Chapter 2 Experiment

2.1 The Fabrication of the Thin Films

2.1.1 The Sol-Gel Method

2.1.1.1 Introduction to Sol-Gel Method

Sol-gel method is one of the promising processes to prepared high quality thin films at relative low temperatures compared to other depositions. The first step to form the gels in the sol-gel process is hydrolysis. In the step of hydrolysis, a hydroxyl attached to the metal atoms as in the following reaction:

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \qquad (2\text{-}1)$$

The R and ROH represented a ligand and an alcohol. The second step of sol-gel process is polymerization which was achieved by two partially hydrolyzed molecules linked together, such as

$$M(OR)_n + M(OR)_{n-1}(OH) \rightarrow M_2O(OR)_{2n-2} + H_2O \qquad (2\text{-}2)$$

Thus a huge chain molecule could be obtained from the reaction of hydrolysis and polymerization mentioned above. Since the coating ability and preferential direction of thin films depend on the molecules, the reaction of solution plays an important role in the preparation of thin films. In organic systems, the solute is usually the metal alkoxide, such as $M(OR)_n$ which R is an alkyl (CH_3, C_2H_5, …, etc.).

As a result of the sol-gel solution still maintains liquid phase before gelation, it is easy to coat thin films on various substrates. There are three coating methods, such as dip coating, spray coating, and spin coating. The properties of the thin films were influenced by the coating conditions for each of the coating method.

Among all of the coating approaches, spin coating is the easiest way to obtain uniform thin films. There are four procedures of spin coating: deposition, spin on, spin off, and evaporation. Firstly, the solution is dripped on the substrates, and then the solution drifts outward by the centrifugal forces, and the excess solution is spun out of the substrates. Finally, the formation of the thin films is achieved by the evaporation of the solvent. The quality of the thin films is influenced by several coating conditions of spin coating, including the cleanliness of the substrates, the chemical properties of the solution (viscosity, stability, and volatile rate), the speed and time of spin, and the adhesion between the solution and substrates. The most significant disadvantage of spin coating method is that it is unsuitable for small and asymmetric substrates.

In general, there are many advantages of the conventional sol-gel method. The processing temperature of sol-gel method is relatively lower, and this could avoid the diffusion between all materials. Furthermore, the cost and maintenance of the facilities of the sol-gel are much lower than that of vacuum techniques such as sputtering or chemical vapor deposition.

Besides the lower processing temperature, the expense of sol-gel method is quite low. In addition, the precursor solution prepared by sol-gel method could be purified by crystallization and distillation methods; thereby the high purity thin films could be obtained.

2.1.1.2 Synthesis of the Precursors

Mixtures of zinc acetate 2-hydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], magnesium chloride anhydrous [$MgCl_2$], and zirconium isopropoxide {$Zr[(CH_3)_2CHO]_2$}, used as the sol-gel precursor, were dissolved in 2-methoxyethanol and monoethanolamine (MEA) and stirred at 60°C for 30 min to form the sol-gel solution. The total concentration of the metal ions was maintained at 0.75 moles per liter. The $Zn_{(1-x)}M_xO$ (M = Mg, Zr) films were deposited on substrates by dip coating in the solution three times. The coated films were then dried at 400°C for 30 min and annealed at 500°C realizing a thickness of 0.1 μm. The flow chart of the precursor preparation is shown in Figure 2-1.

2.1.2 The Radio Frequency (rf) Sputtering System

In our study, several electrodes (including metal and oxide electrodes) and high-k dielectric thin films were prepared by radio frequency (rf) magnetron sputtering system. Figure 2-2 shows the photography of the rf magnetron sputtering system. The sputtering system is composed of several segments:

(1) Sputtering chamber: including the targets, sputter gun, shutter;
(2) Vacuum pump system: including a mechanical pump and a cyro pump for low and high vacuum, respectively.
(3) Gas supply, mass flow control, and flow meter: offering the precise gas flow ratio;
(4) Gauge meter: involving low and high vacuum meter and heater controller and detector;
(5) Power supply system: consists of a rf power generator and a rf power matching box;
(6) Substrate holder and halogen lamp heater: the holder was designed for 3 and 4 inch wafers and the heater provides a maximum deposition temperature of 500°C.

