

擬似的微小重力環境で電析された ZnO ナノワイヤー配列の光学特性

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Optical Properties of Electrochemically Processed ZnO Nanowire Array in Quasi-Microgravity Condition

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ABSTRACT: Free standing ZnO nanowire array was successfully synthesized on ITO/FTO substrate by template-free method in $\text{Zn}(\text{NO}_3)_2$ aqueous solutions. 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 the microgravitational environment, because macroscopic natural convection is not induced. PL of ZnO nanowire array was measured. More uniform nanowires 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.

Introduction

Zinc oxide (ZnO) is a large band-gap (3.30 eV¹ at room temperature) semiconductor. Many applications are planned in the field of optoelectronics devices (e.g. laser diodes and light-emitting diodes, optical waveguides, optical switches, transparent ultraviolet (UV)-protection conducting film, acousto-optic and surface acoustic device², etc). It is well known that the free-exciton binding energy corresponds to 60 meV³, 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 thresholds⁴⁻⁸.

In general, the materials processing of ZnO films has been engaged by pulsed laser deposition⁹, sputtering¹⁰, gas phase deposition¹¹, metal organic chemical vapor deposition (CVD)¹², molecular beam epitaxy¹³ and spray pyrolysis¹⁴. Solution methods such

as sol-gel synthesis¹⁵, chemical solution deposition¹⁶, hydrothermal synthesis¹⁷, anodic oxidation¹⁸ and electrodeposition have also been reported. It is noteworthy to describe that the electrochemical deposition of ZnO films in $\text{Zn}(\text{NO}_3)_2$ or ZnCl_2 aqueous solution have been reported by Izaki et al.¹⁹⁻²³ and Lincot et al.²⁴⁻²⁷. 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 now one of the most fashionable research subjects. However only few measurements have been performed on electrodeposited ZnO. In the present study, ZnO nanowire array is electrodeposited in $\text{Zn}(\text{NO}_3)_2$ 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/\square , 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 \times 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 Zn²⁺ Concentration

ZnO nanowire array was electrodeposited in aqueous electrolyte solution containing 0.1 M LiNO₃ and 0.5 ~ 10 mM Zn(NO₃)₂. PL spectra of ZnO nanowire were measured at room temperature. In the lower Zn²⁺ 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 excitons through an exciton-exciton collision process²⁸. 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.²⁹

In the higher Zn²⁺ 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.³⁰ ZnO nanowire array is not uniformly electrodeposited 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 Zn²⁺ concentration to the PL characteristics. The nanowires synthesized in solution containing 1 mM Zn²⁺ 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(NO₃)₂ - 0.1 M LiNO₃ 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 configuration³¹. It may simulate the μ -g environment.

Fig. 1 shows the room temperature PL spectra for Zn(NO₃)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.

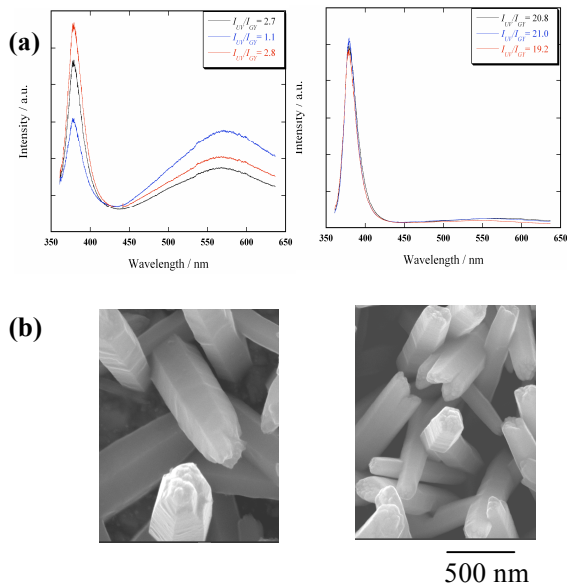


Figure 1. (a) PL spectra from ZnO electrodeposited in aqueous solution. (b) SEM images of deposited nanowire. (left) A/C, (right) C/A

Temperature Dependence of Photoluminescence

The ultraviolet and visible photoluminescence (PL) of as grown nanowire arrays deposited in 1 mM $\text{Zn}(\text{NO}_3)_2 - 0.1 \text{ M LiNO}_3$ solution was measured in the temperature range $17 \text{ K} \leq T \leq 300 \text{ K}$. As the temperature decreases, two peaks significantly grow with freezing-out of phonons and quenching of nonradiative recombination processes (Fig. 2). A 61 meV blue shift of the band-edge emission over this temperature range (as seen in an inset in Fig. 2) is caused by the thermal contraction of the lattice and changing electron-phonon interactions.³² The orange peak ($\sim 600 \text{ nm}$) 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,³³

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

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 $E_A = 73 \text{ meV}$ 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 ³⁴. 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.

