

Chapter 3

Dry Film Photo-resist

Thick film photo-resists are used for fabricating electroplating molds and MEMS (Micro-Electro-Mechanical System). Dry film photo-resist is one type of thick film. Although its resolution and aspect ratio are not very high compared with the other types of thick film, it is still attractive in the applications which do not require high resolution and high aspect ratio. This chapter will go through the history development, structure, composition, reaction mechanism, process procedure, and experiments of the dry film photo-resist in this thesis.

3.1 Development and Characteristics of the Dry Film

“Printed Circuit Board” industry origins from “Silk Screen Printing” technology. This is the reason why it is called PCB (Printed Circuit Board). With the driving force of high density, high accuracy and low cost, printing method had reached its limitation. In 1968, DU-Pont Inc developed dry film photo-resist. Since then, dry film technology replaced most of the traditional image transfer technology. In early stage of the dry film development, photo-resist is solvent type, it needs solvents for development and caused many inconvenience. As time goes on, it gradually became aqueous type and improved resolution. After that, packaging industry joined to use the dry film for research and process applications. Up to the present, dry film is still the best choice for PCB industry. New types of dry film are being fabricated toward higher aspect ratio for various

applications. Table 3.1[30] is reference for the detailed development history of the dry film photo-resist.

Dry film photo-resist has numerous advantages. It is possible to laminate dry film simultaneously on several substrates with various contour shapes. It is also possible to laminate multilayer on single substrate due to its planarization effect. Low exposure energy (typically $50\text{mJ}/\text{cm}^2$ for $50\mu\text{m}$ thickness) and wide band UV light make the process easy and fast. In addition, simple development, vertical sidewalls are all the advantages for the dry film. Sodium carbonate solution and sodium hydroxide solution are the only solutions needed in the development step and in the striping step, respectively. That is, there is no need for organic solvents which are harmful to human health. No significant hazards have been reported about dry film [31]. Most important of all, its cost is very low.



However, the resolution is the main disadvantage. Resolution is in proportion to the film thickness. The aspect ratio is limited by its low resolution, hence the dry film can only achieve about 1 to 1.5. This is not as good as other types of thick film photo-resist such as SU8 which has been reported to be as high as 20.

3.2 Structure and Composition

Dry film photo-resist looks quite different than the common liquid photo-resist. From the appearance, it looks like a sandwich. The top layer is a separation sheet, composed of Polyethylene film (PET), the thickness is about $25\mu\text{m}$. The bottom layer is a support or protective film, composed of polyester

(PE), the thickness is also about 25 μ m. The middle layer is a photosensitive layer. Its thickness depends on the application and ranges from few micron to one hundred fifty micron meters. The whole structure is illustrated in Fig. 3.1.

Generally speaking, the components of photosensitive layer are monomers, photo initiators, polymer binder, and some additional additives such as adhesion promoters and dyes. Monomers are the main components of a dry film. A monomer is initially solvable in developer and becomes unsolvable after UV light exposure and heat treatment. Photo initiators generate free radical under the UV light exposure, the detailed mechanism will be discussed in section 3.3. Polymer binders are used as the backbone of the dry film. As implied by its name, polymer binders bind all of the components together to form a solid film (dry film). A polymer binder does not participate in the chemical reaction during polymerization process but it does enhance the surface adhesion and plating-resist ability. Usually, dyes are being added to increase the process convenience for the sake of easy inspection.

3.3 Reaction Mechanism

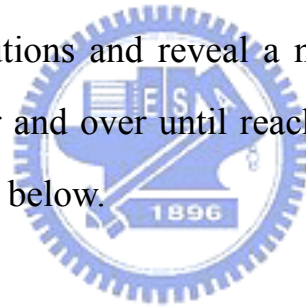
3.3.1 Reaction Mechanism of Exposure

When a dry film is exposed under UV light at 365nm or broad band wavelength, photo initiators absorb UV energy and generate free radical. The monomers, initially spread uniformly in a dry film, start to polymerize under the stimulation of these free radical. After that, polymers cross link to each other and become unsolvable in developer solution. Fig. 3.2 illustrates the chemical structure before and after UV exposure. In the region (a), UV light is been

blocked by the opaque part of the mask and there is no free radical to stimulate polymerization reaction. Hence, the monomer remains solvable. On the contrary, in the region (b), UV light transmits through transparent part of mask and creates a lot of free radical from photo initiator. Therefore, polymerization reaction starts and makes region (b) unsolvable in the developer.

3.3.2 Reaction Mechanism of Developing and Stripping

When an exposed dry film is ready for development, it will be immersed or spread under developer, which is usually composed of 1-3% sodium carbonate solution. The sodium carbonate then reacts with hydroxyl ion on the binder polymer and produces solvable polymer. These solvable polymers will be taken away by liquid solutions and reveal a new surface for developer. These two reactions happen over and over until reach the bottom of photo-resist. The reaction equation is shown below.



A developed region also called pattern can be used as the electroplating mold or etching mask. After plating or etching process is finished, the dry film is no longer needed and has to be stripped off. The stripper is usually composed of 3-5% sodium hydroxide. Although the monomer has polymerized, it still can be transformed to solvable polymer under high concentration hydroxyl ion. The stripper will penetrate into the interface between the dry film and the substrate, make it easily to be stripped or dissolved. Finally, after DI water cleaning and N₂ gas blowing, dry film is fully removed. The developing and stripping

mechanisms are illustrated in Fig. 3.3.

3.4 Process Procedure

This section will go through the detailed process step of the dry film photo-resist. As mentioned in last section, dry film is usually used for plating, tenting, and etching processes. The standard procedures are listed as follow.

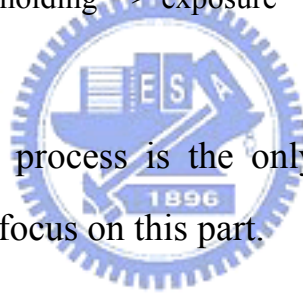
For plating processes

Preprocess → laminating → holding → exposure → holding → developing → plating → stripping

For tenting and etching processes

Preprocess → laminating → holding → exposure → holding → developing → etching → stripping

Because the plating process is the only one being used in this thesis, following discussions will focus on this part.



Preprocess:

The preprocess step depends on the underlying metal material. For silicon based devices, aluminum and copper pads are the common choices. However, for III-V devices, gold pad is the most common one. When gold is chosen for the pad material, the preprocess step is relatively easy. It needs only basic clean process to fully remove the surface dusts and particles. Air shower is necessary before going into next step.

