Chapter Three

Experimental procedure

3.1 Slide pre-treatment

In order to enhance the adhesion of the thin film, first, commercially available glass slides were cut into one inch squire pieces, then were pretreated to remove possible contaminants and to form a silicon dioxide layer or OH groups on the surface of substrate. Glass slides were soaked in ultra sonic cleaner containing de-ionized water for 4 hours, dried at 60 °C for about 2 hours. After that, samples were soaked in butanol for 15 hours (over night). Finally, the substrates were taken from the butanol container, and further dried at 60 °C for 4 hours.

3.2 Chemicals Reagents

The chemicals used for this project were tetraethoxysilane (TEOS, $C_4H_{16}O_4Si_4$), ethanol (EtOH, C_2H_6O), and malonic acid ($C_3H_4O_4$) obtained from Fluka. Acetic acid was (CH_3COOH) obtained from R&M chemical, maleic acid ($C_5H_5O_4$) and butanol [$CH_3(CH_2)_3OH$] were obtained from Merck. The propionic acid (C_2H_5COOH) was obtained from Hopkin & William Ltd.

3.3 Instruments

3.3.1 Spin coater

Several methods can be used to make sol-gel coatings with the sol-gel process. Spin coating and dip coating are two basic techniques used to deposit sol-gel coatings. Spin coating produces a one-sided coating, while dip coating yields a double-sided coating. Both techniques are used in manufacturing to make different coatings and thin films. Spin coating is used for many applications where relatively flat substrates or objects are coated with thin layers of material. For example, several cathode ray tube (CRT) manufacturers use the spin coating method to make anti-glare or anti-reflection coatings. In spin coating, the material to be made into coating is dissolved or dispersed into a solvent, and this coating solution is then deposited onto the surface and spun off to leave a uniform layer for subsequent processing stages and ultimate use. In this project, portable spin coater manufactured by Ika is used for general applications.

There are three key stages in spin coating:

Stage 1: The deposition of the coating fluid onto the substrate

Stage 2: Aggressive fluid expulsion from the substrate surface by the rotational motion

Stage 3: Gradual fluid thinning

3.3.2 Atomic Force Microscope (AFM)

AFM is a powerful technique used to study the morphology of surfaces on the nanometre scale. It usually requires no sample preparation, does not require a vacuum and can give quantitative information. There are several statistical methods of quantifying the surface texture, the most widely used is the average surface roughness (Ra) but there are others, which may be better for particular applications. The two most commonly used modes of operation are contact mode AFM and Tapping Mode AFM, which are conducted in air or liquid environments. Contact mode AFM consists of scanning the probe across a sample surface while monitoring the change in cantilever deflection with the split photodiode detector. In this project used Contact mode AFM (C-AFM).

The AFM is also used in the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The AFM can be used to investigate a variety of materials, which include thin and thick film coatings, ceramics, composites, glass, synthetic and biological membranes, metals, polymers and semiconductors. The AFM may be used to image surfaces at atomic resolution as well as to measure forces at nano Newton scale. With the AFM, it is further possible to study the friction behaviour of composites by applying very low normal forces to the tip within a range from μN down to nN (in contact mode), during scanning the surface topography with a quantitative determination. The image processing software attached to the AFM presents the results in the form of a colored friction contrast and topography.

The advantages of AFM are:

- Quantitative surface roughness measurements
- Can image any solid surface
- Measurement of physical forces
- Compared to scanning electron microscopy (SEM), the AFM provides accurate topographic contrast, direct height measurements and no coating necessary.

Compared with transmission electron microscopy (TEM), AFM images are obtained without expensive sample preparation and yield far more complete information that the TEM profiles available from cross-sectioning samples. In C-AFM the tip makes physical contact with the sample. As the tip is moved across the sample, the contact force causes the cantilever to bend according to changes in topography.

3.3.3 Scanning Electron Microscope (SEM)

If damage such as cracks or fractures occurs in sol-gel synthesis materials, it is important to know which kind of fracture occurred, fatigue or static-overload. These investigations can be carried out in a SEM. Fracture-surface-investigations with a scanning-electron-microscope (microfractography) give information about the nature of the fracture, the direction of applied force, the direction of fracture propagation, and about environmental attacks such as temperature, radiation, or chemicals.

