Chapter 3 Experimental Methods

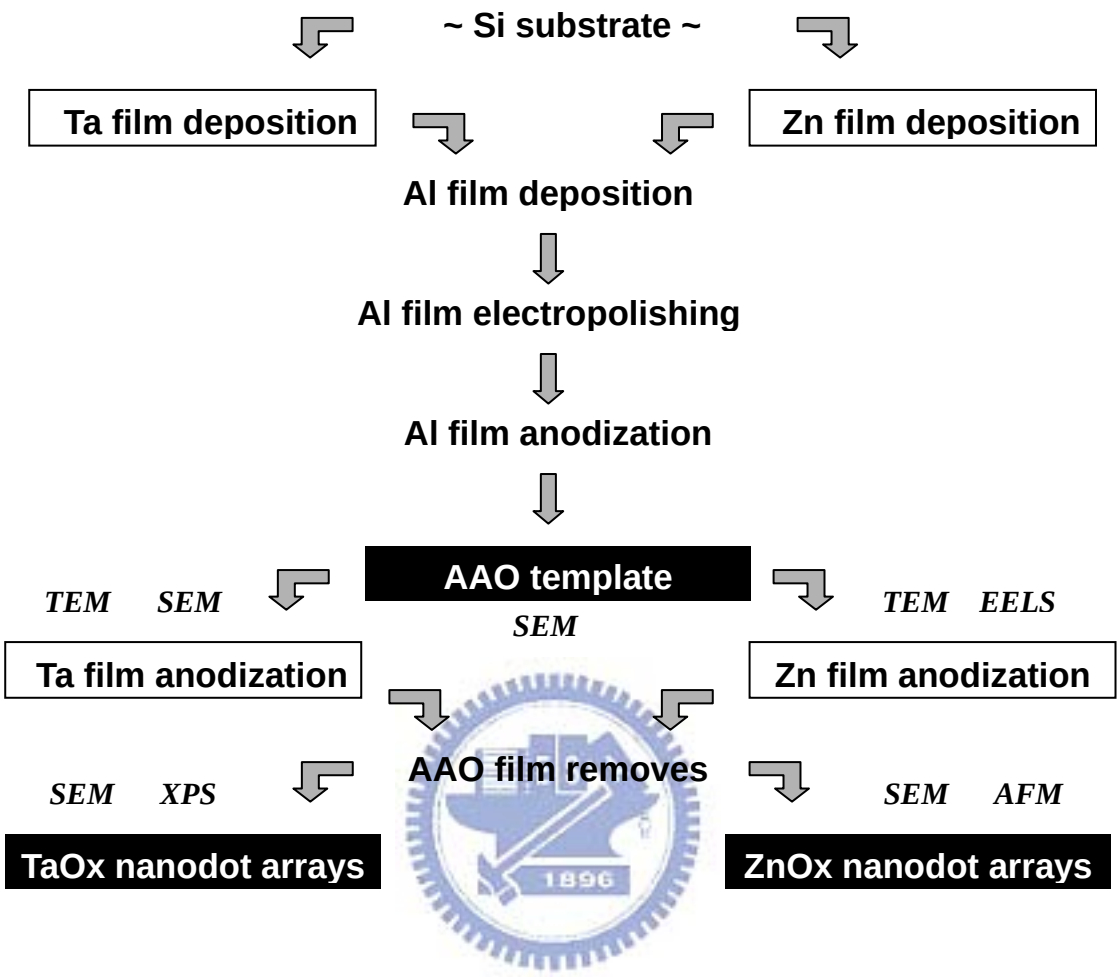

Figure 3-1 Experimental flowchart for the fabrications and analyses of metal oxide nanodot arrays.

Figure 3-1 shows experimental flowchart for the fabrications and analyses of metal oxide nanodot arrays. The AAO templates were prepared by the two-step anodization of the aluminum films. The metal oxide nanodot arrays were prepared by the anodization of the Al/Ta and Ai/Zn bilayer films. The microstructure of the AAO templates was studies by scanning electron microscopy (SEM). The microstructure, bonding structure, chemical composition, and crystallinity of metal oxide nanodots were investigated by SEM, atomic force microscopy (AFM), transition electron microscopy (TEM), electron energy loss spectroscopy (EELS) and X-ray

photoelectron spectroscopy (XPS). Figure 3-2 shows the schematic diagram of fabrication of metal oxide nanodot arrays.