Laminating:

Laminating is the most important step in dry film process. It has great influence on the quality of the patterns and the further processes. The method to

“coat” dry film photo-resist is quite different from liquid photo-resist. In the dry film case, a laminating machine is adopted to paste a dry film on a substrate. The main structure of a laminating machine is illustrated in Fig. 3.4. Several pairs of rollers are mounted on the top and the bottom sides of the machine, separately. Rollers can be heated by electric coil and the ordinary temperature is ranging from 100°C to 150°C. Temperature, pressure, and speed of a laminating machine are set according to the type of the dry film and the environment conditions. The separator sheet has to be removed prior to lamination. After that, a substrate with dry film is loaded together into one side of the laminator under proper temperature and pressure. The dry film achieves its glass transition temperature and becomes liquid thus capable of adhering to the surface. If the temperature is too high, dry film tends to become brittle and hard to develop. If the temperature is too low, the poor adhesion will result in poor pattern and bad plating quality. The speed of laminating depends on temperature; ordinary speed is about 1.0 to 3.5 meters per minute. A successful lamination should result in air bubble free between the surface and dry film.

Holding:

After laminating, the substrate should hold for 5 minutes to 2 days. The purpose is to wait for the substrate cooling down to the room temperature. There are two points should be noticed in this step. First, substrate should be kept in the yellow room under proper temperature and humidity ($21\pm 2^{\circ}\text{C}$, $55\pm 10\%$). If a substrate is kept under white light for a long time, the UV light in the white light may cause the dry film polymerization and hard to develop. Second, the laminated substrate should not stack to each other. If substrates are stacked, heat

is hard to dissipate and may also cause the polymerization reaction.

Exposure:

Exposure step is also important to successfully get a well defined pattern. It uses an ordinary mask aligner, that is to say, the light source is ranging from 300 to 400nm in wavelength. As mentioned before, exposure energy is also an advantage of dry film photo-resist. It only needs about $50\text{mJ}/\text{cm}^2$ compared with other types of thick film photo-resist. Both time and energy can be saved.

Holding:

After exposure, the substrate should hold for 15 minutes to 2 days. The photo-resist needs some time to generate photo acid and stimulate polymerization reaction. For high resolution pattern, immerse the substrate into a 90°C DI water will help increase contrast between exposure and non exposure areas and eliminate the standing wave effect.

Developing:

The developer is composed of 3% sodium carbonate. The developing time is critical and depends on the pattern size. In industry, spray developer is used. A spray developer machine can precisely control the pressure and the temperature. Thus, it is more reliable compared with the immersion method which is used in laboratory. Due to the thickness of the dry film, developer is hard to flow in and out during the process. Therefore, mild shaking is necessary. However, if the shaking force is too large, it may result in larger pattern than desired. After a substrate is taken out of the developer, it should be immediately cleaned by DI water in 30 to 90 seconds in order to remove the residual developer. The last

step is drying the substrate by air shower to remove the residual water.

Electroplating:

This step will be discussed in the next chapter.

Stripping:

The stripper is composed of 5% sodium hydroxide. Dry film will separate from a substrate at 55°C in 3 minutes. Again, DI water and air shower are necessary steps.

3.5 Experiments and Results

In this thesis, a 50µm dry film is supplied by a local vendor. The manufactory is NAN YA Plastics Corporation and the model is A250S. To successfully fabricate a desired pattern, some experiments have to be conducted.

The first thing is finding a good laminating method. As mentioned in section 3.4, a laminator machine is required to paste dry film on a surface. However, there is no such a facility in our laboratory. In the first attempt, a roller without heating function is adopted to manually laminate a dry film. After that, heating is conducted on a hot plate at 90°C in 30 seconds. The 1X and 50X optical microscopy results are shown in Fig. 3.5. It can be seen that the interface between dry film and substrate is full of air bubbles. One possible reason is the non uniform pressure executing on the dry film which fails to get rid of the air bubbles. After few more tries, this approach is concluded to be useless. By further studying the basic principle of a laminator machine, it is found that there is just a little difference between a professional dry film laminator and a

common laminator which is utilized for attaching a protective transparent sheet on a piece of paper. The 1X and 50X optical microscopy results of this approach are shown in Fig. 3.6. There is not any air bubble found as the interface. The surface is still very flat after laminating as shown in Fig. 3.7.

The second thing is to find the best exposure and developing parameters. A test mask is designed with various sizes of patterns on it. The sizes of the patterns are listed in Table 3.2. For a cylindrical hole with 50 μ m diameter, nine tests were conducted with different exposure dose and developing time. Exposure energy is ranging from 40-60 mJ/cm² and developing time is ranging from 2-3 minutes. Fig. 3.8 shows the total nine 50X optical microscopy pictures. From Fig. 3.8, almost every sample is opened excepted for the first condition (40mJ/cm², 2.5min). Further inspection indicates that whatever the exposure energy is, there is always residual scum near the side wall of the developed pattern after 2 minutes developing time. It can be concluded that 2 minutes developing time is not enough for this pattern. For 40mJ/cm² exposure dose with 2.5 & 3 minutes developing time, little distortion of the pattern was found. It implied that the exposure energy is not enough for fully polymerization. The results of the other four conditions look great especially for the middle one of the figure (50mJ/cm², 2.5min). As mentioned in section 3.4, the optimized developing time is in proportion to the pattern diameter. Same methodology can be used to find the best parameter for other sizes of the patterns. Although the vendor claims that the resolution of this type of dry film is only 50 μ m, it is found that by fine tuning the conditions, resolution of 30 μ m can be achieved. Fig. 3.9 shows the 50X optical microscopy pictures with the same exposure and developing conditions. Over half of the test samples failed to be developed. The

sample with $40\text{mJ}/\text{cm}^2$ exposure dose and 3 minutes developing time is only partially developed. Same result is observed for $50\text{mJ}/\text{cm}^2$ exposure dose with 2.5 minutes developing time. The best results come from the sample with $50\text{mJ}/\text{cm}^2$ exposure dose and 3 minutes developing time. The pattern size is plotted versus developing time in Fig. 3.10 with fixed amount of exposure energy. It is observed that the smaller the diameter, the longer the developing time. This phenomenon may be attributed to the different aspect ratio for the pattern with different diameters. Higher aspect ratio makes the developer more difficult to flow in and out, thus takes longer time to fully develop a pattern. Fig. 3.11 shows the several SEM pictures with various pattern sizes. It is also shown a cross section photo of a $77.5\mu\text{m}$ diameter pattern. Near vertical side wall is observed. The result is desirable for further processing.



