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High Yields and Low Costs Liquid Resists

Danny K. L. Cheung and Brian D. Amos
Rohm and Haas Electronic Materials Asia Ltd.
Hong Kong, China

Tina Marabello, Kevin Horgan and Kevin Cheetham
Rohm and Haas Electronic Materials LLC
Marlborough, MA

Introduction

In the multilayer PCB industry, the process of making the inner layer is the first step in a number of complex steps that results in the production of a printed wiring board. This imaging manufacturing step comprises of a number of subprocesses that together allow for the metal interconnect pattern to be formed. The steps by themselves are small and can seem irrelevant, however a good balance of precision and synchronization of all processes is required to guarantee a high yielding reproduction of the circuitry pattern. To ensure the process has the ability to function in any of the selected production environment the selection of raw materials is key to the functionality of the chosen photoresist.

20 years ago, the Inner Layer Photoresist market is being dominated by dry film. However in recent years a significant move towards liquid photoresist has been noted. The main drive for liquid resist was the increased needs for resolution without the need for investment in new equipment. The cost of dry film is relatively high and cannot match the low cost and high resolution of today's liquid resist market offerings.

The industry is demanding a leading edge liquid resist that can balance the formulation of the raw materials used to a ensure a low cost resist formulation that can maintain stable, reproducible, high yielding processes that work in conjunction with the various equipment sets used in the industry today.

In this paper, the first section will be allocated to a discussion on the various equipment / process issues. The second section will be focused on the trade offs in formulation to meet those requirements. The final section will discuss the engineering of a formulation that address the issues discussed.

Equipment

The equipment used in the imaging process has an important role to play in gaining the optimum high yielding results that are demanded by customers. The role of the equipment is as important as that of the resist itself. Traditionally the innerlayer processing equipment has been designed to process dry film. Dry film has a protective film (Mylar) that protects the imaging layer prior to the developing process and therefore protects the fragile photosensitive layer. Liquid resist has no such protection film and so must withstand the mechanical influences that would not affect a typical dry film product. This section will outline some of the significant ways that equipment sets can influence the performance of even the best photoresist.

First of all, cleanliness is also a primary concern for the photolithography process. Without the correct controls in place to minimize the generation of particles the end yield will lower than expected. The main areas for contamination control are seen as:

Yellow room contamination / cleanliness class – include areas for application of Photoresist, drying and the exposure area. **Solution filtration** – include Pre-clean line chemistry, Liquid Photoresist filtration, Develop-etch-strip (DES) line chemistry and the filtration must include all the rinsing water. **Product handling** – the use of tacky rollers (automatic or hand-held). Minimizing handling with the use of automated operation; specifically, for in-line equipment, the alignment of the preclean step, roller coater, oven, automatic loading and unloading machine will all improve the cleanliness.

Preclean

Preclean is the foundation for all the future steps of the Imaging process. Only an appropriately cleaned substrate with surface treatment will allow for good adhesion between the photoresist and the substrate, therefore allowing for a good final yield. All laminates, when they arrive at the PCB shop will contain some level of contamination.

The major role of the Preclean process is to modify the surface roughness so as to promote adhesion between the base copper and the photoresist. This is done by a combination of chemical treatments that lead to increasing the roughness index while removing contaminates from the surface.

In the Preclean process the panels are typically processed in a horizontal fashion. The gears and conveyor parts are classed as wearable parts and therefore over time will produce particulate matter that can be deposited onto the copper surface. To ensure that these particles are removed from the solutions and rinses it is typical to add sub 10 micron filters to the final rinse sections of the Preclean process.

