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Effects of exposure wavelength and surface preparation conditions on the generation of blister defects in organic insulator layer

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Abstract−We report a new factor for blister formation on organic photoresist (PR) and an improvement of this process. We have studied blister formation from more different standpoints, such as processes and instrumentation, than did previous reports. Unexpectedly, we observed radical blister formation in an experiment that involved exposure without any ultraviolet (UV) filters. After a series of experiments, the data showed that the organic PR blister problem was most likely caused by the specific wavelength of the UV light field on exposure. Surface preparations using wet and dry treatments prior to coating a thin film of organic PR on silicon nitride (SiNx) glass wafer were studied. By comparing exposure to different spectra, both with and without a UV filter, we confirmed the key point of blister formation in case of the organic PR. Additionally, various treatments of SiNx prior to the coating of organic PR were primarily performed to improve organic PR adhesion to SiNx glass substrate.

Key words: Blister, Adhesion, Organic Photoresist, Silicon Nitride, TFT Process

INTRODUCTION

First used in small screens, such as those found in cellular phones and laptop PCs, thin-film transistor liquid-crystal displays (TFT-LCDs) are now used to produce large flat-panel displays (FPD), such as those found in computer monitors and full-high-definition (FHD) televisions. The demand for large liquid-crystal display televisions (LCD TVs) has been growing of late in the FPD market, requiring new advanced technologies to achieve high resolution, fast responses, low power consumption, and integrated driving circuits in peripherals [1,10].

There is a specific application of certain polymers, known as organic PR, in the micro-fabrication of TFT substrate for large LCD display panels [1-4]. In TFT-LCD mass production, achieving high-quality and defect-free pattern formation has recently become an increasingly important issue. Blister formation in organic PR during exposure of large scale integration (LSI) circuit pattern to UV light was first reported in 1979 [5]. In recent years, this phenomenon has often been observed in commercially available organic PR, which achieves a high aperture ratio in vertical alignment (VA) mode [6].

A PR blister is a small pocket of fluid within the upper layers of a substrate, typically caused by out-gassing on the interface between two layers. Most PR blisters are filled with a nitrogen gas, and they badly affect the patterning of each layer during the photolithographic process. Previous literature [7] has explained the formation mechanism of blisters at the PR substrate interface during exposure to UV light. We agree that the mechanism of blister formation strongly depends on the following factors: (i) photo-active compound (PAC) concentration of the PR film and (ii) adhesion energy between the PR film and the substrate. This is based on the assumptions that (i) if the generation rate of nitrogen gas is greater than the release rate from the top of the PR film, all of the nitrogen gas generated will be concentrated in the area of the resist substrate interface, and (ii) blister formation requires only the nitrogen gas generated in the PR area where the blister occurs. However, the ability to control PAC concentration in order to inhibit a blister is limited by the photochemical property of the PAC concentration in PR. In this research, we paid special attention to other factors in the photolithography process: (i) the cleaning process and (ii) the exposure to UV light process. Additionally, we checked whether blister formation depends on whether PAC is present or not.

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EXPERIMENTAL SECTION

1. Instrumentation

Photolithography of an organic PR was performed in this study using a mirror projection alignment (MPA), a proximity aligner, a spin coater, a puddle-type developer, an organic cleaner, a UV cleaner, a trimethylammonium hydroxide (TMAH) cleaner, a D.I cleaner and a proximity bake for the processing of a first-generation glass substrate. It was thermally treated under a nitrogen atmosphere in a convection oven for curing the organic PR. Dry etching was performed with a plasma etcher. The contact angle of test substrates was measured with a drop shape analysis system (Kruss Co., Germany). The pattern image was measured by using an inspection microscope (Seoul Engineering Co., South Korea). The thickness difference was measured with the surface profiler scanning electron microscope (SEM) and SEM images were captured by FEI (Quanta 3D). Atomic force microscope (AFM) images were captured by SPA-500 (Seiko Co., Japan). All of the instruments were situated and used in a clean room.