The third thing is to resolve the underplating problem. Generally speaking, dry film is used for plating pure metal or alloy such as copper and lead tin which are conducted under room temperature. In these cases, hard bake is unnecessary. However, gold is one of the materials experimented in this thesis and gold ion has to be reduced to atom state under 70°C during plating process. If hard baking is not performed, dry film itself may not survive under cyanide gold plating bath at high temperature. Also, it may cause contamination of the plating bath. The first attempt of hard baking parameter was 190°C for 2 minutes as suggested by the vendor. The result shows a serious underplating phenomenon as depicted in Fig. 3.12. It can be seen that all of the bumps were electrically connected by the electroplated gold even after the seed layer etching. If longer etching time was used, gold bump will lose its adhesion on the surface separate

from the substrate. To resolve this problem, six test conditions were conducted under different baking temperatures and baking times as listed in Table 3.3. The results indicate that high baking temperature such as 190°C may cause the deformation of dry film and result in the loss of the adhesion. By reducing the baking temperature to 110°C, alleviation of the underplating phenomena was observed. Further reducing the baking temperature to 90°C can totally resolve this problem. Therefore, the hard baking condition was chosen to be 90°C, 6 minutes.

To further exam the influence of baking conditions on the flatness of the dry films. A sample with optimized hard baking condition was investigated by AFM. Fig. 3.14 shows the AFM diagram after hard baking at 90°C in 6 minutes. It can be seen that, compared with Fig. 3.7, surface roughness (Ra) increases from 0.272nm to 1.44nm.

Finally, double layering of the dry films was attempted. After the first layer dry film was laminated and patterned, the second layer dry film was laminated and patterned again on top of the first one with the same process conditions. From Fig. 3.15, it can be seen that the pattern size of the upper layer is bigger than the lower layer especially at the interface. The possible explanation is the penetration of the developer into the interface. Process with care in details may resolve this problem.

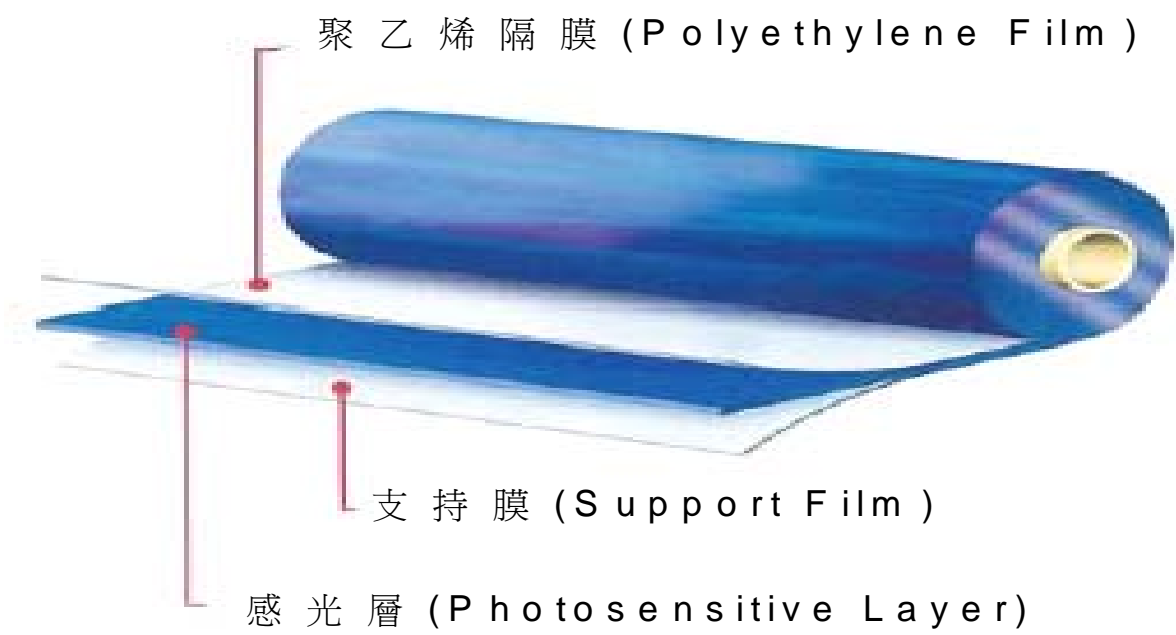


Fig. 3.1 Structure of the dry film photo-resist.

