微細配線形成向け電解めっき用ネガ型レジストの開発

Development of Fine pitch Negative Tone Resist for Electro-Plating

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3D-TSVや2.5Dおよびフリップチップ実装などの高密度実装の実現には，より微細な再配線層（RDL）を形成できる電解めっき用レジストが必要とされている．一般にラジカル架橋システムを用いたネガ型レジストは，酸素による重合阻害がパターン形成をする上で大きな問題となっており，特に微細な再配線層の形成に使用される薄膜条件においてその影響が顕著となる．著者らは，光重合開始剤の感度とポリマーの現像液への溶解速度を制御することで，10 um以下の薄膜条件下においても矩形な微細パターン（2 um L/S，アスペクト比＞3）が形成可能であることを見出し，新規ネガ型レジストを開発した．

High density packaging such as 3D-TSV, 2.5D interposers and Flip-chip wafer bumping requires fine pitch redistribution layers (RDL). In order to satisfy these requirements, we developed a novel negative tone resist for RDL. Generally, oxygen inhibition for cross-linking reactions is a major issue for negative tone resist, especially at film thickness conditions of <10um. We found that the sensitivity of the photo initiator and the developing speed of the polymer have major effects on patterning performance. In this study, we developed a new negative tone resist which shows high resolution (<2.0 um line and space), and high aspect ratio (>3) with straight pattern profiles even under 10 um film thickness conditions.

1 Introduction

In recent years, novel electronic products, like mobile phones and personal computers, have become dramatically smaller and more highly functionalized. Parallel to these market trends, packaging structures for semiconductors are also required to become smaller, thinner and more complicated. To satisfy various requirements, packaging technologies such as 3D-TSV, 2.5D interposers, and Flip-chip wafer bumping are under development[1–5]. These packaging structures require multilayered and/or fine-pitched Cu redistribution layers.

To form Cu redistribution layers, several types of photo resist have been used such as positive tone diazonaphthoquinone （DNQ） resist[6], positive tone chemically amplified resist and negative tone acrylic resist. Among these, negative tone acrylic resist is expected to provide excellent plating resistance for various solutions such as Cu, Ni, Sn/Ag and Au due to their cross-linking systems. Plating resistance and profile control are important key requirements for electro-plating materials. To achieve good patterning performance, it is important to control the cross-linking reactions in the resist formulation, because radical cross-linking systems are influenced by oxygen in atmosphere. Oxygen is well known as an inhibitor for radical polymerization reactions[7,8]. Espe-

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cially in thin film thickness targets below 10 um, the impact of this interaction cannot be ignored in terms of patterning performance such as photo speed, resolution and patterning profiles.

In this paper, we developed a new negative tone resist, which shows faster photo speed (<100 mJ/cm2), higher resolution (<2.0 um) and better strippability with straight pattern profiles at thin film thicknesses, and report possible mechanisms for solving this issue.

1.1 Design concept of negative tone resist

We have adopted negative tone free-radical type resists due to their excellent resistance for electroplating. The design concept of our negative tone resist is shown in Figure 1. The main components of our negative tone resist consist primarily of acrylate resin as a base polymer, cross-linkers such as vinyl compounds, and photo-initiators. As a cross-linking mechanism, i-line (365 nm) irradiation generates radical components from photo-initiators and induces a cross-linking reaction directly between the double bond of the vinyl compounds. The chain growth reaction forms a cross-linked network with the binding base polymer, which shows to be less soluble in alkali developer. This exposed area formed with three-dimensional cross-linking structures in negative tone resist is strongly expected to provide excellent resistance for various plating solutions. Controlling the transparency of the acrylate resin is also important in forming straight pattern profiles.

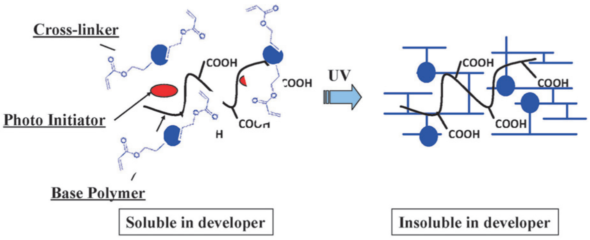


Figure 1 Cross-linking system of the negative tone resist.