2. Materials

The organic insulator material, a solution of acrylic resin and PAC with the positive tone napthanquinone-diazo (DNQ) in diethylene glycol methyl ethyl ether (EDM) and propylene glycol mono-methyl ether acetate (PGMEA) solvents, made use of a photo-definable organic PR for mass production. The developer used TMAH solution diluted by deionized water. We used gases such as sulfur hexafluoride (SF6), hydrogen and oxygen gases at over 99.98% purity for the dry etch process.

3. Surface Treatment of SiNx Substrates

We performed the following test to examine the reproducibility of blister formation and to search for conditions under which no blister formation occurred in our test instruments. The surface treatment of SiNx substrate is shown in Table 1. Different doses-500 and 1,000 mJ/cm^2-were used to verify the dependency of exposing energy under the same treatment conditions. The captions will help readers to understand the details of the cleaning process.

Table 1. The condition of surface treatment in each silicon nitride substrate

Surface treatment	Cond. 1/ Cond. 2	Cond. 3/ Cond. 7	Cond. 4/ Cond. 8	Cond. 5/ Cond. 9	Cond. 6/ Cond. 10
Ex. UV[a]	-	OK	-	-	-
TMAH[b]	-	-	OK	-	-
Organic[c]	OK	-	-	-	OK
DI Water[d]	-	-	-	OK	-
HMDS[e]	OK	-	-	-	-
Lamp	Luminance: 2,100 mW/cm^2				
DOSE (mJ/cm^2)	1000 (Cond. 1, 3-6)				
	500 (Cond. 2, 7-10)				
Blister	No	Yes	No	No	No

[a]Ex. UV treatment: 27 sec at R.T., Lamp Power: 10 kW, Luminance: 30-40 W/cm^2

[b]TMAH treatment: 35 sec at Room Temperature (R.T.=25 °C), TMAH 0.3%

[c]Organic treatment: Organic and DIW Rinse 80 sec at Temp. 70 °C, Chemical: LCS-1000

[d]DI Water treatment: Rinse 80 sec at R.T.

[e]HMDS: 30 sec at Temp. 85 °C

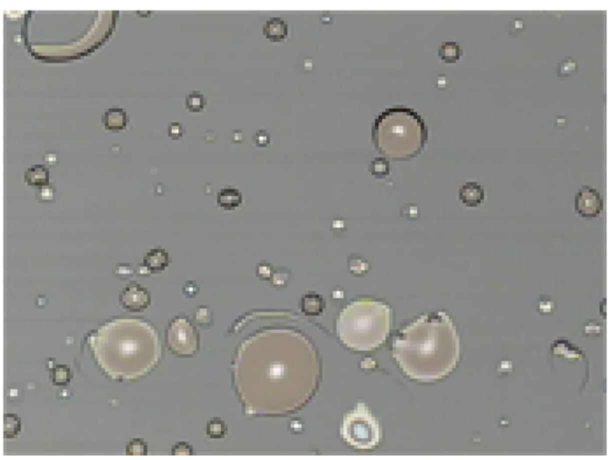


Fig. 1. Blister defects of organic insulator with 10-15 μm size.

4. Organic Insulator Process

The substrates were prepared from SiNx deposited by chemical vapor deposition (CVD). To these substrates, we applied various surface treatments in the photolithographic process. The substrates were coated with an organic PR at a constant thickness using a spin coater. The spin-coated organic PR was dried again by heating it in an oven, after which a suitable dose of it was exposed in an aligner. The exposed organic PR was developed using the TMAH solution, after which its entire surface was exposed to UV irradiation. The organic PR was cured by thermally treating it under a nitrogen atmosphere in a convection oven. The cured substrates were treated with SF6 gas, and then the pixel process was performed.

