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Near Infrared Photolithography and its Photoresist

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ABSTRACT

Novel photolithography using NIR (Near Infrared) exposure and its photoresist are developed. Using NIR's extreme high transparency to photoresist polymer layer, photoresist with very high photosensitivity and vertical profile can be achieved. Adding organic black pigment that blocks UV/Visible light but is transparent to NIR, a black photoresist with vertical profile and high film thickness can be made.

1 Introduction

1.1 Current photolithography

In current photolithography, mainly UV light including g-line (436nm), h-line(405nm), and i-line(365nm) are used for exposure. To achieve finer resolution, shorter wave length exposure, such as KrF (248nm) and ArF(193nm) lithography, is a trend of photolithography.

However, photoresist polymer easily absorb UV light, so the photo-energy decreases by the time UV light reaches the bottom of the photoresist layer. Consequently, most photoreaction occurs only at the surface part of photoresist, and the bottom part of photoresist cannot receive enough photo-energy. This causes a mountain-shape tapered profile for positive photoresist and an overhung-shape for negative photoresist. Stronger exposure (i.e., using higher light intensity lamps or longer exposure time) can slightly reduce this phenomena but not perfectly.

1.2 Near Infrared Lithography

Infrared (IR) including near infrared (NIR) light can penetrate most polymer materials very easily. If we can use IR or NIR light for photo-lithography, very high photoresist photo-sensitivity is expected, and the photoresist profile would be more vertical even with very high film thickness. Therefore, we have focused on using NIR for photolithography and formulating a new type of photoresist for NIR exposure. In this paper, NIR is defined as 700nm-1000nm wave length light.

1.3 Black photoresist for NIR exposure

UV light absorption by photoresist film is a more serious problem for black photoresist. Carbon black, which is normally used as the black segment in black photoresist, blocks UV light perfectly. As a result, negative black photoresist only cure at the very surface part and the bottom part will be only weakly cured. In some cases, black photoresist patterns are washed away by alkaline developer.

We found a special organic black pigment that blocks the UV/Visible light the same as carbon black, but is transparent at near IR wave length. Adding this organic black pigment into the abovementioned NIR photoresist results in photosensitive black photoresist with very high optical density (OD) performance and vertical profile even when its film thickness is high.

2 Experiment

2.1 Photoresist preparation

New type of negative photoresist is formulated as below.

(1) Negative Photoresist

We developed a new negative photoresist which has sensitivity to NIR wave length by mixing ingredients as listed below into solvent PGMEA (propylene glycol monomethylether acetate).

- Acrylic polymer (Matrix Polymer)
- Monomer (DPHA)
- Photo initiator
- NIR-sensitive Dye

This formulation is a radical polymerization system. Most photo initiators are sensitive to UV wavelength, but not to NIR. However, by adding a special dye which is sensitive to NIR, the photoresist becomes curable by NIR.

(2) Black Photoresist

Current black photoresist contains carbon black to achieve its black color and high OD. Black photoresist containing carbon black can block light penetration well, so the OD is usually around 4 or higher by 1-3 um black photoresist film thickness.

However, due to this high OD, even UV light for exposure is blocked easily. Instead of carbon black, we chose some special organic black pigment which blocks UV/Visible light but is transparent at NIR wavelength. We formulated a novel black photoresist by mixing this organic black pigment with the abovementioned negative NIR photoresist.

2.2 Photo-lithography

Photo-lithography was applied as shown in Table 1 to the photoresist samples which were prepared as above.

Table 1. Photo-lithography Process Conditions

Process	Conditions	Method / Machine
Substrate	4-inch Si wafer or glass wafer	
Photoresist Coating	Spin, 1300rpm x 15sec.	Spinner
Prebaking	110℃ x 2min.	Direct Hot Plate
Exposure	50-300mJ/cm2	850nm LED exposure tool (self-produced)
Development	1.19%TMAH aq solution, 30sec.	Puddle

Photoresist was coated on a wafer by spin coating and dried on a direct hot plate. Then 850nm NIR exposure was applied through pattern-designed Cr mask. A self-produced NIR Exposure tool equipped with a 850nm LED lamp in a flash light type enclosure. Then, the wafer was developed by alkaline solution (1.19%TMAH) .

2-3 Observation

Patterned photoresist's profile was checked by optical microscope and SEM. For black photoresist, optical density was measured by X-rite OD meter.

3 Results and discussion

After obtaining pattern by photo-lithography, photolithographic performance was checked.

