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New Positive Working Dry Film Resist

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Abstract
We will present a new positive working dry film resist system that is suitable for high accuracy use. The new positive working dry film resist is composed of base polymers with active hydrogen functionality, and a multifunctional vinyl ether compound plus a photo acid generator, and makes use of a chemical amplification method to allow imaging at low exposure levels of UV light.

At the pre-bake stage, a ketal structure is formed by an additive reaction between the active hydrogen functional groups and the vinyl ether. Consequently, the base resin is cross-linked and the resist becomes insoluble in an alkaline developer.

At the UV exposure stage, the photo acid generator forms a strong acid and the area of exposure becomes soluble in alkaline developer via an hydrolysis reaction. This new chemistry makes it possible to form a high reliability image with high contrast in comparison with conventional positive- and negative-acting systems. The new positive working dry film resist achieves on the order of 10µm Line/Space patterns plus the ability to tent 5mm diameter through holes with a resist as thin as 10µm.

Introduction

The Trend of The Printed Wiring Board (PWB) Industry

Recently, miniaturization and improved fabrication efficiency of electronic products are demanded with progress of information technology. The minimum line width in 10 years is forecasted to be 10µm [1)].. High resolution photoresist material needs to be developed.

The concentration on fabrication of multi-layer PWBs has further importance because of the same miniaturization and improved efficiency needs of electronic products. Multi-layer PWBs have through holes in order to conduct signals between layers.[1), 2)]

One of the important functions of photoresist materials is to protect through holes from copper etchants. In order to protect the through holes, the negative type dry film resists utilize the tenting method, and the liquid resists make use of an electro-deposition coating method. The performance comparison of negative type dry film resists and liquid resists is shown in Table 1. Negative type dry film resists are very easy to apply with a dry process, and the cost of equipment is relatively inexpensive. Moreover, protection of the through holes can use the tenting method. For that reason, the largest consumption of photoresist materials is of the negative-type dry film resists. However, because the thickness of a negative- type dry film resist needs 40 µm - 75 µm to protect the through holes from the etchant, high resolution is difficult. Liquid resists are very hard to apply in a wet process, and the costs of equipment are substantial. Protection of the through holes can use the electro-deposition coating method. However, for the electro-deposition coating method, management of the liquid resist is difficult. The conventional liquid resists can't protect the through holes from etching liquid because it is impossible for liquid resists to coat into the barrel of the through hole. However, because the thickness of a liquid resist is able to change freely, high resolution is possible. Accordingly, a new positive working dry film resist system, with high resolution was developed.

Imaging Chemistry Used With the New Positive Working Dry Film Resist

The purpose of developing a new positive working dry film resist system is to obtain a very workable resist with high resolution. The thickness of the new positive working dry film resist was determined to be 10µm in order to give the same resolution as liquid resists. The new positive working dry film resist has to protect through holes from copper etchants with a film thickness as thin as 10 µm. The development work was targeted at building the molecular weight of the base resin, while adding a cross-linked structure to keep tenting capability.

The reaction mechanism model of the new positive working dry film resist is shown in Figure 1. The new positive working dry film resist is composed of a base resin with active hydrogen functionality plus a multifunctional vinyl ether compound and a photo acid generator.

Table 1 - The Performance Comparison of Negative Type Dry Film Resists and Liquid Resists

	negative type dry film resists		Liquid resists	
Board having T/H	Possible	(tenting)	Impossible	(difficult to coat into T/H)
Usage	Easy	(dry process)	Hard	(wet process)
Cost of the process equipment	cheep	(laminator)	Expensive	(spray / roll coater)
VOC	Low	(solid)	High	(NV 20% or less)
Film thickness	Thick	(not cross linked)	Thin	(It is possible to change thickness)
Resolution	Low	(thick film)	High	(Thin film)

