This article was downloaded by: [University of Haifa Library]

On: 09 August 2012, At: 14:46 Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,

UK



# Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: <a href="http://www.tandfonline.com/loi/gmcl20">http://www.tandfonline.com/loi/gmcl20</a>

### Development of Slit Coating Photoresist with High Coating Speed Property

Shuichi Takahashi <sup>a</sup> , Shunji Kawato <sup>a</sup> , Junichi Shimakura <sup>a</sup> & Seiji Kurihara <sup>a</sup>

<sup>a</sup> Department of Applied Chemistry & Biochemistry Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto-shi, Kumamoto, Japan

Version of record first published: 22 Sep 2010

To cite this article: Shuichi Takahashi, Shunji Kawato, Junichi Shimakura & Seiji Kurihara (2007): Development of Slit Coating Photoresist with High Coating Speed Property, Molecular Crystals and Liquid Crystals, 470:1, 57-62

To link to this article: http://dx.doi.org/10.1080/15421400701492598

#### PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable

for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 470, pp. 57–62, 2007 Copyright © Taylor & Francis Group, LLC ISSN: 1542-1406 print/1563-5287 online

DOI: 10.1080/15421400701492598



## Development of Slit Coating Photoresist with High Coating Speed Property

Shuichi Takahashi Shunji Kawato Junichi Shimakura Seiji Kurihara

Department of Applied Chemistry & Biochemistry Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto-shi, Kumamoto, Japan

The faster coating speed is required to the photoresist for slit coating process. When the photoresist is coated at high coating speed, the film thickness uniformity becomes worse. The carboxylic acids and the ester compounds with long alkyl chain were added into photoresist for the slit coating process. Such photoresist showed really good film thickness uniformity of photoresist film on the glass substrate at high coating speed condition.

Keywords: carboxylic acid; ester compound; photoresist; slit coating; solid content; viscosity

#### INTRODUCTION

The manufacturing of LCD-TFT panels uses very large size of glass substrates at sixth generation and seventh generation factories. The size of glass substrates are more than  $2 \times 2$  meters. TFT panel makers want to coat the photoresist on such glass substrates within short time, because of the shortening production time. When the photoresist was coated on the glass substrates at high scanning speed of slit

We received many useful advices for this study from Dr. Kurihara. Some of the authors appreciate his kind support for us.

We made use of AFM at Hamamatsu Industrial Research Institute of Shizuoka Prefecture. Authors appreciate the cooperation by Mr. Shinya Takoh.

Address correspondence to S. Takahashi, FPD Material Development Team, R&D Department 2, Shizuoka Technology Center, AZ Electronic Materials (Japan) K.K., 3330, Chihama, Kakegawa-shi, Shizuoka, 437-1412, Japan. E-mail: shuichi.takahashi@az-em.com

nozzle, some problems appeared. One of the problems is an unevenness of the coatings.

Lowering of photoresist viscosity was effective to improve the coating unevenness problem. But such method caused new problems. The unevenness of photoresist film thickness and the increasing dispense volume of photoresist were shown. We focused on the density of photoresist film after drying process, and we evaluated the matrix compounds to improve the uniformity of photoresist film thickness.

#### **EXPERIMENTAL**

We reported that the acrylic copolymers were the effective compounds as matrix compounds to improve the uniformity of photoresist film thickness [1]. This time we added the carboxylic acid and the ester compounds with long alkyl chain into photoresist. Table 1 showed the photoresist formulation of each sample.

The photoresists were coated by the large size of slit coater made by Toray engineering. The size of glass substrate was  $1100 \times 1300$  mm. The width of slit nozzle was 1093 mm, and the gap between substrate and slit nozzle was  $150\,\mu\text{m}$ . The film thickness (F.T.) of photoresist after the vacuum drying process was  $1.8\,\mu\text{m}$ . We checked the film thickness of photoresist film by the Nanospec-6500 made by Nanometrics. The observation of coating unevenness in the photoresist film was done by Teknos-5000 K made by Teknos. The unevenness of photoresist film thickness was observed by Atomic Force Microscope (AFM, SPI-3700 made by Seiko Instruments Inc.).

#### **RESULTS AND DISCUSSION**

The photoresist added the acrylic copolymer showed very good uniformity of photoresist film thickness after drying process, but the photospeed was slower than normal photoresist. We thought that

TABLE 1	Additives of Each	Sample
C1-	IZ: J £	Т

Sample name	Kind of additive	Loading amount of additive (wt%)
A	none	
В	Lauric acid	B1(5), B2(10)
$\mathbf{C}$	Oleic acid	C1(5), C2(10)
D	Methyl stearate	D1(5), D2(10)
E	Ethyl stearate	E1(5), E2(10)

the acrylic copolymer acted as a matrix compound for novolak resin. Then we tried to search better compounds as the matrix compounds without slower photospeed phenomena. We already reported the effect of compatibilizer for photoactive over coating material [2]. The compatibilizers were evaluated as the matrix compounds at this study. The viscosities of all samples were adjusted to 4.0cP. Table 2 showed the test result of the fastest coating speed and the uniformity of photoresist film thickness. The calculating equation of film thickness uniformity was as follows;

Uniformity =  $(MaximumF.T. - MinimumF.T.)/AverageF.T./2 \times 100$ 

The test result in Table 2 indicated that there wasn't much difference about the fastest coating speed by the change of additives. We judged that the fastest coating speed depended on the viscosity of photoresist. Moreover we checked the correlation between additives and uniformity of film thickness. The uniformity was calculated by excluding the edge area of substrate. D2 showed the flat surface of photoresist film at all area, and the uniformity was below 2.0%.

