

Synthesis of electrodeposition photoresist resin and study for its photoimaging properties

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Abstract:

An electrodeposition photoresist was synthesized in this paper. The waterborne acrylic copolymer was synthesized by free radical polymerization in the presence of N'N'-azobis(isobutyronitrile) (AIBN). Partial blocked isophorone diisocyanate (PB-IPDI) was prepared using hydroxyethyl acrylate (HEA) as blocked agent, dibutyl tin dilaurate (DBTDL) as catalyst and 2,6-di-tert-butyl-4-methylphenol (DBHT) as inhibitor. PB-IPDI was grafted to the waterborne acrylic resin to obtain electrodeposition photoresist. The water solubility of the photosensitive waterborne resin was tested by Zeta potential & radii analyzer. The radii and its distribution of aqueous dispersion has average micelle size of 40~220nm. For using the polymer as negative photoresist material the rate of photocrosslinking of the polymer was measured under the influence of different photoinitiator dosage. Photocrosslinking nature of the polymer sample was carried out in the presence of various photoinitiator dosages under high pressure mercury lamp. Also the electrodeposition process and photoimaging properties were studied.

Key words: Electrodeposition photoresist; photoimaging; UV curing; waterborne

1 Introduction

Electroplating of photoresist or photoresist electrodeposition (ED) is a powerful technique employed for several years to coat 3D structures^[1, 2].

Compare with spray and spin coating techniques^[3, 4], this new technique has obvious advantages: the most critical part to be coated like the obtuse top corner and concave bottom corner of the cavities are covered by a layer of the same thickness as on the surface of the substrate. For that reason, ED coating is the most suited technique to pattern structures that run in and across cavities or when a smaller line width is required. Especially recent years, traditional techniques and materials could not match the need of PCB manufacture: micromation, lightweight, high-capacity, high density and high reliability.

In the standard technology, spin coating produces highly uniform layer on a planar surface. However, in the case where wafer through-hole or deep recesses are present the coating is rich in striations and holes are filled with photoresist, which causes non-uniform coating. On such coating, lithography could not be successfully performed. Recent years, Shipley corporation has led the current due to its sophisticated product PEPR2400 and EAGLE2100^[5]. ED coating technique allows uniform photoresist coverage on highly textured surface.

ED coating technique combines the advantage of UV curable and electrodeposition. In this paper, it took three procedures to prepared electrodeposition photoresist. First was the preparation of waterborne acrylic resin via the insertion of hydroxyl and tertiary amine groups to main chain; second was the preparation of isocyanate prepolymer which contains unsaturated group that would

be inserted into waterborne acrylic resin to give photosensitivity to target product. The last procedure was the insertion of prepolymer into waterborne acrylic resin. This novel resin can be used as the material of pattern transfer in the PCB procedure.

2 Experimental details

2.1 Materials

Dimethylaminoethyl methacrylate (DMAEMA), Methyl methacrylate (MMA), Ethylhexyl acrylate (EHA), Butyl acrylate (BA), Hydroxyethyl methacrylate (HEMA) and Phenylethylene (St) were purchased from The First Shanghai Chemical Reagents Co. without further purification. Isophorone diisocyanate (IPDI) was obtained from Degussa. N, N'-azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use. ITX & Irgacure907 were supplied by Ciba Company.

2.2 Preparation of waterborne acrylic copolymer (Resin A)

EA (15.00 g, 0.17 mol) was charged into a four-neck round bottom flask which was equipped with a mechanical stirrer, a thermometer, a dropping funnel and a reflux condenser. After the solvent was heated to 77 °C, the mixture of DMAEMA (10.00 g, 0.06 mol), EHA (14.00 g, 0.08 mol), HEMA (13.00 g, 0.10 mol), St (10.00 g, 0.10 mol), MMA (6.00 g, 0.06 mol), BA (15.00 g, 0.12 mol) and AIBN (1.50 g, 0.01 mol) initiator was added through a dropping funnel over a period of 2.5~3 h.

2.3 Preparation of partial blocked isocyanate (PB-IPDI)

Isophorone diisocyanate was charged into a three-neck flask which was equipped with a thermometer, a reflux condenser, and a mechanical stirrer. After the flask was heated to 25 °C, the mixture of hydroxyethyl acrylate, dibutyl tin dilaurate and 2,6-D 1-tert-butyl-4-methylphenol were added through a dropping funnel over a period 2 h. The end point of this step was indicated by the fact that 11.60 wt% -NCO value of the reaction mixture was obtained.