RESULTS AND DISCUSSION

1. Analysis of Blister Formation

Nitrogen gas was generated in the organic PR film by photoreaction of PAC during UV light exposure. The organic PR film peeled away from the SiNx substrate surface with generation of nitrogen gas in the organic PR film, upon the destruction of the adhesive bond between the organic PR and the substrate. Unexpectedly, we discovered radical blister formation in the experiment in which exposure occurred in the absence of UV filters.

Fig. 2 shows a macroscopic photograph and microscopic images of blisters formed at the interface of organic PR and silicon nitride substitute during UV light irradiation. The blisters have diameters of 50 μm to 3 mm. Not only are there visible fringes, showing where excess nitrogen gas pulled the organic PR away from the substrate surface, but there are also many cracks on the organic insulator thin film. In the center region of the glass wafer, blister formation occurs more often. Formation is most likely to occur with a light field and less likely to occur with a dark field. Therefore, the exposure mechanism described previously indicates that the nitrogen released during exposure could be the cause of this blister formation. Initially, when an organic PR is irradiated by UV light, a PAC rapidly decomposes with nitrogen gas and acidic compound from the ballast compound. Then, the concentration of nitrogen gas radically increases at the organic PR and substrate interface after UV light irradiation. Next, the nitrogen gas continually diffuses into the interface. After that, cohesive destruction of organic PR film on the substrate occurs. Finally, blister formation occurs.

As shown in the images of SEM and AFM for a blister in Fig. 3, blisters occur in a variety of sizes and shapes. Simultaneous and random defect problems often involve many factors. We speculate that blister formation might not only result in a large number of blisters, but also from micro-sized to millimeter-sized defects that grow bigger through penetration into the interface of the organic layer and silicon nitride layer because of the 3 μm-thick thin organic insulator film.

2. The Dependence on Wavelength and Intensity of Incident UV Light

We closely examined the difference in the light spectra of the exposure lamp with/without a UV filter. The comparison of the spec-

