Chapter 3

Experimental Methods

3.1 Experimental flowchart

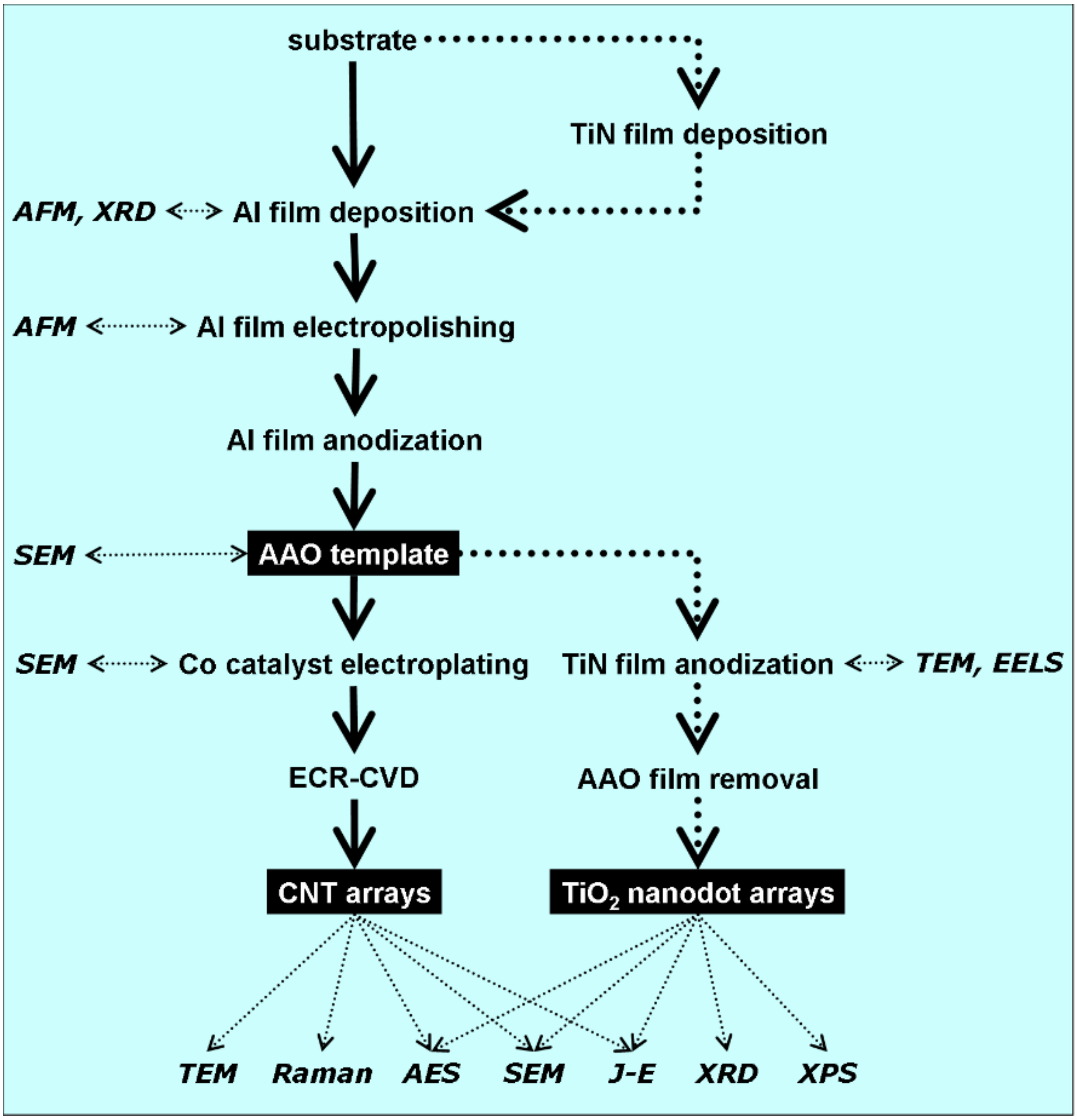

Figure 3-1 Experimental flowchart for the fabrications and analyses of the AAO templated CNT and TiO_2 nanodot arrays.

