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Characterization of imprinting polymeric temperature variation with fluorescent Rhodamine B molecule

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Abstract

The method to measure the imprint temperature variation of resist film with fluorescence probe technique was established. The maximal Rhodamine B concentration was 8×10^{-4} M to achieve higher sensitivity and avoid precipitation problem. The temperature effect was a critical parameter on the temperature sensing, while imprinting pressure was not. The fluorescence intensity of Rhodamine B linearly decayed with time at various temperatures due to the formation of lactone-containing molecule during thermal stressing. The usual imprint time of less than 20 min was not affected by the signal decay effect due to limited percentage of signal variation during 100–200 °C. The technique based on fluorescence probe method was successfully applied to measure the resist temperature variation of the imprint on the resist film of 6-in. wafer.
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1. Introduction

In the current context of nanotechnology, obtaining nanometer scale feature on large area is an important requirement. Nowadays, nanostructure in photoresist can be routinely achieved due to electron beam lithography [1] and nanoimprint lithography [2] (also called hot-embossing). In these two methods, resist heating problem [3,4] will lead to unsatisfied results such as the pattern deformation and critical dimension variation owing to the fact that polymer film structure is sensitive to the temperature fluctuation, especially near the glass transition temperature (T_g) of resist. In the electron beam lithography, high energy electrons enter resist film to induce the crosslink reaction or decompose the polymer backbone. The energy transfer of electron beam between the substrate and the polymer leads to the local heating problem for the polymer film and deteriorate the pattern resolution. As for the nanoimprint lithography, a polymer is heated above the glass transition temperature and deformed by pressurizing a template into a polymer. When the imprinting temperature is near the glass transition temperature of the resist film, the imprint temperature and time need to be under careful consideration [4]. For example, if the imprint temperature or time is too low, the problem of residual resist confines the succeeding reactive ion etching process. On the contrary, if the imprint time or temperature is too high, the pattern defects will be seen. Based on these reasons, it is inevitable to establish a reliable temperature sensing technique during the lithography processes.

Previous attempts made to measure the film temperature can be divided into two groups, the contact mode and the remote mode, respectively. For the contact mode, thermal couple is attached to any regions of interest. This method faces the problem: if we need to measure a couple of regions, we need to install many thermal couples. In addition, the contact method restricts the design and application to resist film sensing. To overcome the problem, the scanning joule expansion microscopy [5] coupled with the

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scanning probe microscopy (SPM) can measure down to several nanometers owing to excellent spatial resolution itself. But the method has inherent limit, the sensing time will be too long for large area mapping. Otherwise, the potential risks of pattern collapse usually arise from the contact measurement. As to the remote mode, it can characterize the electromagnetic spectrum variation of material under different temperature ambiances, such as ultrasonics [6], infrared pyrometry [7], or fluorescence spectrometry [8–10]. In the ultrasonic technique, ultrasonic velocity in a hot body is converted to temperature by means of a precise measurement on velocity, i.e., temperature relation. In infrared pyrometry, the radiant energy emitted from the polymer film is used to reveal the temperature inside the material. Aside from the two methods, the fluorescence probe technique is a non-intrinsic temperature response of material that needs addition of a thermal sensitivity fluorescence dye as a temperature indicator. Conventionally, the thermal sensitive fluorescence molecules such as EuTTA [11,12] and Dy:YA [13] have high sensitive and long linear range for temperature measurement, but the chemical is metal-organic compound and the structure is very complicated. The metal-containing materials are not suitable for adding to the polymer film, especially for the resists. The metal ions in the resist will migrate to the underlying substrate as temperature stressing [14] and influence the device performance. Hence, metal free molecules are required for the fluorescence probe technique to detect the temperature of imprint process.

In this work, we demonstrate a temperature measurement technique for the resist films by using the fluorescence probe. The thermal sensitive organic molecule is mixed with the imprinting resist for the purpose of the resist temperature characterization during imprint process. The effect of imprint temperature and pressure on the Rhodamine B-based resist films is carefully studied.

2. Experimental

2.1. Preparation of resist with fluorescence dye

The fluorescence dye (Rhodamine B, Aldrich) was dissolved in propylene glycol monomethyl ether acetate (PGMEA, Merck) solvent under ultrasonic stirring. The different amounts of Rhodamine B solution were mixed with the electron beam resist (NEB-22A, Sumitomo Chemical) for imprinting lithography [15] and spin coating onto the wafer. The desirable resist film thickness was controlled by the spin rate of the coater. An imprint tool was developed by Nanonex Company. After imprint process, the fluorescence intensity from the resist film was measured by the developed optical system.

