Study on Preparation and Photolithography of Negative-work Photosensitive Polyester Acrylate

Kun-Lin Hsu and Wen-Tung Cheng*

Department of Chemical Engineering, National Chung Hsing University
250 Kou Kuang Road, Taichung 402, Taiwan
*wtcheng@dragon.nchu.edu.tw

This study aims to investigate fabrication and photolithography of negative-work photosensitive transparent insulation material for one glass solution (OGS) applying in touch panel. In this work, two reactive monomers, namely, dipentaerythritol hexaacrylate (DPHA) and tri (propylene glycol) diacrylate (TPGDA), were respectively blended with the mixture of 50% 1-hydroxy-cyclohexyl-phenyl-ketone and 50% benzophenone, and polyester acrylic oligomer in propylene glycol monomethyl ether acetate (PGMEA); and the photolithography of resulted negative-work photosensitive transparent insulation materials with different solid content was determined by characteristic curve and the optical microscope (OM). As shown in the results, it was found that the photolithographic resolution, which is termed by the ratio of line width to line space, is significantly affected by the solid content of as-prepared negative-work photosensitive polymer. Based on 8 µm line width and space at 1 µm film thickness, the photolithographic resolution of photosensitive polyester acrylate containing 19.7 wt% solid content could reach 1.1 after irradiating by 600 mJ/cm² ultraviolet visible light and developing by 0.01 wt% KOH solution for 60 seconds in this explore.

Keywords: Preparation, Photolithography, Negative-work photosensitive polymer, Reactive monomer, Polyester acrylate, One glass solution

1. Introduction

In decade, the smart 3C products, namely, computer, consumption and communication goods, have occupied daily life around world. With the rapid development of the global optoelectronic industry, negative-work photoresist was widely used in the printed circuit board, semiconductor element, black matrix, color filter and so on. Due to a huge manufacturing flux and cost problem, negative-work photo-resist still dominates the material market for fabricating the optical and electrical devices [1-4].

Among the variety products, touch panel is one of a key component for advanced color thin film transistor flat panel display (TFTFPD), which types can be divided into resistive, capacitive, infrared ray, optics, and surface acoustic wave [5]. In respond to the trend of convenience, one glass solution (OGS) is a kind of outstanding method to overcome the problems of panel thickness and response sensitivity. It allows complex modules stacked structure turn to slim type by means of reducing the thickness of display. It removes one of the layers of glass substrate from the traditional capacitive touch screen stack. Therefore, a thin layer of transparent insulating material is needed to replace the touch module glass [6]. In the application, the transparent photoresist insulating material primarily was coated inside glass substrate and acted as insulting layer between the x-axis and y-axis sensors, which are made from indium tin oxide (ITO), for avoiding the short circuit.

Furthermore, it is important to pattern the micro-circuit on the photosensitive material by photolithography process [7]. Generally, there are some factors like acid value of oligomer, exposure time, UV light intensity, type of developers, development time, hard baking temperature and so on, to influence the
resolution of pattern [8-10]. In this study, we attempt to explore the pattern resolution of negative-work photosensitive polymer by regulating the solid content of polyester acrylate.

2. Experimental
2.1. Materials
Commercially available polyester acrylate (Mw = 1000 g/mol), dipentaerythritol hexa-acrylate (DPHA) and tripropylene glycol diacrylate (TPGDA) were obtained from Qualipoly Chemical Co. Taiwan. The mixture of 50% 1-hydroxycyclohexyl phenylketone and 50% benzophenone as the radical-type photoinitiator (PI) was purchased from BASF. Propylene glycol monomethyl ether acetate (PGMEA) as a solvent was supplied by Lancaster. All these chemicals were used without further purification. The chemical structures of used materials were sketchily indicated by Scheme 1.

2.2. Preparation and photolithography of negative-work photosensitive polymer
The negative-work photosensitive polyester acrylic resin was homogeneously mixed by magnetic stirrer (Model MS-211, Taiwan), which formulation is listed in Table 1. The resulted photosensitive polymer was coated on glass substrate (Corning 1737) with the size of 2 cm × 2 cm by spin coater (AGS-0206S, Taiwan). Spin coating processes were performed by the first rotation speed of 250 rpm for 10 seconds to distribute liquid drops on substrate uniformly, and the second rotation speeds ranging from 500 rpm to 2500 rpm for 30 seconds based on solid content of negative-work photosensitive polymer in order to control the film thickness at 1 µm. After soft baking in oven at 90 °C for 3 minutes, the photo mask was covered on the dried negative-work photosensitive polymer and irradiated by different exposure dose of mercury lamp (Acticure 4000). Then, 0.01 wt% of KOH solution was applied for development under various times at 25 °C. Finally, the obtained photosensitive polymer patterns were carried out by post baking in oven (Muffle Furnaces DF30) at 200 °C for 30 minutes.

2.3. Characterization
The viscosity of as-prepared negative-work photosensitive polymer solution was determined by rheometer (DV3T, Brookfield). The film thickness of cast polymeric film was measured by the optical instrument (MP100-M, Mission Peak Optics Inc.) after post baking.
The solid content of negative-work photosensitive polymer was measured according to standard test method (ASTM D 2369-10). Additionally, the images of patterned negative-work photoresist with a magnitude of 200X were observed from optical microscope (BX51, Olympus). The contrast ($\gamma$) of negative-work photosensitive polymer was defined by equation (1),

$$\gamma = \left( \log_{10} \frac{D_{100}}{D_0} \right)$$

where, $D_0$ is exposure dose required for the remaining film thickness at the initial state, and $D_{100}$ is exposure dose required for the film without thickness loss at the final state. All measurements have an average of three runs.

