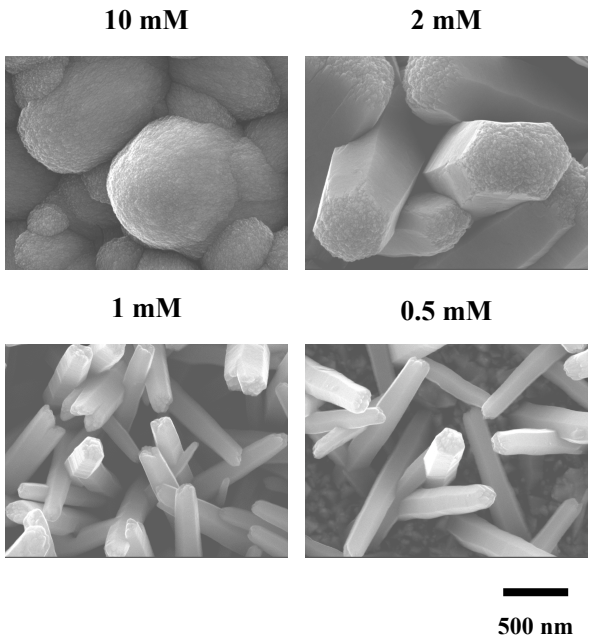

Figure 1. SEM images of electrodeposited ZnO from aqueous electrolyte containing 0.1 M NO_3^- and various Zn^{2+} concentrations.

Figure 2 shows TEM images of a ZnO nanowire. The diameter of nanowire is about 250 nm. Electron diffraction pattern is taken from these nanowires (Fig. 2 inset) and this result confirms its high crystallinity. TEM images of body and top are shown in Fig. 3. ZnO nanowire is structurally uniform and contains no noticeable defects such as dislocation and stacking faults. The lattice spacing of 0.26 nm shows the (002) crystal planes of wurtzite ZnO, confirming that the ZnO nanowires have preferential growth orientation in the c-axis direction. Surface of top is very rugged and rounded shape, however, the structure is very uniform. These results confirm that deposited nanowire is highly crystallized and (002) plane is directed to axial

direction of nanowire.

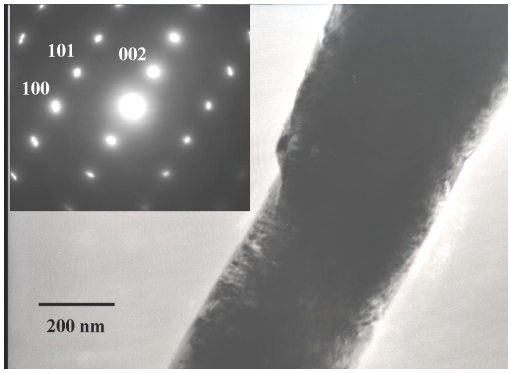

Figure 2. FE-TEM image of electrodeposited nanowire and (inset) SAED pattern.

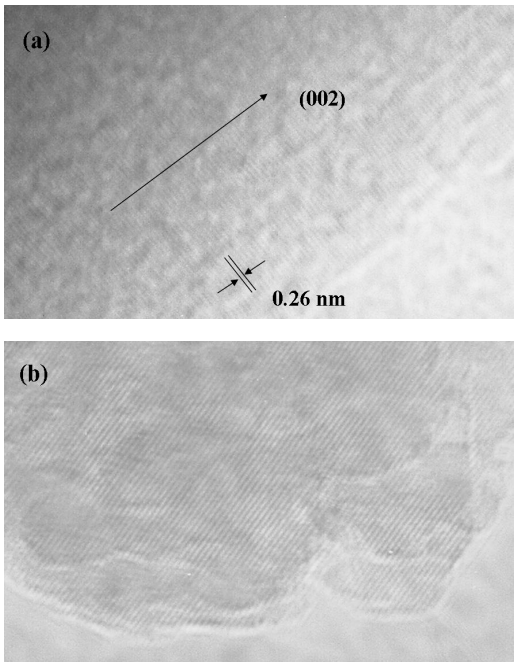

Figure 3. FE-TEM images of electrodeposited nanowire. (a) body and (b) top of nanowire.

Some deposits are anomalously deposited (deposit A) on the nanowire (deposit B). μ-Raman spectroscopy was carried out on each deposit. Fig. 4 shows μ-Raman spectra and SEM images for electrodeposited ZnO nanowire arrays. From deposit B, the peak appears only at 436.76 cm^{-1}. On the other hand, in Raman spectrum from deposit A, two peaks emerge at 436.76 cm^{-1} and 613.5 cm^{-1}.