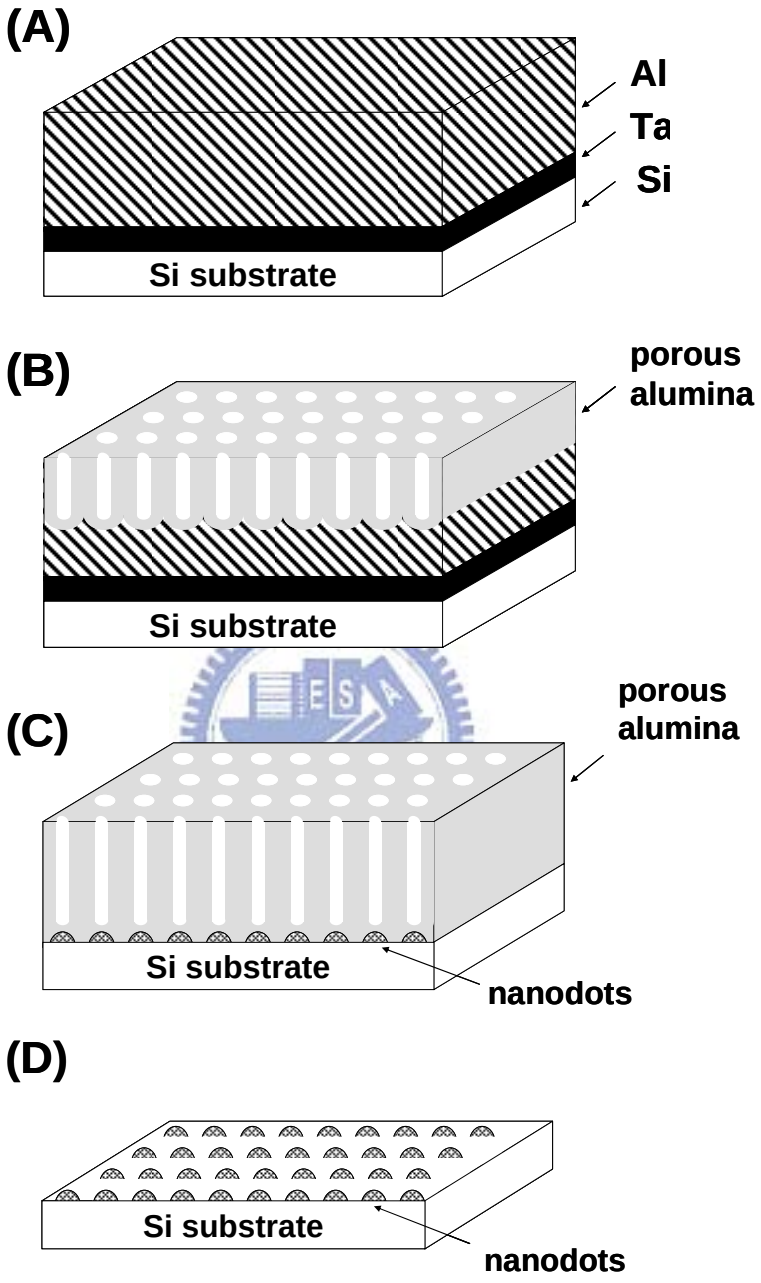

Figure 3-2 Schematic diagram of fabrication of the tantalum oxide nanodot arrays: (A) prestructured sample, (B) first anodic oxidation step, (C) second anodic oxidation step and metal oxide nanodot arrays formation, and (D) metal oxide nanodot arrays after removing alumina film.

3.1 Films Deposition

The tantalum films for the tantalum oxide nanodots production were deposited on a cleaned 6 inches (100) *n*-silicon wafer by ultrahigh vacuum dc sputtering system (ULVAC SBH-3308) with a base pressure of 5×10^{-9} Torr. The Ta target used was 99.9999% pure. The Ta films were prepared at argon gas. The Zn films for the zinc oxide nanodots production were deposited on a cleaned 6 inches (100) *n*-silicon wafer by a thermal evaporation system (ULVAC CRTM-6000) with a base pressure of 2×10^{-6} Torr. The zinc target used was 99.999% pure. Subsequently, an aluminum films was deposited onto the Ta (Zn) films by a thermal evaporation system (ULVAC CRTM-6000) with a base pressure of 2×10^{-6} Torr. to form Ta/Al (Zn/Al) bilayer sample. Tungsten boats were used in melting and evaporating the aluminum and zinc ingots. The tungsten boats were cleaned in a mixed solution of 20 vol.% hydrogen fluoride (HF) and 80 vol.% nitric acid (HNO_3). The sample was annealing at 400^{o}C in a vacuum furnace with H_2/N_2 purge for 4 hr to recrystallize. The wafer was then cut into piece of 3×3 cm^2 and electropolished in a mixed solution of 10 vol.-% H_3PO_4 and 10 vol.-% H_2SO_4 with constant current 0.15 ampere.