Table 2-1 summarizes the specification of the rf magnetron sputtering system. The base pressure of the vacuum system is maintained below 5×10^{-6} torr. There are two US guns tilted 30° toward the center of the substrate, one is the 2-inch and the other is 3-inch. The substrate holder, which is designed for 3 and 4-inch wafers, is rotated by the dc rotary motor and heated by four lamps. The deposition temperature is sensed by a *k*-type thermal couple. The rf power supply operated at a frequency of 13.56 MHz and tuned by an automatic matching network box to obtain the minimum reflection power.

2.2 The Fabrication of the Thin Film Transistors

The thin film transistors were fabricated by the following sequence of processes. The metal chromium was deposited by sputtering on the glass substrate as a bottom gate electrode. Silicon dioxide served as the gate insulator with a thickness of 3000 Å by using plasma-enhanced chemical vapor deposition (PECVD). The source and drain electrodes were made up of indium-tin oxide (ITO) and channel width and length were 500 μm and 50 μm, respectively. Finally, the $Zn_{(1-x)}M_xO$ (M = Mg, Zr) thin films were deposited by spin coating with the same processing parameters mentioned above. The process flow of the thin film transistors is shown in Figure 2-3.

2.3 Analysis of Material Characteristics

2.3.1 X-ray Diffraction (XRD)

The crystallization of the thin films was examined by a Siemens D5000 Diffractometer with Cu Kα radiation. The operation voltage and current were 30 kV and 40 mA. The θ-2θ measurement provides crystal diffraction information such as the crystallization, structure, and the orientation of the thin films.

2.3.2 Scanning Electron Microscope (SEM)

The surface morphologies and thickness of the thin films were observed by a SEM (Hitachi S-4700). The electron energy is 2 keV.

2.3.3 Atomic Force Microscopy (AFM)

The roughness and surface morphologies of the thin films were characterized by an AFM (Digital Instruments Nanoscope III). The scan area in our study ranged from 1 × 1 μm to 3 × 3 μm.

2.3.4 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES)

The stoichiometry of the thin films was determined by the ICP-AES (Perkin Elmer Optima 3000 DV).

2.3.5 X-ray photoelectron spectroscopy (XPS)

The XPS was taken to investigate the binding energy between each element of the thin films. By absorbing a photon, an atom gains an energy amount equal to hν. It then releases an electron to regain its original stable energy state. The released electron retains all the energy from the striking photon. It can then escape from the atom, and even further from matter and kinetic energy keeps it moving. With XPS, incident photons usually carry an energy ranging from 1 to 2 keV.

2.4 Analysis of Electrical properties

2.4.1 Current-Voltage (*I-V*) Measurements

Figure 2-4 shows the block diagram of current-voltage (*I-V*) measurement system, which consisted of the probe station, the semiconductor parameter analyzer (HP 4156A), the remote computer, and the heater controller. This *I-V* measurement is used to characterize the metal-insulator-metal (MIM) structure and the performance of the thin film transistors. Since this system equips with heater controller, it could measure the *I-V* behaviors at various temperatures ranged from RT to 300°C.

2.4.2 Capacitance-Voltage (*C-V*) Measurements

Figure 2-4 also shows the block diagram of capacitance-voltage (*C-V*) measurement system, including the instrument of HP 4284. Besides HP 4284, this system also contains Keithley 590 *C-V* Analyzer, a 595 *C-V* Quasi Meter, and a 230 Voltage Source. The *C-V* measurement could also perform at RT to 300°C.

The entire experimental flow chart by using various analyses is shown in Figure 2-5.

