

CHAPTER III EXPERIMENTAL

3.1 Materials

Due to the sensitivity of reactions and products to moisture and air, all glassware used for these experiments was dried in hot air oven at 110°C over night. Starting reagents and solvents were dried prior to use, and reactions were carried out in an inert atmosphere, nitrogen gas.

-Acetonitrile (CH_3CN) and Methanol (CH_3OH)

They were used as precipitating agents, They were purchased from Labscan Company Limited and purified by distillation over calcium hydride and magnesium activated with iodine, respectively.

-Fused Silicon Dioxide or HI-SIL 927 Silica (SiO_2)

The silica with a surface area of 182 m^2/g was donated by PPG Siam Silica Co., Ltd. It was dried in hot air oven until a constant weight was obtained before used at 110°C and kept in desiccator.

-Ethylene Glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, EG)

EG was purchased from Labscan Company Limited. It was distilled in fractional distillation set and used as both reactant and solvent in the synthesis reaction.

-Pentamethylene Glycol ($\text{HO}(\text{CH}_2)_5\text{OH}$, PG)

It was procured from Aldrich Chemical Co.Inc. and kept in desiccator to avoid humidity. It was used as received.

-2-Chloroethylmethyldichlorosilane [$(\text{Cl})_2\text{Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{Cl})$]

It was purchased from Fluka Company Limited. This chemical reagent was extremely sensitive to moisture and thus always kept under N_2 atmosphere in desiccator to prevent reaction between moisture and this reagent.

-Sodium Hydroxide (NaOH)

NaOH was bought from AKZO Nobel Co.,Ltd. and kept in desiccator containing silica gel. It was used as received.

-Triethylenetetramine ($\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)\text{H}$, TETA)

This reagent was used as a base catalyst and purchased from Farsai Chemical Company Limited. It was distilled under vacuum prior to use.

3.2 Equipment

3.2.1 UV Exposure Source

265 nm wavelength of UV source was H44GS-100 Sylvania Par 38 mercury lamp. It was equipped inside the black acrylic sterilizing box, and

set 2 inch height away from the sample box. The whole system was kept under N₂ to control experimental environment.

3.2.2 Mass Spectroscopy (MS)

Mass spectra (MS) were obtained using a VG Autospec Model 7070E from Fison Instrument with VG data system. Samples were run using the electron impact mode (EI⁺- MS) and PFK was used as calibration peaks. The mass range was set from $m/z = 20$ to 2000.

3.2.3 Thermal Analysis (TA)

Thermograms were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) mode. They were carried out on a Du Pont instrument, DSC 910s and TGA 2950, respectively. Hermetically sealed aluminum pans were used in the DSC, while platinum pans were used in the TGA. Sample sizes were typically 5-25 mg, and experiments were carried out in N₂. For TGA measurements, the purge flow rates for N₂ were set at 60 ml/min and O₂ were 40 ml/min. The temperature analysis range in the TGA was from 100° to 900°C, with a heating ramp rate of 10°C/min, while DSC measurements were conducted from 20° to 500°C at a heating rate of 10°C/min

3.2.4 Nuclear Magnetic Resonance (NMR)

¹H-NMR and ¹³C-NMR spectra were performed on a Bruker 400 MHz spectrometer at room temperature. The samples were pulsed at 400 MHz for ¹H-NMR with spin rate of 21 rpm. A relaxation delay time was 1 sec with a sweep width of 3105 Hz, using a pulse of 45 μsec. Deuterated dimethyl

sulfoxide (DMSO-d₆) was used as standard solvent. 16 scans were run for ¹H-NMR, while ¹³C-NMR samples were more than 400 scans. Tetramethylsilane (TMS) was used as the reference for chemical shift measurements in both proton and carbon NMR.

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained on a Equinox 55 Bruker instrument. For the solid samples, they were prepared by mixing with dried KBr at an approximate ratio of 1:5 sample:KBr, while the liquid samples were prepared by wiping on the ZnSe pellet. The solid samples were therefore characterized by using KBr as reference background, and the liquid samples using ZnSe as a reference background. The moisture in the chamber was controlled using silica gel. The resolution for this method was ± 4 cm.

3.2.6 Thickness Meter

Thickness meter used for thickness measurement was obtained from a thickness meter (Peacock PDP-12N type SIS 6). The samples were measured as prepared after exposure process. The units of sample measurement were reported in micron scale.

3.3 Procedure

3.3.1 Cleaning Process of SiO₂ Wafer

3.3.1.1 *Removing Metal Scrap on Wafer Surface*

Concentrated HNO_3 was heated up to 90°C using hot plate. After that the SiO_2 wafer was dipped into the heated HNO_3 solution for 10 minutes, and washed with water until HNO_3 solution was completely removed from the surface of SiO_2 wafer. The SiO_2 wafer was then dried on hot plate and kept in a desiccator to control moisture.

3.3.1.2 Cleaning Hydrophobic Chemicals on Wafer Surface

Boiled trichloroethylene was prepared by using hot plate to 80°C , followed by dipping SiO_2 wafer into this solution for 10 minutes. Continuously, the SiO_2 wafer was washed by acetone at room temperature. The same wafer was dipped into water to remove any reagents from the surface, dried on hot plate, and kept in a desiccator. A pair of twizzer was used to handle throughout the process.

3.3.1.3 Oxidizing Surface of SiO_2 Wafer

50:50 % V/V. of hydrogen peroxide mixed with sulfuric acid solution was quickly heated to 100°C SiO_2 wafer was then dipped into this solution to oxidized the surface. The oxidization would go on till no bubble occurs on the surface, which would take about 30 to 60 minutes. After oxidizing process, the oxidizing agent was removed from the wafer surface by washing with water, and then the wafers were dried in an oven at 60°C . The wafer was brought to produce pattern immediately without touching the wafer surface.

