Viscous Finger Pattern Formed in Photoresist Film during Heat Treatment

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1. Introduction

When a gas is pushed through a fluid of high viscosity, the liquid breaks through in the form of highly branched patterns called viscous fingers (VF).[1,2] The role of VF pattern has recently become one of the central questions in the studies of spreading of viscous fluid such as resist film coating. The VF behavior has been recognized to be a very useful tool for the experimental invisibility. We report in this paper the two-dimensional experimental results of VF pattern formed in a resist layer which is interposed with two substrates. We pay special attention to the relation between formation mechanism of the VF pattern and surface energy of the substrate.

2. Experiment

A photoresist material which contains novolak resin was used. A solvent contained in the photoresist layer was ethylcelluloseacetate (ECA) which boiling temperature was 156 °C. As a substrate, indium tin oxide (ITO) film was formed by the sputtering method. The resist layer was interposed with two ITO substrates. Subsequently, the samples were heated at 150°C for 5 min on a hot plate. Figure 1 shows a schematic of cross sectional view of the samples in which the VF pattern is formed. The gap width d between two substrates was adjusted with a silica particles to be 1.0, 5.0 and 10.3 μm. Various surface treatments, exposing to O2 plasma treatment and hexamethyldisilazane (HMDS) vapor were performed on the ITO substrates. The optical microscope images of the VF pattern were taken by the recording system.

Usually, surface energy γ of a condensed matter is defined as a sum of two components, London dispersion γd and Keesom polar γp, as follows.

$$\gamma = \gamma^d + \gamma^p$$  \hspace{1cm} (1)

The interfacial energy γrs and the adhesion energy Wrs between two materials (Resist and Substrate) can be expressed as the following equation.

$$\gamma_{rs} = \left(\sqrt{\gamma^d_R} - \sqrt{\gamma^d_S}\right)^2 + \left(\sqrt{\gamma^p_R} - \sqrt{\gamma^p_S}\right)^2$$  \hspace{1cm} (2)

$$W_{rs} = 2\sqrt{\gamma^d_R}\sqrt{\gamma^d_S} + 2\sqrt{\gamma^p_R}\sqrt{\gamma^p_S}$$  \hspace{1cm} (3)

By measuring a contact angle on a sample surface by using standard liquids which surface energy and components are known, surface energy and its components of the sample can be obtained. The details of surface energy measurement are described in the reference. [3]
3. Results and Discussion

Figure 2 shows the component map of surface energy of the materials used for VF investigations. Dispersion component of resist film is relatively high comparing with polar component. By the oxygen treatment, the polar component of the ITO film increases, but it decreases by the HMDS treatment. From the surface energy data, the interface energy $\gamma_{RS}$ and adhesion energy $W_{RS}$ can be estimated.

![Component map of surface free energy](image)

Fig.2 Component map of surface free energy.

(a) ITO (Non treatment)
\[
\begin{align*}
\gamma_s &= 46.7 \text{ mJ/m}^2 \\
W_{RS} &= 87.6 \text{ mJ/m}^2 \\
\gamma_{RS} &= 1.3 \text{ mJ/m}^2
\end{align*}
\]

(b) HMDS treatment
\[
\begin{align*}
\gamma_s &= 36.6 \text{ mJ/m}^2 \\
W_{RS} &= 75.0 \text{ mJ/m}^2 \\
\gamma_{RS} &= 3.8 \text{ mJ/m}^2
\end{align*}
\]

(c) O$_2$ plasma treatment
\[
\begin{align*}
\gamma_s &= 58.6 \text{ mJ/m}^2 \\
W_{RS} &= 93.0 \text{ mJ/m}^2 \\
\gamma_{RS} &= 7.8 \text{ mJ/m}^2
\end{align*}
\]

Figure 3 shows the optical microscope images ofVF pattern formed in each sample. It can be observed that the VF pattern becomes large as increasing the interface energy of the ITO substrate. Consequently, the resist fragment becomes small as the growth of the VF pattern.

![Saffman-Taylor model for viscous fingering](image)

Fig.4 Saffman-Taylor model for viscous fingering.

The motion of the interface between the solvent gas and the resist layer placed between two close parallel plates is determined by the pressure distribution in the resist layer. The resulting VF instability was defined as a fractal growth phenomenon. The physical mechanism might be considered as the interaction between the interface $\gamma_{RS}$ and the viscosity $\eta$ of the resist material as shown in Fig.4. By Saffman-Taylor model, the formation factor of VF pattern can be expressed as follows.[3]

\[
\frac{R}{d} \propto \sqrt{\frac{\gamma_{RS}}{\eta'}}
\]

It can be explained that the radius of VF pattern apex $R$ increases as increasing interface energy $\gamma_{RS}$. Therefore, the dependency of VF pattern size on interface energy, as shown in Fig.3, can be explained.

4. Conclusion

The VF pattern becomes large as increasing the interface energy of the resist film and the ITO substrate. These results have enabled to discuss the coating process of a resist film on a substrate.

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References