Development of New Photoresist Stripping Agent

Ching-Yi Chu, Te-Jung Hsu, Tzu-Hsing Chiang, Yung-Ming Wang, Shiu-Chin Wang, Ping-Feng Yang, Jen-Kuang Fang

Chemical Lab, Advanced Semiconductor Engineering. Inc., Nantze Export Processing Zone, 811

Te-Jung_Hsu@aseglobal.com

ABSTRACT

Optical lithography is one of the most extensively used technologies in the fabrication of a printed circuit board (PCB) or a semiconductor device. In recent years, as the demand for smaller sized electronic appliances increases and the cost of the stripping agents keeps escalating, higher standard and requirement on existing photoresist stripping technology is demanded for the semiconductor industry. In conventional techniques, photoresists can be removed by simple hydroxides based stripping agents. Proprietary stripping agents which are predominantly based on amine chemistry have attracted much attention because of their proven ability to make the photoresist film particulate into small features thus to show faster and improved stripping efficiency. However, the photoresist stripping ability of known stripping agents is insufficient to tackle the newly developed fine process and short time treatment in the production of semiconductor devices and liquid crystal display panels. Moreover, these known stripping agents are reported to show negative effect on the PCB production process with problems such as high metal corrosion rates which can lead to tin transfer and etch retardation. Therefore, it has been a high demand for further improvement of the stripping ability.

Up to date, the stripping agents we used are capable of dry films removal processes within a short period of time. However, the existing stripping agents are not powerful enough to clean the liquid photoresists efficiently. The liquid photoresists removal process performs much worse with high level of residues which requires a second exposure and lead to unacceptable scrap rates after etching. Furthermore, corrosive attack on copper substrate by these existing stripping agent results in an uneven wire width after gold plating. In order to resolve such issues, development of the next generation of photoresist stripping agent which can be applied to both dry and wet film with minimal attack on the metal base is an urgent issue in the immediate future.

In this paper, a photoresist stripping agent containing a combination of amine compounds in aqueous alkaline based solutions is proposed. By using this new photoresist stripping agent, the circuit appears to have been fully stripped of all dry film with increasing stripping rate and the production was increased by 60%. New product is also capable of completely removing the liquid photoresists without secondary processes, and the production was increased by 25%. The use of new formulation avoids any undesirable metal attack. In addition, the cost of the new formulation is much less than the existing stripping agent. With the advantages of lower cost, better stripping ability and increase of production rates, the new stripping agent is aimed to replace the older stripping agent in order to produce high quality product.

INTRODUCTION

A photoresist is a light-sensitive material utilized in the lithographic production of wide range of devices such as integrated circuits, LCD display devices, printed boards, micro machines, and DNA chips. To form a circuit pattern on a substrate, a semiconductor wafer is periodically coated with photoresist in order to fabricate various layers of circuitry, electrical devices, vias and interconnects. After the development and usage of photoresist, etching and washing are performed, and these processes will result in residues that have to be removed before further processing.

In traditional procedures, photoresist strippers are used to remove unwanted photoresist and the residues from etching and washing. The conventional stripper compositions for a photoresist include widely used organic and inorganic alkaline solutions. Ideally, photoresist strippers should show good ability to completely remove the unwanted components while preventing the corrosion of the metal chips. However, in reality it is difficult to achieve such goal. Most of the photoresist strippers are unable to selectively remove the photoresist or etching and washing residues without damaging the desired circuit structures. Consequently, the production yields are severely limited because of the damage to the chip optical properties. Thus there is an urgent need to develop a photoresist stripper composition with low metal corrosions.

So far, the photoresist stripping agents that are currently available can only remove the dry films in a short period of time. With wet films, these agents are unable to clean out unwanted residues at once and require a second stripping process, which is very time-consuming and thus increase production cost. In addition, as finer line gradually gained its popularity in the semiconductor industry, and as the developments in films and inks has led to better adhesion and stability, the commercially-available photoresist stripping agents can no longer meet the needs for fine line photoresist removal. Therefore, a more cost-effective stripping agent with good ability to remove fine line photoresist is in high demands for the industries.

