Chapter four

Result and Discussion

In this project, four different weak acids namely acetic acid, propionic acid, malonic acid, maleic acid were used as catalyst. The precursor and organic solvent used in this project are tetraethoxysilane (TEOS) and ethanol (EtOH) respectively. Various sols are prepared by varying the concentration and volume of weak acid while the volume of TEOS and EtOH keep constant for all sol preparation. The composition of sols in volume described in table 1, 2, and 3. Thus, different acid catalysts were used to produce thin films through similar sintering process at different temperature has been studied. The surface morphology of thin films was investigated by employing AFM and SEM.

In this project the study of surface morphology of thin films that is finding surface cracking, the nature of sol distribution, thickness and roughness of films, were investigated by SEM, which is available at physics department, University of Malaya and contact mode AFM from digital instruments Ltd, which is available in Colloids and Surfaces research laboratory.

On most thin films, the SEM and AFM produce a similar representation of the sample surface. A common application of surface investigations of thin films consists of determining changes in morphology with variations of deposition parameters, such as temperature, pressure and time.

The three-dimensional nature of the AFM can be used to calculate changes in roughness and surface area variations due to differences in deposition parameters. SEM provides important information about the surface structure. The SEM produces image by raftering a finely focused electron beam over a sample's surface and using secondary electrons produced by the primary beam to modulate the intensity of a CRT display. The SEM microscope provides a tremendous improvement because of the far higher magnifications, resolution and depth of field that result from using and electron beam instead of a light beam. SEM micrographs can be taken at a magnification as high as 200,000X for many types of samples.

SEM is the only technique, which provides elemental analysis, however, both SEM and AFM are associated with techniques that can provide compositional information through analyzing materials and physical properties of the sample. Furthermore, by using two techniques, which are complementary, one technique will often compensate for the imaging artifact of the other technique. SEM and AFM are complementary techniques that provide a more complete representation of a surface when used together than if each were the only technique available. The results, which obtained through the SEM and AFM, are later described.

4.1 Acetic acid catalyzed sol coated thin films

Homogeneous and crack free acetic acid catalyzed coating were successfully deposited using spin coating technique. Figures 8, 10, 12, 14 and 16 represent the micrograph of the coating microstructure at magnification 20.00K obtained by SEM (model ISI SX-40, electron accelerating voltage 20 KV). Thin film is composed of 5 μm, 3 μm, 1 μm spheroid grains, which are uniformly distributed on the surface.

SEM inspection revealed that the formation of crack free films was strongly dependant on the composition of the sol. To get good coverage of the surface coating the solutions composition were to keep between 12 mol dm^{-3} and 10 mol dm^{-3} respectively as shown in figure 8, 10, and 12. Good surface coverage monolayer thin film was obtained using a solution of 10 mol dm^{-3} concentration as shown in figure 12. In the case of 8 mol dm^{-3} concentrated acetic acid catalyzed thin film surface, a slight scratch is found but homogenized surface formation is achieved as shown in figure 14. While in the case of 6 mol dm^{-3} concentrated acetic acid thin film not homogenized surface is formed as shown in figure 16.

The film thickness was also influenced by the solution concentration and was found to vary between 155.71 nm and 283.61 nm as according to AFM study. The average thickness and roughness of the thin films achieved is illustrated in table 5.

Table 5: The thickness and roughness of various acetic acid catalyzed thin films

No	Acid catalyzed thin films	Roughness	Thickness
1	12 M acetic acid catalyzed thin film sintered at 300 °C	1.579 nm	235.85 nm
2	12 M acetic acid catalyzed thin film sintered at 250 °C	1.293 nm	283.61 nm
3	10 M acetic acid catalyzed thin film.sintered at 250 °C	1.483 nm	250.51 nm
4	8 M acetic acid catalyzed thin film sintered at 250 °C	2.730 nm	228.00 nm
5	6 M acetic acid catalyzed thin film sintered at 250 °C	2.952 nm	155.71 nm

The smoothest and thickest thin film is achieved by 12 mol dm^{-3} acetic acid sol coating, sintering at 250 °C followed by 12 mol dm^{-3}sintering at 300 °C (in above table sample no 2 and 1) respectively. The second good thin film is 10 mol dm^{-3} acetic acid sol coating, sintering at 250 °C (sample no 3).