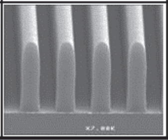
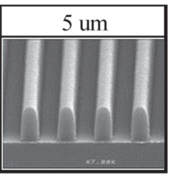
Coating Film thickness	10 um	5 um
Pattening profile @L/S=2.0 um/2.0 um		

Figure 2 Pattern profiles of our conventional resist for RDL at 10 um and 5 um film thickness.

Negative tone acrylic resists have high potential as electro plating resists for various film thickness targets. However, the patterning performance at thin film thicknesses, especially below 10 um, is a concern. Oxygen inhibition can have a significant effect on pattern profile. Figure 2 shows patterning profile comparisons of our conventional resist at 10 um and 5 um film thicknesses. These patterns showed relatively round top profiles, and tapered profiles are obvious at 5 um film thickness. This result suggests that oxygen inhibition impacts resist profiles, especially for thin film thickness applications.

A simulation study was conducted to determine which resist properties impact pattern profiles at thin film thickness. Figure 3 shows the results of patterning profile simulations with different developing speeds of photo resists. Each simulation was conducted with Porith X4.2(KLA Tencor). Model-A and -B have same developing speed at un-exposed areas(Rmax:1000 nm/s). Model-A has slower developing speed at exposed area (Rmin:25 nm/s) compared to Model-B(Rmin:60 nm/s). The simulation result of Model-A has rectangular profiles with a high remaining film thickness ratio. On the other hand, the profile results of model-B, those having higher developing speed at exposed areas, show tapered profiles with low remaining film thickness. These simulation results suggest that controlling resist developing speed and increasing remaining film thick-

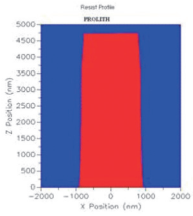
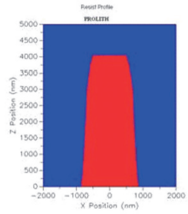
	Model-A	Model-B
Rmax [nm/s]	1000	1000
Rmin [nm/s]	25	60
Patterning Image		

Figure 3 Patterning profile simulation of Model-A and-B.

ness after development are important factors to obtaining straight pattern profiles.

2 Experimental sections

Table 1 shows the standard process conditions. First, each resist was coated onto a Cu sputtered Bare-Si wafer to target the optimum coating film thickness, then soft baked at 90 ℃ for 2 min on the hot plate and then exposed with an i-line stepper. Finally, these sample films were developed with 2. 38 wt% TMAH aqueous solution for 20 sec. After O_2 ashing 100 W/60 sec, a Cu plating evaluation was conducted using EEJA Microfab Cu300 solution and the remaining resist was stripped with DMSO/TMAH base stripper at 23 ℃ for 10 min.

3 Results and discussion

In this section, we discuss the results of a photo initiator and polymer study, which have major impact on lithography performances. The study was targeted at maximizing remaining film thicknesses and developing speeds for improvement of thin film lithography performances at targeted film thicknesses (5 um coating film thickness).

3. 1 Study for Photo initiator

Table 2 shows the properties of the photo initiators that were tested. Three kinds of photo initiators, having different quantum yields (ϕ) and molar absorption coefficients (ε) were tested. Evaluation samples were prepared with two different loading amounts of photo initiators while keeping same ratio of other ingredients to compare absorbance at 365 nm (Table 3). Each sample was checked for remaining film thickness after exposure and development process steps. Figure 4 shows the remaining film thickness behaviors though exposure dose amount. Regarding remaining film thickness, higher absorption samples, Samples 4 and 5, especially with higher loading amounts of photo initiator showed higher remaining film thicknesses compared with Samples 1 and 3. Sample 2, having photo initiator I–B, showed the highest remaining film thickness ratio under absorbance 0. 2 conditions. However the loading