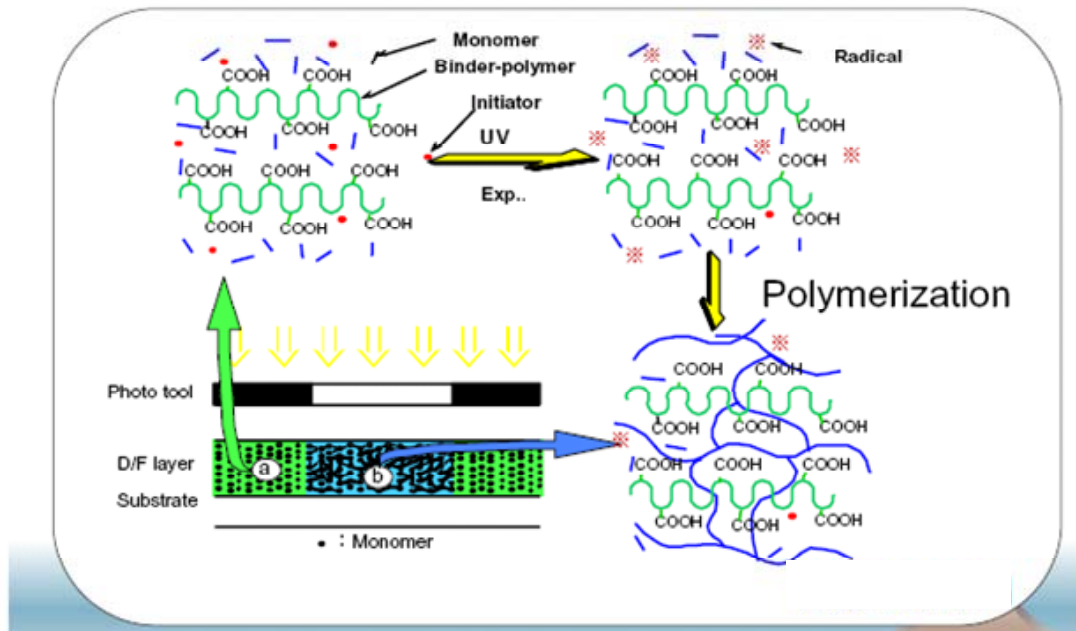


Fig. 3.2 Dry film reaction mechanism for exposure

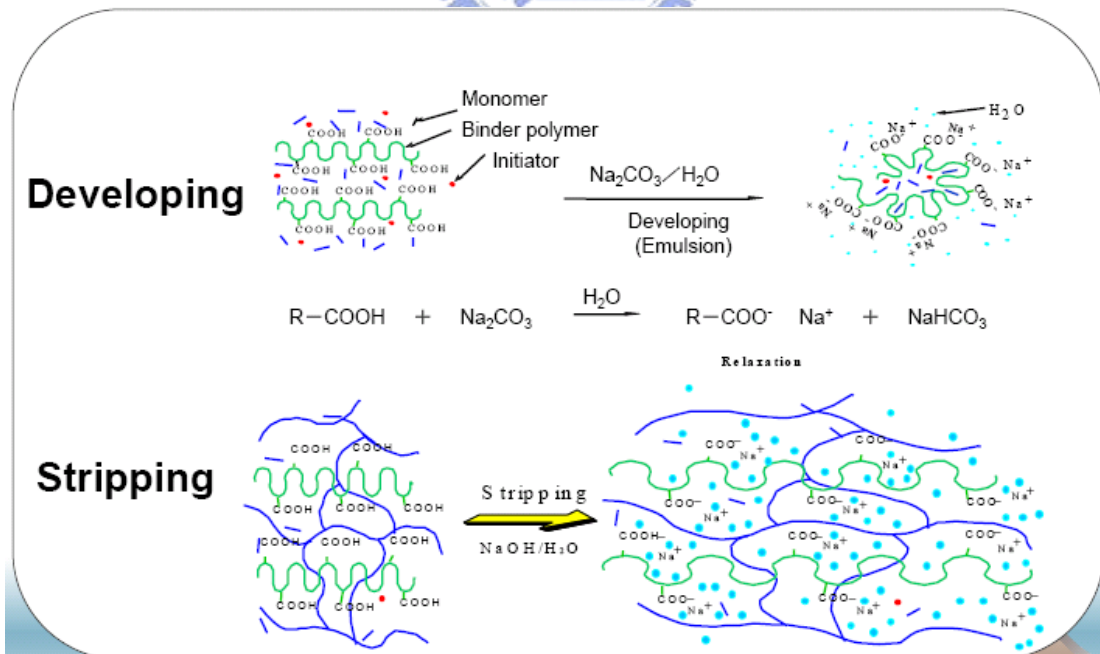
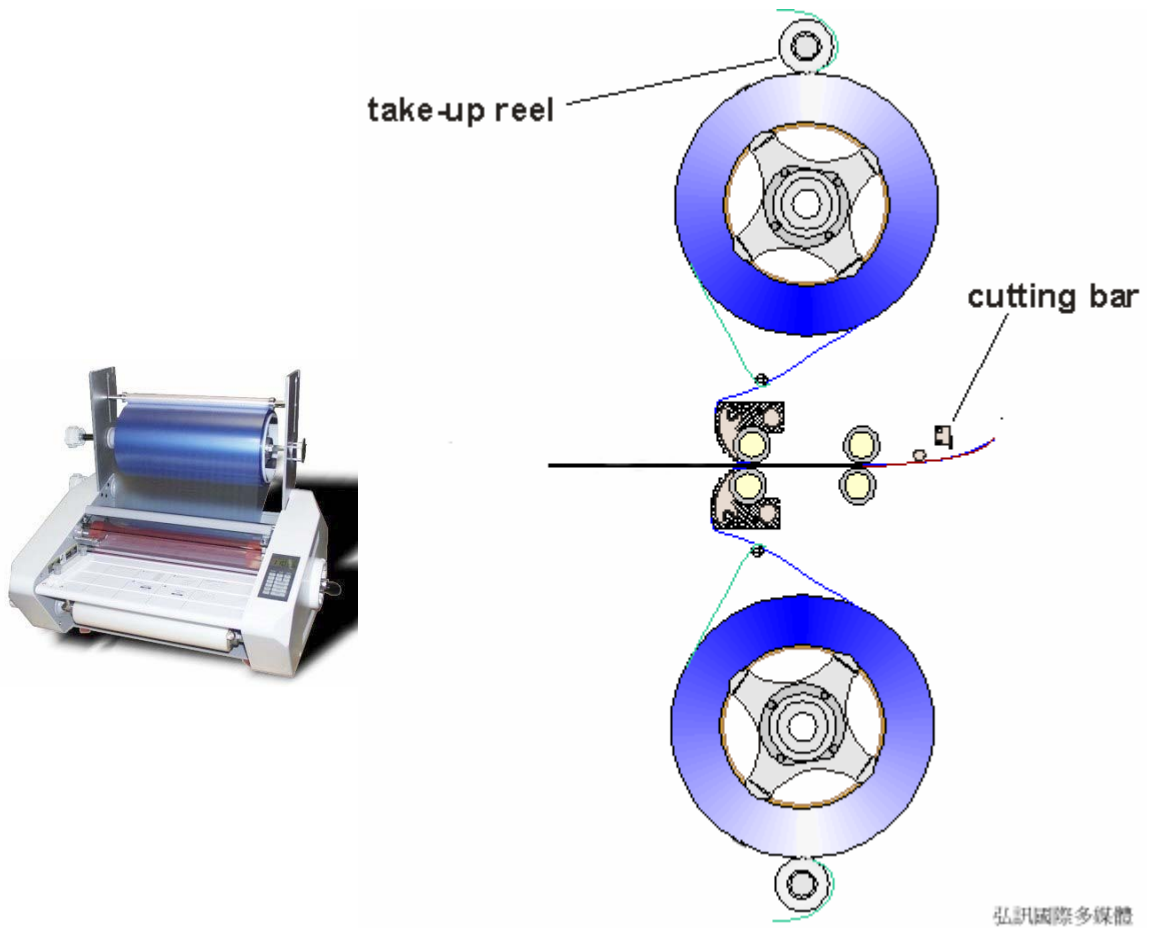


Fig. 3.3 Dry film reaction mechanism for developing and stripping.

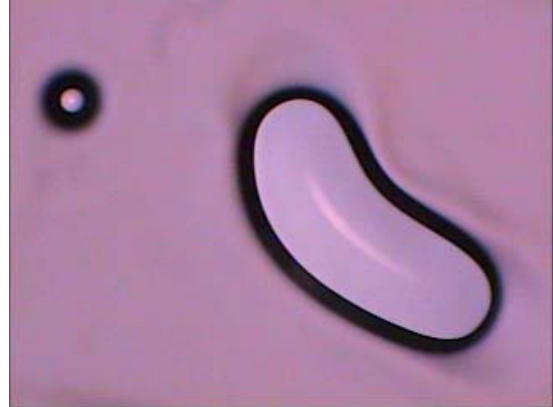


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Fig. 3.4 Structure of a dry film laminator.