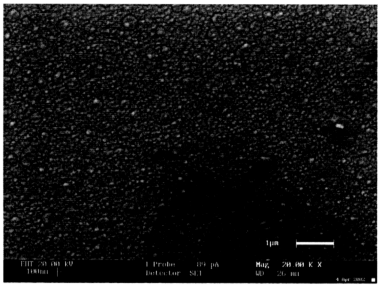

Fig 8: SEM micrograph of 12 mol dm^{-3} acetic acid catalyzed thin film after sintering at 300 °C

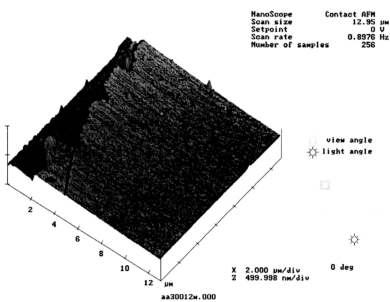

Fig 9: AFM micrograph image of 12 mol dm^{-3} acetic acid catalyzed thin film after sintering at 300 °C

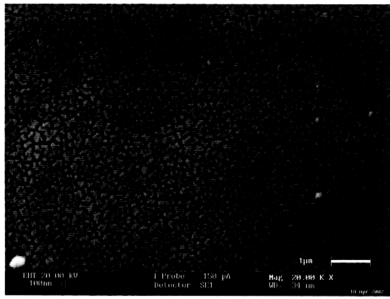

Fig 10: SEM micrograph of 12 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

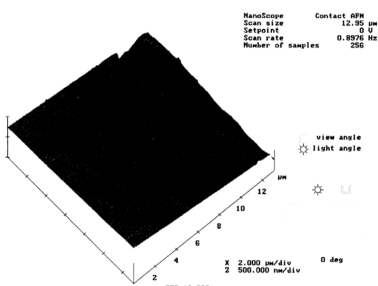

Fig 11: AFM micrograph image of 12 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

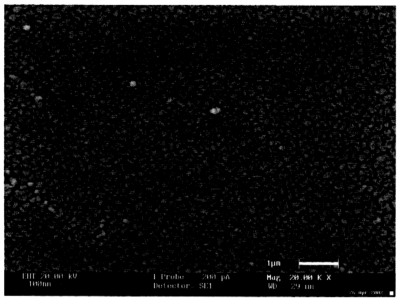

Fig 12: SEM micrograph of 10 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

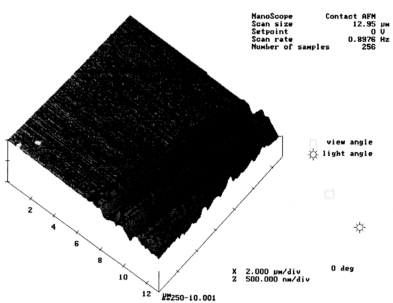

Fig 13: AFM micrograph image of 10 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

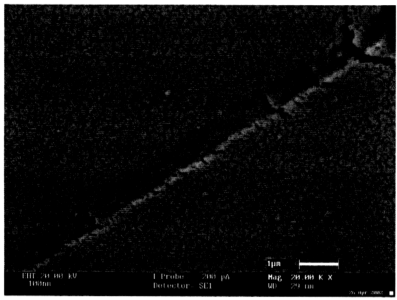

Fig 14: SEM micrograph of 8 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

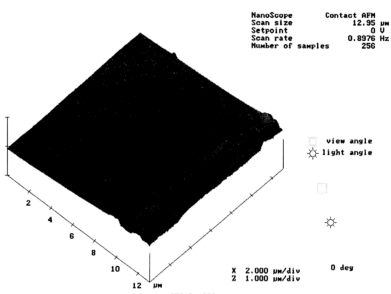

Fig 15: AFM micrograph image of 8 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

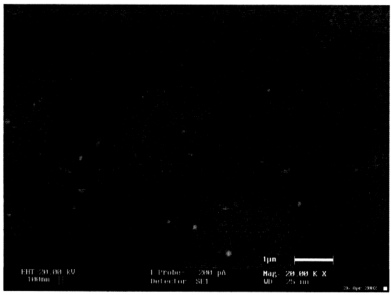

Fig 16: SEM micrograph of 6 mol dm^{-3} acetic acid catalyzed thin film sintering at 250 °C

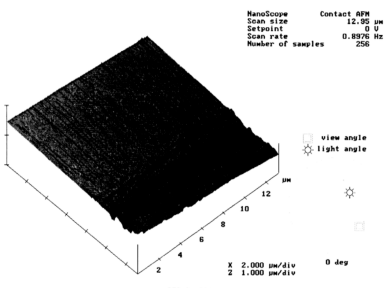

Fig 17: AFM micrograph image of 6 mol dm^{-3} acetic acid catalyzed thin film after sintering at 250 °C

4.2 Prop ionic acid catalyzed sol coated thin films

In the case of propionic acid catalyzed sol coating thin film development, homogeneous and crack free coating were also successfully deposited using spin coating technique. Thin film is composed of 5 μm, 3 μm, 1 μm spheroid grains, which are uniformly distributed on the surface.