Figure 3-1 shows the experimental flowchart for the fabrications and analyses of the anodic aluminum oxide (AAO) template assisted arrays of carbon nanotubes (CNTs) and titanium oxides. The AAO templates for the CNT growth were prepared by the two-step anodization of the aluminum films. After the cobalt catalyst electroplating the CNT growth was performed in a microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD) system. The titanium oxide nanodot arrays were prepared by the anodization of the Al/TiN bilayered films. Atomic force microscopy (AFM) was utilized to characterize the surface morphology of the as-deposited and the electropolished aluminum films. The microstructure of the AAO templates was studies by scanning electron microscopy (SEM). The microstructure, bonding structure, chemical composition, and crystallinity of the AAO templated CNTs and titanium oxide nanodots were investigated by SEM, transition electron microscopy (TEM), electron energy loss spectroscopy (EELS), Raman spectroscopy, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), etc. The field emission measurements (J-E) of the specimens were conducted by the simple diode configuration and performed in high vacuum.

3.2 Depositions of Al and TiN films

In this study, fabrication of the AAO template began with the deposition of an aluminum film on a (100)-oriented *p*-silicon wafer by a high vacuum thermal evaporator with a base pressure of 5×10^{-7} Torr. The deposition temperature ranged from 100 to 300 ^{o}C. Aluminum ingots with a purity of 99.999% were used as aluminum source. Tungsten boats were used in melting and evaporating the aluminum ingots. Prior to aluminum deposition the aluminum ingots were cleaned in a 10 vol.% hydrogen chloride (HCl) solution for 60 sec. The tungsten boats were cleaned in a mixed solution of 20 vol.% hydrogen fluoride (HF) and 80 vol.% nitric acid (HNO_3) for 15 sec.

The titanium nitride (TiN) films for the titanium oxide nanodot production were deposited on a (100)-oriented *p*-silicon wafer by a load-locked multi-chamber ultrahigh vacuum reactive dc magnetron sputtering system (MRC PRIMUS 2500TM), with a base pressure of 5×10^{-9} Torr. The titanium target used was 99.9999% pure. The TiN films were prepared at a gas mixture of argon and nitrogen. During the deposition, the dc power, substrate temperature, and working pressure were set at 10 kW, 300 °C, and 3×10^{-3} Torr, respectively.

Fabrication of the highly uniform titanium oxide nanodot arrays began with the epitaxial growth of a TiN film on (0001)-oriented, 2-inch-diameter sapphire wafers using a reactive dc magnetron sputtering system. The base pressure of the sputtering