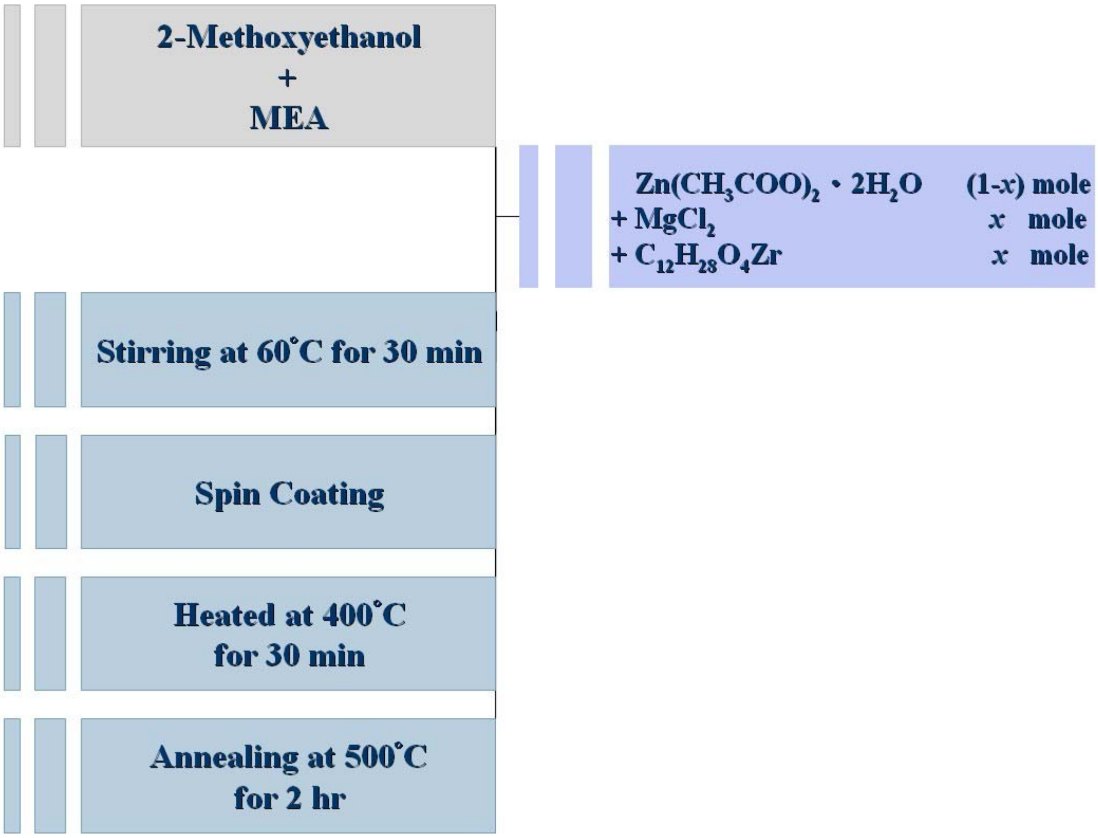


Figure 2-1 Flow chart of the sol-gel precursor preparation.

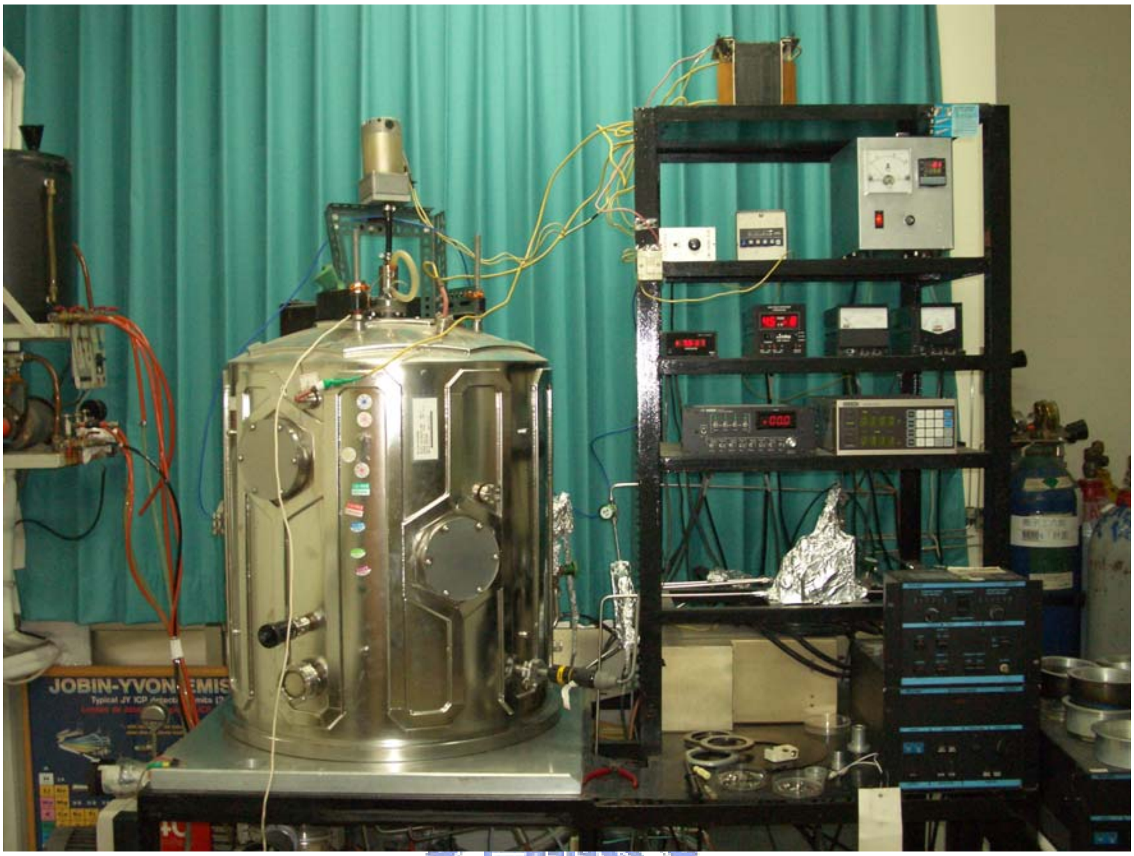
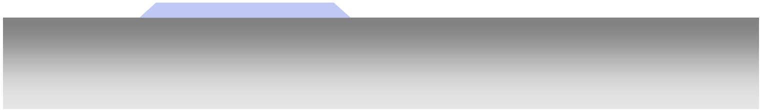
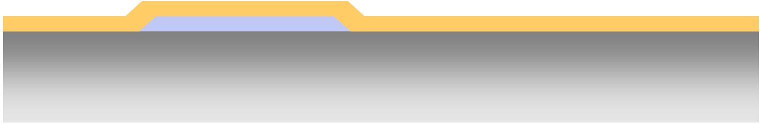


