Dryfilm Photoresists and Photoinitiators for Direct Imaging

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Thick negative photoresists based on photo-radical polymerization have high photospeed are widely used in the area of electronic component manufacturing, and known as dryfilm resists for etching and plating, photosensitive solder resists, photosensitive color filter coatings, photosensitive polyimides, etc. Along with diversity of recent electronic devices and refinement of their manufacturing, designing of photoinitiator systems as key components in the photoresist formulation seems important.

Direct imaging can eliminate photomask preparation and avoid problems inherent to photomasks, and direct imaging for electronic components was firstly proposed more than twenty years ago¹⁾. Recent technical trend is reviewed in this paper.

Though the early blue emission line (488 nm) direct imagers equipped with an Ar⁺ ion laser required safety light condition and visible light sensitive photoresists, a UV laser type direct imagers using the 351 and 364 nm emissions of the argon laser or the third-harmonic (355 nm) of a Nd:YAG laser were proposed²⁾ and accepted in the market. In 2000s, a new type of direct imager based on a micro-mirror array optical processor³⁾ and a gallium nitride laser (405 nm) was introduced⁴⁾.

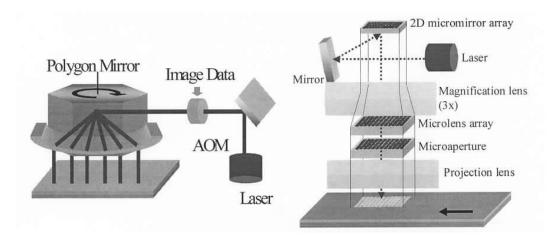


Figure 1. Polygon Type (left) and Mirror Array Type of Direct Imager (right)

Photoresists for direct imagings are required to have a much faster photospeed than convensional type of photoresists. Spectral matching of the photoinitiator absorption with the emission of the light source should be considered. For early visible light direct imagers, the research of visible light sensitive photoinitiator systems has been done⁵⁾. Compounds such as 2,2',4,4',5,5'-Hexaarylbiimidazoles (HABIs)

are known as a class of effective photoinitiators for photoimaging systems when combined with hydrogen donors. Photosensitizers for HABI hydrogen system provide good spectral matching with the light source. Quenching of short lifetime intermediates in various HABIs and photosensitizer was studied⁶⁾. Figure 2 shows the triplet decay of the EAB and the building up of the lophyl radical from 2,6-fluorinated HABI photoinitiator.

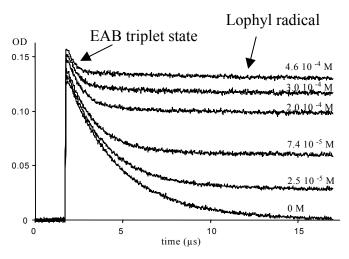


Figure 2. Transient Absorption Signals of EAB with Different [2,6-F-HABI] at 540 nm.

The spectral sensitivity matching to the 405 nm laser source is illustrated in Figure 3, where the spectral matching to 405 nm light is achieved with a minimum yellow light sensitivity 4c).

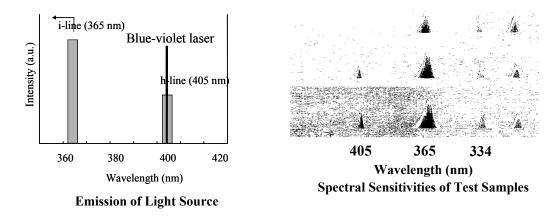


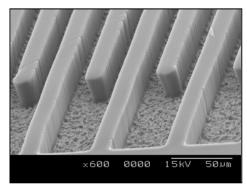
Figure 3. Spectral Matching to Blue-Violet Laser Emission

Photoinitiator systems containing a coumarin dye and a titanocene for 405 nm direct imaging are disclosed⁷⁾. Spectral matching to the UV laser direct imager with argon laser might be achieved similarly to the conventional flood exposure equipments.

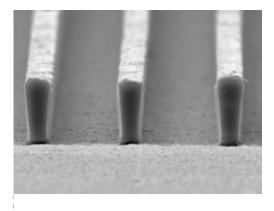
To obtain good resist pattern quality, spot size of the beam and the pixel size are important as primary parameters. Direct scanning imaging gives integrations of many spot light energy profiles.

Considering monochromatic light exposure, photo-reaction to the bottom is different from broadband light exposure⁸⁾.

We have designed spectral matching not only to gallium nitride laser but also to the THG/Nd:YAG. laser light source. Figure 4 shows SEMs of fine line/space resist pattern obtained after aqueous development by using our test dry film photoresist with a mirror-array type direct imager equipped with a 405 nm laser light source and a polygon type direct imager equipped with a 355 nm laser light source. These are showing satisfactory resist resolution and side-wall shape for high density interposer (HDI) applications.



a. Pattern Feature: 15/15 μm line and space Exposure: Micro-mirror array imager (405 nm)



b. Pattern Feature: 10/26 μm line and space Exposure: Solid state UV direct imager (355 nm)

Figure 4. Directly Imaged Photoresist Pattern; 25 µm thick

The recent direct imaging technology and photoinitiator technology are briefly reviewed as advanced electronics materials. The direct imaging is expected to become much more popular than before by technical innovations in electronics and mechanics. And the design of photoinitiating systems will play an important role.

References

- 1. G. C. Koutures, PC '80 WEST, Los Angels, 22-3/001/IMAGING
- 2. a) B. B. Ezra, *Advanced Technologies*, 11. 20, (1998)
 - b) K. D. Dietz, Electronic Circuits World Convention Tokyo '99, PO4-1, 1-4, (1999)
 - c) J. Murry, *PC Fab.*, 22, 22, (1999)
- 3. L. J. Hornbeck, USP 5,535,047, July 9, 1996
- 4. a) A. Ishikawa, USP5,955,776, Sep.21, 1999
- b) A. Ishikawa, *J. Photopolym. Sci. Technol.*, **15**, 707, (2002)7. B. M. Monroe, G. C. Weed, *Chemical Reviews*, **1993**, 1993
 - c) T. Itoh, M. Kaji, *Proc. RadTech Asia* '03, 583, (2003)
- 5. a) M. D. Baum, C. P. Henry Jr., US patent 3652275, 1972
 - b) D. P. Specht, P. A.Matric, S. Y. Farid, Tetrahedron 1982, 38, 1203
 - c) L. Roos and R. Barr, Printed Circuit World Convention IV, 1987, Tokyo
 - d) M. Kawabata, M. Harada, and Y. Takimoto, J. Photopolym. Sci. Technol., 1(2), 222, (1988)
- 6. X. Allonas, H. Obeid, J. P. Fouassier, M. Kaji, Y. Ichihashi, Y. Murakami, *J. Photopolym. Sci. Technol.*, **16**, 123, (2003)
- 7. Mitsubishi, Japan patent 3508310
- 8. Y. Ichihashi, and M. Kaji, J. Photopolym. Sci. Technol., 17, 135(2004)