The advantages are:

One of the key advantages of the SEM with respect to other types of microscopy is its large depth of field. This ability makes it possible to image very rough surfaces with millimeters of vertical information within a single image. The depth of field and small beam size makes it possible to image the fibers far below the top layer. This ability also makes it possible to measure very rough surfaces over larger lateral areas as well. Although the AFM can measure vertical surface variations below 0.5 Å, its ability to measure a tall structure comes from how far the scanner can move vertically. Standard scanners typically have 5 to 6 μm of vertical range, however, in some configurations the vertical range approaches 10 μm or larger. For scanning areas that have heights of greater than 5 to 10 μm of variation, the SEM would be better suited for the analysis.

3.3.4 Thermogravimetric Analyzer (TGA)

Thermogravimetric Analyzer (TGA) measures the weight change of a test sample as the temperature rises. Points along the temperature curve which indicate rapid weight loss are useful in determining at what points along the firing curve time must be allowed to assure safe completion of these reactions. The temperatures at which the reactions occur are also indicators of the compositions involved. Changes in sample weight may be due to oxidation, decomposition, reduction, volatilization, sublimation, and reactions within the sample.

TGA modules are available in temperature ranges from room temperature to 1,700 °C, and in a variety of balance sensitivities from 100 microgram to 0.1 microgram. Atmosphere conditions range from ambient to vacuum and inert to reative. Most modules are configured for digital output and analysis.

TGA measures mass flow into or out of a sample (weight change). Kinetic processes, such as cure and thermal stability, and material composition may be investigated by this technique. Examples include the monitoring of the heating of solder fluxes, and their decomposition. The characterization of moisture release from a sample as a function of temperature and time is often illuminating.

Differential Thermal Analysis (DTA) is a "fingerprinting" technique that detects heat release or heat absorption caused by the chemical and physical changes which occur within the material during heating and cooling. The point along the temperature curve at which the reaction takes place can predict which reaction took place, and the magnitude of deviation of the curve can give an idea of the relative size of the reaction. Changes in the sample which result in a release of heat (exotherm) or absorption of heat (endotherm) may be caused by such detectable phenomena as decomposition, oxidation crystalline phase change, glass transition, curie point, sintering, melting, and other chemical reactions. Both qualitative and quantitative data may be generated. DTA Modules are available in temperature ranges from 170 °C to 1,700 °C, are designed for various atmospheres (ambient air, light vacuum to 1,500 psi, and non-corrosive gasses), and can be configured for either digital or analog output and analysis.

TGA measures the amount and rate of change of sample mass as a function of temperature or time in an inert or reactive environment. This versatile instrument can be used to characterize the thermal and oxidative stability of organic and inorganic materials, the extent and kinetics of gas-solid reactions, the composition of multicomponent systems, moisture and volatiles content, and decomposition kinetics.

The TGA contains a quartz lined sample chamber with a purge gas side arm allowing tests to be conducted in an inert or reactive environment at temperatures up to 1200 °C. During operation, a sample is placed on a balance arm that is maintained in a horizontal reference position by an optically activated servo loop. An LED light source is focused through an aperture slit to strike two vertically mounted photodiodes. When the balance arm is in the reference position, the light strikes both photodiodes equally. As sample mass is gained or lost, the arm becomes unbalanced, causing light to strike the diodes unequally. The unbalanced voltage output from the photodiodes produces a current flow that acts as a restoring force on the balance arm, returning it to the reference position. The magnitude of this restoring current is directly proportional to the change in sample mass.

3.4 Preparation of sol-gel solutions

The precursor selected for the sol-gel is tetraethoxysilane (TEOS). The alcohol selected for the sol-gel solution is ethyl alcohol. The selected acid catalysts for this project are:

1. Acetic acid,
2. Propionic acid,
3. Malonic acid,
4. And maleic acid.

Except propionic acid, the acids available in the laboratory are in solid form obtained from different chemical companies as mentioned earlier. Thus, I prepared acid solution in different molarities. For acetic acid 6 mol dm^{-3}, 8 mol dm^{-3}, 10 mol dm^{-3}, and 12 mol dm^{-3} solutions were prepared. For both malonic and maleic acid 0.7 mol dm^{-3}, 1 mol dm^{-3}, 1.72 mol dm^{-3}, and 2.58 mol dm^{-3} solutions were prepared. In the case of propionic acid the concentration is kept constant that is 12.70 mol dm^{-3}, but varied in volume such as 2.00 ml, 1.50 ml, and 1.00 ml. In the various sol preparation, the ratio of precursor TEOS, alcohol EtOH, and acid catalyst by volume are as mentioned in the following tables.

