

## ***Chapter 2 Experiment***

### ***2.1 Manganese Oxide-Carbon Nanotube Nanocomposite Supercapacitor Electrodes***

The 10×10 mm<sup>2</sup> nickel substrates (Nilaco, Japan) were etched with 20 % HNO<sub>3</sub> solution at room temperature for 10 min to increase the roughness of the surface, cleaned with de-ionized (DI) water in an ultrasonic bath, and dried in a vacuum oven at 90 °C for 24 h. In order to obtain the CNTs with acidic sites on the surface, the CNTs were put in the boiling 70 % nitric acid solution for 1 h and dried in an oven at 90 °C for 24 h before electrophoretic deposition (EPD). The EPD technique was adopted to deposit the CNTs on the Ni substrate. The CNTs were dispersed by ultrasonic agitation in the bath of dimethylformamide (DMF) with a concentration of 0.5 mg/mL. The nickel and platinum sheets were put in this solution as the cathode and anode electrode, respectively. The CNTs were electrophoretically deposited on the Ni substrate after a direct current (DC) voltage of 20 V was applied for 5 min. Then, the MnO<sub>x</sub>·nH<sub>2</sub>O films were deposited onto the Ni and CNTs/Ni substrates by an anodic deposition with a platinum sheet as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in a 0.16 M MnSO<sub>4</sub>·5H<sub>2</sub>O solution with pH of 5.6. Such an amorphous-MnO<sub>x</sub>·nH<sub>2</sub>O film was deposited by the potentiostatic method at 0.4 V for 3 min.. The deposition condition was controlled by an EG&G Princeton Applied Research model 263 potential meter. After deposition, the electrode was cleaned with DI water and dried in a vacuum oven at room temperature for 24 h.

### ***2.1.1 Structural analysis***

The weight of amorphous  $\text{MnO}_x \cdot n\text{H}_2\text{O}$  films was determined by the microbalance with an accuracy of 10  $\mu\text{g}$ . The crystal structure of these samples was examined by X-ray diffraction (XRD, MAC Science, MXP18, Japan) employing a Cu target at an angle speed of  $4^\circ (2\theta) \text{ min}^{-1}$ . The surface morphology and microstructure of these electrodes were studied by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan) and high resolution transmission electron microscopy (HR-TEM, Philips tecani-20) coupled with an energy dispersive X-ray analyzer (EDX, Oxford, England). The measurement of surface area of electrodes was carried out by multi-point Brunauer-Emmett-Teller (BET, Quantachrome Instruments) method using  $\text{N}_2$  gas.



### ***2.1.2 Electrochemical characterization***

All of the electrochemical test was carried out in a three-compartment cell with a reference electrode of SCE, and a counter electrode of platinum sheet and 0.1 M  $\text{Na}_2\text{SO}_4$  as the electrolyte. Before electrochemical analysis, the cell was purged with argon atmosphere to remove the oxygen. Electrochemical characterizations of  $\text{MnO}_x/\text{Ni}$  and  $\text{MnO}_x/\text{CNTs}/\text{Ni}$  composite electrodes were demonstrated by the potentiostat/galvanostat (EG&G Princeton Applied Research model 263) with the working voltage from 0 to 1 V at a scan rate varied from 5 to 100 mV/s. The constant current discharge (CCD) reaction was carried out chronopotentiometrically at a cathodic current of 0.1 mA after applying a positive potential bias of 1 V for 30 s. The capacitance can be calculated from the equation of

$$c = \frac{i}{(dV/dt)} \quad [2.1]$$

Where  $c$  is the specific capacitance,  $i$  the specific voltammetric charge within the working voltage and  $V$  the potential. The amplitude of the as applied potential signal was 10 mV and the frequency ranged from 10 mHz to 100 kHz.