1X



50X

Fig. 3.5 1X and 50X optical microscopy of dry film surface laminated by a roller.



1X



50X

Fig. 3.6 1X and 50X optical microscopy of the dry film surface laminated by a laminator.

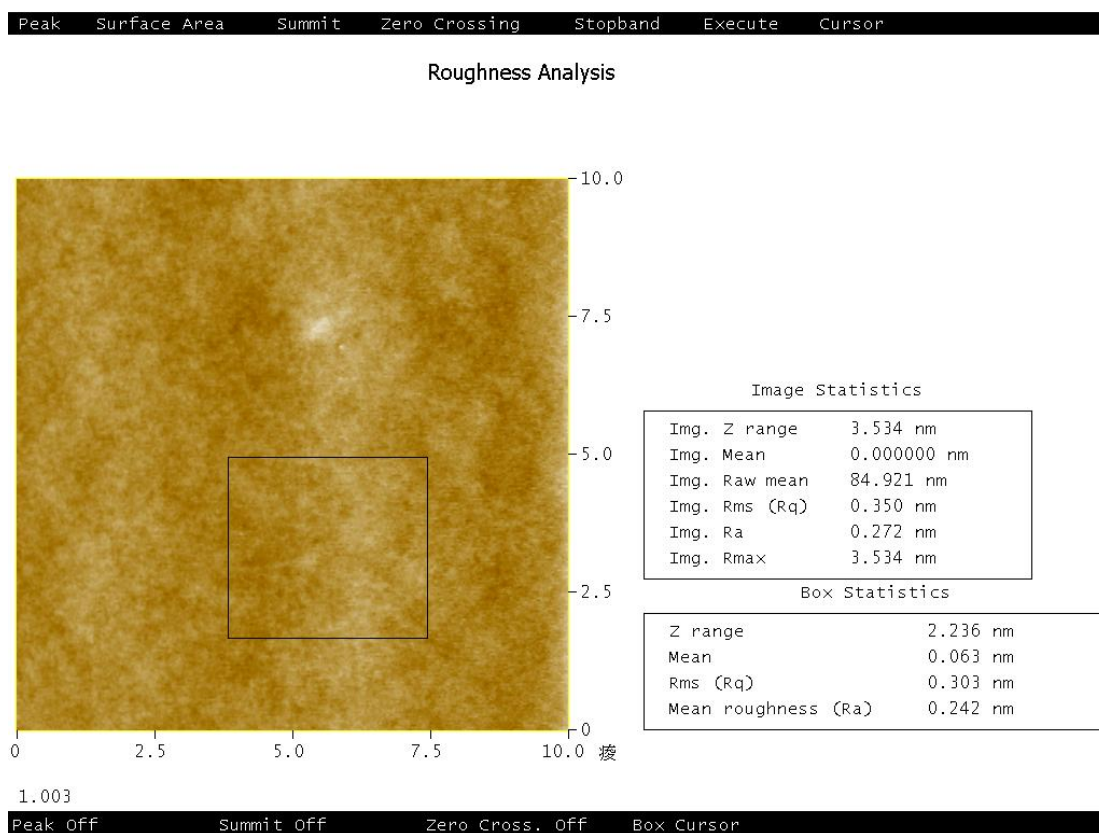


Fig. 3.7 AFM image of as laminated dry film photo-resist.

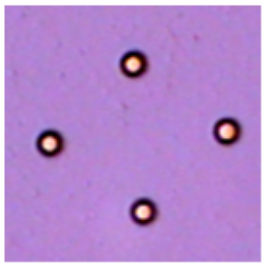
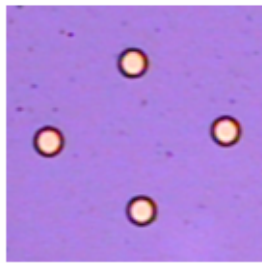
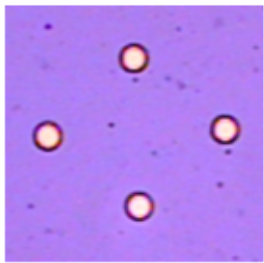
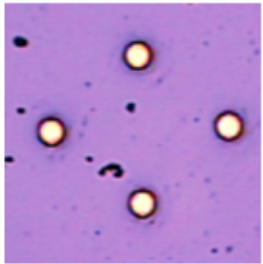
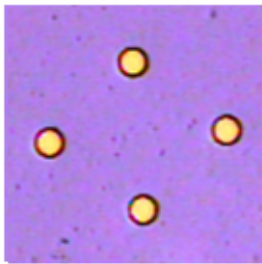
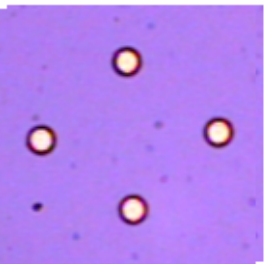
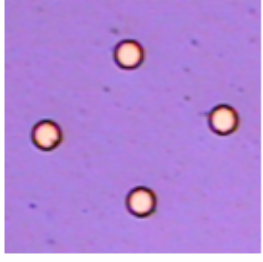
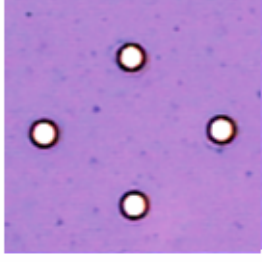
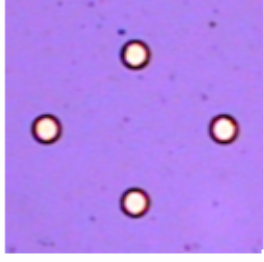
Exposure Dose / Developing Time	Exposure Dose		
	40mJ/cm ²	50mJ/cm ²	60mJ/cm ²
2min			
2.5min			
3min			

Fig 3.8 50X optical microscopy results for the 50µm test pattern with various exposure doses and developing times.