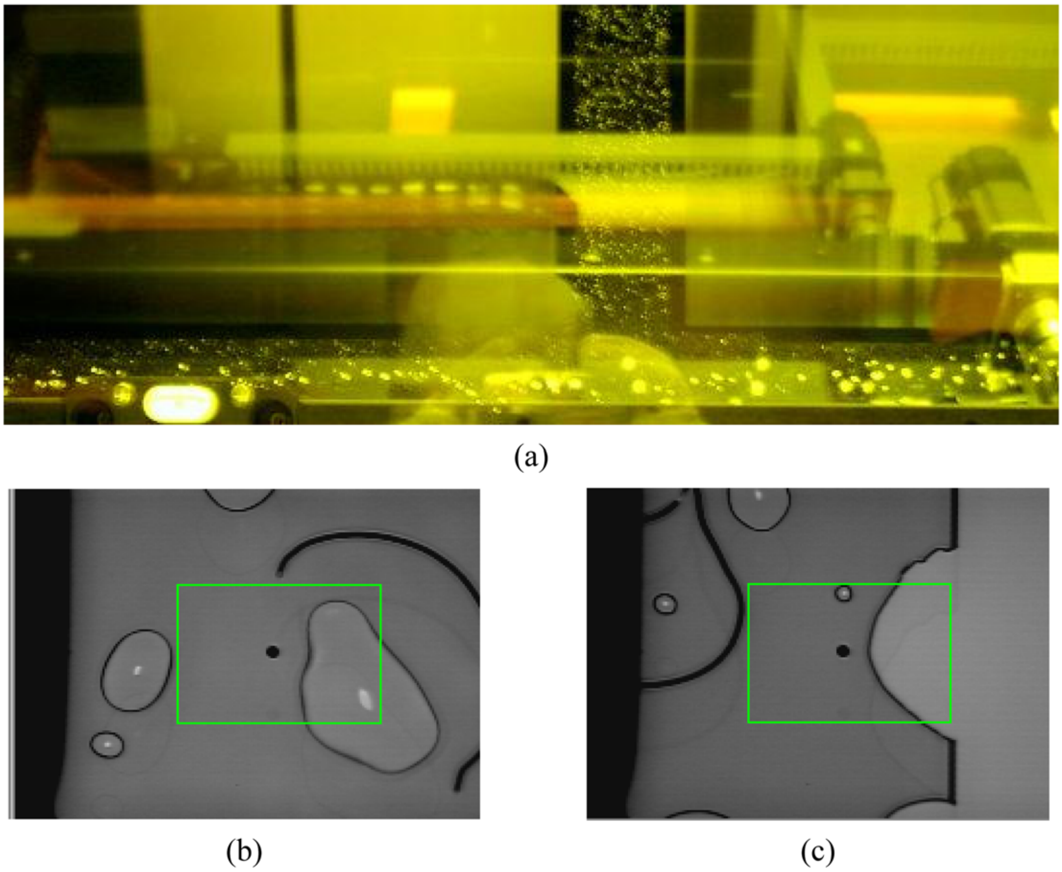
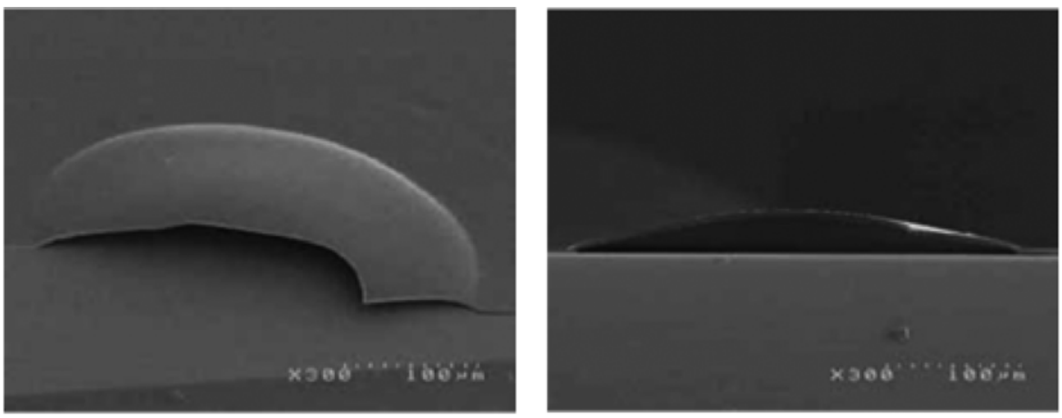


Fig. 2. (a) Macroscopic photograph and microscopic images at (b) center and (c) side of blisters formed at the interface of organic PR and SiNx/glass substitute (blister size: about 10 μm to 3 mm).



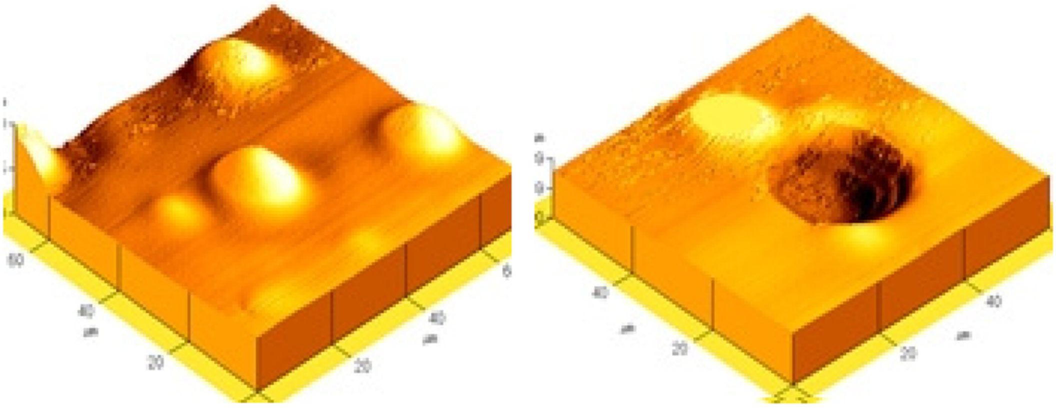
(a) Tilted top view (b) Sectional view

Fig. 3. SEM images at (a) tilted top and (b) sectional view of blisters formed at the interface of organic PR and SiNx/glass substitute (blister size: about 300 μm).