## ***2.2 Synthesis of ZnO Nanowires on Polymer Substrate***

Before deposition, the PET substrates (ES301911, Goodfellow) were cleaned by acetone in an ultrasonic bath for 10 minute, and ITO layers served as the conducting layer for field emission cathode with a sheet resistance of  $50 \Omega/\square$  were sputtered on the PET substrates. Some of the ITO/PET substrates were deposited with ultra thin seeding ZnO film ( $\sim 70 \text{ \AA}$ ) by rf-sputtering (13.56 MHz) under 20 mTorr Ar atmosphere. The ITO/PET and ZnO/ITO/PET substrates were put into their respective sealed vessels, which contain an aqueous solution (Milli Q,  $18.2 \text{ M}\Omega\text{cm}$ ) of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.01 M) and hexamethylenetetramine (HMTA,  $\text{C}_6\text{H}_{12}\text{N}_4$ , 0.01 M) for ZnO NWs hydrothermally grown at  $75 \text{ }^\circ\text{C}$  for 30 min..

### ***2.2.1 Structural analysis***



The surface morphologies of ZnO NWs were observed by field emission scanning electron microscopy (FE–SEM, Hitachi S–4700I, Japan) and high resolution transmission electron microscopy (HR–TEM, Philips tecani–20). The crystal structure was examined by X–ray diffraction (XRD, MAC Science, MXP18, Japan). Room temperature optical properties were measured by the UV–visible spectrometer (UV–VIS, Hitachi 557, Japan) and photoluminescence analyzer (PL, Hitachi F–4500, Japan) with Xe lamp as an excitation source (325 nm).

### ***2.2.2 Electrical characterization***

The field emission characterizations were measured with a Keithley 237 source–measure unit in a vacuum chamber at a base pressure of  $1 \times 10^{-6}$  Torr at room

temperature. The light-assisted field emission measurement was carried out under the illumination with a 30 W incandescent lamp. A copper electrode probe adopted as an anode with an area of  $7.1 \times 10^{-3} \text{ cm}^2$  was placed at a distance of 350  $\mu\text{m}$  from tips of the NWs. The anode-NW distance was adjusted by a vernier with an accuracy of  $\pm 0.1 \mu\text{m}$ .



## ***2.3 Influence of Dopants on Hydrothermal growth ZnO Nanowires***

### ***2.3.1 Influence of Mg Dopant on ZnO Nanowires***

To prepare the NWs by hydrothermal method on a ITO glass substrate (Ritec Co.,  $40 \Omega/\square$ ),  $70 \text{ \AA}$  ultra-thin ZnO film was deposited on the substrate by rf-sputtering (13.56 MHz) under Ar sputtering gas at 20 mTorr. Then, the coated glass substrates were put into an aqueous solution (Milli Q,  $18.2 \text{ M}\Omega\text{cm}$ ) of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.01 M), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and hexamethylenetetramine (HMTA,  $\text{C}_6\text{H}_{12}\text{N}_4$ , 0.01 M) in the sealed vessel at temperatures from 75 to  $105 \text{ }^\circ\text{C}$  for various reaction times from 10 min. to 2h. The surface morphologies of these samples were observed by atomic force microscopy (AFM, DI NS3a) in order to realize the crystal growth in the course of the process. The microstructure and properties of the 2 h synthesized NWs that have been cleaned with deionized (DI) water and dried in the vacuum oven at room temperature for 5h were investigated. The chemical composition of formed MZO NWs was controlled by changing the pH and the Mg concentration in the aqueous solution (Table 2.1).

#### ***2.3.1.1 Structural analysis***

The chemical composition and microstructures were confirmed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan) coupled with an energy dispersive X-ray analyzer (EDX, Oxford, England) and high resolution transmission electron microscopy (HR-TEM, Philips tecani-20), respectively. The crystal structures of the MZO NWs were examined by X-ray diffraction (XRD, MAC Science, MXP18, Japan). Room temperature optical properties were confirmed by the

UV-visible spectrometer (UV-VIS, Hitachi 557, Japan) and photoluminescence analyzer (PL, Hitachi F-4500, Japan) with Xe lamp as an excitation source (325 nm).

### ***2.3.1.2 Electrical characterization***

A Keithley 237 source-measure unit was used for measuring the current-voltage ( $I$ - $V$ ) and field emission characteristics. The field emission characterizations were carried out in a vacuum chamber at a base pressure of  $1 \times 10^{-6}$  Torr at room temperature. A copper electrode probe adopted as an anode with the area of  $7.1 \times 10^{-3}$  cm<sup>2</sup> was placed at a distance of 450  $\mu$ m from tips of the NWs which was adjusted by a vernier with an accuracy of  $\pm 0.1 \mu$ m.