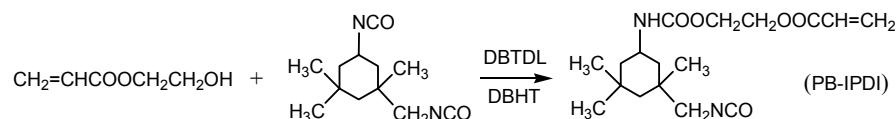
2.4 Preparation of urethane acrylate (Resin B)

The prepolymer (PB-IPDI) prepared in procedure 2.3 was added into waterborne acrylic resin at 65 °C for 3h until the peak at 2267 cm⁻¹ for isocyanato group disappeared as shown in Fig.2. The peak at 1635 cm⁻¹, 810 cm⁻¹ and 1531 cm⁻¹ indicated methacrylate group and N-H respectively.

2.5 Preparation of cathodic electrodeposition photoresist (Resin C)

The product Resin B was neutralize by lactic acid at 60 °C, after the flask was cooled to 40 °C, ethylene glycol monobutyl ether and photoinitiator ITX & Irgacure907 was charged into it. The resulting mixture was stirred at 30 °C for 5 min, and then further reduced to 10% percent (wt/wt)

by addition of deionized water giving an aqueous dispersion of amine-functional, photosensitive resin.



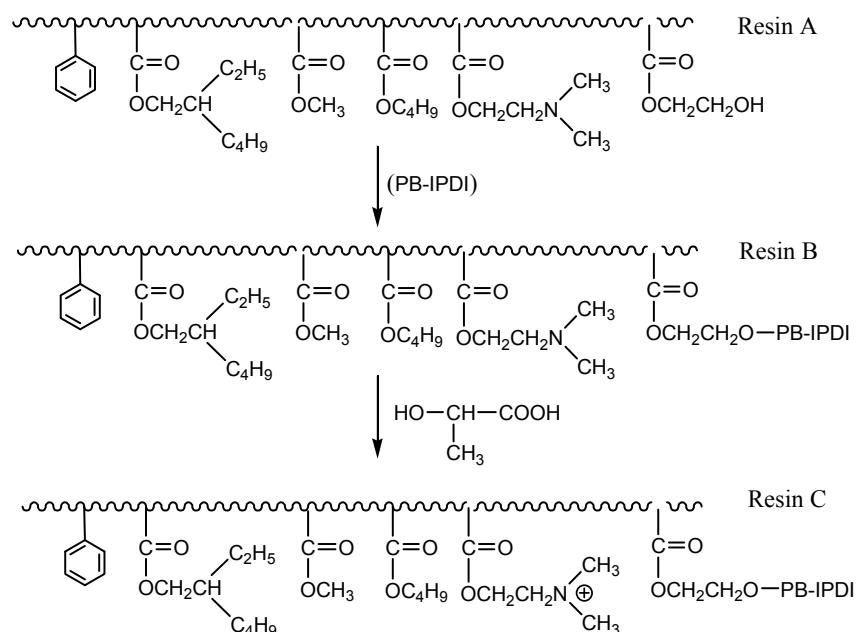


Fig. 1. Reaction scheme of the electrodeposition photoresist

3 Results and Discussion

3.1 FTIR spectra

Fig. 2 shows FTIR spectra of waterborne acrylic resin and urethane acrylate resin. The C=C stretching vibration mode at 1635 cm^{-1} and =CH out-of-plane bending modes at 810 cm^{-1} were observed. Absorption peak at 3423 cm^{-1} , assigned to the stretching vibration of N-H stretching vibration. Also, the absorption peak of -NCO group at 2270 cm^{-1} disappeared, this is indicative of graft reaction of -OH and -NCO. It is also can be seen, the stretching vibration at 2956 cm^{-1} , 2875 cm^{-1} , 1731 cm^{-1} , 1245 cm^{-1} , 1166 cm^{-1} belongs to the -CH₃, -CH₂-, C=O, C-O respectively. The prepolymer PB-IPDI was grafted to the acrylic resin successfully.