3.2 Electrochemical Process

Figure 3-2 shows the schematic diagram of experimental setup for the aluminum electropolishing and anodization. A specially designed one-electrode cylindrical cell double layer glass cup was used which can let cooling water flow through. The anode was the aluminum film specimen and a graphite flake 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 1.5 cm^2 on the cylinder, and there was an O-ring clipped between the specimen and the tank fixed by a jig. GW laboratory power

supply (model GPC-3060D) was used as the anodizing source. Table 3-1 shows conditions for the preparation of metal oxide nanodot arrays. Anodization was carried out in 1.8M sulfuric acid (under 5, 10, 15, 20, 25 and 30 constant polarization voltages), 0.3M oxalic acid (under 10, 20, 30, 40, 50 and 60 constant polarization voltages) and 5wt-% phosphoric acid (under 100 constant polarization voltages). During all anodizing process, the temperature of the electrolytes was at 3^{o}C and stirred adequately. When the anodization was nearly complete, here was a distinct color change in sample surface and decreasing in the current. Then the alumina film was removed in 5wt-% phosphoric acid solution in room temperature.

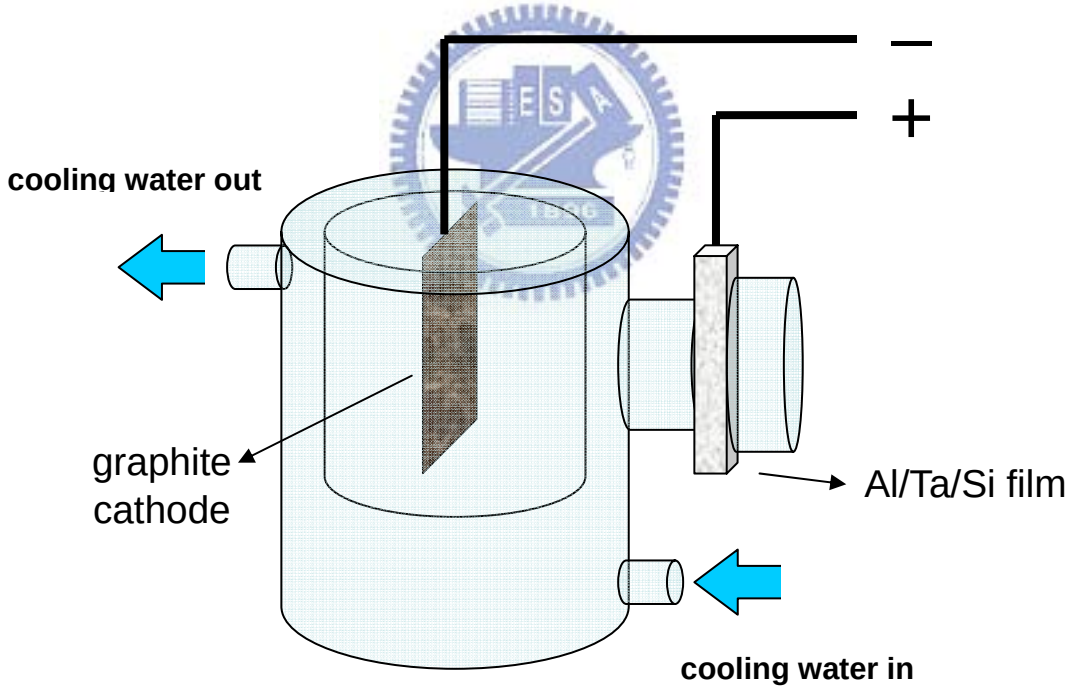

Figure 3-2 The schematic diagram of experimental setup for the aluminum electropolishing and anodization.

Table 3-1 Anodization conditions for the preparation of metal oxide nanodot arrays.

Sample	Voltage	Electrolyte	Concentration	Metal Film
A	5 V	H_2SO_4	1.8 M	Ta
B	10 V	H_2SO_4	1.8 M	Ta
C	15 V	H_2SO_4	1.8 M	Ta
D	20V	H_2SO_4	1.8 M	Ta
E	25 V	H_2SO_4	1.8 M	Ta
F	30 V	H_2SO_4	1.8 M	Ta
G	10 V	$C_2H_2O_4$	0.3 M	Ta
H	20 V	$C_2H_2O_4$	0.3 M	Ta
I	30 V	$C_2H_2O_4$	0.3 M	Ta
J	40 V	$C_2H_2O_4$	0.3 M	Ta
K	50 V	$C_2H_2O_4$	0.3 M	Ta
L	60 V	$C_2H_2O_4$	0.3 M	Ta
M	100 V	H_3PO_4	0.5 M	Ta
N	40 V	$C_2H_2O_4$	0.3 M	Zn

3.3 Specimen analysis

(A) SEM

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. In this study, the morphology and microstructure of the porous alumina films and nanodots were all characterized by a field-emission SEM (FE-SEM) (JEOL-6700) operating at 15 kV accelerating voltage.