3.1 Negative photoresist

Several formulations and photolithographic process conditions were tested as shown in Table 2.

Table 2. Photo-lithography Result

Experiment No.	Formulation				Photo-Lith	Result
	Matrix Polymer	Monomer	Photo Initiator	Dye	Exposure	
1	Acrylic	DPHA	PI-A	NIR-Dye	850nm	Well Patterned
2	Acrylic	DPHA	PI-A	(None)	850nm	Not curable
2-2	Acrylic	DPHA	PI-A	(None)	i-line	Curable
3	Acrylic	DPHA	PI-B	NIR-Dye	850nm	Not curable

Experiment 1 (Exp.1) showed high photosensitivity and good pattern profile by applying NIR(850nm) exposure. However, Exp.2, using photoresist that doesn't contain the dye, could not show patterns, that is, photoresist was not cured by NIR exposure, although this photoresist is curable when UV (i-line) exposure is applied (Exp.2-2). This suggests that the dye, which is sensitive to NIR, receives NIR photo-energy and once excited, then the energy transferred to photo-initiator.

In Exp.3, a different type of photo initiator (PI-B) was used with the NIR-Dye, but this formulation did not work by applying NIR exposure. This suggests that not any combination of photo initiator and NIR-Dye works for this NIR photolithography. Needs a specific combination of Dye and photo-initiator.

3.2 Black photoresist

Black pigments (Carbon black, Ti black and the special organic black pigment) were added to Exp.1 formulation in Table 2, respectively. Then photo-lithographic performance was tested applying NIR (850nm) exposure.

Special black organic pigment contains black photoresist showed very high photosensitivity and good profile as shown in Fig. 1. Even with thick film (20um) , patterns are well formed, showing that NIR wavelength light penetrates the black photoresist film without being absorbed. However, if carbon black or Ti black is used as a black segment, photoresists were washed away by alkaline developer, that is, NIR light is absorbed at the surface of the photoresist. As shown in Fig. 2, carbon black or Ti black blocks NIR wave length light. In contrast, although the special organic black pigment blocks the UV/Visible light enough, its transparency at NIR wave length area becomes very high.

There is no NIR exposure machine on the market. The Exposure tool used in this paper is a hand self-produced tool combining 850nm LED with flash light enclosure. Therefore, 850nm light is not perfectly parallel light exposure. If we could get a parallel NIR exposure machine, pattern profile of Fig.2 would be very vertical.

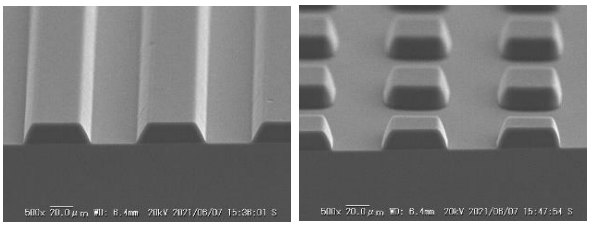

Fig. 1 SEM Observation of Exp. 1 formulation
(Left: 25um L&S, Right: 25um Dot, Resist:20um thick)

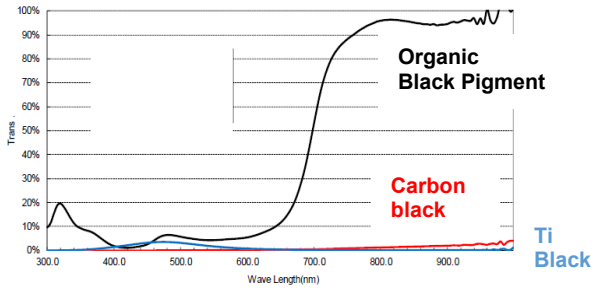

Fig. 2 Black materials transparency

4 Conclusion

We achieved to establish a novel photo-lithography process applying near IR exposure and formulate special NIR photoresist. And by containing specific organic black pigment which blocks the UV/Visible light but is transparent to NIR, we could formulate a novel black photoresist which potentially shows high photosensitivity, high vertical profile, and high OD.

References

[1] G. Imai and D. Kojima, “Research and Development of Novel Posi-type resist system for Thermal Laser imaging” Research of Paint, No. 142, pp. 50-54 (Sept. 2004).

[2] A. Shiraishi, “Development of Cure System using Near Infrared Light” Photo-polymer Conference News Letter, No. 83, pp. 7-9 (2018).