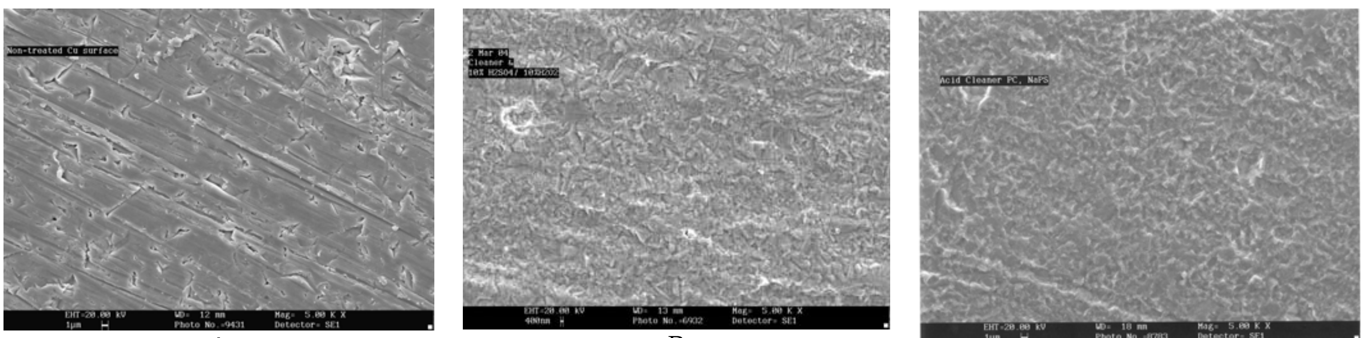
There are three major cleaning processes available in the market, namely: mechanical cleaning, chemical cleaning and electrolytic cleaning.

Mechanical Cleaning

Usually, mechanical equipment utilizes a slurry of particles to physically abrade the copper surface. Both pumice and aluminum oxide are used as slurry materials. The boards must have a sufficiently thick layer of copper so that a loss of 50 µi does not impact the final conductor height. Since it is a purely physical process, it is quite difficult if not impossible to mechanically clean very thin or frail panels. Periodic maintenance of this equipment is very important since the brushes deteriorate with use and the slurry also will degrade.

Chemical Cleaning

Chemical cleaning has become increasingly important since it can provide several solutions to tackle different type of contaminants and it require minimal maintenance apart from replenish or make up of new solutions. Typical chemistry includes: soap for oil and grease, micro-etch for removal of anti-tarnish treatment of different chemistry and mild acidic cleaning solution for oxide removal. Figure 1 shows the SEM pictures showing the difference between untreated copper and post treatment using H_2O_2 and sodium persulphate.



A B C

Figure 1 - SEM Pictures showing the Difference between a) A; Non-Treat Copper Surface; b) Bt; Treat with 10 % Sulfuric Acid and 10 % H_2O_2; c) C; Treat with Sodium Persulphate

Electrolytic Cleaning

This process utilizes a rectifier that is typically found in the copper electroplating plating line. However in this environment it is used to reverse plate (strip) the copper from the surface so as to de-plate and remove the typical surface contaminates. To further enhance the copper surface a micro etch is recommended to modify the surface roughness.

Photoresist Application and Dry

The current method of deposition for the liquid resist is roller coat and dry. This process has been around in the industry for 40 years. The horizontal method of resist application and drying was the predominate method however in the last five years the more recent equipment technology being purchased by the market is a vertical application method.

Application

The deposition of liquid films onto the board surface occurs by transferring the liquid resist from a set of grooved application rollers. The substrate is passed between two grooved application rollers that are held in a state of “compression”. This compression facilitates a controlled release of the liquid resist contained in the groove and with the correctly balanced resist, a contaminant and defect free coating is deposited then dried. In the two typical modes, Vertical vs. Horizontal, different challenges are encountered. The main area of concern is that during the coating process a resist wedge is formed. When in the horizontal mode this wedge “drips” into the resist tray however in the vertical mode it is possible that this may drip onto the next panel.

There are a number of other factors which will also affect the coating quality and coating thickness. These include: the physical configuration of the rollers, groove size (wide, depth and configuration) and the viscosity of the photoresist. Please refer to Table 1 for the comparison between the two modes of coating methods.

Table 1 - Application Comparison between the Horizontal and Vertical Roller Coaters

Roller Coating Application		
	Horizontal Roller Coater	Vertical Roller Coater
1. Dripping	No dripping occurs	Dripping occurs when application roller pressure is adjusted incorrectly. Increases the running cost.
2. Gripper points	The Photoresist present at the gripper point would be minimal due to the design of scraper blade.	With the vertical method it is not possible to reduce the resist thickness in that area and therefore layer of Photoresist is present in the gripper area.
3. Stand-by mode	With the added options of a viscosity controller and the standard recirculation of Photoresist back to sump. The resist will not dry on the roller even for few days idle time	Viscosity control is not an option supplied or easily retrofitted to the vertical machines and therefore resist will dry on the roller after 2 days idle time
4. Thickest panel can use	1.6 mm	The panels will drop easily within the oven
5. Thinnest panel	0.05mm	The transfer gripper may not clamp on the panels due to the lack of stability of a thin panel when held in the vertical mode.