According to SEM inspection revealed that the formation of crack free films was dependant on the composition of the sol and according to AFM study the film thickness was also influenced by the solution concentration and was found to vary between 175.66 nm and 250.46 nm. The average thickness and roughness of the thin films achieved is illustrated in table 6.

Table 6: the thickness and roughness of propionic acid catalyzed thin films

No	Propionic acid catalyzed thin films	Roughness	Thickness
1	2.0 ml propionic acid catalyzed thin film sintered at 300 °C	3.956 nm	192.91 nm
2	2.0 ml propionic acid catalyzed thin film sintered at 250 °C	3.560 nm	234.56 nm
3	1.0 ml propionic-acid catalyzed thin film sintered at 250 °C	5.668 nm	158.97 nm
4	2.0 ml propionic-acid catalyzed thin film sintered at 120 °C	3.477 nm	250.46 nm
5	1.5 ml propionic-acid catalyzed thin film sintered at 120 °C	2.419 nm	223.71 nm
6	1.0 ml propionic-acid catalyzed thin film sintered at 120 °C	5.598 nm	175.66 nm

In order to get good coverage of the surface coating, the solutions composition were to be kept between 2.00 ml and 1.50 ml of propionic acid respectively. Good surface coverage monolayer thin film was obtained using a solution of 2.00 ml of propionic acid containing sol, sintering at 250 °C as shown in figure 20.

The best thin films in this series are: 2.00 ml propionic acid thin film sintering at 120 °C followed by 2.00 ml sintering at 250 °C and 1.50 ml sintering at 120 °C (sample no 2, 4, and 5 in table 5) respectively and as illustrated in figures 20, 24, and 26.

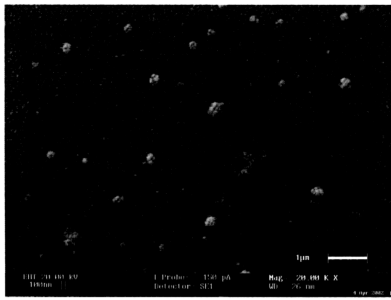

Fig 18: SEM micrograph of 2.0 ml propionic acid catalyzed thin film after sintering at 300 °C

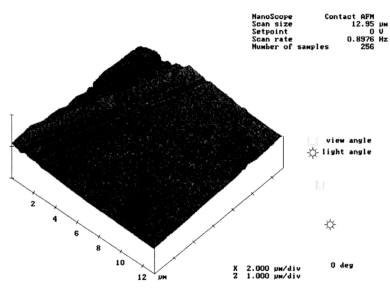

Fig 19: AFM micrograph image of 2.00 ml propionic acid catalyzed thin film after sintering at 300 °C

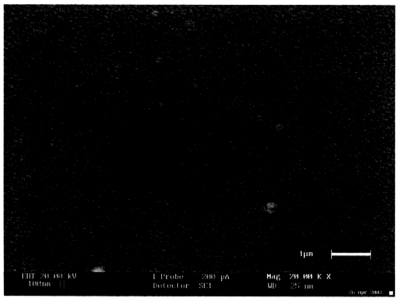

Fig 20: SEM micrograph of 2.0 ml propionic acid catalyzed thin film after sintering at 250 °C

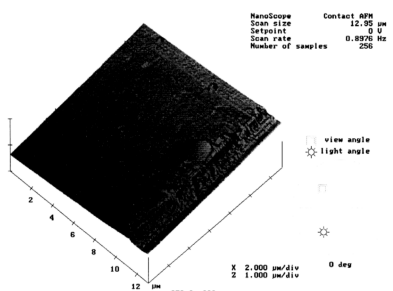

Fig 21: AFM micrograph image of 2.00 ml propionic acid catalyzed thin film after sintering at 250 °C