2.2. Optical system design and measurement

The optical system for fluorescence measurement is illustrated in Fig. 1. Excitation light from a 100 W Hg arc lamp was extracted by blue-glass filters (533 nm) where only a band of interest that corresponds to the absorption wavelength of the dye molecule was transmitted. This filtered light (excitation light) was focused by lens on the sample at a normal angle. A fraction of the resulting fluorescent light traveled into the same lens and splitter. After filtering the unwanted light, the feedback signal was recorded by a photomultiplier tube (PMT).

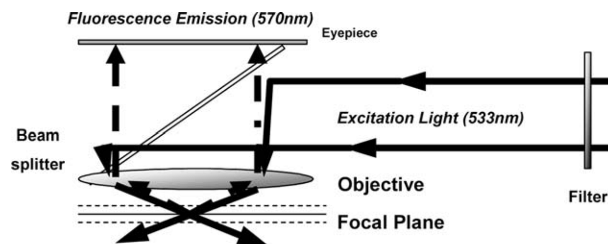

Fig. 1. Optical system design for the fluorescent intensity measurement.

3. Results and discussion

3.1. Temperature dependence of fluorescence molecule

The relationship between the applied temperature and the fluorescence intensity needs to be established for elucidating the thermal effect on Rhodamine B. We prepare the samples by dissolving 6×10^{-4} M Rhodamine B in PGMEA solvent and NEB resist, respectively, and spin coating the sample onto the silicon wafer. Prior to fluorescence intensity measurement, these wafers are heated on a calibrated hot plate at various temperatures for 5 min. Fig. 2 indicates that the fluorescence intensities of both samples linearly decrease with the temperature up to 250 °C. This observation suggests that the baking temperature is a critical issue for the fluorescence probe technique. The correlation coefficients (R^2) of both lines are higher than 0.96, but the slope of Rhodamine B in PGMEA solvent is 7% lower than that in NEB resist. The phenomenon is attributed to the following reason. The resist has a higher

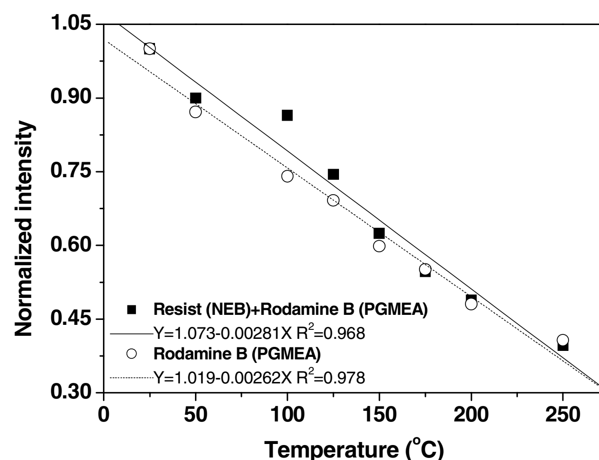

Fig. 2. The effect of imprint temperature on the fluorescent intensity.

viscosity than the PGMEA solvent owing to the constituent of the polymer. Hence, most of the Rhodamine B molecules in PGMEA solvent are spinning out of the wafer surface.

In addition to the effect of imprint temperature, the concentration of fluorescence molecule also influences the performance of temperature measurement using fluorescence probe technique. If the fluorescence signal is too low, the fluorescence probe does not afford to sense the thin resist film with a thicknees of several hundred nanometers. The way to solve the low signal problem is to increase the concentration of Rhodamine B in the resist. However, the precipitation problem of Rhodamine B in the resist may occur. Once the fluorescence molecule precipitates in the resist, the fluorescence intensity after resist spin-coating decreases. To optimize Rhodamine B concentration and the precipitation problem, we add different amounts of the Rhodamine B to the resist from 0.5×10^{-4} to 12.5×10^{-4} M, and evaluate the usable linear range. Fig. 3 depicts that the fluorescence intensity linearly increases with Rhodamine B concentration up to 8×10^{-4} M, and has a correlation coefficient of 0.995 at the resist film thickness of 600 nm. If the concentration of Rhodamine B is higher than 8×10^{-4} M, the curve in Fig. 3 deviates away from linearity due to the unwanted precipitation of Rhodamine B. The observation suggests that the upper concentration of spiking Rhodamine B into resist is 8×10^{-4} M. The detection limit (based on three times the standard deviation of the minimal concentration, i.e., 0.5×10^{-4} M) of the concentration of Rhodamine B in the resist by the fluorescence probe technique is estimated to be 0.038×10^{-4} M.