Drying

The drying step of the process is the key to the formation of a good, robust photosensitive coating that can withstand the abrasion from handling and process equipment, while still maintaining a fast exposure speed. The historical trade-off has between to get good handling-stacking attributes and exposure speed is that you would need to reduce the capability of one to achieve the other. With the introduction of the vertical coating method, a third issue has now been added: equipment design. In Table 2 a description of differences seen in the physical and thermal drying conditions is provided.

Table 2 - Drying Comparison between the Horizontal and Vertical Roller Coaters

Item	**Horizontal**	**Vertical**
Internal Oven Dimension	$1.356m^3$	$4.346m^3$
Air Exhausted	200CFM	100CFM
Number of air Turnovers	956 per hour	150 per hour
Air Temperature	120 -1408ºC	100 -1308ºC
Board Surface Temp Max.	120 - 1308ºC	110 - 1158ºC
Time above 908C	60 –70 sec	240 – 360sec
Panel ramp rate	3 – 58C per sec	0.5 – 18C per sec
Dwell time in Oven	70 – 90 sec	300 – 480 sec
Panel Transportation	Panels are gripped firmly on two edges and transported through the oven.	Panels are gripped on one edge.
Air flow design	Air knife 908 impingement to the board surface.	Laminar flow from the top of the oven.
Typical Resist hardness measure by pencil hardness method.	3-4 H	1-2 H

The data in the table shows that further formulation balance is needed to have a resist that can dry in low impingement, low temperature, long dwell drying oven but also perform in horizontal mode where the drying process is more aggressive, shorter and optimized to remove the solvent in fast, effective manner. The photoresist formulation should be balanced so as not to over dry when used in either process, as the photo-reactive material will start to degrade with a prolonged expose to high temperature. A shorted exposure in the drying oven may also have an advantage to reduce the chance for the resist to be contaminated by airborne particles. If the customer intends to stack the panels after coating then the drying and the control of this step are of utmost importance.

It can also be noted that the Vertical type of drying process does not produce the same hardness of the resist surface when using the same product for both application methods. Post drying the vertical mode has a pencil hardness of 1-2H and the Horizontal mode is 3-4H. Neither can compare to the 6H hardness that is required to affect the Mylar coated dry film.

The photoresist should also be dry enough in order not to contaminate the phototool during exposure and is especially important if PCB shops intend to stack up the panels. Apart from drying, cooling is also necessary to achieve stability.

Expose
This is the process for image formation. In the discussion, we would separately discuss light source and phototool use.

Light source
For the PCB industry, usually contact exposure tools are used. This places the phototool and the panels in direct contact and draws a vacuum between the pieces. Often, a mercury arc lamp is chosen as the light source for its high-intensity output. Non-collimated sources are used as the intensity is greater, resulting in a decrease in the exposure time and improved line definition. Line definition is different for fineline definition of which collimated sources are preferred. Good contact between the phototool and the panel is the most important factor in fineline definition. Gap will result in reduced resolution. Nowadays, as driven by the increased demand for products with fine features of 3 mil and less, non-contact exposure equipment is proposed and this is beyond the discussion of this paper.

Phototools
There exist three types of commonly available photo tools: Glass, Polyester, Diazo. Polyester and Diazo are currently the two industry accepted products for today's resolution challenges. They differ from each other mainly by the optical properties, dimensional stability with respect to temperature and humidity, and their durability. The impact on the exposure using the glass as a reference is given in Table 3.

The data shows that if you were to use a Diazo artwork then longer exposure times of up to 30% would be expected.

