Micro Bubbles Captured at Micro Defect on Resist Film

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1. Introduction

Recently, removal and adhesion control of micro bubbles formed on a resist film surface have become important in order to realize high quality resist pattern.[1] In the pattern development process, micro bubbles on the resist surface cause a certain development failure. In this paper, we pay attention to micro bubble capture at a micro defect formed on the resist surface. It is indicated that the micro bubble is more likely to capture at the micro defect due to pinning effect.

2. Experiment

A resist material consisting of acryl resin as a base polymer was used for the investigation. By a spinning method, the resist film of 300nm thickness was formed on a Si(100) substrate. As a dipping water, deionized (DI) water (ρ = 0.2 μS/cm) was used. Figure 1 shows a schematic of micro bubble capture at a micro defect. As the micro defects, polystyrene latex (PSL) particle were used. The size of PSL particle was ranging from 0.29 to 5.15 μm. The micro bubbles were observed with the optical microscope.

In order to analyze the capture mechanism of micro bubble, the wetting property of the resist films and the PSL particle were measured by the contact angle method. The surface energy γ can be expressed as a sum of two components, dispersion γ and polar γ. As the test liquid, deionized water, ethyleneglycol and diiodomethane were used for the contact angle measurement. [2-3]

3. Results and Discussion

Figure 3 shows the component map of surface energy of the resist film, PSL and DI-water. The dispersion component γ of the PSL is relatively high comparing with polar component γ. On the other hand, the polar component of DI-water is considerably high. The components of the resist material are the intermediate values.

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Fig. 1 Schematic of micro bubble captured at micro particle.

Fig. 2 Component map of surface energy for materials used for the investigation.
Figure 3 shows the typical photographs of micro bubbles captured at the PSL particles on the resist film surface. It is clearly observed that the micro particle gives rise to capture the micro bubble. The minimum size of the captured bubble, which can be confirmed with the optical microscope, is approximately 15 μm. Figure 4 shows the size distribution of the captured bubbles. The maximum frequency of the captured bubbles is about 4 pieces/cm². As decreasing the bubble size, the bubbles are more likely to adhere to the micro particle on the resist surface.

(a) Bubble 1  (b) Bubble 2

Fig. 3 Photographs of micro bubbles.

![Size distribution of captured bubble on resist film.](image)

Fig.4 Size distribution of captured bubble on resist film.

Free energy change and buoyancy can be considered as the factors for bubble capture. The free energy change per unit area $\Delta G$ can be expressed as the following equation.

$$\Delta G = \Delta S \cdot \gamma_L (1 + \cos \theta),$$

where, $\Delta S$ and $\gamma_L$ represent area change of bubble and surface tension of liquid. The symbol $\theta$ represents contact angle of bubble.

Figure 5 shows a schematic of pinning effect of bubble on a defect. In Fig.5, symbols $\theta_1$ and $\theta_2$ indicate contact angles of bubbles on the defect and at the corner respectively. In general, the advance contact angle $\theta_2$ of bubbles becomes small as compared with that of stationary bubble $\theta_1$, that is, $\theta_1 > \theta_2$. The surface area change $\Delta S$ of bubble increases by advancing of the bubble. Therefore, free energy change per unit area $\Delta G$ becomes large, when the bubble moves around the corner of the defect. In thermodynamic, it can be considered that the capturing of bubble at the defect is stable, that is, pinning effect.

![Schematic diagram of pinning effect model.](image)

As the another factor, the ascending force due to buoyancy $F$ acts to remove the micro bubble from the PSL particle. The buoyancy of bubble can be expressed as the following equation.

$$F = \frac{4}{3} \pi r^3 \rho g$$

The ascending force of bubble is proportional to bubble size $r$. Therefore, as increasing the bubble size, the number of captured bubble decreases as shown in Fig.4.

4. Conclusion
The micro bubbles are more likely to adhere to the micro defect on the resist surface. The capture mechanism of micro bubbles at PSL particle is analyzed based on the pinning effect and buoyancy. The control of micro bubble capture and removal would become important in micro device fabrication.

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References