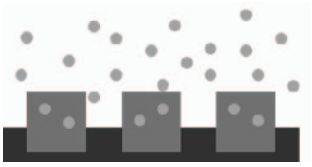
In this study, a series of new photoresist stripping agents which consist of a quaternary ammonium hydroxide, an alkanolamine and an alkali metal hydroxide for a semiconductor device has been prepared. The newly

 IEEE Catalog Number: CFP1459B-ART ISBN: 978-1-4799-7727-7

developed stripping agents show high efficiency for dry film and wet film removal. They are aimed to replace the currently available commercial agents, and be further applied in the semiconductor industry.

PHOTORESIST STRIPPING MECHANISM

Because of the presence of the carboxylic acid groups within the binder system of both dry and liquid photoresist, stripping process can be carried out through a simple neutralization reaction with strong alkali media or amine based solutions. The stripping mechanism can be summarized as the following four steps.



Step 1: diffusion
The stripping solution starts to diffuse into the dry film layer. Ion repulsion between COO- and COO- makes the film swelling. The hydrophobic nature of the film will greatly affect the diffusion.

Step 2: neutralization
The basic stripping solution reacts with the carboxylic group within the dry film to form soluble polar salts. This step further accelerates the diffusion of the stripping solution into the film.

Step 3: rupture
Internal stress of the film increases because of the presence of the water and the polar salts within the film. As a result, the film begins to rip itself apart (rupture) and particulate.

Step 4: film lift and strip
Stripping solution keeps penetrating through the film as it rupture. Interface attack of the film layer and the copper surface by the stripping solution results in the film lifts from the panel and becomes "stripped".

With the amine based stripper system due to the diffusion rate is slower, higher degree of salt will form during the stripping process. Subsequently, much more internal stress will appear within the film and therefore smaller particle size will achieved with amine based strippers.

RESULT AND DISCUSSION

In recent years, shortening the stripping time in a semiconductor device production process has become an important task in stripping technology. Conventionally, a mixed system of an alkanolamine and an organic solvent has been widely utilized as a photoresist stripping agent.[1-2] However, this formula does not have sufficient stripping ability and always exhibits high metal corrosion rate. In addition, stripping solution employing tetramethylammonium hydroxide (TMAH), hydrogen peroxide and a nonionic surfactant requires a high temperature and a sufficiently long period of time for removal of a photoresist.[3] Furthermore, a stripping agent containing potassium hydroxide, a water-soluble organic solvent and a metal corrosion inhibitor can perform stripping in short period of time, but high temperature is always necessary.[4] More importantly, the chemical used as corrosion inhibitor, benzotriazole, will cause a high level of environment burden and therefore should be avoided in device production.

Many attempts have been made in order to develop an efficient stripping system with high photoresist removability in mild condition. Stripping solutions 1 to 6 having the compositions shown in Table 1 were prepared. A segment (3cm x 3 cm) from the patterned wafer was immersed in each of the solutions. The immersion test was carried out at 55 ^{o}C in a temperature-controlled water bath. The segment was taken out after the immersion test and then washed with DI water and dried with N_2. After immersion test, the sample was evaluated by optical microscope in order to determine the presence of any photoresist residues. The stripping ability of new formulations and optical microscope results for dry film and liquid photo resist are summarized in Table 1.