Table 1:The components ratio of various acetic acid sol-gel solutions

No	Molarity	Volume of TEOS	Volume of EtOH	Volume Acid
1	6 M	2 ml	0.5 ml	4 ml
2	8 M	2 ml	0.5 ml	4 ml
3	10 M	2 ml	0.5 ml	4 ml
4	12 M	2 ml	0.5 ml	4 ml

Table 2: The component ratio of various malonic and maleic acid sol-gel solutions

No	Molarity	Volume of TEOS	Volume of EtOH	Volume Acid
1	0.70 M	2 ml	0.5 ml	1 ml
2	1.00 M	2 ml	0.5 ml	1 ml
3	1.72 M	2 ml	0.5 ml	1 ml
4	2.58 M	2 ml	0.5 ml	1 ml

Table 3: The component ratio of various propionic acid sol-gel solutions

No	Volume of TEOS	Volume of EtOH	Volume Acid
1	2 ml	0.5 ml	1.00 ml
2	2 ml	0.5 ml	1.50 ml
3	2 ml	0.5 ml	2.00 ml
4	2 ml	0.5 ml	2.50 ml

3.4.1 Methodology for sol preparation

All the sol-gel preparation conducted as above-mentioned tables that is for example, in preparing acetic acid sol the ratio between the TEOS: EtOH: acetic acid is 2.0 ml: 0.50 ml: 4.0 ml respectively. The same ratio in volume is applied for all acetic acid, (12 mol dm^{-3}, 10 mol dm^{-3}, 8 mol dm^{-3}, and 6 mol dm^{-3}) sol preparation. The working procedure is firstly, pippetted out 2.0 ml of TEOS, transferred it into a test tube, then add 0.5 ml of EtOH, stirred it on a mini-shaker of IKa at 1100 rpm for 1 minute in order to homogenize the solution. Subsequently add 4.0 ml of acid of interest (e.g.12 mol dm^{-3}), then further stirred it for 15 minutes. Then the test tube is sealed nicely and left it in intact for 18 hours for aging. The same working procedure applied for all acid sol preparation according to volume ratio as described above tables 1-3.

3.5 Spin coating

The most common methods of applying a thin film coating of sol-gel glass on to substrate are spin coating and dip coating. Both involve coating the substrates with a well-mixed sol and then allowing the sol to polymerize, dry, and sinter on the surface of the substrate. Spin coating is the method used in this experiment for applying a layer of TEOS-based sol onto the substrates. The Spin coating process involves simply spreading the sol onto the substrate and then spinning it. The thickness of the subsequent coating depends on the chemistry of the sol, the properties of the substrate, and environmental factors.

3.5.1. Developing thin films

As soon as the aging period of sol, 18 hours is over, it is the time for developing thin films. The sol spread properly on treated substrate, and waits exactly 90 second of time in order to stabilize the sol on surface. As soon as 90 second is over, run the spin coater exactly for 30 second. Next, the thin film was labeled and sealed in a petry-dish, leaves it for 48 hours in order to polymerization. The next step is drying and sintering the thin films.

3.5.2 Drying and sintering

The already prepared substrates were heated at different temperature as 75 °C, 120 °C, 250 °C, and 300 °C. The temperature rate of heating is set 0.1 °C per minute. The constant duration time between the segments is set at 2 hour 30 minutes. Successful drying leaves the interconnected metal oxide structure intact while replacing the interstitial liquid phase with air: as a result, the sample is prepared for the sintering process. During sintering, the sample is brought to high enough temperature to collapse its skeleton like structure into a higher density vitreous state. The required sintering temperature for full densification is considerably less than the temperature required for making similar glass by fusion. The primary disadvantage with the sol-gel technique is the cracking that is likely to occur during the gel drying stage. Evaporation of the interstitial liquid phase from the gel generates large stresses that often induce cracking, but drying is a necessary step for the gel to vitrify.

3.5.3 The effect of temperature

In order to evaluate the effect of temperature regarding to the thin film thickness gained, monolith of two samples were investigated with Thermo gravimetric analyzer (TGA) at the laboratory of Mettler Toledo (M) Sdn Bhd. The results of the thermograms are attached the following pages. The Thermogravimetry is a technique for the measurement of mass change as a function of temperature. The TGA results reveal that the temperature affects the mass weight of TEOS. The weight loss is directly proportional to the temperature that is at the higher temperature the weight loss is high. Therefore, the higher the sintering temperature, the lesser the thickness of thin films gained. The evidence is clearly seen from the following table. In the table, the comparison between 2 and 1, when the temperature increased 50 °C, the thickness of thin film reduces about 48 nm; likewise between sample 4 and 3, it also reduces about 42 nm. This effect of temperature with regarding to the thin film thickness as illustrated in table 5 and 6 in chapter four (result and discussion). It is clear that at higher temperature the thickness gained is less than lower temperature.