Table 3 - Comparison of the Optical Transmission of Various Phototool Materials (Source: Kodak Technical Literature (ACCUMAX 2000) for Polyester film; *Tables of Physical and Chemical Constants*, Longman, London, 1973, p. 254

Property	Diazo	Polyester	Glass
Absorbance at 365 nm	0.271	0.107	0.047
Transmission at 365 nm	54%	78%	90%
% increase in exposure time vs. glass	40	13	0

Develop
This process utilizes the solubility difference between the exposed and unexposed portions of the Photoresist. The total dwell time is set to approximately double the time to clear, that is 50 % breakpoint. The variable includes solution temperature, spray pressure and concentration of the developer solution. Photoresist images should be distinct with vertical sidewalls. Any failure means the set points require adjustment. Images larger than the phototool may mean incomplete development, overexposure, or poor contact at expose. Where as smaller images may mean underexposure or the development chemistry being too aggressive.

Horizontal spray conveyor is commonly utilized by PCB shop. Most of the time, antifoam agent is recommended to be added into the developer chamber. To maintain cleanliness, solution must be filtered to remove the suspended resist particles. Replenishment keeps the developer solution in a working condition and minimizes or maintains a consistent resist loading level. In addition, hard water often improves the photoresist image and the yield.

Formulation of Photosensitive Materials
This component within the liquid photoresist is essentially the same as that of dry film, which is composed of: backing materials, photoinitiators, photoreactive materials, dyes and other additive to give specific properties. The most obvious difference between liquid photoresist and dry film is the solvent content that is present at less than 1 % in a dry film but up to 60% in a liquid resist formulation.

The first problem encountered is to find a suitable solvent that can dissolve all the solid raw materials and at the same time does not react with the photoreactive materials and cause complications with the application rollers. The next criterion for a good solvent is one that can dry fast enough within a short period of time. Since the solvent may go directly into the environment, it is very important to choose an environmental friendly solvent. The liquid photoresist is targeted to be less costly than dry film and as the solvent is the major component, this decision is a key to attaining the cost model. However the current choice of solvent that meets these expectations is limited.

The typical PCB shop within China has chosen a manual type production process. This puts an emphasis on the process of stacking the coated panels. The stacking process is typically achieved by using a traditional 70º Tote. Depending on the PCB shop, the stack time can reach up to 48 hours before being exposed, and some PCB shop require to stack for up to 60 hours to allow for logistic arrangement. Then comes the second problem, for dry film, there is always an outer backer sheet of polyethylene (Mylar) present to protect the film but not for liquid photoresist.

The stackability of a resist can vary due to the level of solvent that remains in the dried film layer. This solvent content will vary depending on the set and style of each oven used. If too much solvent is left in the resist then it will have a short stacking time and too little solvent gives a strong indication to over drying and therefore a reduction in the photospeed and typically longer developing times. To counter this problem, a high level of formulation focus has been placed on determining the correct ratio of backing materials to photoreactive materials. This will then minimize the retained solvents contribution to the stacking issue and ensure all other function of the resist remain at optimum. Apart from the formulation, stacking performance is very dependent on the effectiveness of the drying oven.

The next formulation issue is related to the surface properties of the photoresist layer and since most of the PCB shop are running a largely manual process, a high degree of manual movement and transfer of the coated panels after drying is seen. Dry Film has a Mylar protection cover and therefore the manual movement would not cause any defects on the resist layer whereas it will easily form scratches on the Liquid Photoresist surface. In order to have a product that exhibits a high degree of scratch resistance, the strategy is to mix in specific additives that reduce the resist's tendency to be affected by the manual movement and therefore reduce the scratching defects. The choice of chemicals within the market is even more extensive than the backing materials and the photoreactive materials and formulation effort to find the best product and which concentrates to use is long and complex task.

Another property all the PCB shops want the Photoresist to have is a fast photospeed. That is a fast response to UV light centered around 365 nm, this wavelength coincides with the major emission wavelength of the mercury arc lamps. That would decrease the exposure time and hence increase productivity or reduce the investment on placing additional exposure machines. In response to this, we need to find more reactive materials and also a suitable photoinitator that absorbs the wavelength and has a high quantum yield. For the photoinitator, there are some really low cost and highly effective ones available, unfortunately it is quite difficult to decompose in the environment and would cause harm to the environment. Rohm and Haas Company places environmental, health and safety issues above cost considerations.

The amount of photoreactive material present has a large effect on the photospeed. This is also one of the major components apart from solvent and backing material. Increasing the amount will mean decreasing the ratio of backing material and hence sacrificing stacking properties. Figure 2 illustrates this relationship.