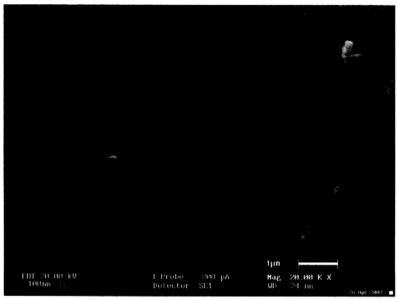

Fig 22: SEM micrograph of 1.00 ml propionic acid catalyzed thin film after sintering at 250 °C

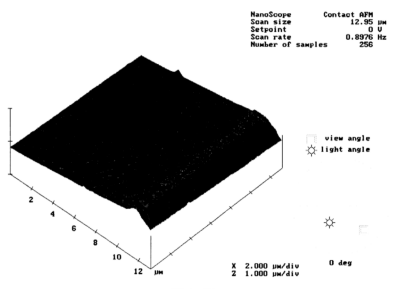

Fig 23: AFM micrograph image of 1.00 ml propionic acid catalyzed thin film after sintering at 250 °C

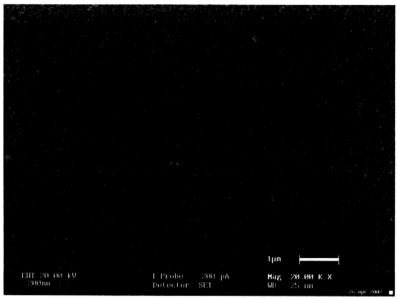

Fig 24: SEM micrograph of 2.0 ml propionic acid catalyzed thin film after sintering at 120 °C

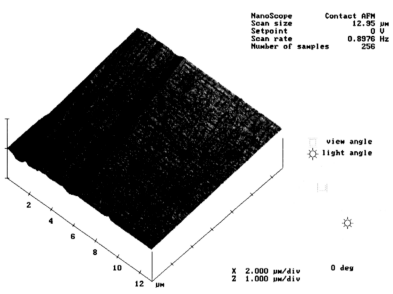

Fig 25: AFM micrograph image of 2.00 ml propionic acid catalyzed thin film after sintering at 120 °C

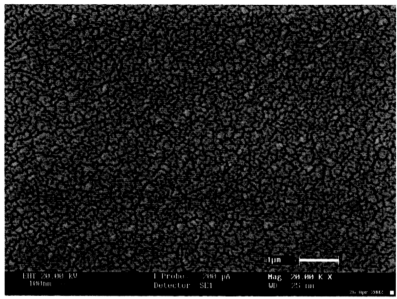

Fig 26: SEM micrograph of 1.5 ml propionic acid catalyzed thin film after sintering at 120 °C

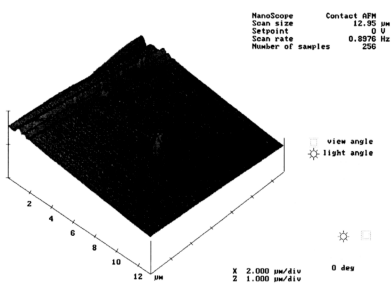

Fig 27: AFM micrograph image of 1.50 ml propionic acid catalyzed thin film after sintering at 120 °C

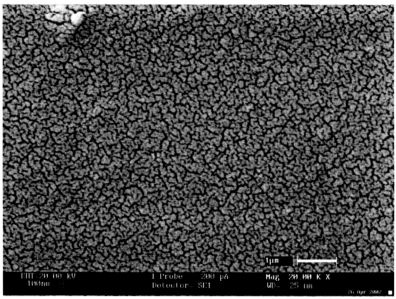

Fig 28: SEM micrograph of 1.00 ml propionic acid catalyzed thin film after sintering at 120 °C

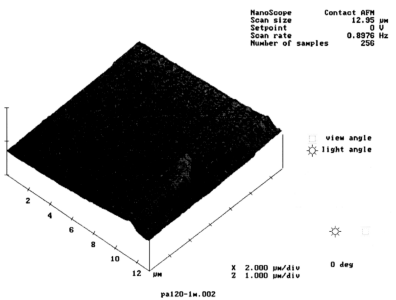

Fig 29: AFM micrograph image of 1.00 ml propionic acid catalyzed thin film after sintering at 120 °C

4.3 Malonic& Maleic acid catalyzed sol coated thin films

In case of malonic and maleic acids thin film, development there no homogeneous and crack free coating were successfully deposited. For both acid I work on similar concentration rage 0.70 mol dm^{-3}, 1.00 mol dm^{-3}, 1.72 mol dm^{-3}, and 2.58 mol dm^{-3}, and the composition ratio in volume regarding TEOS and EtOH is as shown in table 3.