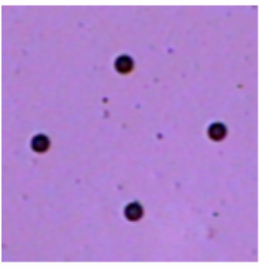
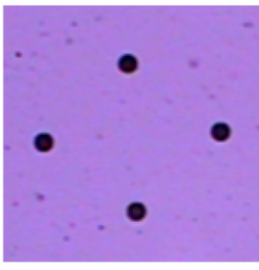
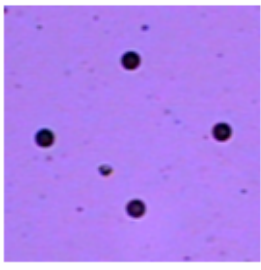
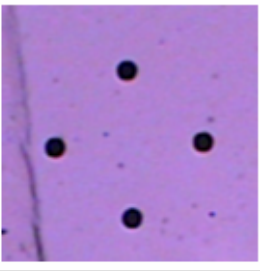
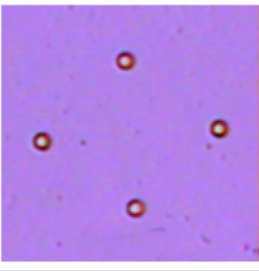
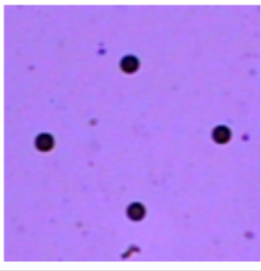
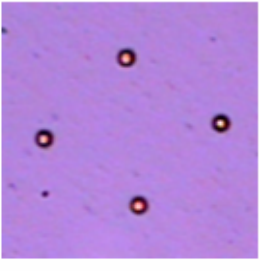
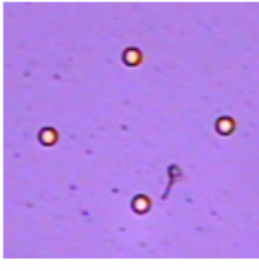
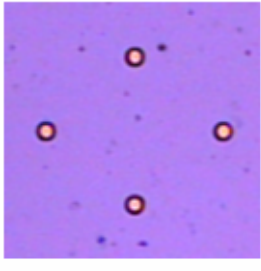
Exposure Dose / Developing Time	Exposure Dose		
	40mJ/cm ²	50mJ/cm ²	60mJ/cm ²
2min			
2.5min			
3min			

Fig 3.9 50X optical microscopy results for the 30µm test pattern with various exposure doses and developing times.

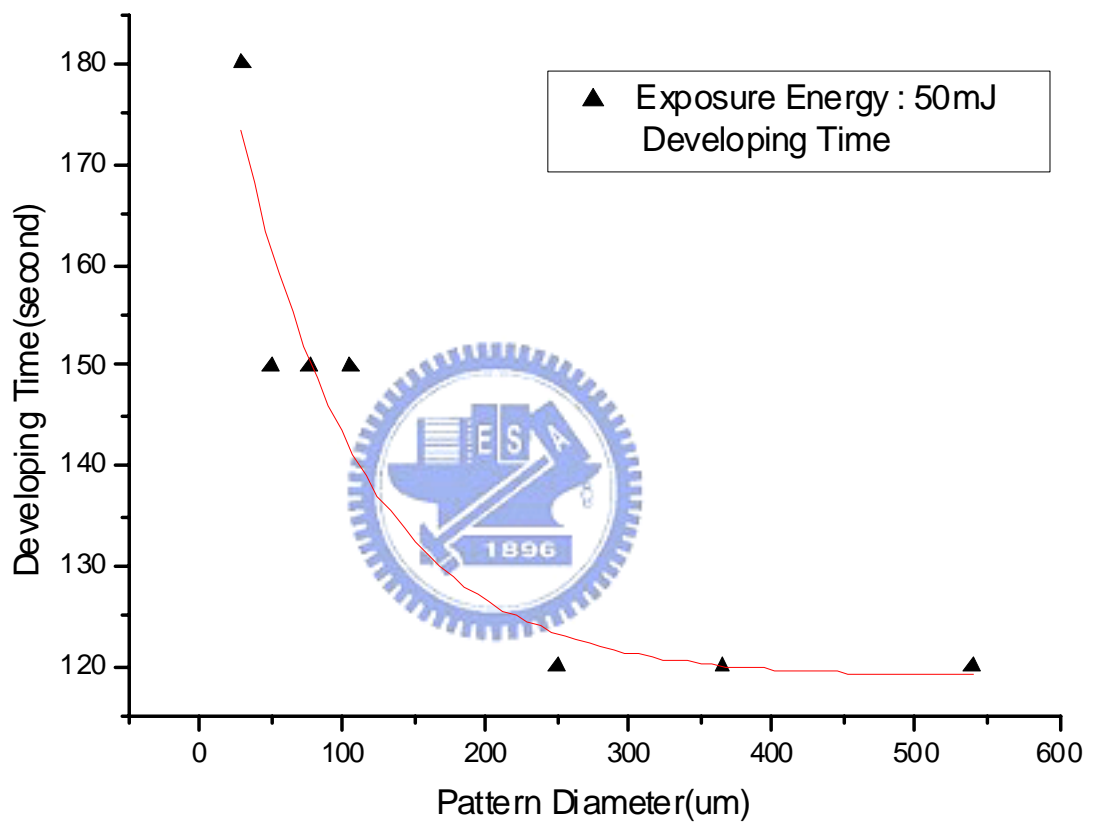


Fig. 3.10 Optimized developing time for various pattern diameters.