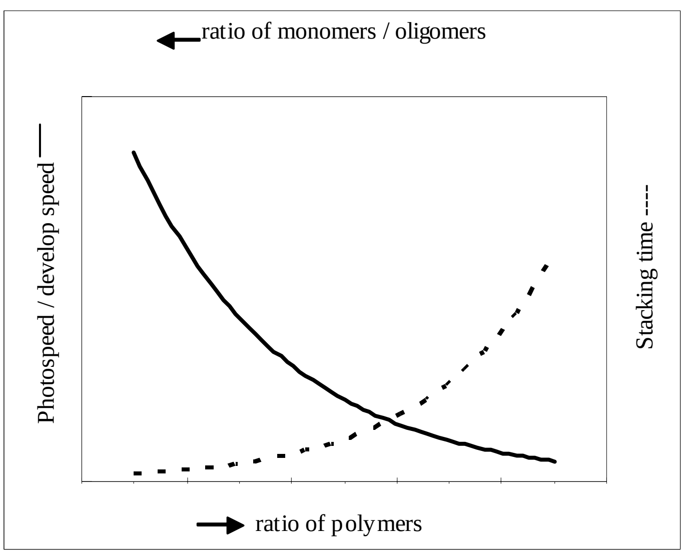


Figure 2 - Relationship between the Ratio of Backing Material, Photoreactive Material, Photospeed, develop Speed and Stacking Time

Another requirement from customers is that they like to have a product that can develop fast to increase in the productivity in the DES process. A good solution to this problem is to decrease the portion of backing material, but it will sacrifice the stacking ability. Therefore a good balance between the two components, backing materials and photoreactive materials is needed. A fact that needs to be clarified is that after setting the developer line too fast, the rinsing section may not be sufficient and this may cause difficulty in the latter process stages. The rate determining step in the DES line is typically the etcher section.

Most formulators tend to ignore the sludge that tends to form in the developer line – either on the developing chamber or the rinsing chamber. If it is too extensive, it results in copper spot or even opens in the resulting panels. According to our findings, if a customer uses deionized water or reverse osmosis water for the developer chamber, the sludge problem can be reduce to a minimum. In formulation, this must be taken into account. There are a lot of components present in the photoresist which will cause this problem. Reduction in sludge formation components can somewhat sacrifice the photospeed.

In the discussion with the properties desired by the PCB shop, the reader can find there are a lot of compromises in the formulation of Liquid Photoresist. There cannot be a single resist that can perform perfectly in every aspect of the properties discussed above.

The Imaging process comprises so many steps and both the chemistry of Photoresist and equipment employed will affect the yield. There is so much balance needed between them that it is difficult to say which type of chemistry or equipment is the best for the market. The best path forward is to ensure good coordination between the PCB shop, material supplier and the equipment supplier for the maintenance of good yield. Table 4 gives the summary of the interaction between the chemistry and equipment affected.

Table 4 - Showing the Impact of each Component on Different Processes

	Monomers	**Polymers**	**Additives**	**Solvent**
Application	High	High	High	Medium
Drying	High	High	Low	High
Imaging	High	Medium	Low	Low
Developing	High	High	Low	None
Stripping	High	High	None	None

Experimental Findings for a New Generation of Liquid Photoresists

It is important to place considerable effort to meet the market requirements for a stable, reproducible, high yielding, and low cost Photoresist. Over the past decade, many Photoresists (Ref#1) have shown improvements in the areas of scratch resistance and stackability, while retaining the resolution of the product. The resist must also be suitable to run in most of the equipment available in the market, both fully automatic and manual handling processes. Hereby, we present some of the experimental findings.

For example, with reference to the requirement of stacking time, we do try to have a formula that after drying would have minimal surface energy. As we believe that there is an indirect relationship between lower the surface energy and resist transfer. Figure 3 shows our progress in surface energy through the development of different versions of resist.