### ***2.3.2 Influence of P Dopant on MgZnO Nanowires***

Before deposition, the  $p$ -type Si substrates were cleaned by RCA clean process to remove native silicon oxide on the substrate surface. Ultrathin ZnO seeding film ( $\sim 70$  Å) was deposited on the Si substrate by rf-sputtering (13.56 MHz) method under Ar sputtering gas at 20 mTorr. Then, the coated Si substrate was put into an aqueous solution (Milli Q, 18.2 M $\Omega$ cm) of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.01 M), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.06 M) and hexamethylenetetramine (HMTA,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) with pH value of 7.2 in a sealed vessel at 75 °C for 1h. After this hydrothermal reaction, the MZO NWs can be formed on the Si substrate and the color of the product was gray. The microstructure and properties of the synthesized MZO NWs that have been cleaned with deionized (DI) water and dried in the vacuum oven at room temperature for 5 h were investigated. To fabricate the PMZO NWs, the MZO NWs were exposed to  $\text{PH}_3$  plasma for 120 s. The plasma

treatment was carried out in an inductively coupled plasma (ICP) reactor using a 3 kW ICP power supply. The processing conditions were under 10 mTorr working pressure, 200 W ICP, 200°C reaction temperature, both Ar (99.5 %) and PH<sub>3</sub> (99.5 %) with 100 cm<sup>3</sup>/min flow rate. Then, these NWs were rapid thermally annealed (RTA) at 300 °C for 30 min. in the oxygen atmosphere.

### ***2.3.2.1 Structural analysis***

The crystal structure of the NWs was examined by X-ray diffraction (XRD, MAC Science, MXP18, Japan). The surface morphologies of the NWs were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan) and high resolution transmission electron microscopy (HR-TEM, Philips tecani-20). The chemical composition of the NWs was analyzed by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250). Room temperature optical properties characterizations were performed by UV-visible spectrometer (UV-VIS, Hitachi 557, Japan) and photoluminescence analyzer (PL, Hitachi F-4500, Japan) with Xe lamp as an excitation source (325 nm). The conducting behaviors of MZO and PMZO were characterized by the Hall effect measurements (HL500PC) at a magnetic field strength of 0.3 T at room temperature. The samples used for this measurement were bulk materials, which have the same chemical compositions as the NWs.

### ***2.3.2.2 Electrical characterization***

The field emission characteristics of the NWs were measured by Keithley 237 source-measure unit in a vacuum chamber at a pressure of  $1 \times 10^{-6}$  Torr at room



temperature. In the field emission measurement, a tungsten anode with an area of  $7.0 \times 10^{-3} \text{ cm}^2$  was placed at a distance of  $350 \text{ }\mu\text{m}$  from tips of the NWs, which can be adjusted by a vernier with an accuracy of  $\pm 0.1 \text{ }\mu\text{m}$ .



## ***2.4 Characteristics of Field Emission Triode***

### ***2.4.1 Planar Gated Field Emission Triode***

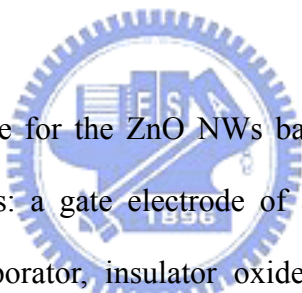
The field emission triode based on ZnO NWs was fabricated on the p-type Si (100) substrate. Figure 2.1(a) illustrates the fabrication flow of a ZnO NWs triode field emission array. The process began with plasma-enhanced chemical vapor deposition (PECVD) of SiO<sub>2</sub> on the Si substrate followed by an electron beam evaporator deposition of gate electrodes, Al. The thicknesses of the insulating oxide and the gate metal were 500 and 100 nm, respectively. The emitter regions were defined by a standard photolithography and wet etching process. An ultra-thin ZnO film (~70 Å) was deposited on the substrate by rf-sputtering (13.56 MHz) under Ar sputtering gas at a base pressure of 20 mTorr, which was used as a seeding layer to prepare the well-aligned ZnO NWs by hydrothermal method. Then, the photoresistance (PR) layer was stripped, and the unwanted seeding above the metal gate layer was lifted off. Last, the substrate was put into an aqueous solution (Milli Q, 18.2 MΩcm) of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.01 M) and hexamethylenetetramine (HMTA, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, 0.01 M) in a sealed vessel at 75 °C for 30 min.. After the NWs were hydrothermally grown on the substrate, the fabrication of triode device is completed.