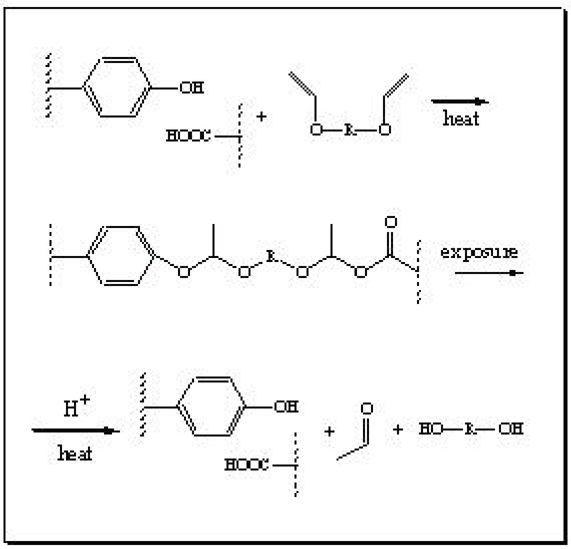

Figure 1 - The Reaction Mechanism Model of the New Positive Working Dry Film Resist

At the pre-bake stage, a ketal structure is made by an additive reaction between the active hydrogen functional groups and the vinyl ether. Consequently, the base resin is cross-linked and the resist becomes insoluble in alkaline developers. At the exposure stage, the photo acid generator generates a strong acid caused by UV light energy. At the post exposure bake (PEB) stage, the acid cuts some cross-linked bonds and an active hydrogen functional group is reproduced (acid hydrolysis reaction). After the PEB stage, the portion of the resist which was exposed becomes soluble in an alkaline developer. The new positive working dry film resist is formed at the pre-baking step from the coating of a liquid resist. The resist layers are tack-free after the pre-baking step, hence the resist doesn't require a cover film. Therefore, the new positive working dry film resist has a two-layer structure, consisting of a resist layer and base film.

Experimental

The pattern formation process is shown in Figure 2. At first, the new positive working dry film resist is laminated onto the substrate (inner layer core or the outer layers of a multi- layer board). The second process step is the exposure. Note: It is recommended to strip the base film before exposure to improve the resolution. Reaction hindrance by oxygen doesn't occur in this new positive working dry film resist system. After exposure, the board with laminated resist is baked using a clean oven or a hot plate. During the PEB process, the acid hydrolysis reaction occurs. The area of the resist which was exposed becomes soluble in an alkaline developer. Then, the conducting pattern is formed after development, etching, and stripping processes.

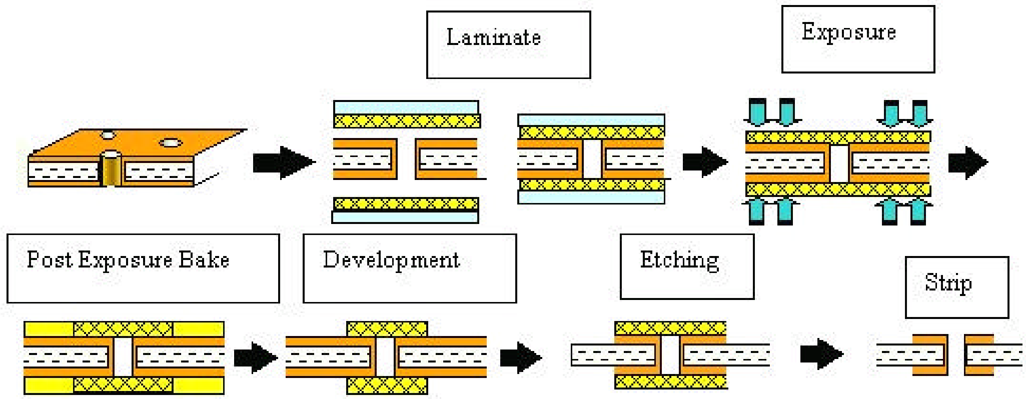

Figure 2 - The Pattern Formation Process

Result and Discussion

Performance of New Positive Working Dry Film Resist

The characteristic curve of the new positive working dry film resist compared to a negative type resist is shown in Figure 3. As for the new positive working dry film resist, the exposure dose required to turn the insoluble part into soluble material is a narrow bandwidth. A typical negative type resist requires a wide bandwidth to accomplish the same result. Because of this narrow bandwidth of UV energy, the new positive working dry film resist has high contrast in comparison with a negative type resist.