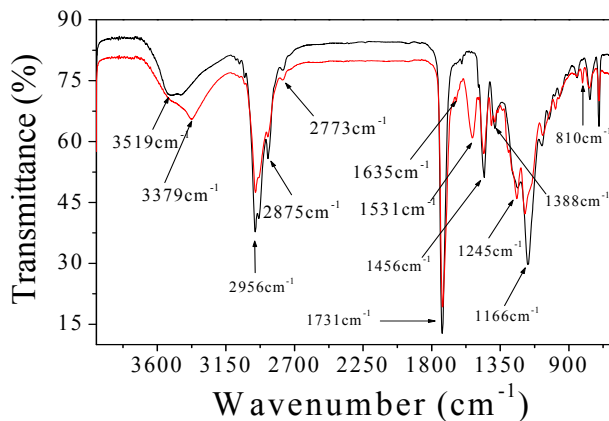


Fig. 2. FTIR absorption spectra of Resin A and Resin B

3.2 Electrodeposition behavior

3.2.1 Electrodeposition voltage and time consideration

Electrodeposition photoresist thickness depends on the applied voltage and time at a fix coating temperature. In the experiment, the potential was varied from 40 to 90 V. As can be seen in Fig. 3, the applied voltage and thickness has nearly linearly relationship. Lower voltage is not enough to deposit a good layer, and higher potential will result in the penetration of the film, the film could be easily withdrawn from the metal surface.

The electrodeposition of photoresist is a self-terminating procedure because the polymerized resist forms an insulating layer. After the process starts, the electrical field at the surface of the resist and the current decrease. After 90 s, only small amounts of the resist are still deposited on the surface and lead to an improvement of the mean roughness. Longer time results in a slight increase of thickness.

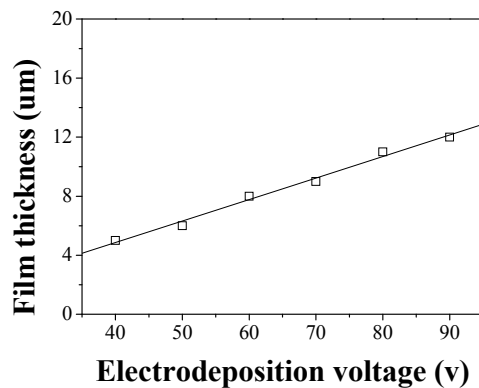


Fig. 3. Film thickness vs. electrodeposition voltage

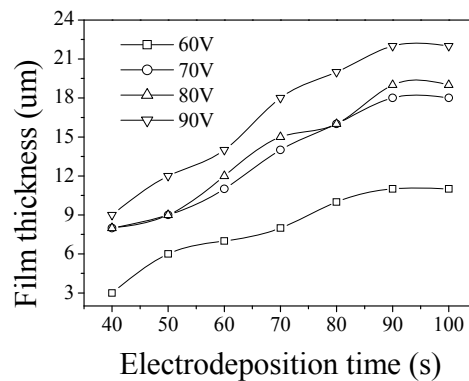


Fig. 4. Film thickness vs. electrodeposition time

3.2.2 Bath temperature consideration

The influence of bath temperature on resist thickness and dispersion conductivity has been characterized as illustrated in Fig. 5. As thin but uniform layers are highly desirable for pattern transfer on copper surface, coating bath temperature range of 25~30 °C is chosen. As temperature lower than 21 °C, it is difficult to control the expected resist thickness as a minor change in temperature can lead to a large variation on resist thickness. On the other hand, high temperature results in faster degradation of the emulsion^[6].

