Spreading of Liquid Drop on Resist Film Surface

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Liquid drop spreading is effective phenomenon for understanding nature of wetting processes such as pattern development, etching, cleaning, immersion lithography and so on. Liquid spreading can be measured by contact angle measurement. Spreading coefficient c in Neumann model is estimated for each film surface. Results obtained in this experiment indicate that the liquid drops on resist surfaces are more likely to spread compared with those on the inorganic substrates.

Keywords: resist, contact angle, Neumann spreading model, spreading coefficient

1. Introduction

In LSI production, resist films were treated in various wet processes such as pattern development, substrate etching, plating and so on. It is important to understand the spreading phenomenon of liquid drop for designing the wet process conditions. In this study, the time dependency of spreading was investigated by contact angle measurement based on Neumann model [1].

2. Experiment

As the substrate materials, eight kinds of novolac resists were used. The resist films were formed by the spin method. As the references, various inorganic films were prepared. As the liquids, DI(deionized) water, TMAH (tetramethyl-ammoniumhydroxide) 2.38% aqueous solution, ethanol and acetic acid were used. Contact angles of liquid drop were measured after making a contact.

Fig.1 Schematic of liquid drop spreading.

Figure 1 shows a schematic of liquid drop spreading. Neumann derived the model for contact angle variation during liquid drop spreading [1].

$$\cos \theta_t = \cos \theta_\infty (1 - ae^{-ct}) \quad (1)$$

where θ_t and θ_∞ is contact angle at t (s) and infinite, symbol a is empirical constant, and c is spreading coefficient (s^{-1}) of liquid drop.

3. Results and Discussion

The contact angle change of DI-water after dropping is shown in Fig.2. As the lapse of time, the contact angle decreases gradually.

Fig.2 Contact angle of DI-water on substrates.

Fig.3 Relationship between $1 - \cos \theta_t / \cos \theta_\infty$ and passage time after dropping of DI-water.

The resist and bare Al surfaces indicate hydrophobic but doped poly Si surface. These experimental results can be plotted in Neumann formula as shown in Fig.3. The Neumann formula can be expressed as follows.

$$\ln(1 - \cos \theta_t / \cos \theta_\infty) = \ln a - ct \quad (2)$$

The slope value in Fig.3 corresponds to spreading coefficient c of liquid drop. The analysis method is explained in detail in previous report [2]. The spreading coefficient of DI-water on the novolac resist is relatively larger than that of the bare Al substrate. The poly Si and doped poly Si substrates indicate lower spreading property.

Figure 4 shows spreading coefficient on various resist materials. The DI-water and TMAH developer indicate relatively high spreading property. However, higher wetting liquids, alcohol, indicate lower spreading property. The spreading coefficient c is mostly same among resist materials.

As shown in Fig.5, the spreading coefficient for inorganic substrates is drastically changed. On the Al substrate, DI-water droplet spreads rapidly. On the contrary, Al substrate with oxygen plasma treatment indicates lower spreading property. It can be considered that the hydrophobic surfaces indicate relatively higher spreading, which means contact angle decreases rapidly. On the other hand, the lower spreading properties are appeared in the Al surfaces treated with O_2 plasma. Therefore, the hydrophilic surfaces show relatively lower contact angle change. One can safely state that Neumann model is effective to analyze

Fig.4 Spreading coefficient of various liquids on resist materials. The resists A, B, C, and D are novolac type in commercial available. The resists E and F are surfactant containing resists, G and H are dye-containing resists.

Fig.5 Spreading coefficient of various liquids on inorganic substrates. I :bare Al, J: Al+ O_2 plasma, K: Al+n-butyl acetate rinse, L: Al+HMDS primer, M: poly Si, N: doped poly Si, O: WSi_2 , P: $MoSi_2$, Q: SiO_2 , R: PSG, S: BPSG, T: CVD-SiN.

the dynamic wetting of liquid drop on the substrates.

4. Conclusion

Spreading coefficient of liquid drops is analyzed on various resist and inorganic substrates based on Neumann model, and it is effective to characterize surface wetting property of resist thin film.

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