Figure 4 shows the relation between a 50µm line width and the exposure dose. The new positive working dry film resist has sufficient management width of exposure dose, which can form a stable 50µm line width.

Figures 5 through 8 show the new positive working dry film resist's pattern capability as the PEB temperature is varied. For the new positive working dry film resist, the PEB process is critical. During the PEB process, the acid hydrolysis reaction is promoted. The PEB process causes the cross-linked structure to decompose, and cause that portion of the resist which was exposed to the UV light to become soluble in an alkaline developer. Pattern images were also observed during the variation in temperatures with the PEB process. Figure 5 shows such a pattern image with a temperature of 130 °C, Figure 6 also shows a pattern image appearing with a PEB temperature of 120 °C, and Figure 7 shows a pattern image with a temperature of 110°C and Figure 8 shows a pattern image with a temperature as low as 100 °C. The lower the PEB temperature is, the better defined are the patterns.

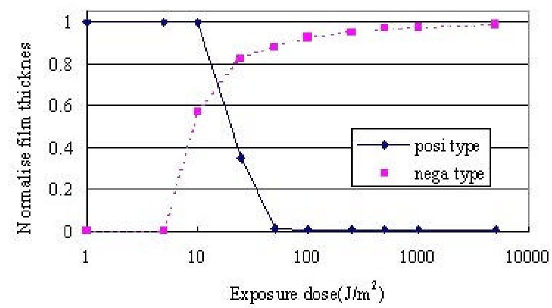

Figure 3 - The Characteristic Curve of New Positive Working Dry Film Resist and Negative Type Resist
Laminate: 120°C 0.4MPa 1m/min PEB: 120 °C 10minites
Development: 25 °C 0.75% Na_2CO_3 30sec

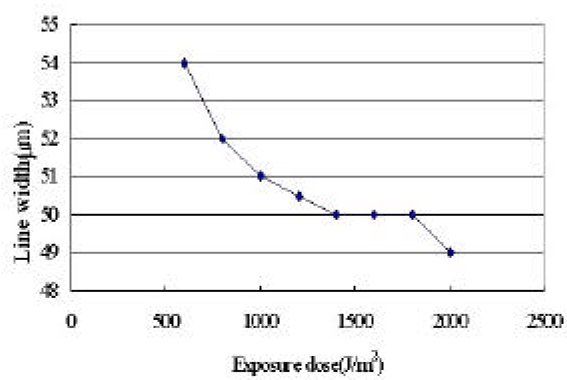

Figure 4 - The Relation Between 50mm Line Width and Exposure Dose
Laminate: 120°C 0.4MPa 1m/min PEB: 120 °C 10minites
Development: 25 °C 0.75% Na_2CO_3 30sec

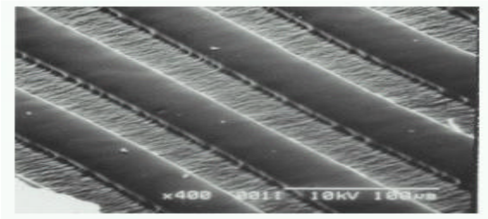

Figure 5 - The Pattern Image of PEB Temperature: 130 ^{o}C (Line/Space=50/30μm) Laminate: 120 ^{o}C 0.4MPa 1m/min - Exposure: 1000J/m^2 PEB: 130 ^{o}C 10minites Development: 30 ^{o}C 1.0% K_2CO_3 60sec

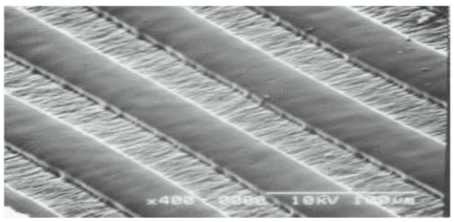

Figure 6 - The Pattern Image of PEB Temperature:120 ^{o}C (Line/Space=50/30μm) Laminate: 120^{o}C 0.4MPa 1m/min Exposure: 1200J/m^2 PEB: 120^{o}C 10minites Development: 30 ^{o}C 1.0% K_2CO_3 60sec

