In-situ Monitoring of TMAH Developer Intrusion into Resist Film by C-V Method

Hodaka Shirataki and Akira Kawai*

Department of Electrical Engineering, Nagaoka University of Technology,
1603-1 Kamitomioka, Nagaoka, Niigata, 940-2188 Japan
*E-mail : kawai@nagaokaut.ac.jp

The TMAH developer (2.38 wt% aqueous solution) intrusion into a resist film is analyzed by the typical current-voltage (C-V) method. As well known device structure, Metal / Insulator / Semiconductor (MIS) structure is employed, and a resist film (novolak resin base) is adopted to an insulator material. During the TMAH developer dropping on the Au mesh electrode, an increase of the capacitance and a parallel shift towards a negative gate bias voltage region in a C-V curve can be clearly observed. At the first stage of dropping, these signal changes in C-V curve are relatively large. Refractive index of the resist film slightly increases after the TMAH developer dropping, which reflects the condensation of polymer resin due to the TMAH developer intrusion. A contact angle decrease of the TMAH developer after dropping is also monitored. A spreading coefficient $c_S$ of TMAH developer decreases gradually as the time elapse. Particularly, the capacitance change clearly indicates the intrusion of the TMAH developer as the function of time elapses. These dynamic measurements of the intrusion will be effective to analyze the liquid intrusion mechanisms into polymer materials.

Keywords: liquid intrusion, TMAH developer, photoresist, MIS structure, C-V curve, dielectric constant, refractive index, contact angle, spreading coefficient, in-situ monitoring

1. Introduction

Recently, the intrusion mechanism of tetramethylammoniumhydroxide (TMAH) developer into a resist film has been studied by many researchers because the accuracy of the nano scale patterning of the resist film has been required [1-11]. It is well known that the various dissolution and insoluble mechanisms are clarified due to the liquid-resin interactions [1,2]. Recently, the dynamic observation of resist pattern development in real time by using High Speed Atomic Force Microscopy [3]. Authors already reported a hardened layer formation of a resist film surface after the TMAH development analyzed by the tip indentation technique [4]. Moreover, some effects on the adhesion or strain characteristics of the TMAH developer intrusion has been reported [5-8]. Various property changes of of resist film, such as refractive index, film thickness and electrical resistance, will occur due to the intrusion of TMAH developer [9-11]. In addition, the liquid intrusion can be observed not only the TMAH developer but also 0.5 wt% HF aqueous solution [12].

In this paper, we discuss the analysis of the TMAH developer (2.38 wt% aqueous solution) intrusion into the resist film by the typical current-voltage (C-V) method. Usually, the C-V method is often employed for evaluating the LSI device operation or detect some impurity ions in the insulator film [13-15]. It is well known that the C-V characteristic reflects a slight change of dielectric constant sensitively. Moreover, an in-situ monitoring of C-V characteristic is available in order to analyze liquid intrusion phenomena. Particularly, it was possible to observe the capacitance change which will reflect the intrusion phenomena as the function of time elapses.

2. Experiment

2.1. Dielectric dispersion measurement of resist film

In order to determine a stable frequency region of a dielectric constant $\varepsilon$ and lower value of $\tan\delta$ of the resist film, the frequency dispersion measurement of resist film was carried out by a parallel plate capacitor method. A gold base electrode thin film was fabricated on a SiO$_2$ film formed on a p-type silicon substrate by using the
radio frequency (RF) magnetron sputtering system (SVC-700RF II, SANYU ELECTRON Co.LTD.). Then, the resist film was coated on the Au film by a spin coating process of 5000 rpm for 30 sec. Finally, the upper Au electrodes of 2 mm × 2 mm square were fabricated by using the RF magnetron sputtering system. A thickness of the both Au electrodes is about 0.48 µm. The frequency dispersion characteristic was measured by using the LCR tester (IM3570, HIOKI E.E. CORP.).