Table 1 Standard process conditions

Item	Condition
Film thickness	5-10 um
Soft bake	90 ℃ 2 min
Exposure	i-line stepper (N.A=0. 50, σ=0. 50)
Development	20sec/2. 38 wt % TMAH w/o surfactant
Rinse	60sec / DI water
Ashing	O_2, 100 W/60 sec
Plating	EEJA Cu300, 3ASD
Stripping	DMSO/TMAH base, 10 min@23 ℃

Table 2 Properties of photo initiators (Catalog values)

Photo initiator	I-A	I-B	I-C
Type	(Oxime type)	(Acylphosphine type)	(Aminoketone type)
ρ	0. 8	0. 6	0. 3
ρ	$8*10^3$	$5*10^2$	$8*10^3$

Table 3 Resist formulation properties

Sample	1	2	3	4	5
Photo initiator	I–A	I–B	I–C	I–A	I–C
Absorbance@365 nm	0. 2	0. 2	0. 2	0. 4	0. 4
Remaining film thickness ratio @400 mJ/cm^2 [%]	74	79	65	85	79

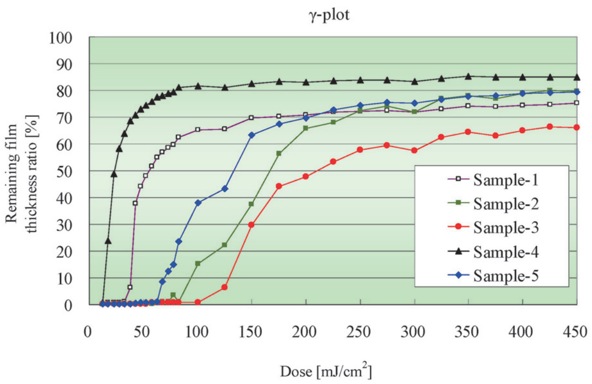


Figure 4 γ-plot (x-axis: exposure dose, y-axis; Remaining film thickness ratio)

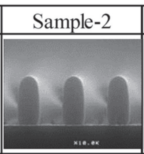
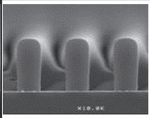
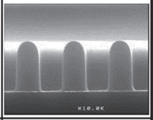
Sample	Sample-2	Sample-4	Sample-5
Petterning profile			
Remaining film thickness	4.0 um	4.4 um	4.0 um

Figure 5 Cross-section SEM observations of Sample 2, 4 and 5.

amount of I–B into the resist formulation was limited due to a lower absorption coefficient. Formulation of a sample for absorbance 0.4 was not possible. As a result, Sample 4, which includes I–A photo initiator having the highest quantum yield with large absorbance at 365 nm, showed the best performance for remaining film thickness. The patterning profiles comparison among Samples 2, 4 and 5 are shown in Figure 5. Sample 4 has rectangular top profiles compared with Samples 2 and 5 showing relatively top round profiles. These results suggest high quantum yield and large absorbance is necessary to obtain good patterning properties under thin film thickness condition.

3.2 Study for Polymer screening

As described in the previous section, high sensitivity photo initiator plays an important role in controlling pattern profiles for thin film negative tone resists. However, to meet fine pitch patterning requirements, further formulation study is needed to determine the optimum solubility behavior for resist formulation under for use with high sensitivity photo initiator existence. The resist solubility behavior is mainly affected by the properties of the base polymer. Table 4 shows polymer screening samples including three different types of polymers. Samples 6, 7 and 8 are formulated to show different developing speeds with the same optimized photo initiator composition based on the previous section. Samples 7 and 8 contain higher developing speed polymers and show better resolution (<1.5 um). However, these samples with higher developing speed tend to show lower remaining film thicknesses. Based on this result, Sample 7, having P–B polymer has the most balanced performance in terms of resolution and remaining film thickness.

Table 4 Properties of Polymers and resist samples

Sample	6	7	8
Polymer	P–A	P–B	P–C
dev speed*	0.3	1	1.4
Remaining film thickness ratio [%]	89	88	85
Resolution [um]	2	1.3	1.4

*Normal ized values as Sample 7 is 1.

3.3 Lithography performance

Sample 7 shows higher resolution with higher remaining film thickness to achieve our target properties. The lithography performance of this novel negative tone resist, Sample 7, is below.