tra is shown in Fig. 5. In the original spectrum of the lamp, the light intensity of the G (436 nm), H (405 nm), I (365 nm), J (334 nm), and K (314 nm)-line peaks can be clearly seen. However, we cannot see the light of the K-line peak in the filtered spectrum of the lamp, and there is only a very small J-line peak. This result raises the possibility that one of the main factors in blister formation is intensive UV irradiation at a wavelength of 350 nm.

In Table 2, the blister was formed under non-filtered lamp (40 mW/cm^2) conditions in a sample that included 5% PAC. These results show a wide variation in the effects of PAC and UV filters on the exposure process. The blister is independent of exposure energy under 1,000 mJ/cm^2. However, the blister is dependent on the presence of PAC and the intensity of UV light at the J or K-line.

In the FT-IR transmittance spectra, there is no difference between them, curve (a), (c) and (d), except for curve (b). The difference on fingerprint region was two stretching vibration peaks at IR spec-



(a) Various sizes and shapes of blisters (b) Blister formation next to contact hole

Fig. 4. AFM images of (a) various sizes and shapes of blisters and (b) blister formation next to contact hole at tilted top view of blisters formed at the interface of organic PR and SiNx/glass substrate (blister size: about 10-20 μm).

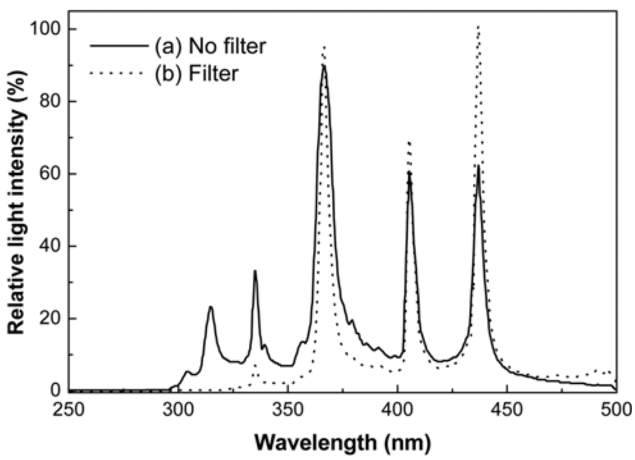


Fig. 5. Comparison with (a) original and (b) filtered spectra of exposing lamp.

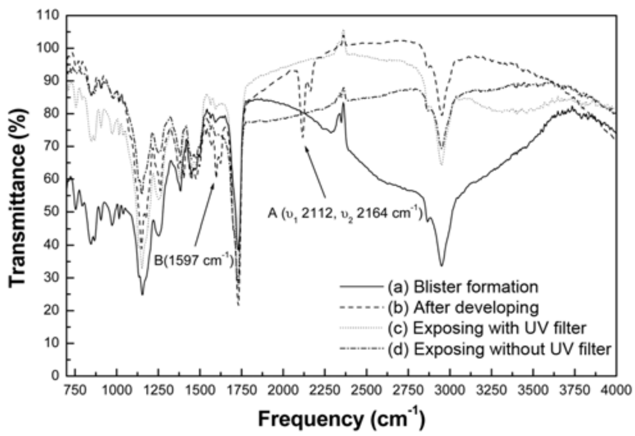


Fig. 6. The comparison of FT-IR transmittance Spectra of (a) blister film, (b) film after developing, (c) film after exposing through UV filter and (d) film after exposing without UV filter.