2.2. C-V curve measurement of MIS structure

Figure 1 shows a schematic structure of the Metal / Insulator / Semiconductor (MIS) capacitor used for C-V curve measurement. In this study, a positive novolak resin based photoresist film was employed as an insulator layer. As shown in Fig. 1a, a gold electrode in a mesh structure was formed. A schematic cross sectional structure of MIS device is shown in Fig. 1b. The fabrication processes of the MIS capacitor and the intrusion experiment of the TMAH developer are as follows. A native oxide film on the p-type silicon (100) wafer was removed by dipping into a HF (5 wt%) aqueous solution for 10 min. Then, an i-line positive photoresist was coated on the silicon substrate by a spin coating process of 5000 rpm for 30 sec. Then, the resist film was baked at 200 °C for 15 min. A thickness of the resist film becomes 2.91 µm. After that, a Au electrode was fabricated on the resist film by a direct current (DC) sputtering system. As shown in Fig. 1a, the four square pieces of the electrode are connected each other. A TMAH developer was dropped on the electrode by using a syringe. Figure 2 shows the photographs of the MIS capacitor and the LCR tester. The bias voltage applied to the gate electrode was changed at ±2.5 V and the alternating current (AC) voltage of 0.05 V at 100 kHz was employed as the measurement signal.

2.3. C-V measurement of Metal / Oxide Semiconductor (MOS) capacitor

The C-V characteristic of MIS capacitor is compared with a traditional MOS capacitor. A typical dielectric Ta₂O₅ film of 17 nm thickness was fabricated by the RF magnetron sputtering system. Then, the Ta₂O₅ film was annealed in a vacuum condition by an infrared rapid thermal annealing system (IVF298W, THERMO RIKO CO.). Then the Cu electrodes were fabricated on the Ta₂O₅ film by the RF magnetron sputtering system. The measurement conditions of C-V characteristic were almost same with those of the MIS capacitor as mentioned above.
2.4. Refractive index and contact angle measurements
The resist film was coated on a p-type silicon (100) substrate by a spin coating process of 5000 rpm for 30 sec and baked at 200 °C for 15 min. After dipping into the TMAH developer, a refractive index $n$ was measured by using an Ellipsometer (DVA-FL, MIZOJIRI OPTICAL MACHINE CO.) at 632.8 nm wavelength. A contact angle of the TMAH developer on the resist film was measured in order to analyze the intrusion phenomena of TMAH developer. The contact angle of the TMAH developer (2.38, 5.00, 7.50 and 10.00 wt% aqueous Solution) and the deionized (DI) water were measured by the half angle method of a contact angle meter.

3. Results
3.1. Frequency dispersion of resist film
Figure 3 shows the frequency dispersion of dielectric constant and $\tan\delta$ of the resist material in the range from 100 kHz to 1 MHz. The capacitance of the resist material indicated mostly constant value around 37.8 nF. The amount of $\tan\delta$ increased gradually, and no influence for the liquid intrusion experiment can be considered. It can be discussed that the dielectric dispersion and relaxation of resist polymer material will reflect in these results. Therefore, the frequency of AC bias voltage used for the C-V measurement was set to be 100 kHz.

3.2. C-V characteristics of MIS and MOS capacitors
Figure 4a shows the C-V curves of the MIS capacitor after dropping a TMAH developer on the resist film. It is clearly observed that the C-V curve before dropping the TMAH developer became flat in the ranging of the bias gate voltage change. After dropping the TMAH developer, the capacitance increased in the whole range of the gate bias voltage, and typical C-V curve such as capacitor gradient around zero bias clearly appeared. Moreover, a certain amount curve-shift toward negative bias can be clearly observed. In this case, dielectric constant of the resist film will become large and equivalent to that of depletion layer. On the other hand, no change of C-V curve and curve-shift can be observed in the case of DI water dropping as shown in Fig. 4b.

Figure 5 shows the dependency of MIS capacitance on dropping time both of the TMAH developer and DI-water. It is clearly observed that the capacitance after dropping the TMAH developer increased instantly. On the other hand,
the capacitance after dropping DI-water increased gradually. At the initial stage of contacting the TMAH developer with the resist surface, a certain characteristic change should occur due to TMAH intrusion phenomena.

The result of the C-V measurement of MOS capacitor is shown in Fig. 6. It can be observed that the typical C-V characteristics of the p-type silicon base MOS capacitor can be confirmed. A large amount of capacitance gradient can be observed clearly. No curve shift of the C-V curve is also observed, which means a slight ionic defect existence.