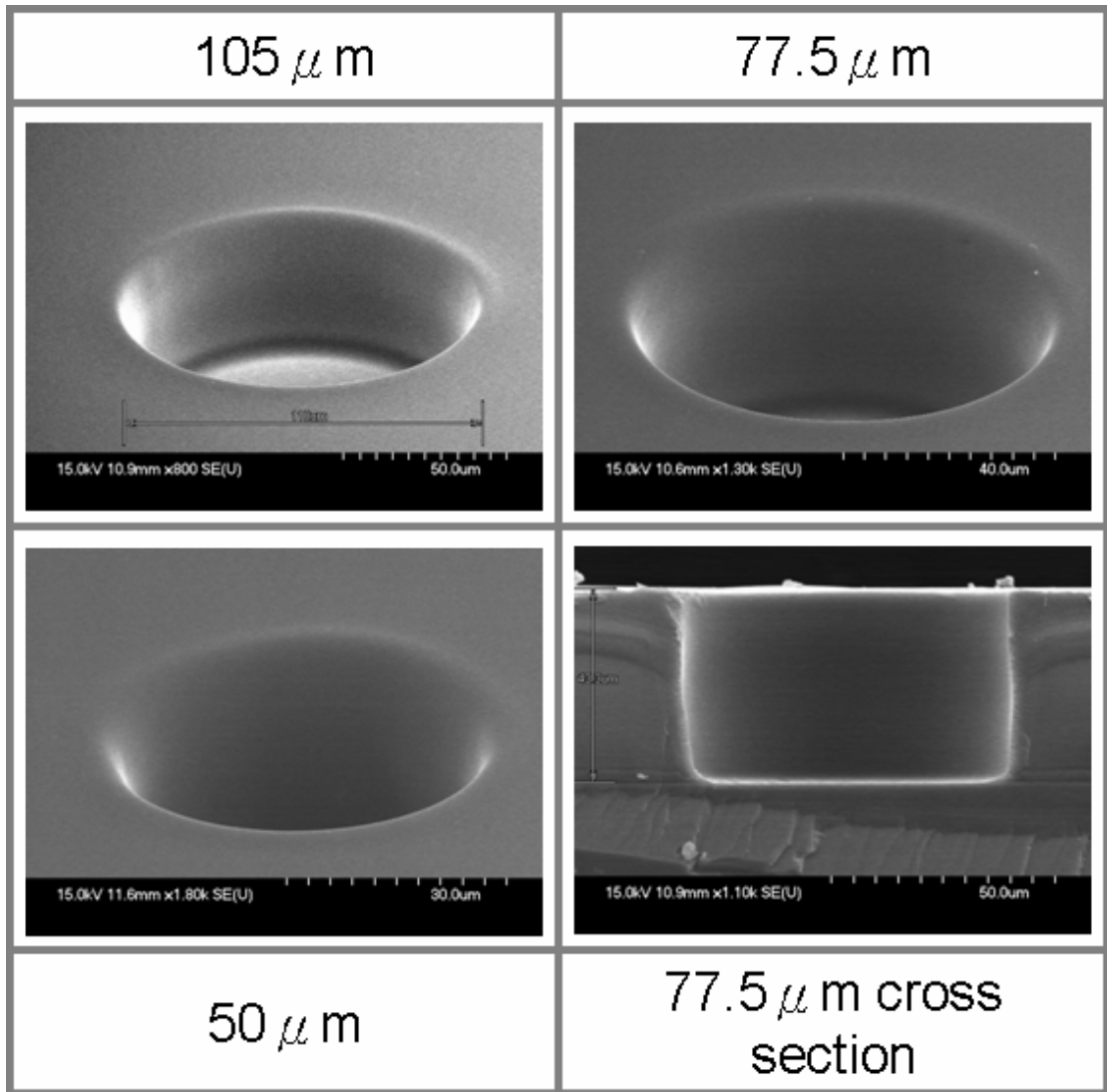


Fig. 3.11 SEM pictures of the as developed dry film with various pattern sizes

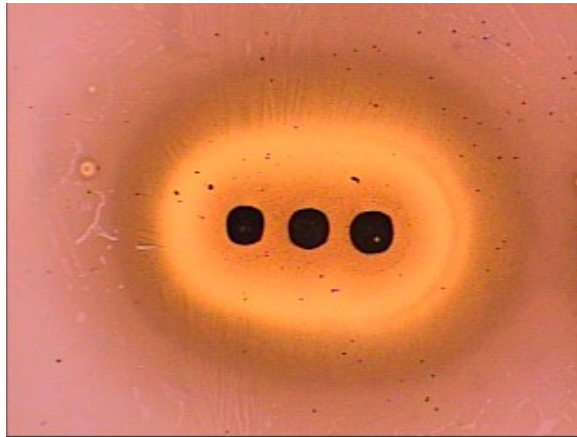
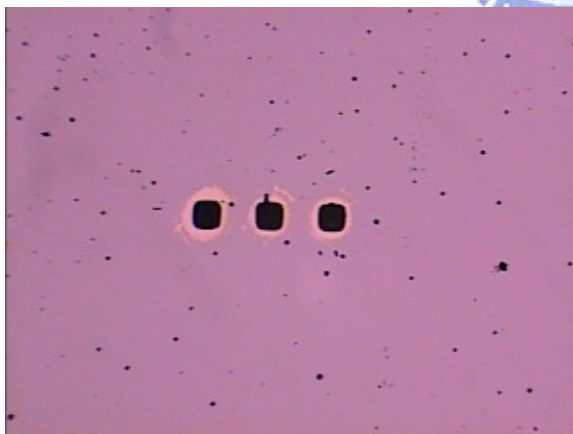
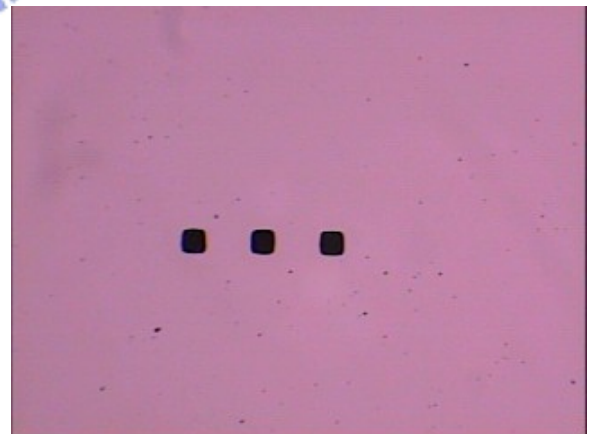


Fig. 3.12 Patterns with underplating for the dry film with hard bake condition of 190°C , 2 minutes.



(a)



(b)

Fig. 3.13 Patterns without underplating for the dry film hard baked at the conditions of (a) 110°C , 6 minutes (b) 90°C , 6 minutes.