Figure 2-2 Photography of the rf magnetron sputtering system.

(a) Cr deposition and patterning as

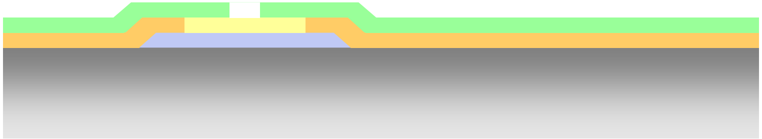


(b) SiO_2 deposition



(c) Contact hole patterning

(d) ITO deposition and patterning



(e) $Zn_{(1-x)}M_xO$ deposition and annealing

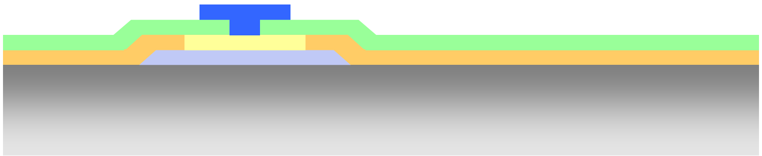


Figure 2-3 Process flow of the thin film transistors.

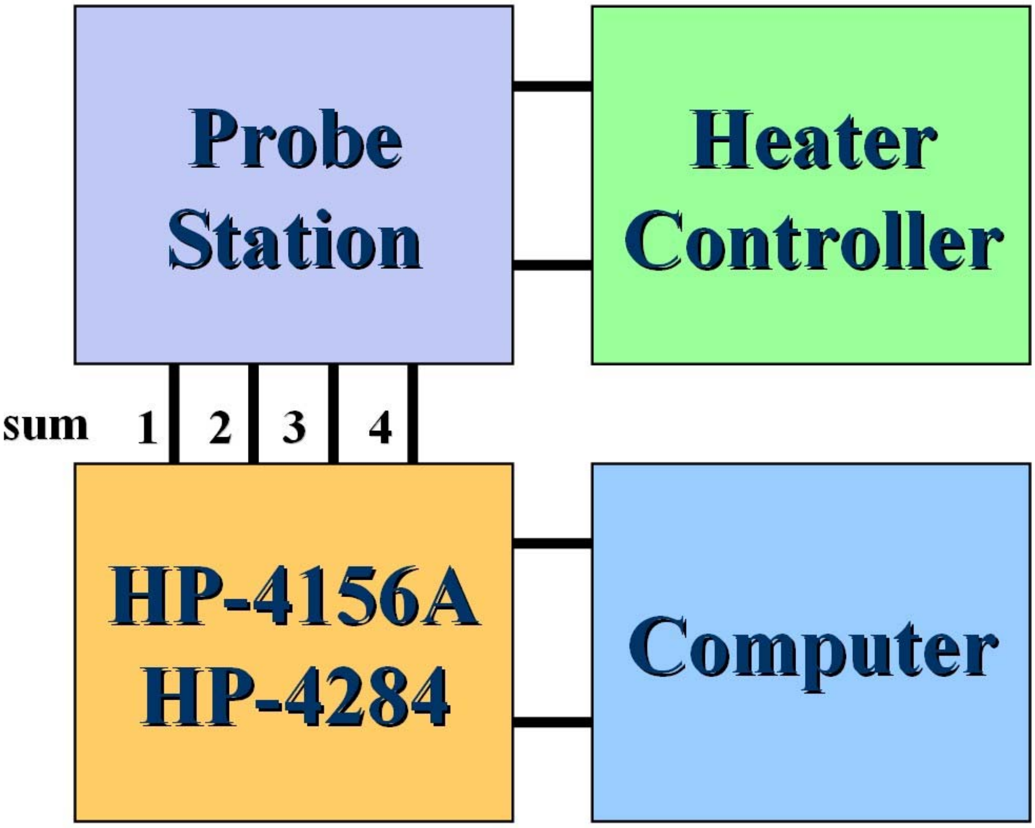


Figure 2-4 Block diagram of current-voltage (*I*-*V*) and capacitance-voltage (*C*-*V*) measurement.

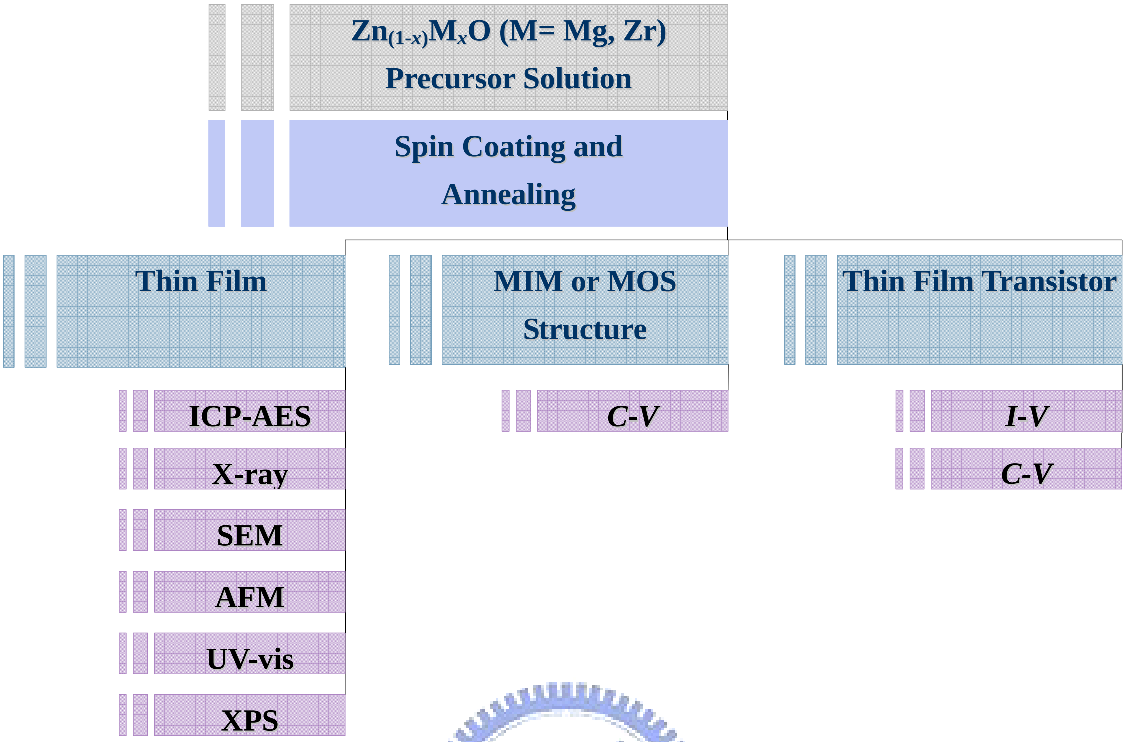


Figure 2-5 Experimental flow charts by using various analyses.

Table 2-1 Specifications of rf magnetron sputtering system.

Components	**Specifications**
Chamber size	100 cm of diameter and 120 cm of height
Pump	Mechanical pump and cryo-pump for low and high vacuum, respectively
Base pressure	$< 5 \times 10^{-6}$ torr
Power	rf power generator (rf plasma prodicts Inc., model: RF 5S)
Mass flow controller	4 channel mass flow controllers (MKS, type 1259C, argon: 50 sccm and O_2: 10 sccm)
Sputter gun	2 or 3-inch US gun
Substrate holder	Available for 3 or 4-inch wafers
Heater	Four halogen lamps heaters up to 500°C