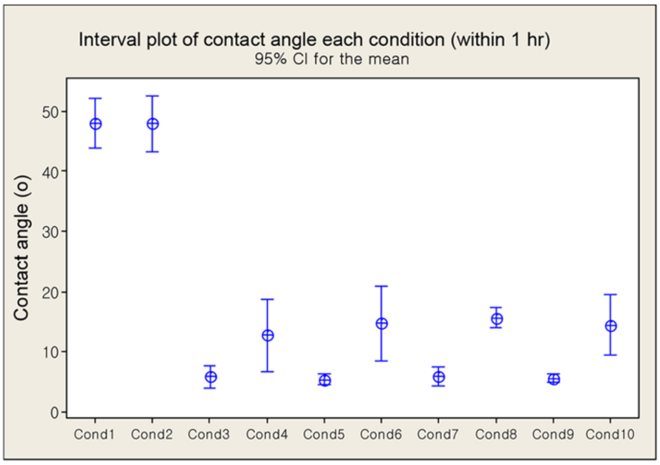
trum after developing of organic PR. The stretching vibration band (A) for the diazo group in DNQ is represented by a doublet (ν_1 and ν_2) in the region 2,100-2,200 cm^{-1} [8]. The low-frequency band of the doublet, ν_1, shows additional splitting, which appears in relation to the donor-acceptor nature of the substituent and the solvent polarity. The stretching vibrations (B) of carbonyl (C=O) and C=C group of DNQ are represented by a doublet at 1640-1550 cm^{-1} [9].

3. Surface Treatment and Adhesion Improvement

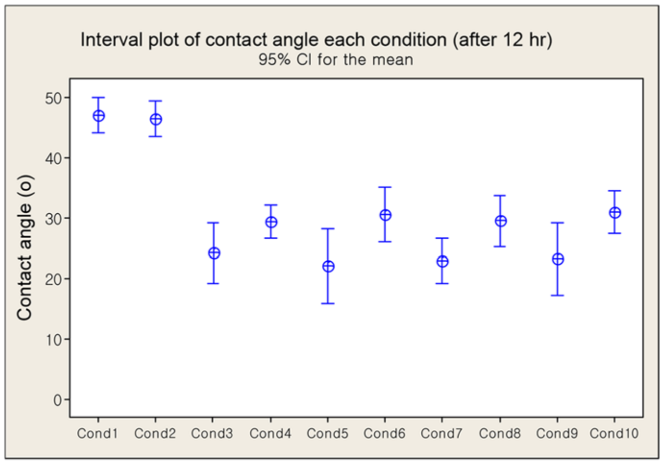
In the organic and hexamethylenedisilazane (HMDS)-treated surfaces, conditions 1 and 2 are hydrophobic and the average contact angle is 49°. In contrast, the one-condition treated surfaces are hydrophilic and have a contact angle that ranges from 5° to 35°. The greater the contact angle, the fewer water molecules adsorb on the surface. The dehydration bake helps to reduce the amount of water molecules on the substrate; however, the cooling step following the dehydration bake reintroduces water molecules onto the substrate. Both organic and HMDS-treated and one condition-treated surfaces showed no organic PR blister defects except for condition 3. The values of contact angle on reference samples are much greater than those of other conditions under different cleaning process. After 12

Table 2. The test results of blister formation with/without UV filter

Lamp	Sample	Exposure energy (mJ/cm^2)			
		150	300	600	1000
Original Lamp, 40 mW/cm^2	PAC 5%	Blister	Blister	Blister	Blister
	PAC 0%	No blister	No blister	No blister	No blister
Filtered Lamp, 5 mW/cm^2	PAC 5%	No blister	No blister	No blister	No blister
	PAC 0%	No blister	No blister	No blister	No blister