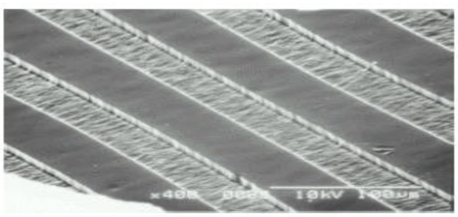

Figure 7 - The Pattern Image of PEB Temperature: 110 ^{o}C (Line/Space=50/30μm) Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1600J/m^2 PEB: 110 ^{o}C 10minites Development: 30 ^{o}C 1.0% K_2CO_3 60sec

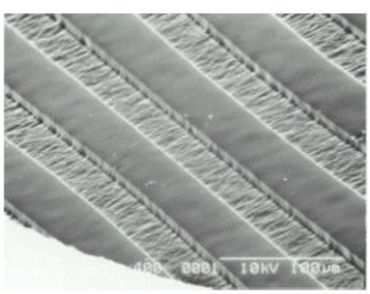

Figure 8 - The Pattern Image of PEB Temperature: 100 ^{o}C (Line/Space=50/30μm) Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure 1800J/m^2 PEB: 100 ^{o}C 10minites Development: 30 ^{o}C 1.0% K_2CO_3 60sec

Figure 9 shows a characteristic curve with varying the concentration of the developer. Although the concentration of the developer is varied from 0.5% to 1.0%(25ºC Na_2CO_3), the resist's characteristic curves do not change. The result of this experimentation is that the resist contrast of this new positive working dry film resist does not depend on the concentration of the developer, over reasonable ranges.

Figure 10 shows the relation between developing time and line width, where the photo mask line width is nominally 20μm. Even if the development time is changed, it does not influence the line width. Figures 11 and12 show the relation between developing time and line quality. The pattern quality doesn't depend on development time. The new positive working dry film resist's resistance to variations in development time is excellent

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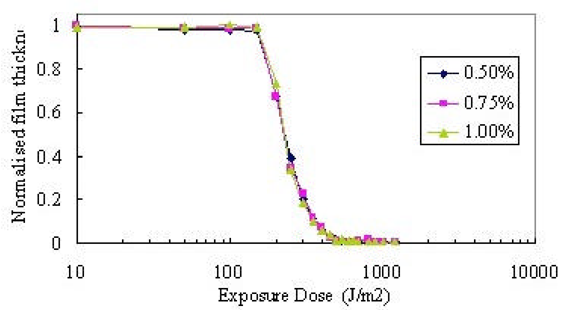

Figure 9 - The Characteristic Curve at Changing Concentration of Developer Laminate: 120^{o}C 0.4MPa 1m/min PEB: 120^{o}C 10minites Development: 25 ^{o}C 0.5%, 0.75%, 1.0%Na_2CO_3 30sec

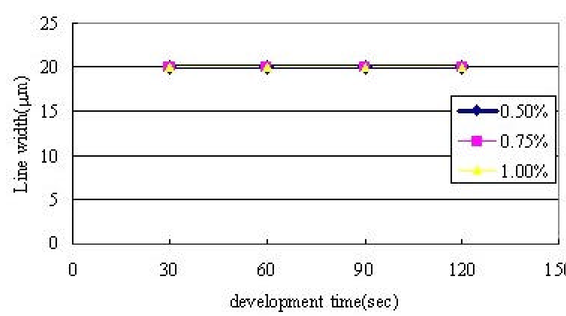

Figure 10 - The Line Width of the Resist Pattern at Changing Development Time Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1200J/m^2 PEB: 120 ^{o}C 10minites Development: 25 degree 0.75% Na_2CO_3