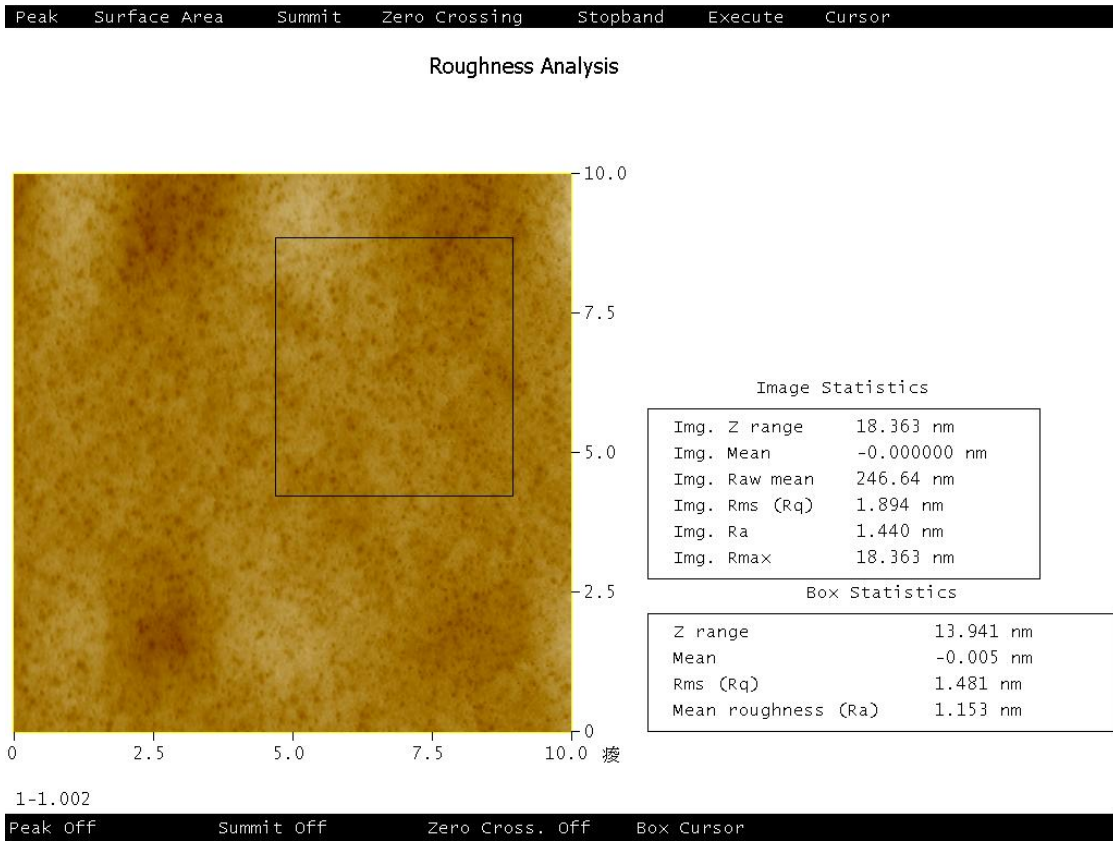


Fig. 3.14 AFM image of hard baked dry film photo-resist with optimized baking condition.

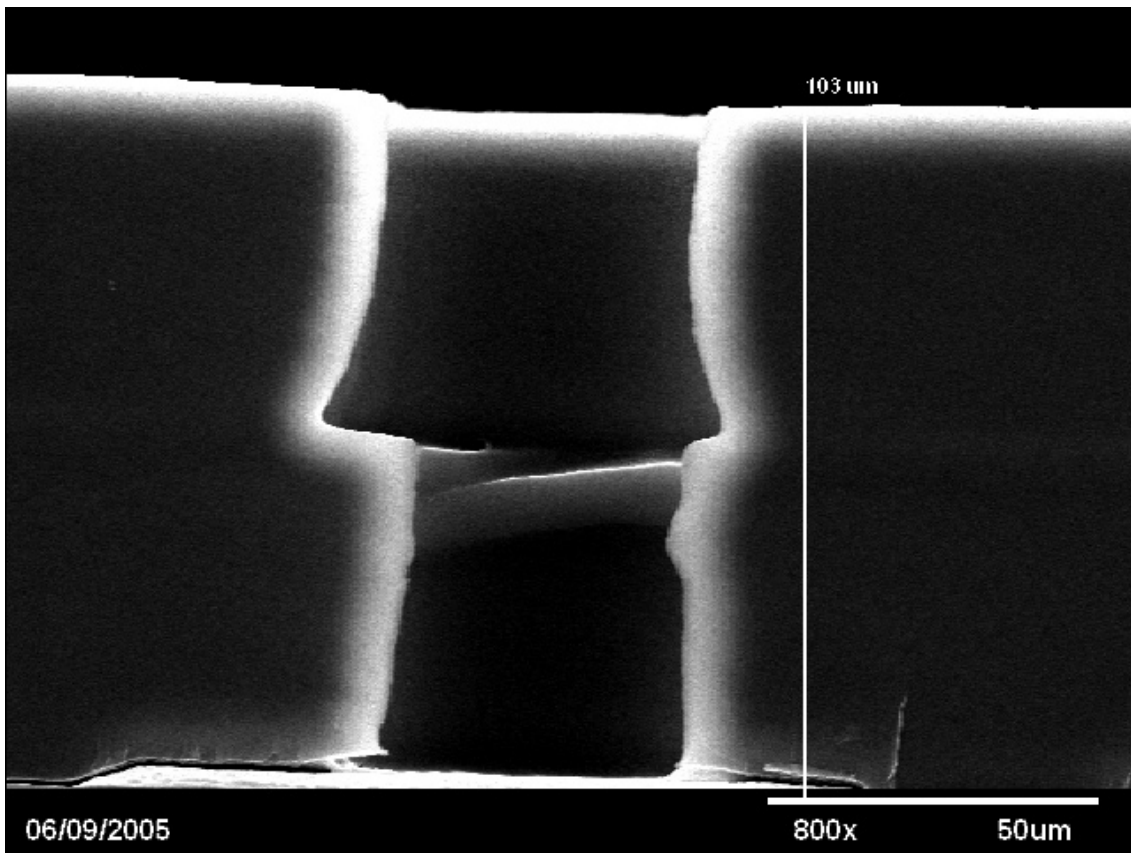


Fig. 3.15 Double layer dry film after developing.

Year	Dry film type	Characteristics and applications
1968	Solvent Type	<ol style="list-style-type: none"> 1. Substitute for liquid photo-resist and silk printing 2. Uniformity in thickness 3. Improved yield 4. Suit for secondary copper plating
1970	Aqueous Type	<ol style="list-style-type: none"> 1. More environment friendly 2. Low cost 3. Reduce the use of solvent 4. Waste is easy to handle
1973	Semi-Aqueous Type	<ol style="list-style-type: none"> 1. Extend the range of electroplating 2. Suit for plating nickel and gold
1978	Improve Aqueous Type	<ol style="list-style-type: none"> 1. Popular in PCB industry, packaging industry 2. Better characteristic and improvement in process
1984		Expiration of DU-Pont Inc' s patent
		Many company begin to fabricate dry film photo-resist

Table 3.1 Development history of the dry film photo-resist

Various Pattern Sizes on a Test Mask
540 μ m
365 μ m
260 μ m
105 μ m
77.5 μ m
50 μ m
30 μ m

Table 3.2 Various pattern sizes on a test mask.

Baking temperature	Baking time	Underplating
90°C	2min	No
90°C	6min	No
110°C	2min	A little
110°C	6min	A little
190°C	2min	Yes
190°C	6min	Yes

Table 3.3 Hard baking conditions with various baking times and temperatures.