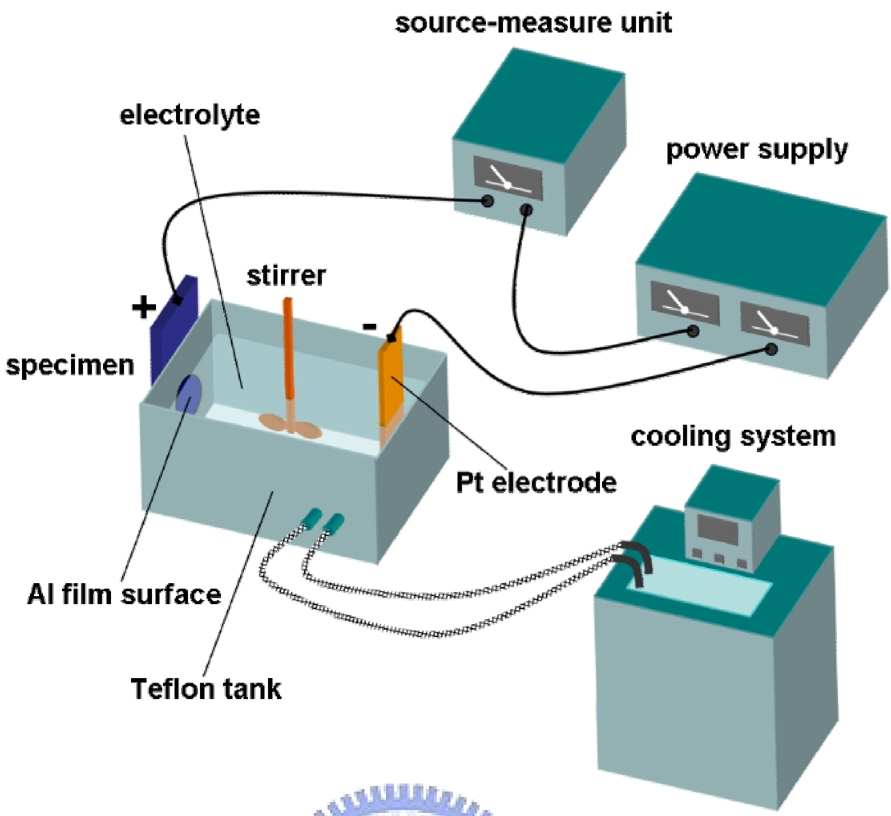

Figure 3-2 Schematic diagram of experimental setup for the aluminum electropolishing and anodization.

chamber was 5×10^{-7} Torr. The TiN layer was deposited by dc magnetron sputtering at 300 °C using a titanium target (99.9999%) in a mixed nitrogen and argon atmosphere (N_2:Ar = 3:50) under a working pressure of 1×10^{-3} Torr. The sputtering voltage was 345 V and the sputtering current was 0.55 A. The deposition rate was about 1.7 nm/min.

3.3 Electrochemical processes

Figure 3-2 shows the schematic diagram of experimental setup for the aluminum electropolishing and anodization. The experiments were carried out in a Teflon tank. The anode was the aluminum film specimen and a platinum foil was used as the cathode. Because edges of the aluminum film undergoing stronger electric field have a faster reaction rate than center, only a part of the film was exposed to the electrolyte through an open circle with an area of about 1.3 cm^2 on the tank, and there was an O-ring clipped between the specimen and the tank fixed by a jig. The electrolyte for the aluminum electropolishing was a mixed solution of 25 vol.% perchloric acid ($HClO_4$) and 75 vol.% ethanol (C_2H_5OH). A constant polarization voltage of 40 V was applied to force the electropolishing reaction. The electrolytes for the aluminum anodization were