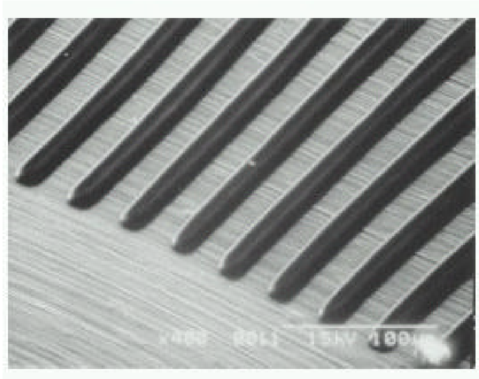

Figure 11 - The Line Pattern Image of Short Development Time
Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1200J/m^{2}
PEB: 120^{o}C 10minites Development: 25 ^{o}C 0.75% Na_2CO_3 20sec

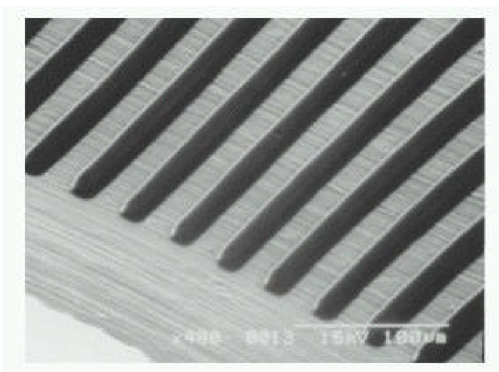

Figure 12 - The Line Form of Long Development Time
Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1200J/m^{2}
PEB: 120 ^{o}C 10minites Development: 25 ^{o}C 0.75% Na_2CO_3 60sec

Since the thickness of the new positive working dry film resist is 10μm, it is possible to resolve an image to a high degree of precision. This high pattern resolution is shown in Figure 13. The new positive working dry film resist achieves Line/Space patterns in the order of 10μm.

Since the thickness of the new positive working dry film resist is 10μm, there have been concerns about the etching tolerance of the copper foil. Figure 14 shows the new positive working dry film resist's pattern after development (before etching) and Figure 15 shows the pattern in the copper foil after etching. Because the new positive working dry film resist has a cross-linked structure, it is very resistant to the etching liquid. The resist yields very little side etching, because the thickness of the resist is so thin (10 μm). Therefore, the resist is very capable of forming fine conductive patterns.

A special feature of this new positive working dry film resist is the tenting capability with such a thin film. The tenting strength of this new positive working dry film resist was measured. Figure 16 shows tenting strength. A through hole of 5mm diameter was punctured with a pin of 1.5mm diameter at an insertion rate of 5mm/min. The result showed good strength of 3.2N with an elongation of 3.5mm before final rupture. The new positive working dry film resist has a strong tenting strength. Moreover, it has been observed that the occurrences of broken tents during actual processing is essentially zero. The evaluation of the appearances of broken tents was done after the development process (25^{o}C; 0.5% Na_2CO_3; pressure 0.15Mpa for 30sec) and after the etching process cupric chloride at 50^{o}C and a pressure of 0.2Mpa for 105sec. The occurrences of broken tents were seen to be 0% for 15,000 through holes. Therefore, this new positive working dry film resist has sufficient tenting strength to protect the through holes from the developer and etching processes. Figure 17 shows a pattern image which is a tented film after development and etching.

Figure 13 - The Line Form of Line/Space=10 / 10μm Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1200J/m^{2} PEB: 120 ^{o}C 10minites Development: 25 ^{o}C 0.75% Na_2CO_3 30sec

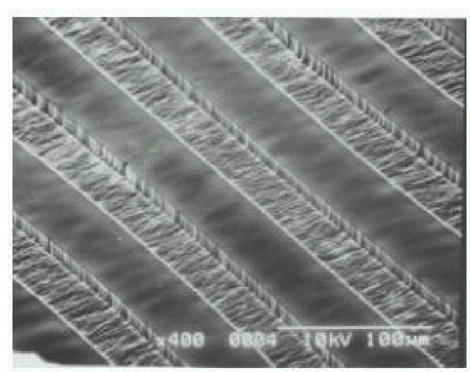

Figure 14 - The Pattern Image of New Positive Working Dry Film Resist after Development (before etching) Laminate: 120 ^{o}C 0.4MPa 1m/min Exposure: 1200J/m^{2}
PEB: 120 ^{o}C 10minites Development: 25 ^{o}C 0.75% Na_2CO_3 30sec