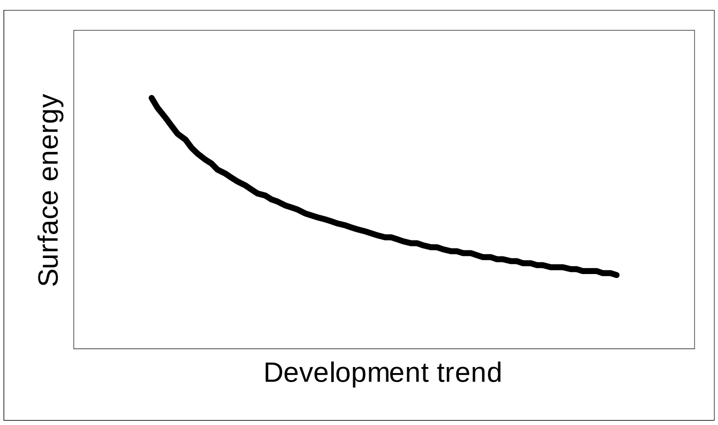


Figure 3 - Graph showing the Development Tend towards Lower Surface Energy Resist

In measurement of the scratch resistant, we have developed a test called Fingers of Depth – both dry and wet. Figure 4 shows how it works and the principle is scratching the panel using a single point of pressure loaded with different weights. This is to simulate scratch during manual handling or accidentally present sharp and point substances within the DES line. Figure 5 shows the results after the Fingers of Death experiment. The resist and hence the circuit remains with no damage greater than 5 % of the line width.

Although, we have formulated a resist that shown the requirement of 72 hours stack time on 70˚ tote, 6 inch stack height with strong scratch resistant, we do not sacrifice any resolution for making any compromise. Figure 6 and Figure 7 show the 3 mil line / space pattern and the lowest resolution possible for a typical liquid resist.