As shown in Table 1, commercially available stripping agent based on alkaline and amine based solution (**CA1**) shows negative stripping result on liquid photo resist. OM image shows photoresist residues after the stripping process. Stripper **RD1** comprises a mixture of organic amine based solution and ethylene glycol monobutyl ether in a ratio of 1:1. Ethylene glycol monobutyl ether is normally employed in the solution to assist the stripping process. It can dissolve the resist material during the stripping process. Therefore adding ethylene glycol monobutyl ether can prevent the frequent plugging of filters and nozzles because its ability to retain the stripped resist in solution. However, the stripper based on this formula was unsuccessful to show good stripping ability on the liquid photoresist. Only dry film can be removed by this agent. Stripping solution **RD2** includes 5 to 7 weight parts of hydroxide based solution; 8 to 12 weight parts of amine based solution; 0.3 to 0.5 weight parts of ethylene glycol monobutyl ether. It turns out that this newly developed stripper is

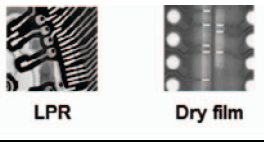
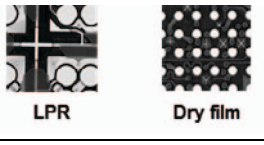
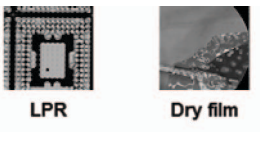
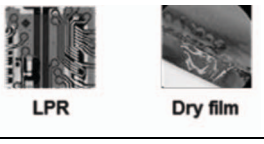
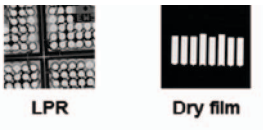
Formula	Stripper components	Weight (%)	Temp. (°C)	Results	OM images
CA1	Alkaline based	15	55	Dry film: passed Liquid PR: failed	
	Organic amine	30			
RD1	Organic amine	3	55	Dry film: passed Liquid PR: failed	
	EGME	3			
RD2	Hydroxide based	5-7	55	Dry film: failed Liquid PR: failed	
	Organic amine	8-12			
	EGME	0.3-0.5			
RD3	Hydroxide based	5-10	55	Dry film: failed Liquid PR: failed	
	Organic amine	5-10			
RD4	Hydroxide based	2-5	55	Dry film: passed Liquid PR: passed	
	Organic amine	2-5			
	TMAH	0.01-0.1			

Table 1. Results for removal of dry film by different stripping solutions.

unsuitable for both dry film and liquid photoresist removal. OM image clearly shows high level of resist residues. Stripping liquids **RD3** having the compositions of 1 to 2 ratios of hydroxide based solution and amine bases gives unacceptable stripping results. Although increasing the amount of amine bases makes the resist particulate into small features, the new stripper still not strong enough to completely remove the liquid photoresist. Stripper **RD4** was constructed from 1 to 1 ratio of hydroxide based solution and organic amine bases plus 0.01 to 0.1 weight parts of tetramethylammonium hydroxide. The adding of small amount of quaternary ammonium hydroxide salts in our new stripper gives excellent stripping result. New stripper exhibits improved stripping results by reducing occurrence of photo resist residues. Two types of resists were successfully removed in a short period of time. Most importantly, the new formulation not only passes the beaker test in the lab, it has been installed in our production lines to replace the original stripping agent.

CONCLUSION

Since photo imageable dry films and liquid inks are widely used in the PCB industry, the need for capable photo resist stripper has greatly increased. So far, the photoresist stripping ability of commercially available stripping agents is insufficient for rapidly developed fine process and short time treatment in the production of semiconductor devices.

Therefore, a cost-effective stripping agent with good ability to remove fine line photoresist is under a high demand from the industries. In conventional techniques, different strippers should be chosen for the dry films or liquid photo resists removal. Our ultimate goal is to develop a single stripping system suitable for both fry film and liquid inks. In this paper, a new photo resist stripping agent with enhanced stripping ability is successfully prepared. The newly development stripper show no tendency to attack the metal substrate. Most importantly, the new formula replaced currently available commercial agents and has now been production and show improved results with reduced occurrence of photo resist residues.

REFERENCES

1. US Patent No. 7998914B2
2. US Patent No. 7888300B2
3. US Patent No. 20090082240A1
4. US Patent No. WO2013025619A2

 IEEE Catalog Number: CFP1459B-ART ISBN: 978-1-4799-7727-7