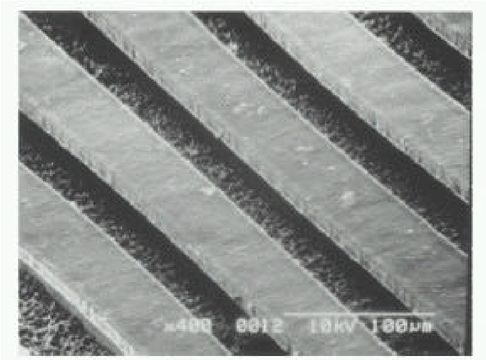

Figure 15 - The Pattern Image of New Positive Working Dry Film Resist after Etching Laminate: 120 °C 0.4MPa 1m/min Exposure: 1200J/m
PEB: 120 °C 10minites
Development: 25 °C 0.75% -Na_2CO_3 30sec
Etching: copper(II) chloride 50 °C 90sec

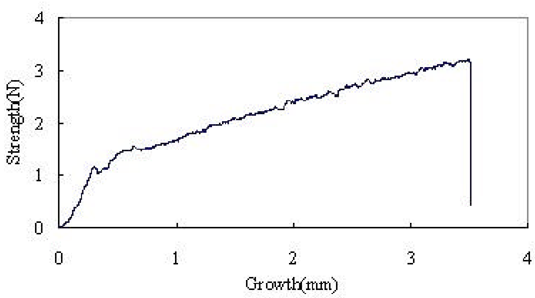

Figure 16 - Tenting Strength Test T/H (5mm diameter) Sticking with Pin (1.5mm diameter) by 5mm/min Laminate: 120 °C 0.4MPa 1m/min PEB: 120 °C 10 minutes T/H (5mm diameter) was stuck with pin
(1.5mm diameter) by 5mm/min

Figure 17 - The Pattern Image of Tenting Film Laminate: 120 °C 0.4MPa 1m/min Exposure: 1200J/m^2 PEB: 120 °C 10minites Development: 25 °C 0.75% Na_2CO_3 30sec Etching: copper (II) chloride 50 °C 90sec

Other Applications of the New Positive Working Dry Film Resist

The use of LDI (laser direct imaging) has been reported. The conventional mask exposure system requires exposure, development, etching, and strip process after the circuit data design, mask creation, and mask inspection. LDI (laser direct imaging) can skip the mask design and inspection processes. It can expose directly from the circuit data design by CAD/CAM.

Moreover, high positional accuracy, improved yields, multiple types of production, short delivery times and a fully-automated process are all advantages of LDI. Pattern formation by LDI has been conventionally performed using visible light (488nm Ar^+ laser and 588nm YAG-SHG laser). Recently, a 365nm Ar^+ laser was developed. In order to develop the film after exposure using LDI, a high sensitivity resist is indispensable. Changing the amount of the photo acid generator in the film causes changes to the sensitivity of the film. A pattern was formed using a commercially available 365nm Ar^+ LDI laser. A Line/Space pattern of25/25µm was formed by using 80 J/m^2 (Figure 18). Therefore, the new positive working dry film resist has shown that it is very compatible with the use of the UV-LDI process. There are variations in the resolution between LDI and a photomask process, because optimization of the exposure with LDI has not been performed. But, it is expected that the same resolution can be obtained with the LDI process as with a photomask process with proper optimization.

It is forecast that the need for further fine pattern formation will be increasing in the future. The mainstream method used today to form conductive patterns is a subtractive technique. However, side etching influences the resolution obtained with the subtractive process. The semi-additive process is gathering attention as the better technique for forming high resolution circuitry. Part of the evaluation of the semi-additive method of the new positive working dry film resist was testing the resist in a copper plating bath. The result is shown in Figures 18through 21. The resist film thickness was 20µm for this test. Figure 19 shows the Line/Space pattern was 20/20µm after development. Figure 20 shows the pattern after copper plating. Figure 21 shows the pattern after the resist was stripped and a soft etching step. A Line/Space pattern of a 20/20µm conductive pattern can be formed using this new positive working dry film resist. The new positive working dry film resist will be evaluated and is expected to be successful with using it in a semi-additive plating process.