Table 4: The temperature effect on thin film thickness

No	Thin films	Sintered at	Thickness gained
1	12 M acetic acid catalyzed thin film	300 °C	235.85 nm
2	12 M acetic acid catalyzed thin film	250 °C	283.61 nm
3	2.0 ml propionic acid catalyzed thin	300 °C	192.91 nm
4	2.0 ml propionic acid catalyzed thin	250 °C	234.56 nm

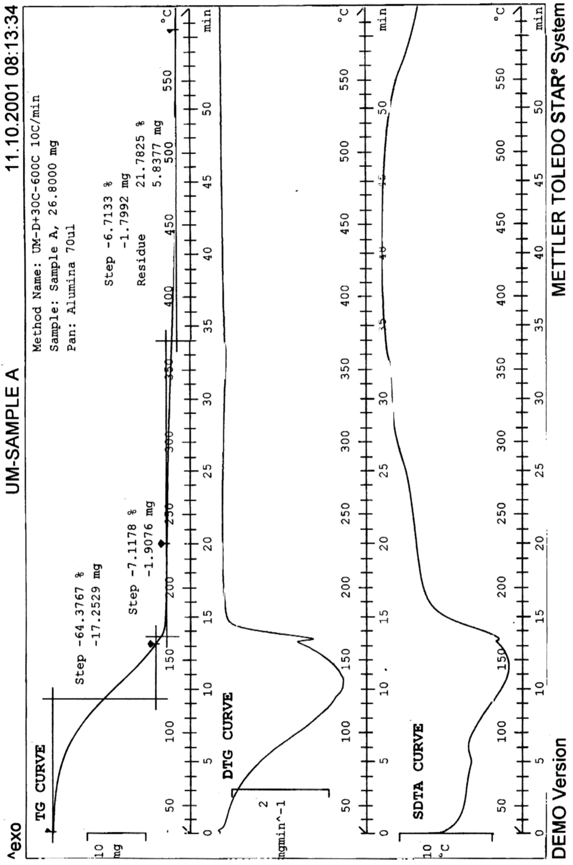

Figure 2: The thermogram of Sample A (TEOS + EtOH + Acetic acid)

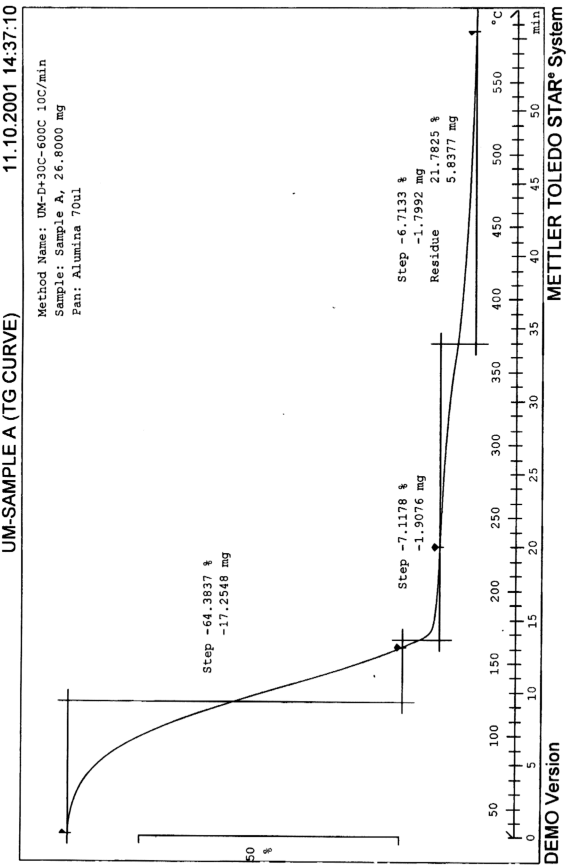

Figure 3: TG curve showing mass reduce of sample A (TEOS+ EtOH + acetic acid) due to heat