3.3.2 EG Spirosilicate Photoresist

3.3.2.1 Synthesis and Characterization of EG Spirosilicate Monomer

Synthesis of EG spiro-silicate monomer was carried out by adding 15.00 g (250 mmol) of SiO₂, 18.28 g (125 mmol) of TETA, 0.4 g (4 % of SiO₂) of NaOH and 150 ml of excess EG into a 250 ml three-necked reaction flask equipped with a simple distillation set. The reaction mixture was mechanically stirred and heated at the boiling point of EG (about 200 °C) to distill off ethylene glycol and by-product water produced during reaction. The reaction mixture turned clear after 6 hours of heating, and at this point the mixture was also clear when it was cooled down to room temperature, meaning that the reaction was completed. Synthesized 5 ml. solution was precipitated in 2.5% of dried MeOH in dried CH₃CN.

3.3.2.2 Crosslinking of EG Spirosilicate Monomer

Synthesized 2 ml. of EG spiro-silicate monomer obtained was added onto the petridish which the crosslinking reaction was then took place in a vacuum oven. The vacuo temperature was varied from 80° to 110°C to obtain the suitable temperature.

After obtaining the suitable temperature, EG spiro-silicate was coated on the surface of SiO₂ wafer by laminating method. Four wafers were put into a vacuum oven, at the set temperature. The crosslinking conditions of EG spiro-silicate monomer were varied by firstly varying the crosslinking time from 3 to 12 hours with taking each wafer sample out every 3 hours. Finally, all samples were characterized the ability of crosslinking by FTIR, DSC and TGA techniques.

3.3.2.3 Pattern Process of EG Spirosilicate on SiO₂ Wafer

The cleaned wafer coated with EG spiro-silicate monomer, and exposed by UV radiation under N₂ atmosphere for variation of exposure time range from half to 2 hours. Then the sample was kept in desiccator avoiding moisture for further etching process.

3.3.3 PG Spirosilicate Photoresist

3.3.3.1 Synthesis and Characterization of PG Spirosilicate Monomer

Synthesis of PG spiro-silicate monomer was started by using 15.00 g (250 mmol) of SiO₂, 18.28 g (125 mmol) of TETA, 0.4 g (4 % of SiO₂) of NaOH and 150 ml of excess PG into a 250 ml three-necked reaction flask equipped with a simple distillation set. The reaction mixture was mechanically stirred and heated at boiling point of PG (240°C) to distill off pentamethylene glycol and by-product water produced during reaction. The reaction mixture turned clear when the reaction was allowed to heat for 6 hours, and at this point the mixture was also clear when it was cooled down to room temperature, meaning that the reaction was completed. Some part of the product mixture was precipitated in dried CH₃CN.

3.3.3.2 Pattern Process of PG Spirosilicate on SiO₂ Wafer

Cleaned SiO₂ was used as substrate for laminating with PG spiro-silicate monomer. The laminated wafer with PG spiro-silicate

monomer was separated into two steps of exposure variation as with and without covered photomask. For without covered photomask, the exposure time was varied from half to 2 hours, whereas the covered photomask process the exposure time was varied from 1 to 4 hours. Then the samples were kept in desiccator for further etching process.

3.3.3.3 Etching Process of PG Spirosilicate Photoresist

With covered photomask, exposed films of PG spirosilicate were etched to remove uncrosslinked part on silicon wafer by dipping into 66% concentration of acetic acid in solution for 15-20 minutes. Then sample wafers were measured for thickness and characterized the part left on SiO₂ wafer.

3.3.4 2-Chloroethylmethyldichlorosilane photoresist

3.3.4.1 Pattern Process of 2-Chloroethylmethyldichlorosilane on SiO₂ Substrate

In the step of coating 2-chloroethylmethyl-dichlorosilane monomer on SiO₂ wafer, it was separated into 2 categories as with and without using spincoater before UV exposure.

For without using spincoater process, 2-chloroethylmethyldichlorosilane monomer was coated on SiO₂ wafer surface by laminating method. Immediately, the wafer coated with monomer was exposed to UV radiation under N₂ atmosphere by varying exposure time from 3 to 6 hours.

As for the second case that used spincoater to control smoothness of the monomer film, the suitable condition was firstly varied the speed of spinning from 200 to 500 rpm. After each speed condition, the SiO₂ substrate coated with 2-chloroethylmethyldichlorosilane monomer was immediately covered by photomask and exposed UV radiation by varying exposure time from 3 to 5 hours.

After exposed UV radiation, the SiO₂ substrate was kept into desiccator to avoid moisture and dust for further identification by FTIR, TGA and MS.

3.3.4.2 Etching Process of 2-Chloroethylmethyldichlorosilane on SiO₂ Substrate

Crosslinked 2-chloroethylmethyldichlorosilane on SiO₂ wafers both with and without using spincoater were patterned via developing process. In this process, many chemicals were tested to select the suitable etching solvent and they also were varied etching temperature to find the suitable condition. Then the suitable condition was verified for the suitable etching time. Both with and without using spincoater, wafer samples after developing process were further measured thickness.

3.3.4.3 Effect of Photomask on Pattern of 2-Chloroethylmethyldichlorosilane Photoresist

Many types of photomask were investigated the effect of heat transfer by varying metal types of photomask. From the lowest to the highest thermal conductivity, they were stainless steel, tin, chromium and aluminum photomasks, respectively. All of the constructed photomasks were used in the same process of photoresist that closely covered without any gap

on the surface of polymer film obtained from pre-baking. After developing process, different patterns were resulted, as described in the results and discussion.