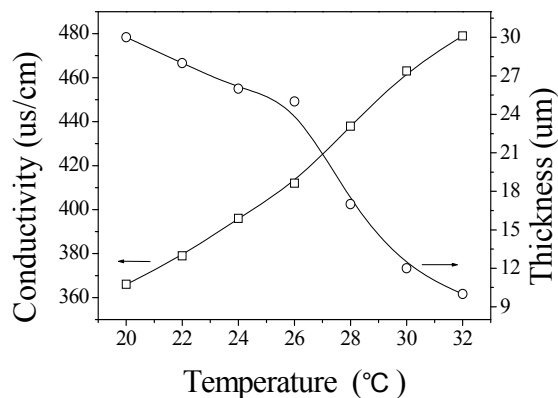


Fig. 5. Electrodeposition bath temperature vs. emulsion conductivity

3.3 Flash-off process

Fig. 6 compares the drying speed of the electrodeposition film under different temperature for a 15 μm thick ED film. The evaporation of water was observed with an oven, which primarily heated the coating. For about 7 min, 90% (wt.) of the water was removed during flash-off process when $t \leq 70^\circ\text{C}$. In contrast, the water content was reduced to zero when $t \geq 80^\circ\text{C}$ and the film had good levelling effect. But higher temperature will destroy photoinitiator, and some C=C double bonds crosslinking. After developing, poor circuit line resolution obtained.

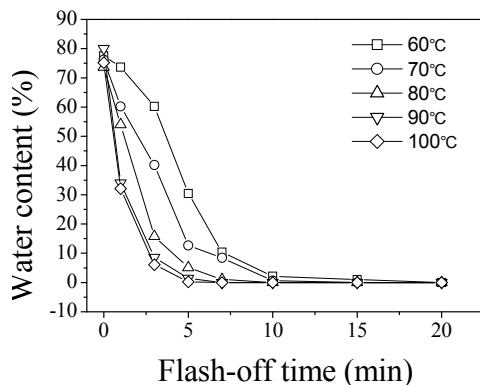


Fig. 6. Comparisons on drying speed of an electrodeposition film under different flash-off temperature

3.4 Conversion ratio of C=C

By exposing to a monomer to an intense ultra-violet (UV) light for a short period time, large amounts of free radicals are generated at once, and initiate an instant polymerization.

The conversion rate of C=C is a measure of the photosensitivity for the photoresist. FTIR spectroscopy is a powerful analytical method for monitoring UV-initiator processes. The present paper this technic was used to study the effect of the photoinitiator dosage on curing degree.

The conversion α was calculated according to Eq. (1).

$$\alpha = \left(1 - \frac{A_{c=c,t} / A_{c=o,t}}{A_{c=c,0} / A_{c=o,0}} \right) \times 100\% \quad (1)$$

Here, $A_{c=c,0}$, $A_{c=c,t}$ was the peak area of =CH at 810 cm^{-1} after 0, t seconds' irradiation respectively. $A_{c=o,0}$, $A_{c=o,t}$ was the peak area of carbonyl group at 1730 cm^{-1} after 0, t seconds' irradiation respectively. Carbonyl group was used as reference peak to eliminate the error of the instrument and sample dosage.

UV irradiation was performed with a 200W high pressure mercury lamp (Blue Sky Special Lamps Development Co., Ltd). The maximum UV intensity in the focus on the surface was 64 mW/cm^2 .

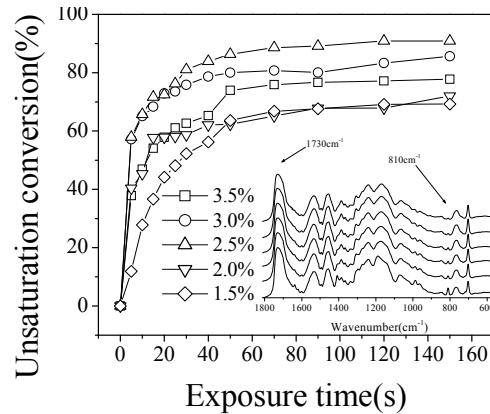


Fig. 7. Unsaturation conversion vs. photoinitiator dosage

It can be seen in Fig. 7, the unsaturation bond conversion rate has similar trend with different photoinitiator dosage. At the 0~20 s, the system cured rapidly and then the conversion rate^[7] considerably slows down. However, when the reaction continues, the increased crosslinking level eventually limits the mobility of monomers and oligomers as well their radicals. The propagation reaction then becomes diffusion-controlled stage along with the radical termination, and the overall polymerization rate begins to decrease. As the mobility of the reaction system further reduces, the reactive species becomes trapped, and the polymerization finally stops. Moreover, conversion will come down when the photoinitiator dosage more than 2.5%wt.