3. Results and discussion

3.1. Analysis of solid content

To improve the pattern resolution, we begin with investigation of the solid content affecting by different formulas of negative-work photosensitive polymer, as listed in Table 1. As a result, when the amount of DPHA and PI were changed, the solid contents were almost constant at 25 wt%. In contrast, as PGMEA was added from 20 g to 40 g, the solid content would remarkably decrease from 25.9 to 16.2 wt% due to the low viscosity of the solvent, as displayed in Fig. 1. This suggests that the solid content could be significantly regulated by solvent in this work.

Table 1. Formula of negative-work photosensitive polyester acrylate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PGMEA (g)</th>
<th>Polyester acrylate (g)</th>
<th>DPHA (g)</th>
<th>TPGDA (g)</th>
<th>PI (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>10</td>
<td>2</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>10</td>
<td>2</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>10</td>
<td>2</td>
<td>1.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

3.2. Property of negative-work photosensitive polyester acrylate

Before examining photolithography, we characterize the viscosity and spinning curve of negative-work photosensitive polymer with different solid content. Figure 2 shows the rheological behavior of as-prepared photosensitive polymer, which viscosity could be obtained by the slope of shear stress to shear rate. As shown in the figure, when the solid content were 16.2 wt%, 19.7 wt%, and 25.9 wt%, the viscosity would correspond to 2.7 cp, 4.2 cp, and 7.5 cp, respectively. In addition, Fig. 3 indicates the relation between spin rate and film thickness varying with solid content. It can be seen that the film thickness will decrease steeply at lower spin rate and tend to level off constant resulting from the film thickness of negative-work photosensitive polymer is inversely proportional to square root of spin rate. In order to study the effect of solid content on photolithographic performance, the film thickness would be fixed at 1 µm. Therefore, the spin rate at the final state were specified at 750 rpm, 1200 rpm, and 2500 rpm, corresponding to solid content with 16.2 wt%, 19.7 wt%, and 25.9 wt%, respectively, in this work.
3.3. Sensitivity and contrast of negative-work photosensitive polyester acrylate

Figure 4 exhibits the wedge curve of as-prepared negative-work photosensitive polymer. As observed from the figure, when the exposure dose was increased from 0 to 1200 mJ/cm², the residual film thickness was gradually increased from 0 to 1 µm because the photosensitive polymer is turned from solubilization to insolubilization after irradiation of UV-Vis light [11]. Furthermore, this result exhibits that the less exposure dose is needed to reach maximum residual thickness for the lower solid content of photosensitive polymer. In the figure the inset is the exposure doses of wedge curve to be narrowed down in the range from 0 and 200 mJ/cm² for obtaining the contrast of negative-work photoresist [12].

The result showed that when solid content was changed from 16.2 wt% to 25.9 wt%, the exposure dose would raise from 68 mJ/cm² to 90 mJ/cm² and the contrast decrease from 1.26 to 0.68, respectively, due to slow polymerization rate caused by high viscosity [13].

3.4. Resolution of photolithography

The resolution of negative-work photosensitive polyester acrylate with different solid content and 1 µm of film thickness was investigated by OM. The resolution of photolithography, namely, the ratio of line width to line space of patterned photosensitive polymer varying with solid content was shown in Fig. 5. As shown in the figure, when solid content was increased from 16.2 wt% to 25.9 wt%, the ratio of line width to line space will promote from 0.53 to 1.49. According to the used the mask with equal line width and space, the ratio of line width to line space of patterned image to be nearly 1 is much better. Therefore, in this work, the negative-work photopolymer with 19.7 wt% of solid content was chosen to meet 8 µm of photolithographic resolution.

Figure 6 shows that the as-prepared photosensitive polymer were irradiated by exposure dose ranging from 400 to 700 mJ/cm², followed by developing with 0.01 wt% KOH for 60 sec. As seen from the images, when the exposure dose was lower than 500 mJ/cm², the line width of the developed photoresist was reduced resulting from underexposure [14]. However, when the exposure dose was set at 700 mJ/cm², the unexposed areas of negative work photo-resist would be difficultly removed due to overexposure. As a result, the best resolution of as-prepared negative-work
photosensitive polymer could be obtained by an irradiation with 600 mJ/cm² of UV-Vis light and development with 0.01 wt% KOH for 60 sec.

![Image](68x610 to 167x693)
![Image](173x610 to 272x693)
![Image](68x516 to 167x597)
![Image](173x516 to 272x596)

Fig. 6. The OM images of patterned photosensitive materials at 19.7 wt% of solid content after irradiating by (a) 400 mJ/cm², (b) 500 mJ/cm², (c) 600 mJ/cm², and (d) 700 mJ/cm², respectively, UV-Vis light, which scale bar is 16 µm.

4. Conclusion

In this study, the negative-work photosensitive polyester acrylate has been successfully fabricated with the different solid content. As shown in results, the significant findings could be remarked as below:

(1) When the solid content of the negative-work photosensitive polymer film with thickness of 1 µm was varied from 16.2 wt% to 25.9 wt%, for the film thickness without reduction, the requirement of exposure dose would increase from 68 mJ/cm² to 90 mJ/cm², to maintain the residual film thickness without film loss, resulting in the contrast is decreased from 1.26 to 0.68 due to the higher viscosity of photoresist to slow the polymerization rate.

(2) By OM observation, the ratio of line width to line space of as-patterned negative-work photosensitive polymer with solid content of 19.7 wt% and 1 µm film thickness was 1.1 after irradiating by 600 mJ/cm² of UV-Vis light, followed by development with 0.01 wt% KOH in de-ionic water for 60 seconds.

References