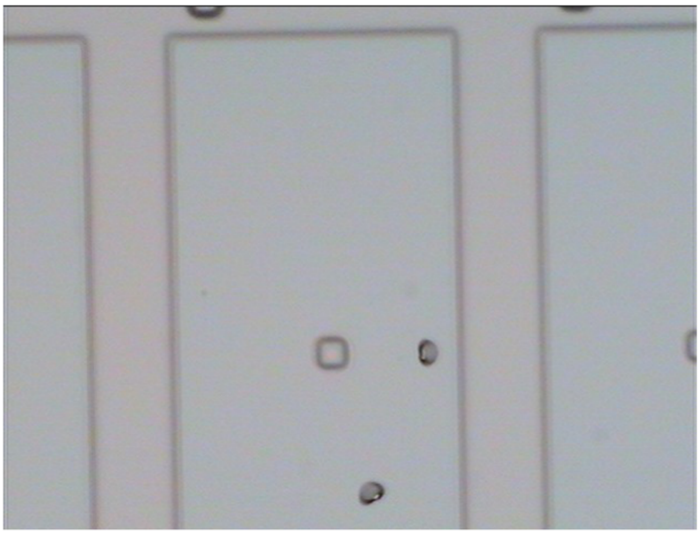


(a)

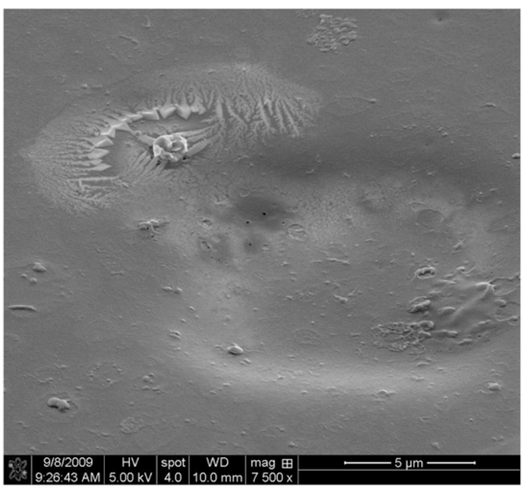


(b)

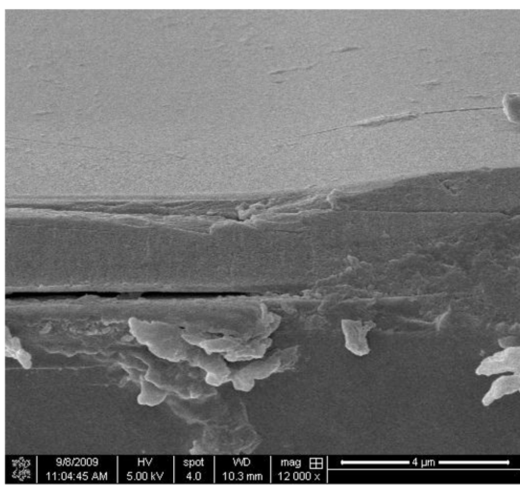
Fig. 7. The results of contact angle (a) within 1 hr and (b) after 12 hrs in each condition. These results are the distribution for 5 points a sample.



(a) Blister reproduction (size: 10~20 ㎛)



(b) Tilted top view image



(c) Sectional view image

Fig. 8. (a) A microscopic image and (b) tilted top view and (c) sectional view SEM images of blisters reproduced in condition 3.

hours, the hydrophobic surface property of references is not changed; however, the hydrophilic surface properties of the other condition substrates all changed to become more hydrophobic than was previously the case.

We checked the reproduction of blisters on only one condition, condition 3, as illustrated in Fig. 8. The size of the blisters reproduced is about 10-20 μm in diameter. The blisters on organic PR were inflated during the photolithographic process and then shrank during preparation of the scanning electron microscope (SEM) sample in Fig. 8(b), Fig. 8(c), showing that the organic PR has separated from the SiNx layer.

CONCLUSION

In this work, to solve the blister problem we have paid special attention to other factors on process and instruments. In conclusion, the main factor is the existence of PAC. In organic PR and intensive UV irradiation under 350 nm, a specific wavelength like J or K-line of UV light brings the blister. Also, the adhesion of organic PR to silicon nitride glass wafer was significantly improved through the pretreatment of organic and HMDS.

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