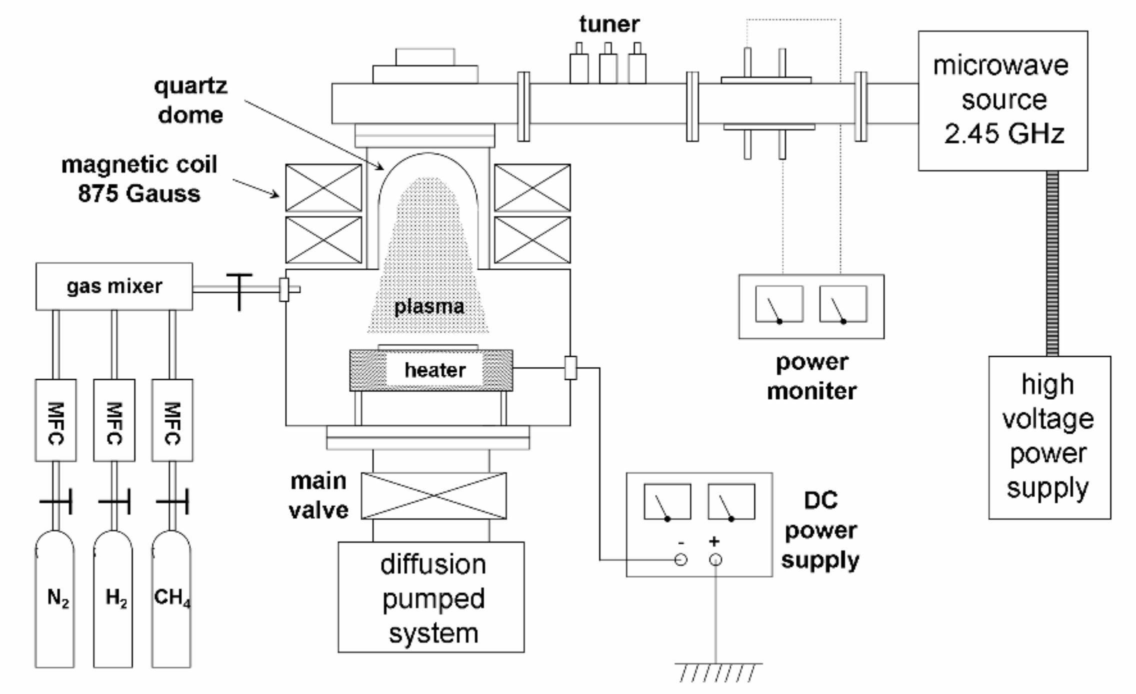

Figure 3-3 Schematic diagram of the microwave plasma ECR-CVD system for CNT growth.

0.3 M oxalic acid ($H_2C_2O_4$), 0.6 M sulfuric acid (H_2SO_4), and 1.2 M sulfuric acid for constant voltages of 40, 20, and 8 V, respectively. The electrolyte was violently stirred and maintained at a constant temperature of 21 ^{o}C by a cooling system. The anodic current was measured by a source-measure unit (Keithley Model 196).

3.4 Microwave plasma ECR-CVD system

The schematic diagram of the microwave plasma ECR-CVD system for the CNT growth is shown in Figure 3-3. Microwave power (2.45 GHz) was supplied to a plasma chamber through a quartz dome entrance window. A magnetic field of 875 Gauss for ECR plasma excitation was generated by the coils surrounding the resonance volume and was applied perpendicularly to the substrate surface. A negative dc bias was applied to the substrate holder. The plasma stream was introduced into the deposition chamber, which had previously been pumped down to a base pressure of about 10^{-6} Torr by a diffusion pump system. The catalyst pretreatment conditions were: microwave power 700 W, -150 V substrate bias, working pressure 2×10^{-3} Torr, sample temperature 600 ^{o}C, H_2 flow rate = 20 sccm, and treatment time 15 min. The gas mixture of CH_4 and H_2 was used as carbon source for CNT growth. The total gas flow rate was kept at 22 sccm. The other CNT growth conditions were: microwave power 700 W, -150 V substrate bias, working pressure 2×10^{-3} Torr, deposition temperature 600 ^{o}C, and growth time 7-30 min.

ECR is the coupling of microwave energy at the natural resonance frequency of an electron gas in the presence of a static magnetic field. It is well known that the microwave plasma ECR-CVD system takes the advantages of high dissociation percentage of precursor gases, high uniformity of plasma energy distribution, and large deposition area (lager than 13 inch^2 in our system). The ECR plasma can be characterized by the magnetic field (B_{m}) and electric field (E). The electrons in the plasma are accelerated by electric field to the direction perpendicular to magnetic field, and orbited in a plane perpendicular to magnetic field and with a cyclotron radius (r_{c}). If the microwave angular frequency (ω) is the same as the angular frequency of the orbit, the electrons will be in phase with the field at both $+E$ and $-E$. This phenomenon is known as ECR. Resonance occurs when the electron cyclotron frequency equals to the microwave frequency ($\omega = B_{\mathrm{m}}e/m_{\mathrm{e}}$, where m_{e} is mass of electron and e is the electron charge). Therefore, at the common microwave frequency of 2.45 GHz, resonance occurs at the B_{m} = 875 Gauss. The cyclotron radius for electrons orbiting in a magnetic field can be expressed by $r_{\mathrm{c}} = m_{\mathrm{e}}V_{\mathrm{e}}/eB_{\mathrm{m}}$, where V_{e} is electron velocity component perpendicular to B_{m}. The spiral motion confines the electrons to the gases, resulting in fewer diffusion losses to the wall at low pressures. As a result, the electrons can acquire high energy before experiencing a collision. Operation at low pressure allows efficient coupling of energy to the electrons so that ion/neutral collision are of sufficient energy to induce ionization. ECR effect is reduced at higher pressures because increasing collision frequency prevents electrons from achieving high energies.