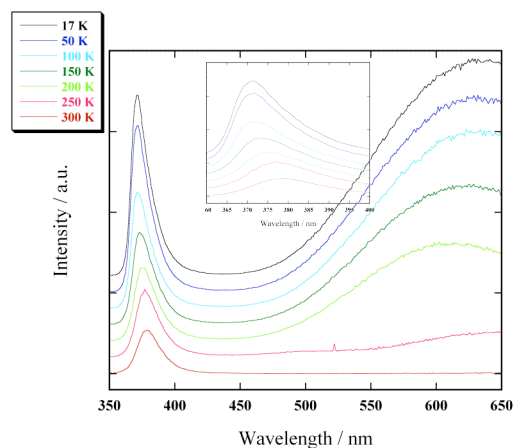


Figure 2 Temperature-dependent photoluminescence of a ZnO nanowire array on ITO/FTO substrate. The inset is a magnification of band edge emission.

Seeding Effect

Several groups have recently grown vertical ZnO nanowire arrays on various substrates. These arrays were synthesized by using the electrochemical deposition (ECD), metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition, or chemical vapor transport (CVT). A substrate having smaller lattice mismatch with ZnO crystal were employed to control the nucleation phenomena. A nucleation phenomenon may be a key issue to determine nanowire alignment.

The hydrolysis processing of zinc salts is an established route to the formation of ZnO colloids and nanocrystals in aqueous solution.³⁷⁻³⁸ A droplet of 0.005 M zinc acetate dihydrate (98%, Aldrich) in ethanol was placed on FTO/ITO substrate. It was rinsed with clean ethanol after 10 s, and then dried with Ar gas stream. This coating step is repeated several times. The substrate, now covered with a film of zinc acetate crystallites, is heated to 350 °C in air for 20 min to produce ZnO islands with (002) planes parallel to the substrate surface.

Fig. 3 (a) is SEM images electrodeposited nanowire grown on the substrate seeded with zinc acetate several times. By repeating the seeding process, the deposited nanowire became highly oriented and the diameter is dramatically decreased. PL spectra were measured at room temperature and 17K (Fig. 3 (b)). No apparent difference is observed regardless of seeding as long as PL measurement at room temperature concerns. However, ZnO nanoparticle seeding significantly restricts the enhancement of orange peak at 17 K. It is probably caused by fewer introductions of atomic defects during crystallization accompanying smaller mismatch between the nanowire and the substrate.

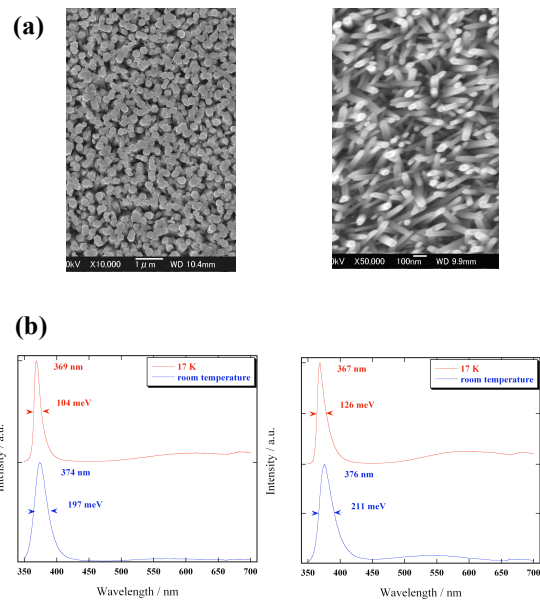


Figure 3. (a) SEM image of ZnO nanowire (b) PL spectra from ZnO nanowire. (left) thin ZnO seed layer (right) thick ZnO seed layer

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.

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