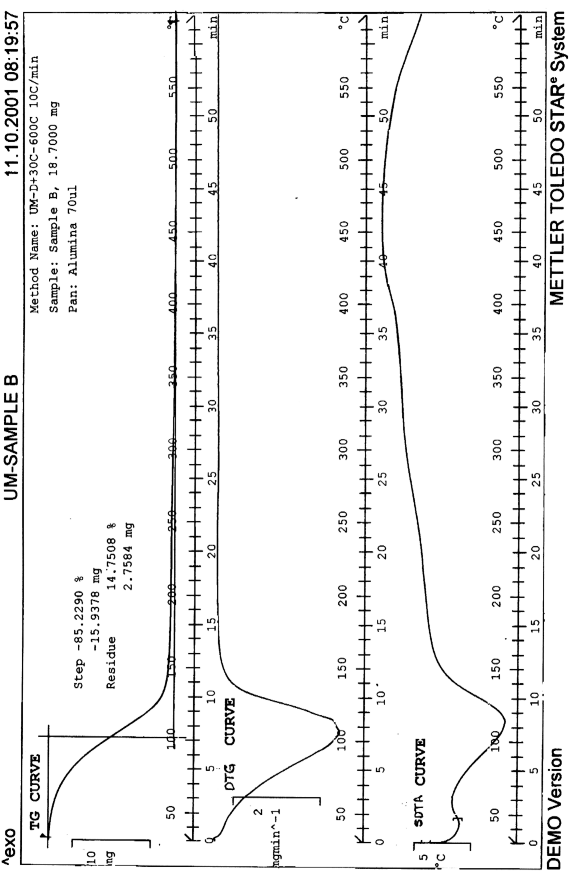

Figure 4: The thermogram of Sample B (TEOS + EtOH + Malonic acid)

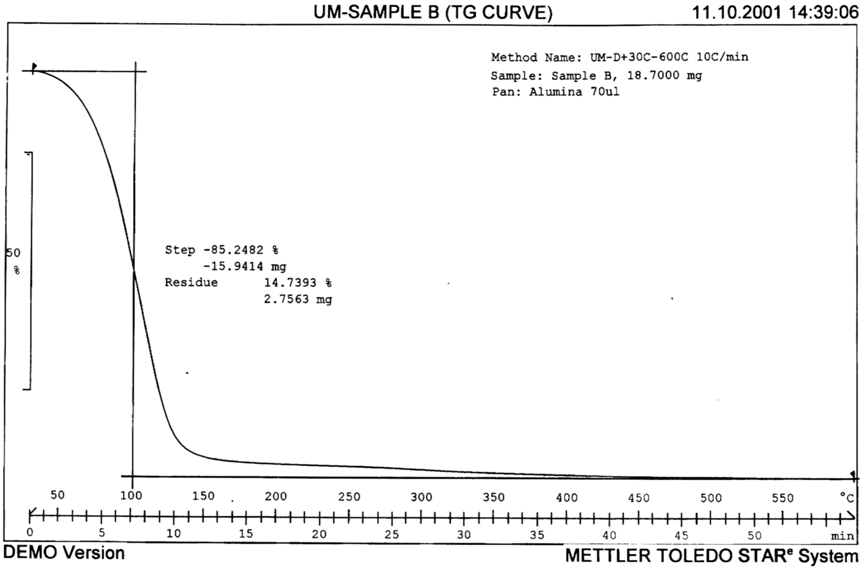

Figure 5: TG curve showing mass reduce of sample B (TEOS + EtOH + malonic acid) due to heat

3.6 Summarization of gel formation route

The monolayer thin film was synthesized by employing tetraethyl tetraethoxy silane (TEOS), ethanol, and acid catalysts (e.g. acetic acid, malonic acid, maleic acid, propionic acid). The processing of gel method via inorganic and organic acid catalyst as follows:

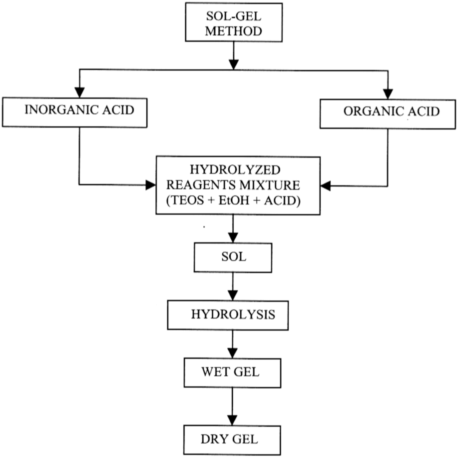

Figure 6: Schematic diagram of organic and inorganic acid catalyzed sol-gel method

3.7 Heat treatment schedule

$C_4H_{16}O_4Si_4$ + EtOH

↓

add acid catalyst (mixed thoroughly)

↓

spin coating

↓

air dried for 48 h

↓ 0.1 °C / min

up to 75 °C for 17.30 h

↓0.1 °C /min

up to 120 °C for 25 h

↓0.1 °C/min

up to 250 °C for 46 h

↓0.1 °C/min

up to 300 °C for 55 h

Figure 7: Schematic diagram showing heat treatment for silica thin films