3.2. Mechanism of Rhodamine B for temperature sensing

Rhodamine B is a kind of xanthene dye, the optical properties of which rely on many factors, such as solvent polarity [16,17], dye concentration [17], and pH value [18] of ambient environment. Generally, it has three molecular forms (Fig. 4a) during various media. In a polar solvent, such as ethanol, the carboxyl groups participate in a typical acid–base equilibrium $RBH^+ = RB + H^+$. Compounds I (RBH^+) and II (RB) are strongly colored and emissive molecules. However, the equilibrium compound of lactone-containing molecule (III) is colorless and exhibits no emission because the conjugate π-electron system in the chromophore is interrupted. As mentioned in Fig. 2, the increase of the temperature facilitates the transformation from RBH^+ (I) and RB (II) to lactone-containing molecule (III) to some extent, and furthermore, Rhodamine B dye may decompose at an even higher temperature. Fig. 4b shows the transmission spectra of Rhodamine B spiked in resist film in the visible region where the resist signal was previously corrected. In different temperature treatments from 50 °C to 250 °C, the transmission spectra consist of a strong transmission band at 564 nm and with a shoulder around 526 nm. It is noted that the absorption intensity of the film decreases with increasing the treatment temperature. The main 564 nm transmission band is due to the Rhodamine B monomer, while the shoulder around 526 nm is from the Rhodamine B dimer [18]. This observation suggests and confirms the structure transformation of Rhodamine B molecules during temperature stressing.

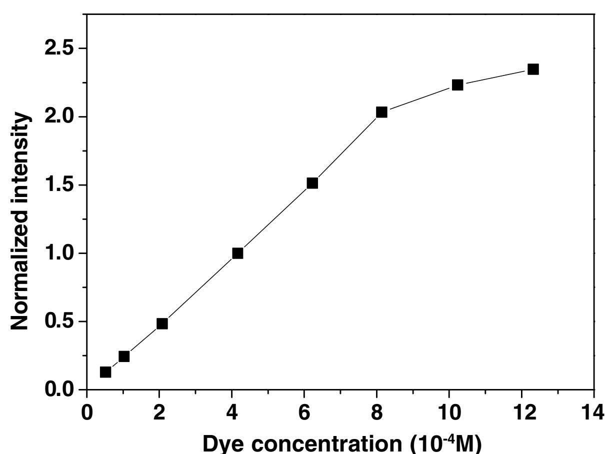

Fig. 3. The effect of Rhodamine B concentration on the fluorescent intensity.

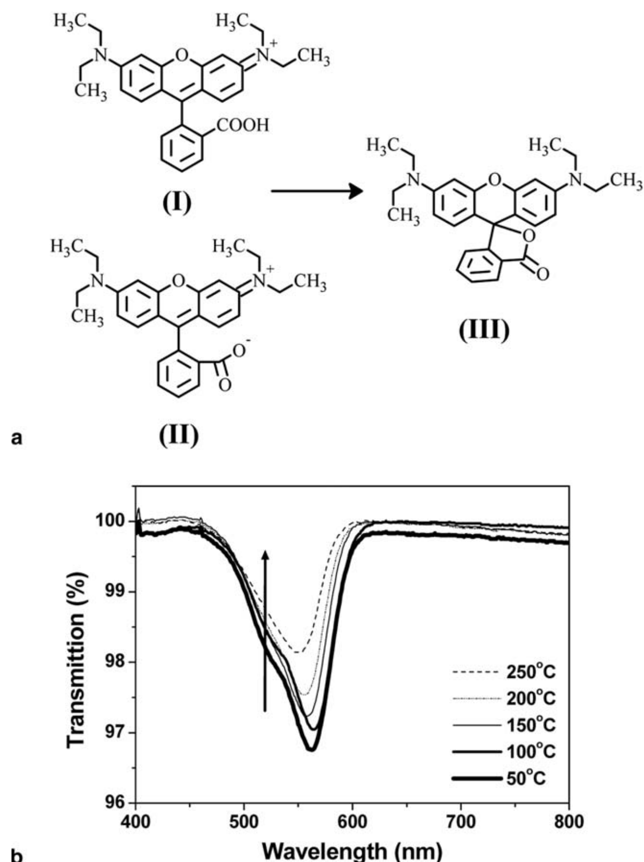

Fig. 4. (a) The Rhodamine B species transformation under thermal treatments. (b) The transmission spectra of Rhodamine B under different temperature treatments.

3.3. Stability of imprint temperature measurement with fluorescence probe technique

Rhodamine B is a thermal sensitive fluorescence molecule if the temperature varies. Because the thermal decomposition is not only from thermodynamics but also from kinetic processes, the effect of reaction time must be considered for understanding the time effect during thermal stressing. Fig. 5 evaluates three imprint temperatures at various durations. We find that the fluorescence intensity of these curves linearly decays with time at three imprint temperatures. This observation clearly indicates the fluorescence decay by thermal stressing followed by a zero-order kinetics reaction. With temperature increase, the decay rate (Δintensity/Δtime) of fluorescence intensity increases due to the higher decay coefficient at higher temperature. It is noted that the temperature variation is very small as if the heating time is below 1 h, regardless of the imprint temperature. Above that, the fluorescence intensity will be decayed under the kinetic control. Hence, there are two cases to measure the imprint temperature by using the fluorescence probe technique from Fig. 5. In the first case, if the imprint time is controlled within 1 h, we can neglect the kinetic-controlled decay due to the limited percentage of signal variation between 100 °C and 200 °C. If the imprint temperature is larger than 1 h, we need to correct the signal variation for different imprint temperatures. However, most of the imprint processes belong to the first case.