3.3. Refractive index and contact angle of resist film

By the ellipsometer measurement, refractive index of the resist film before dipping into the TMAH developer and DI-water were 1.628 and 1.637, respectively. The results are consistent to the typical value of the resist materials as summarized in Table 1 [16-18]. After dropping the TMAH developer and DI-water, the refractive index became 1.738 and 1.638, respectively. The clear increase of refractive index $n$ of the resist film after dropping the TMAH developer can be observed, but no change for DI-water. It is well known that the refractive index change of polymer film reflects the change of numerical density of polymer molecule.[11] The above experimental results will discuss later on the point of surface crossing due to chemical reaction between the polymer and TMAH developer.

Figure 7a shows the measurement results of a contact angle change of the TMAH developer and DI-water on the resist film. The contact angle of the TMAH developer became lower than DI-water, which indicates higher wetability on the resist film surface. A spreading coefficient $c_s$ is calculated from the contact angle data by Newman’s law as shown as follows [19].

$$\cos \theta_t = (\cos \theta_\infty)(1 - ae^{-cs t})$$  \( \text{(1)} \)

where a symbol $\theta_t$ denotes the contact angle of the measurement, a symbol $\theta_\infty$ is the equilibrium contact angle and $\alpha$ is the experimental constant. The results of spreading coefficient are shown in Fig. 7b. In the initial stage after dropping the TMAH developer, the change of spreading constant is relatively large but DI water. These results is similar to those of the MIS capacitance change experiment as shown in Fig. 5.

![Fig. 5. Capacitance change of MIS capacitor at bias voltage of -2.5 V, 0 V and 2.5 V after TMAH developer and DI-water dropping.](image)

![Fig. 6. C-V characteristic of (p-type Si / Ta$_2$O$_5$ / Cu) capacitor.](image)

| Refractive Index of various resist materials. |
|-----------------------------------------------|
| Table 1. Refractive index of resist in this study. |
| Intrusion liquid | TMAH developer | DI-water |
| positive resist (i-line) (using for MIS capacitor) | before dropping | 1.628 | 1.637 |
| after dropping | 1.738 | 1.638 |
| negative resist (SU-8) | 1.650 (\(\lambda =405\) nm) |
| negative resist (AZ5214E) | 1.656 (\(\lambda =436\) nm) |
increase of the MIS capacitance is strongly related with the spreading coefficient derived from the contact angle experiment as shown in Fig. 7. In addition, the gradient of the C-V curve can be confirmed after dropping the TMAH developer. The gradient is obviously shifted to the negative voltage region from the origin position, which indicates the existence of positive ions in the resist film. In general, a flat band voltage $V_{FB}$ shift in MIS structure is shown as follows [15].

$$V_{FB} = \Phi_{ms} - \frac{(Q_f + Q_m + Q_{it})}{C_o}$$

where the symbol of $\Phi_{ms}$ is the work function, $Q_f$ denotes the fixed insulator charge, $Q_m$ is the mobile ionic charge, $Q_{it}$ is the insulator trapped charge and $C_o$ is the sheet charge. When a positive ion is trapped in the insulator film, flat band voltage $V_{FB}$ is shifted to the negative region. In this regard, in Fig. 4a, a certain amount of TMAH positive ions will exist in the resist film and detected by the C-V method, which indicates the TMAH developer intrusion into the resist film.

The refractive index increase of the resist film after dipping the TMAH developer will reflect the surface crosslink layer formation due to the formula of Clausius Mossotti as follows.

$$\varepsilon = n^2 = \varepsilon_0 + \frac{\sum N_i \alpha_i}{1 - \frac{1}{3 \varepsilon_0} \sum N_i \alpha_i}$$

where $N_i$ is the molecular number per volume and $\alpha_i$ is polarizability. From a formula of Clausius Mossotti, reflective index increase indicates a molecular number per volume increase. It has been reported that the refractive index increase because of crosslinking reactions of polymer materials [20,21]. The authors have been confirmed the surface hardened layer formation due to the crosslinking by tip indentation method [22]. In the results of the spreading coefficient in Fig. 7, the TMAH developer will intrude into the resist film easier than a DI-water and intrude instantly from the moment of liquid dropping.

5. Conclusion

An increase of the capacitance and a parallel shift to the negative bias voltage region of a C-V characteristics are observed clearly after dropping the TMAH developer. It is possible to a TMAH developer intrusion by a C-V method in higher
sensitivity. Particularly, it was possible to observe the capacitance change at the beginning of the initial stage of the intrusion. These dynamic measurements by using the MIS capacitor is effective to analyze the study of liquid intrusion mechanism.

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