In typical Raman spectra of ZnO, the peaks at 437 and 579 cm^{-1} can be assigned to be vibration modes of E_2 and E_1 (LO), respectively. The E_2 mode corresponds to band characteristic of wurtzite phase. The appearance of the E_1 (LO) peak has been attributed to the formation of oxygen deficiency, interstitial Zn, and free carrier. Both spectra show peaks corresponding to E_2 mode and no peak corresponding to E_1 mode appears in both deposits. However, the peak observed at 613.5 cm^{-1} is still under examination.

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

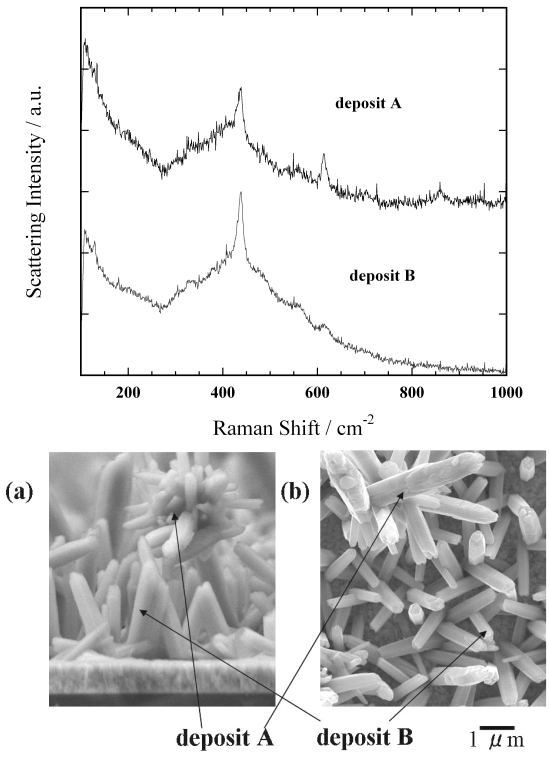

Figure 4. (top) Raman spectrum of two types of deposits. (bottom) SEM images of electrodeposited nanowire electrodeposited in A/C configuration. (a) cross sectional view and (b) top view.

sub-surface lattice of materials.

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).

Fig. 5 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. They clearly demonstrate more uniform film in C/A configuration. A kind of natural convection is induced in A/C configuration. The fluctuating concentration of chemical species may disturb the crystallization process of ZnO nanowire.

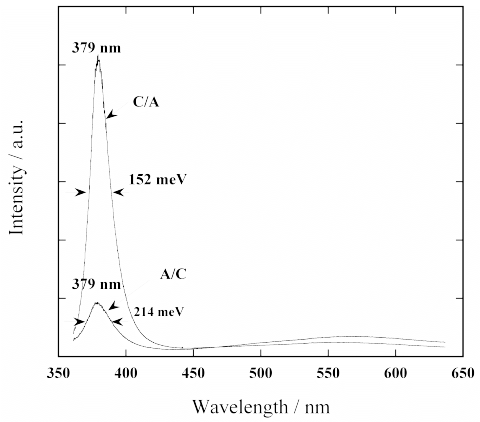

Figure 5. PL spectra from ZnO nanowire arrays electrodeposited in aqueous solution.

Future Research Direction

Z. L. Wang et al. successfully synthesized ultralong beltlike ZnO nanobelts by simply thermal-evaporating commercial oxide powder at 1673K without the presence of catalyst. The as-deposited ZnO nanobelts are structurally uniform and single crystalline free from defects and dislocations (Science, vol. 291, 1947-1949(2001)).

His group further extend their achievements to a new pathway for self-powering of wireless nanodevices (MRS Bulletin, vol. 32, 109-116(2007)). When the elastic deformation energy is suppressed by reducing the thickness of nanobelt, the polar nanobelt could self-assemble into a nanospring, by minimizing the electrostatic energy stemming from the ionic charges on the polar surfaces.

It is surely expected the gravitation effect emerges on the microstructure of nanobelts obtained in terrestrial experiment as long as the present temperature gradient furnace design is employed. The effect of gravitational level to the nanostructured devices must be carefully examined in the long duration microgravity environment. Electrochemical processing of ZnO nanowire is now designed in MGLAB Drop tower, although the duration period is too short to grow ZnO nanowire arrays. Nucleation phenomena are focused as well as the initial stage of electrodeposition under microgravity.

Conclusion

ZnO nanowire array was electrodeposited in aqueous solution containing various Zn^{2+} concentrations under quasi μ-g environment of C/A configuration. Crystallinity of nanowire deposits is the highest when Zn^{2+} concentration is 1 mM. Orange luminescence was observed at low temperature PL measurement. Seeding ZnO colloid particles on the substrate can control diameter or orientation of ZnO nanowire. Orange luminescence was considerably reduced at 17K.

Acknowledgement

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