3.5 Material analysis methods

(a) AFM:

AFM measures inter-atomic interactions between a scanning probe tip and the specimen surface. It can generate topographic images for the specimen surface in atomic scale. In addition, due to its superior vertical and horizontal resolution, AFM are very good for roughness measurement. In this study, in order to illustrate the ability of the electropolishing process, AFM was employed to scan a 5×5 μm^2 area of the aluminum film surface. AFM analyses were performed by a Digital Instruments

NanoScope Ⅱ system with the contact mode using the silicon nitride (Si_3N_4) tips.

(b) SEM, TEM, and EELS:

SEM is a very useful tool for observing surface morphology of specimen. SEM has secondary electrons or backscattered electrons detectors passing the signal to computer and forming image. TEM image is the result of electron transmitting through the specimen. TEM reveals the interior microstructure of the specimen, and it can give the high-resolution lattice image and the electron diffraction pattern as well. In this study, the morphology and microstructure of the AAO films, CNTs, and nanodots were all characterized by a field-emission SEM (FE-SEM) (Hitachi S-4000) operating at 25 kV accelerating voltage and a TEM (JEOL JEM-2010F) operating at 200 kV accelerating voltage. Cross-sectional specimens for the TEM analysis were prepared by mechanical polishing and subsequent argon ion milling. Moreover, EELS (Gatan GIF 2000) analyses were also performed in the TEM system to identify the chemical composition and chemical bonding of the specimens.

(c) AES:

AES analysis technique employs an electron beam (2-30 keV) irradiating the specimen surface to excite Auger electrons which possess specific energy. Through assaying the kinetics energy of the Auger electrons by an electron energy analyzer, one can get to know the element composition and chemical state of the specimen. Because the incident electrons with low-energies (1-3 keV) have very short inelastic mean free paths (5-20 Å) inside the solid phase materials, AES technique is usually used to obtain the information within 50 Å away from the surface (surface analysis). In this study, AES was employed to investigate the bonding structure of the carbon nanostructures and to study the atomic composition of the nanodots as a function of the time of argon ion sputtering (depth profiling). The AES analyses were performed using a VG Microlab 310F Auger system with a Schottky field emission electron source.

(d) Raman spectroscopy:

Raman scattering was discovered by Raman in 1928. If an incident photon occurs inelastic scatter with specimen molecules and causes the energy change of the photon called Raman scattering. By this mechanism, one can measure the difference between incident and scattering light by a spectrometer to obtain the information of element and bonding structure of the specimen. In particular, Raman spectroscopy is useful in identifying carbon-based materials. There are two obvious bands located at about 1330 cm^{-1} (*D* band) and 1590 cm^{-1} (*G* band) which correlate with the vibration of sp^3-bonded and sp^2-bonded carbon atoms, respectively. In order to study the structural characterization of the CNT samples, a Jobin Yvon LABRAM HR Micro-Raman system with a He-Ne laser (wavelength: 632.8 nm) was utilized in the experiments.

(e) XPS:

Surface analysis by XPS involves irradiating a solid in vacuum with mono-energetic soft X-rays and analyzing the emitted electrons by energy. The spectrum is obtained as a plot of the number of detected electrons per energy interval versus their kinetic energy. Quantitative data can be obtained from peak height or peak areas, and identification of chemical states often can be made from exact measurement of peak positions and separations. In this study, XPS was employed to analysis the chemical state of the titanium oxide nanodots. XPS analyses were performed on a ULVAC-PHI 1600 ESCA system with Al-*Kα* (1486.6 eV) excitation. X-ray emission energy was 400 W with 15 kV accelerating voltage. Argon ion with ion energy of 5 keV was used for sputter profiling.