Our first target of the fastest slit coating speed was over 200 mm/s. We evaluated the photoresist with lower viscosity as the next step. Sample A and sample D2 were diluted to 3.0cP. The test result was shown in Table 3. Sample A and sample D2 could be coated on the glass substrate without any coating unevenness at 200 mm/s. When sample A was diluted to 3.0cP, the uniformity of film thickness was worse than 4.0cP of sample. The change of uniformity was 5.2%. But sample D2 diluted to 3.0cP could keep the film thickness uniformity of 4.0cP of sample. The change of uniformity between 3.0cP and 4.0cP sample was 0.44%.

**TABLE 2** Fastest Slit Coating Speed and Uniformity of F.T. of Each Sample

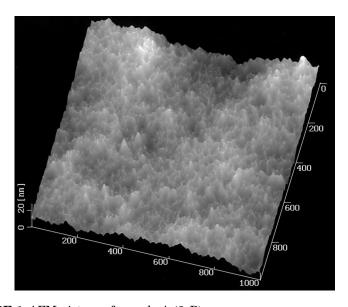
Sample	Fastest coating speed (mm/s)	Uniformity of film thickness (%)			
		w/o 10 mm	w/o 15 mm	w/o 20 mm	w/o 50 mm
A	140	2.77	2.56	2.13	1.58
B1	130	2.96	1.83	1.67	0.84
B2	130	4.55	2.83	1.29	0.63
C1	130	3.79	2.28	1.54	0.90
C2	140	2.92	2.16	1.19	0.48
D1	150	4.42	3.42	1.78	1.15
D2	130	1.87	1.79	1.79	1.78
E1	140	2.70	2.18	0.82	0.97
E2	130	2.39	1.63	1.28	0.75

Sample	Fastest coating speed (mm/s)	Uniformity of film thickness (%)			
		w/o 10 mm	w/o 15 mm	w/o 20 mm	w/o 50 mm
A (4cP)	140	2.77	2.56	2.13	1.58
A (3cP)	210	7.97	6.61	6.34	1.24
D2 (4cP)	130	1.87	1.79	1.79	1.78
D2 (3cP)	220	2.31	1.96	1.55	0.87

**TABLE 3** Fastest Slit Coating Speed and Uniformity of F.T. of Each Sample

We thought that the difference of the change of uniformity by the dilution caused from the density of photoresist film after drying process. When the matrix compound was added into photoresist, the density of photoresist film after drying process increased. As the result, the uniformity of film thickness became good. The AFM was used for observation of the surface of photoresist film. The surfaces of sample A (3cP) and D2 (3cP) were observed. Figures 1 and 2 were shown the AFM picture of each sample.

The observation area was  $1000 \times 1000 \, \text{nm}$ . The vertical scale of Figure 1 was  $20 \, \text{nm}$ , and the scale of Figure 2 was  $2 \, \text{nm}$ . The film surface of sample D2 was very flat and fine pitch compared with sample



**FIGURE 1** AFM picture of sample A (3cP).

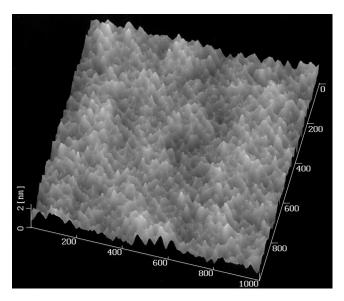


FIGURE 2 AFM picture of sample D2 (3cP).

A. This observation result indicated that methyl stearate increased the density of photoresist film. As the result, the uniformity of film thickness was better than sample without methyl stearate.

Moreover methyl stearate has another effect for Slit coating performance. The higher solid content of photoresist is good for manufacturing of LCD-TFT panels. If panel makers use lower solid content of photoresist to decrease the viscosity, the dispense volume of photoresist increases. The sample D2 (4cP) showed higher solid content compared with sample A (4cP). The solid content ratio of sample A (4cP) was 14.20%, and the ratio of sample D2 (4cP) was 15.28%.

We calculated the effect of saving the dispense volume of photoresist by adding methyl stearate into photoresist. If  $100\,\mathrm{cm}^3$  of sample A needs to coat on one glass substrate, the dispense volume of sample D2 is  $93\,\mathrm{cm}^3$ . 7% of dispense volume of photoresist are saved by using methyl stearate.

#### CONCLUSIONS

The decrease of viscosity of photoresist was effective to increase the fastest slit coating speed, but the uniformity of film thickness became worse. The adding methyl stearate showed good performance to

improve the uniformity of film thickness at high coating speed and to save the dispense volume of photoresist. We thought that such effect caused from increasing the density of photoresist film by the observation of the film surface by AFM.

#### **REFERENCES**

- [1] Kawato, S. & Takahashi, S. (2001). 47th Meeting for presenting research papers about polymer, p. 86.
- [2] Takahashi, S., Zhang, Y., Mochida, K., Ogata, T., & Kurihara, S. (2005). IDW/AD 2005, 1295-1298.