#### ***2.4.1.1 Structural and Electrical Analysis***

The crystal structure of the ZnO NWs was examined by X-ray diffraction (XRD, MAC Science, MXP18, Japan). The surface morphologies of the NWs were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan)

and high resolution transmission electron microscopy (HR-TEM, Philips tecani-20). The test scheme corresponding to the field emission measurement is illustrated in Fig. 2.1 (b). The measurement was carried out in a vacuum chamber (base pressure of  $1 \times 10^{-6}$  Torr) equipped with a valve through which Ar gas flows in to adjust the measuring pressure. A Keithley 237 current-voltage analyzer was used for measuring the field emission characteristics and a power supply was adopted for the control of the gate bias ( $V_g$ ). A copper electrode probe that serves as an anode with the tip diameter of 500  $\mu\text{m}$  was placed at a distance of 500  $\mu\text{m}$  from the tips of the NWs. The electrode distance was adjusted by a vernier with an accuracy of  $\pm 0.1 \mu\text{m}$ .

#### ***2.4.2 Under Gated Field Emission Triode***

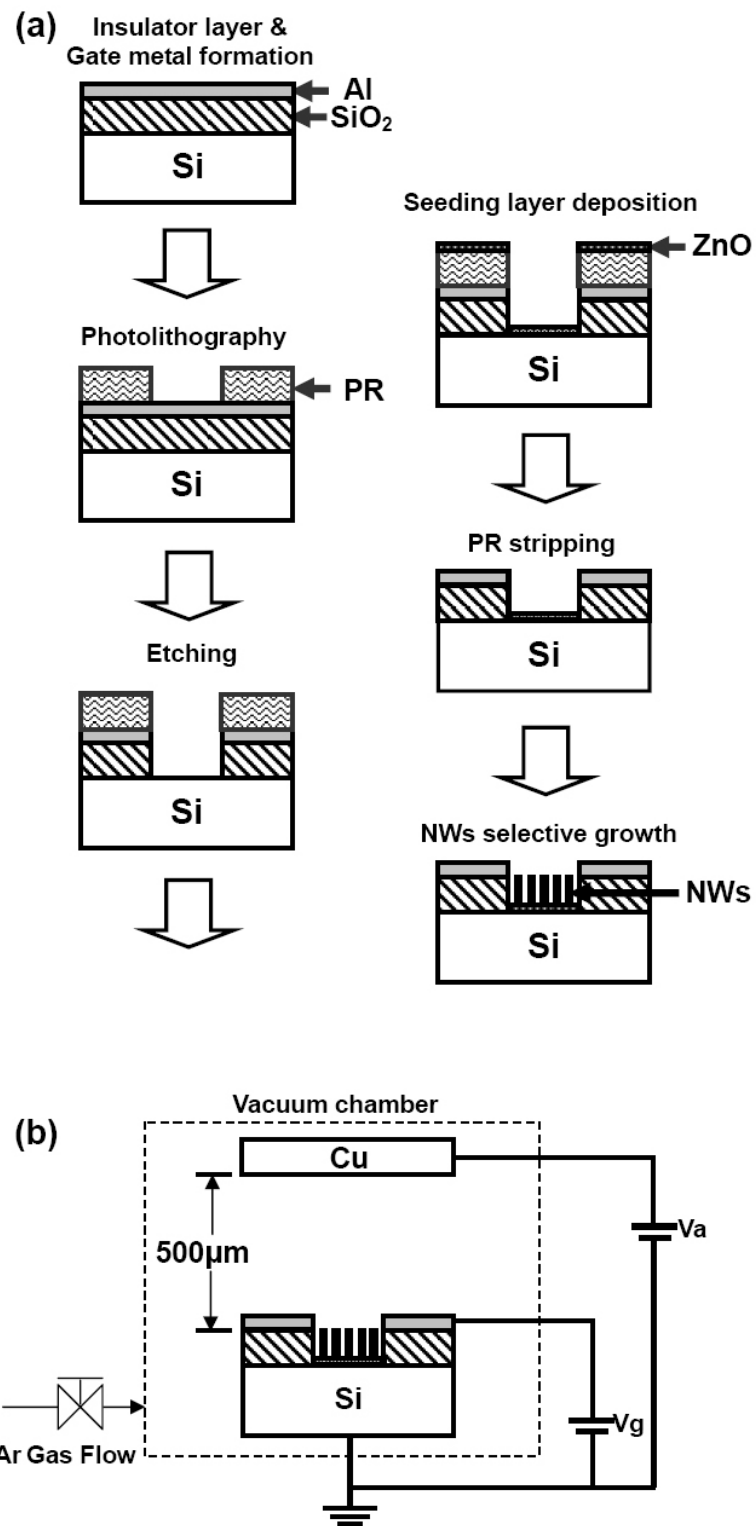


The fabrication procedure for the ZnO NWs based patterning under gate field emission device is as follows: a gate electrode of aluminum (Al) is deposited by electron beam (e-beam) evaporator, insulator oxide of  $\text{SiO}_2$  by plasma-enhanced chemical vapor deposition (PECVD), cathode metal of Al by e-beam evaporator and ultra-thin seeding ZnO film ( $\sim 70 \text{ \AA}$ ) by rf-sputtering on the p-type Si (100) substrate, respectively. Then, the emitter array regions, including insulator, cathode metal and cathode emitter regions, were defined by photolithography and etching. After the photoresistance (PR) layer