3.5 DMAEMA content consideration

In this experiment, DMAEMA as an important monomer introduced to the polymerization was studied from following two aspect: first, as tertiary amino group introduced to the acrylic resin to make the polymer dispersed in the deionized (DI) water after neutralized with lactic acid; second, to make the photoresist developed in the HCl water solution.

3.5.1 Effect of DMAEMA content on water solubility

The acrylic resin can be dispersed in the DI water after neutralized with lactic acid, it play an important role for the resin water solubility and stability. As can be seen in Fig. 8, the micelle average size is at the range of 45 nm and 216 nm with DMAEMA content ranges of 8.82 wt% - 14.71wt%. The decrease in the DMAEMA content will give rise to an increase in particle size which leads to lower hydrophilicity. And the ED film has poor coalescence with substrate.

Increasing the DMAEMA content result in a higher ionic strength per unit area, while its content is greater than 13.24%wt, there are more cation in the bath, which increase the conductivity the velocity of particle deposition.

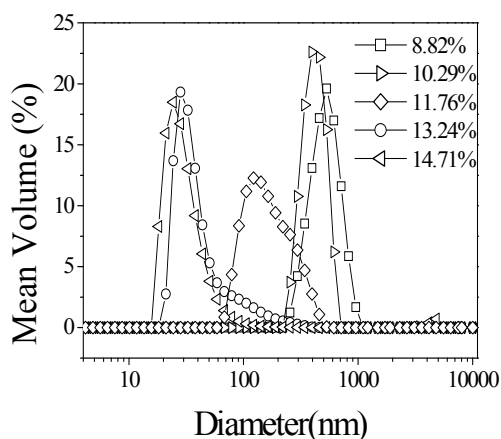


Fig.8. The micelle diameter vs. DMAEMA content

3.5.2 Effect of DMAEMA content on photoimagine properties

After an electrodeposition process, the resist is exposed to UV light and then developed in HCl water solution at 30 °C. The exposed areas of the resist become insolubilized, and less soluble to a developing solution. Hence, there is a solubility differential between the exposed and unexposed areas of the resist film. As can be seen in Fig. 9, DMAEMA matches with the circuit line resolution. The lower DMAEMA content, the poorer the circuit line resolution. When its content $\geq 11.76\%$ wt, the width of line was 150 μm , and the pattern can be transferred easily and clearly. While higher DMAEMA content will result the film swelled even the exposed area, just described as Fig. 9, A serial experiments indicated that 13.24% DMAEMA content can achieve excellent pattern.

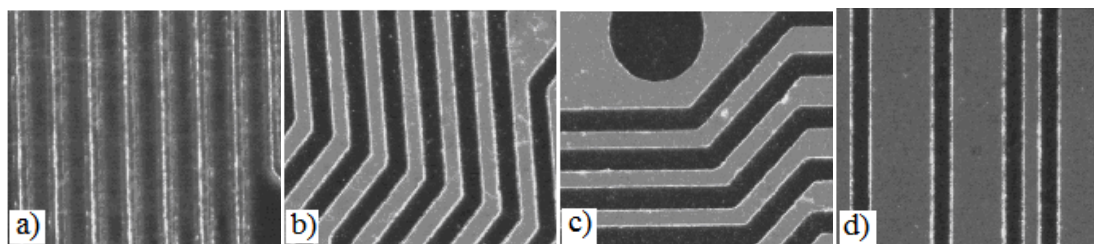


Fig.9. Photo imagines of the electrodeposition photoresist with different DMAEMA content (a: 10.29%; b: 11.76%; c: 13.24%; d: 14.71%) after developed in hydrochloric acid

4 Conclusions

In this paper, we have synthesized a resin for electrodeposition photoresist. The electrodeposition behavior and flash-off process were investigated. By control the experiment condition, uniform ED photoresist and excellent pattern can obtained. Curing speed can be enhanced by adjust the photoinitiator ITX and Irgacure907 dosage, and 2.5% (wt) was the optimized value. The DMAEMA as an important monomer introduced to the polymerization was studied from water solubility and photoimagine properties. The DMAEMA content value less than

11.76% (wt) results in the instability of the dispersion. While 11.76 wt% of DMAEMA content is the demarcation of development, the photoresist represent excellent pattern transfer, the circuit line width was 150 μ m with hydrochloric acid as developer.

5 References

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