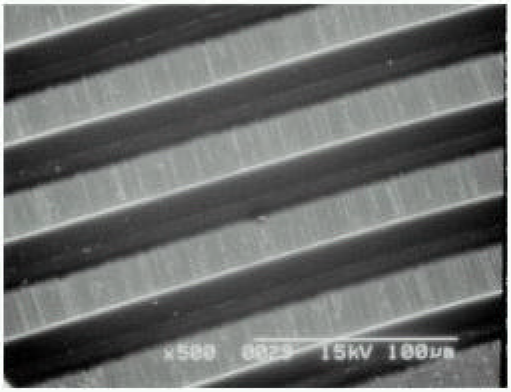

Figure 18 - The Pattern Image Exposed with UV Laser Direct Image Equipment (Line/Space=25/25mm) Laminate: 120 ^oC 0.4MPa 1m/min Exposure: 80J/m^2 (laser direct imaging system DP-100M made by Orbotech Ltd.) PEB: 120 ^oC 10minites Development: 25 ^oC 0.75% Na_2CO_3 60sec

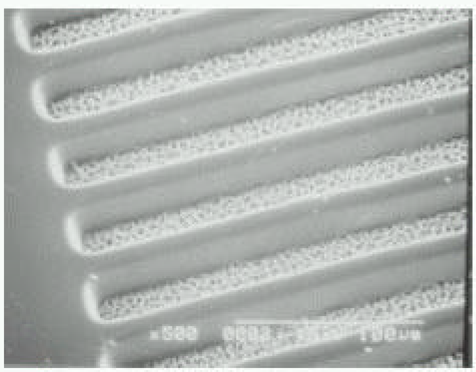

Figure 19 - After Development
Line/Space=20/20mm Pattern Laminate: 120 ^oC 0.4MPa 1m/min
Exposure: 1200J/m^2 PEB: 120 ^oC 10 minutes
Development: 25 ^oC 0.75% Na_2CO_3 30sec

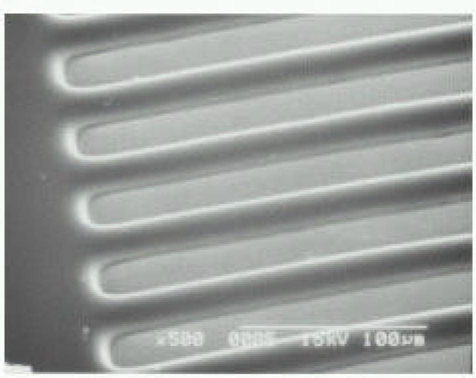

Figure 20 - After Copper Plating
Plating: Acidity Washing; Soft Etching; Acid Treatment;
Elector Copper Plating

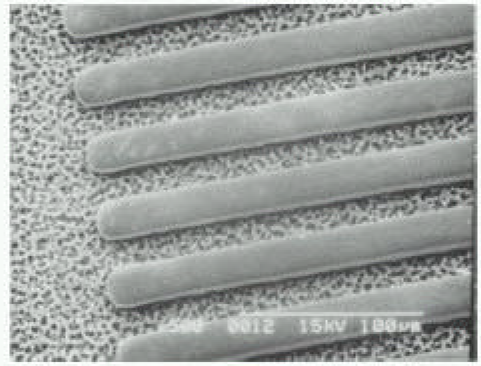

Figure 21 - After Resist Stripping and Soft Etching
Stripping: 50 ^oC, 3% NaOH 3minites

Conclusion

As mentioned above, a new positive working dry film resist was developed having both the characteristics of a liquid resist and a negative type dry film resist. This resist has high resolution, and good workability. Since this new positive working dry film resist has a cross-linked structure, it has excellent tenting strength. Since such a thin-film is possible with this material, the resist has the ability to resolve down to 10µm /10µm Lines / Spaces.

References

1. The electronics packaging technology road map in 2010
2. G. Imai : Electronic Circuits World Convention '99