was stripped, and the substrate was put into an aqueous solution (Milli Q,  $18.2 \text{ M}\Omega\text{cm}$ ) of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.01 M) and hexamethylenetetramine (HMTA,  $\text{C}_6\text{H}_{12}\text{N}_4$ , 0.01 M) in a sealed vessel at  $75 \text{ }^\circ\text{C}$  for 30 min.. The ZnO NWs were hydrothermally grown on the ZnO seeding regions, and the under gate device is completed.

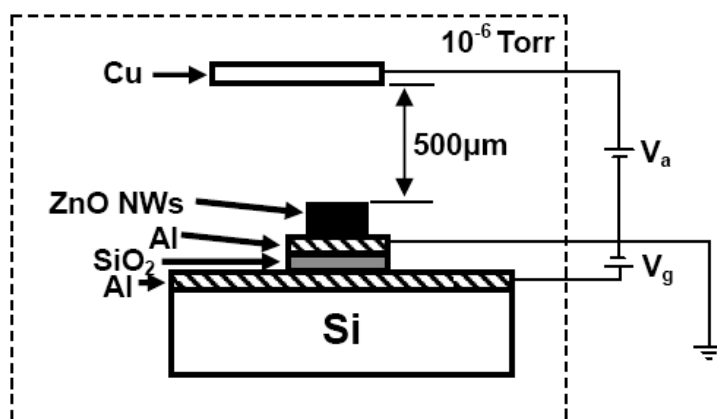
### ***2.4.2.1 Structural and Electrical Analysis***

The surface morphologies were confirmed by field emission scanning electron microscopy (FE–SEM, Hitachi S–4700I, Japan). The test scheme corresponding to the field emission properties is illustrated in Fig. 2.2. A Keithley 237 current-voltage analyzer was used for measuring the field emission characteristics at a base pressure of  $1 \times 10^{-6}$  Torr at room temperature and a power supply was adopted for the control of the gate bias ( $V_g$ ). A copper electrode probe that acts as an anode with the tip diameter of 500  $\mu\text{m}$  was placed at a distance of 500  $\mu\text{m}$  from the tips of the NWs. The electrode distance was adjusted by vernier with an accuracy of  $\pm 0.1 \mu\text{m}$ .





**Figure 2.1** (a) Schematic description of fabrication processes of field emission triode. (b) Test system of the triode mode.



**Figure 2.2** Test system of the under-gate field emission triode.



**Table 2.1** Relationship among composition of synthesized MZO NWs, concentration of Mg in the solution, and pH of the solution.

x value in MZO based on EDX results	Concentration of Mg in the solution (M)	pH of the solution
x = 0.00	0.00	7.0
x = 0.05	0.02	7.0
x = 0.10	0.06	7.2
x = 0.15	0.10	7.2
x = 0.20	0.15	7.4
x = 0.25	0.25	7.4