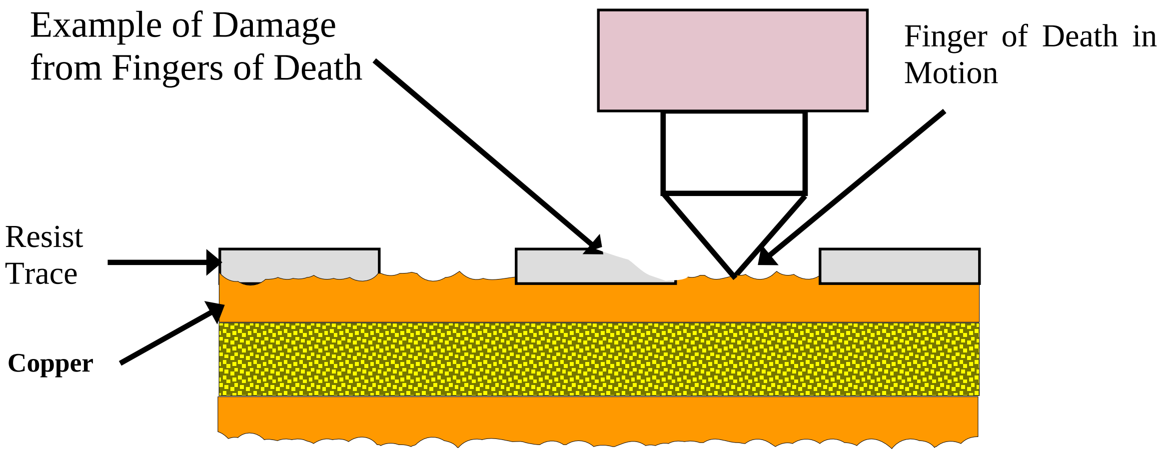


Figure 4 - Drawing shows the Experimental Setup of the Fingers of Death

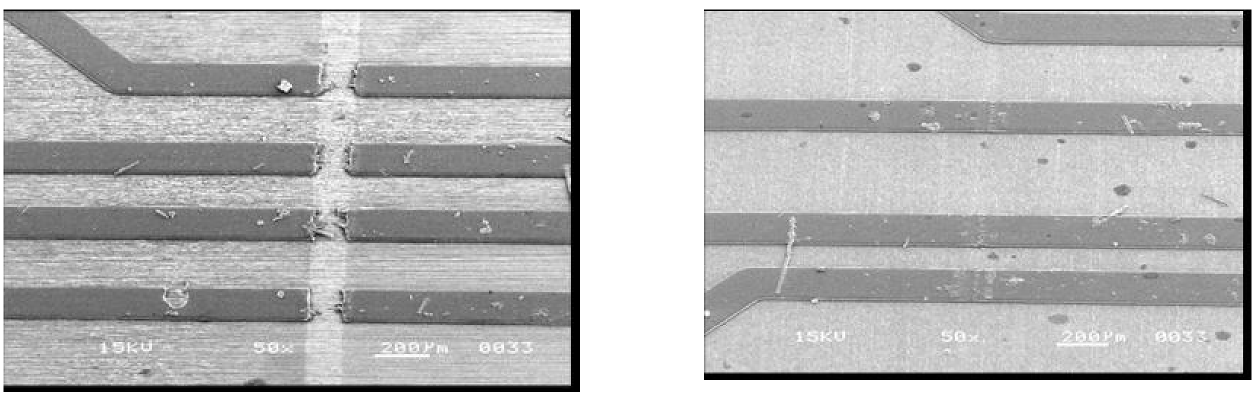


Figure 5 - SEM Pictures showing the Results of Finger of Death a) above, Resist from Competitor; b) below, Latest version of Photoposit@ SN Series

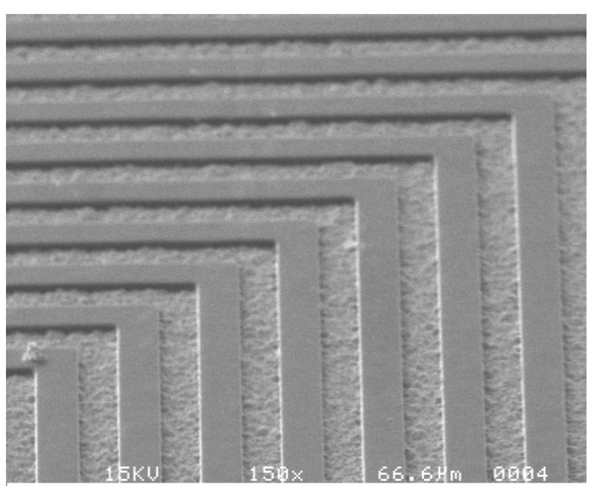
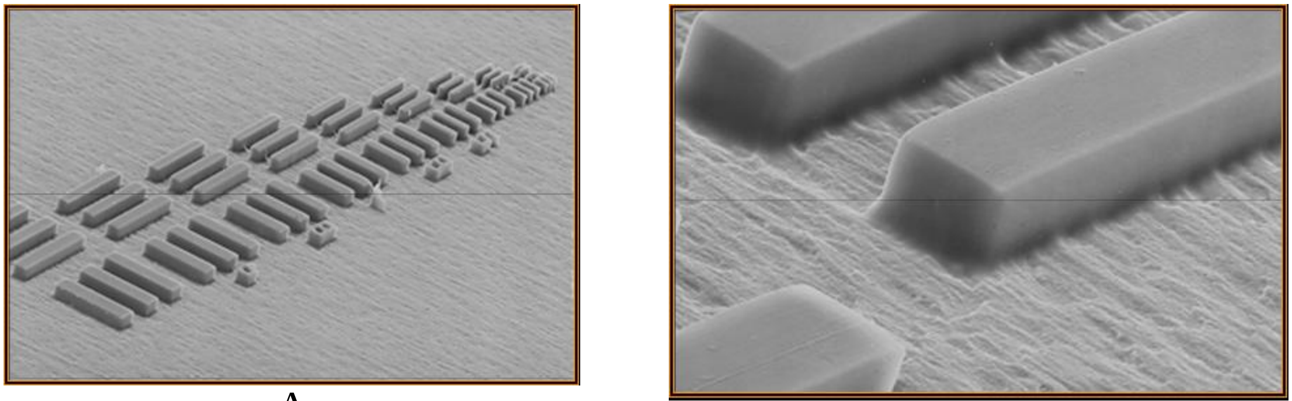


Figure 6 - SEM Picture showing the Line/Space of 3 Mils Line



A

B

Figure 7 - SEM Pictures showing the Resolution of the Latest version of Photoposit[@] SN Series - A: the Line / Space Range shown is between 0.1 to 1.0 mil. B: Close Up SEM Picture

Reference

1. Rohm and Haas' Photoposit[@] SN 35R, Photoposit[@] SN 50A and Photoposit[@] SN 66.