The sintering temperature for these two acids catalyzed thin films is 75 °C, after sintering at so said temperature the coating layer is broken that is stratification is occurred, it was obvious that the coating layer of sol is not adheres well and spread evenly on surface of glass substrates, therefore, the thin films were not treat at further higher temperature.

The photomicrographs of the coating microstructure at different magnification obtained by SEM were illustrated in figures 30, 32, 34, 36, 38, 40, 42, and 44 respectively. SEM inspection revealed that the formation of crack free thin films are impossible by employing these two acids as catalyzed in sol-gel technique.

The film thickness and roughness were varied disorderly. The needle like particle, plate like particle and cracking were seen obviously. The average thickness and roughness of the thin films achieved is illustrated in table 7 and table 8 respectively.

Table 7: the thickness and roughness of malonic acid catalyzed thin films

No	Thin film	Roughness	Thickness
1	0.70 M malonic acid catalyzed thin film sintered at 75 °C	1.961 nm	298.62 nm
2	1.00 M malonic acid catalyzed thin film sintered at 75 °C	13.543 nm	355.15 nm
3	1.72 M malonic acid catalyzed thin film sintered at 75 °C	5.097 nm	306.26 nm
4	2.58 M malonic acid catalyzed thin film sintered at 75 °C	7.558 nm	308.96 nm

Table 8: the thickness and roughness of maleic acid catalyzed thin films

No	Thin film	Roughness	Thickness
1	0.70 M maleic acid catalyzed thin film sintered at 75 °C	1.961 nm	369.76 nm
2	1.00 M maleic acid catalyzed thin film sintered at 75 °C	13.543 nm	331.26 nm
3	1.72 M maleic acid catalyzed thin film sintered at 75 °C	5.097 nm	373.92 nm
4	1.72 M maleic acid catalyzed thin film sintered at 75 °C	7.558 nm	359.25 nm

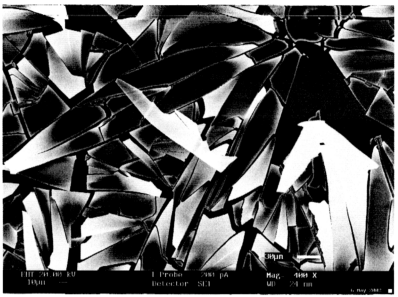

Fig 30: SEM micrograph of 0.70 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

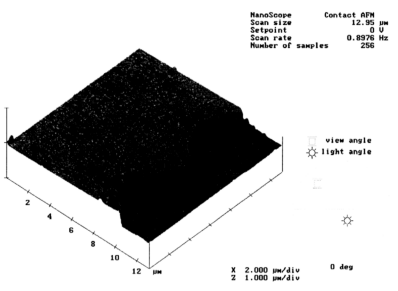

Fig 31: AFM micrograph image of 0.72 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

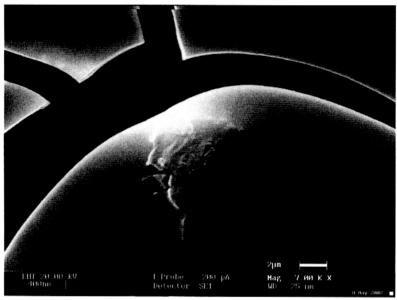

Fig 32: SEM micrograph of 1.00 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

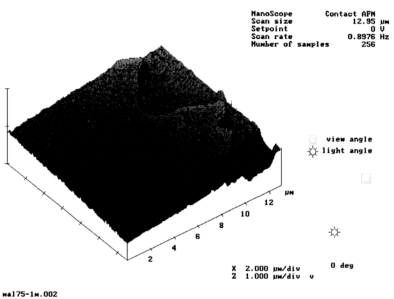

Fig 33: AFM micrograph image of 1.00 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

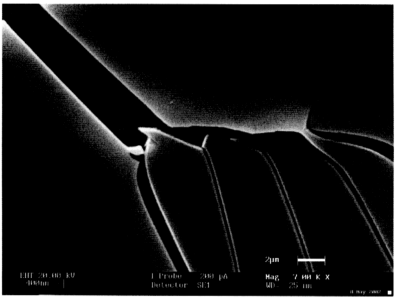

Fig 34: SEM micrograph of 1.72 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