(f) XRD:

In this study, the crystal structure of the as-deposited Al/TiN bilayer films and the annealed nanodots was identified by XRD (Philips X'Pert Pro). The Cu-*Kα* line at 0.1541 nm was used as the source for diffraction. The diffraction angle and the associated peak intensity are the unique characteristic of crystalline materials. Therefore, by using the XRD method, various crystal structure information of the specimen can be determined. XRD θ-2θ scan and rocking curve were utilized to investigate the preferred orientation and crystal quality of the specimens, respectively.

3.6 Field emission measurement

Figure 3-4 shows the instrument setup and the test configuration used during field emission characterization. The measurements were conducted by the simple diode configuration and carried out in a high vacuum chamber pumped down to a pressure of about 10^{-6} Torr with a turbo molecular pump, backed up by a rotary mechanical pump.

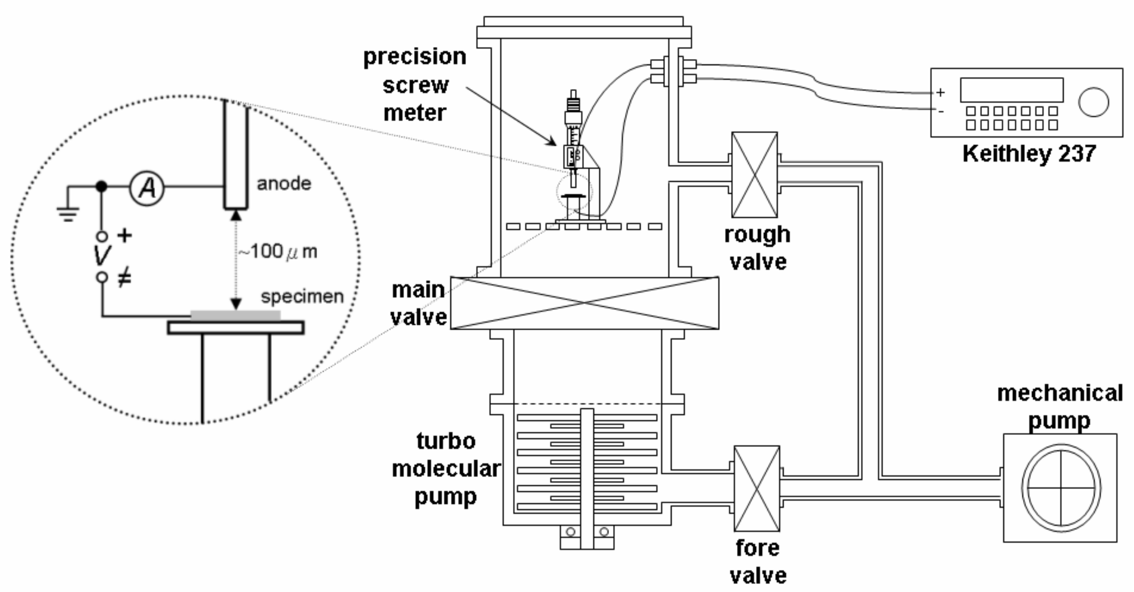

Figure 3-4 Schematic diagram of the field emission measurement setup.

A steel probe with a diameter of 1.8 mm as anode was used for the measurement. The distance between the specimen and anode was about 100 μm controlled by a precision screw meter, and effective field emission area of the specimen was 0.025 cm^2. The specimen (cathode) was biased with a voltage swept positively from 0 to 1000 V at room temperature to extract electrons from emitters. A high voltage source-measure unit (Keithley 237) was used for providing the sweeping electric field (E) and monitoring the emission current density (J). The measurement instruments are auto-controlled by the computer. Prior to the field emission measurement, a high constant voltage of about 600 V was applied to the emitters to exhaust the adsorbed molecules.