3.3.1 Patterning resolution

Figure 6 shows patterning resolution of Sample 7 at a 5 um film thickness. The optimum exposure dose is 70 mJ/cm^2 and a L/S=1.3 um/1.3 um pattern is resolved with straight profiles.

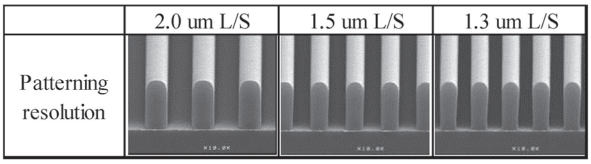


Figure 6 Cross-section SEM observations of patterning resolution of Sample 7.

3.3.2 DOF margin

The redistribution layer consists of several wiring and insulator film layers. As a result, resist for redistribution layers require a wide DOF margin. Figure 7 shows the DOF margin of Sample 7 from + 1 to + 5 um focus (Focus +/− 0 is at film surface; + direction means inside of film). The space CD variation under+/−1.0 um focus shift is roughly 10 % at 2.0 um space CD target. And patterning profiles are kept straight with no scumming. The DOF margin of Sample 7 is expected to be wide enough for redistribution layer processing.

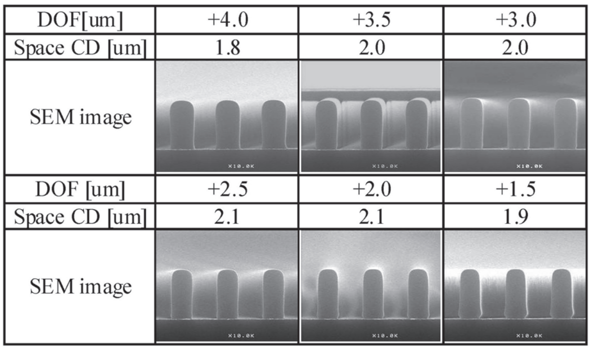


Figure 7 Patterning profile of sample 7 with various film thicknesses from 5 um to 10 um.

3.3.3 FT margin

As a result, Sample 7 achieved straight pattern profiles with a higher aspect ratio(>3). The result demostrates Sample 7 is a good candidate for fine pitch and high aspect Cu wiring (Figure 8).

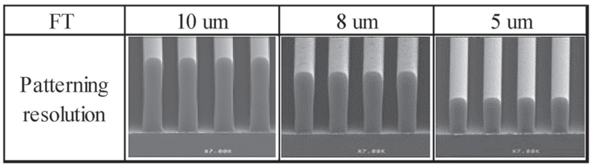


Figure 8 Cross-section SEM observations at various film thicknesses.

3.3.4 Plating performance

Figure 9 shows Cu plating results of Sample 7 with various pitch sizes at 5 um film thickness. The Cu plating solution is EEJA microfab CU300, 3ASD as current density, 2.5 um as Cu plating height. After plating, the test substrate was dipped in a typical stripper such as DMSO/TMAH at 23 ℃ for 10 min and then rinsed with DI water. Straight Cu lines were formed without any stripping residue, irregular plating such as under plating, or rough surfaces. These results showed that Sample 7 has good strippability and plating resistance.

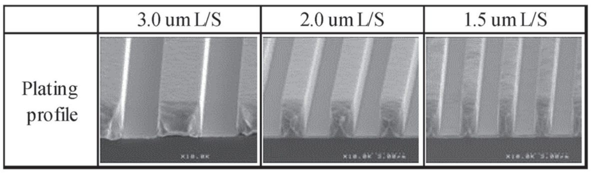


Figure 9 SEM images after plating and stripping.

4 Summary

In this study, new novel negative tone resist was developed to meet the requirements of fine pitch redistribution layers. It was found that a higher sensitivity photo initiator is one of the key item to controlling the remaining film thickness at thin film thickness conditions (<10 um), and developing speed of base polymer has a major impact to obtaining fine patterning resolution. We think that our new resists contribute to the progress of advance packaging such as 3D-TSV, 2.5D interposer and Flip-chip bumping.

Published conference

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