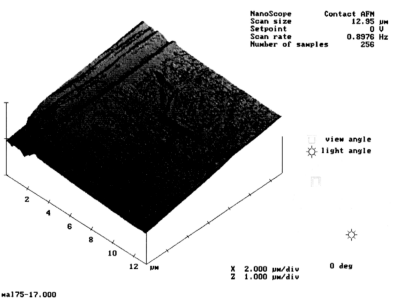

Fig 35: AFM micrograph image of 1.72 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

Fig 36: SEM micrograph of 2.58 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

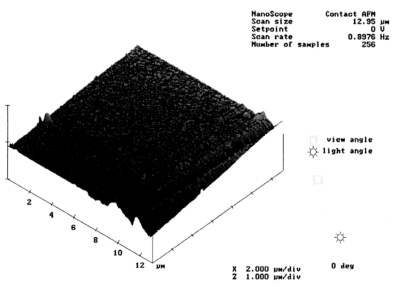

Fig 37: AFM micrograph image of 2.58 mol dm^{-3} malonic acid catalyzed thin film after sintering at 75 °C

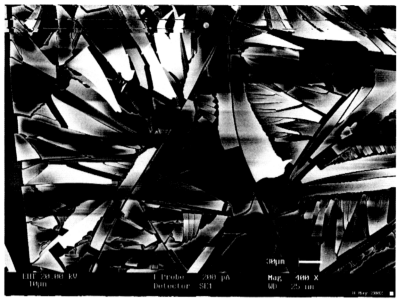

Fig 38: SEM micrograph of 0.70 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

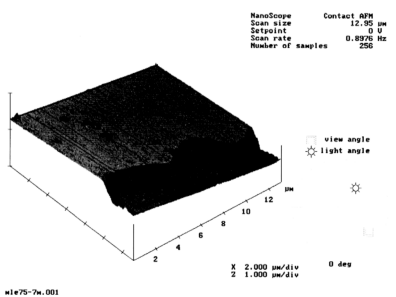

Fig 39: AFM micrograph image of 0.70 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

Fig 40: SEM micrograph of 1.00 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

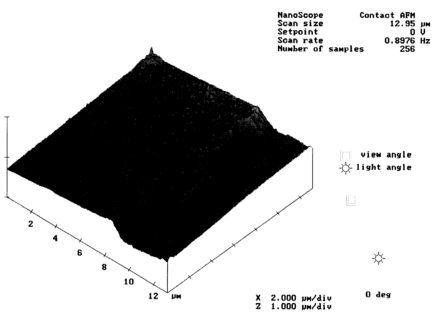

Fig 41: AFM micrograph image of 1.00 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

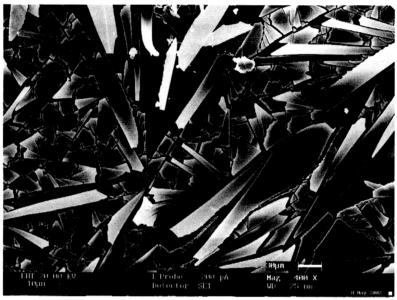

Fig 42: SEM micrograph of 1.72 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

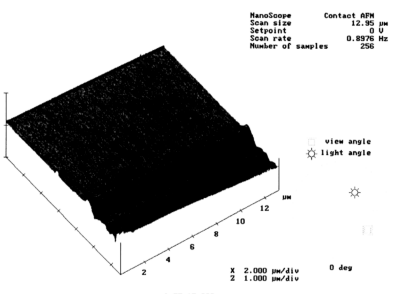

Fig 43: AFM micrograph image of 1.72 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C

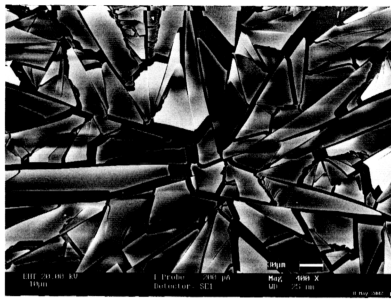

Fig 44: SEM micrograph of 2.58 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C.

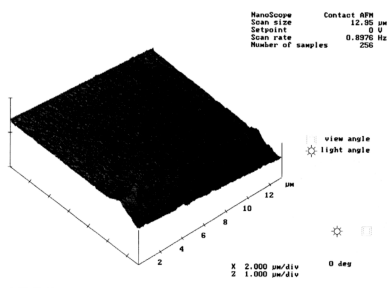

Fig 45: AFM micrograph image of 2.58 mol dm^{-3} maleic acid catalyzed thin film after sintering at 75 °C.