The other critical factor during imprint is the applied pressure between the template and the substrate. We also need to evaluate the pressure effect on the Rhodamine B molecule. Unlike conventional temperature measurement techniques, the imprint process in this study is under high pressure. Fig. 6 illustrates the respective temperature measurements under four different pressures of 200, 250, 300 and 350 psi with 10 min. The three test temperatures of 55, 95 and 155 °C are set on the imprint machine. The temperature for each result is averaged from 10 replicates on the center of 6-in. wafer. This observation indicates that the fluorescence probe technique is not affected under high pressure stressing. The Rhodamine B molecule is very stable up to 350 psi. The finding suggests that Rhodamine B is a suitable molecule for temperature sensing without the pressure influence.

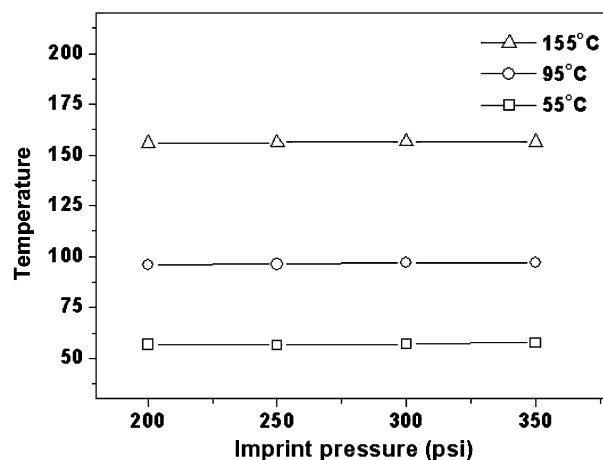

Fig. 6. The effect of imprint pressure on the fluorescence temperature.

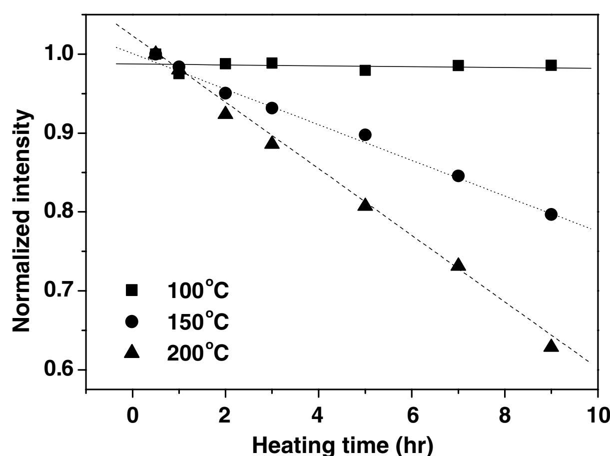

Fig. 5. The effect of imprint heating time on the fluorescence intensity for various temperature conditions.

3.4. Application of fluorescence probe technique to measure the resist imprint temperature

Previous reports point out that the temperature difference effect will lead the resist pattern to deform after the imprint [4]. The uniformity of imprint temperature is an important parameter to ensure the process reliability. If the temperature bias makes the temperature of imprint area lower than the T_g of resist, the aspect ratio of imprint pattern will become lower. As a consequence, the etch resistance under dry etch process will be challenged. On the contrary, if the imprint temperature is biased up, the resist has the chance to decompose and lead to out-gassing problem.

To explicit the temperature detection by Rhodamine B during the imprint processes, we mix the resist with Rhodamine B molecule which has optimized concentration and spin coating on the wafer. The Δ°C refers to the temperature difference of fluorescence probing area and wafer center area. After imprint at 120 °C, the temperature on the wafer recorded by fluorescence probe technique is listed in Fig. 7. The solid line reflects the temperature difference along X direction and dash line represents the variation of Y direction. The temperature variation in the Y-axis is higher than X-axis, suggesting that the heating system in Y-axis need to be adjusted. The range of temperature variations on the whole wafer can rise up to 8 °C. It leads to a problem that if the setting temperature of imprint tool is near the T_g point of the polymer, the risk from temperature bias-up will lead to pattern deformation owing to the flow characteristics of resist. The flow behavior (defect mechanism) will become significant when there

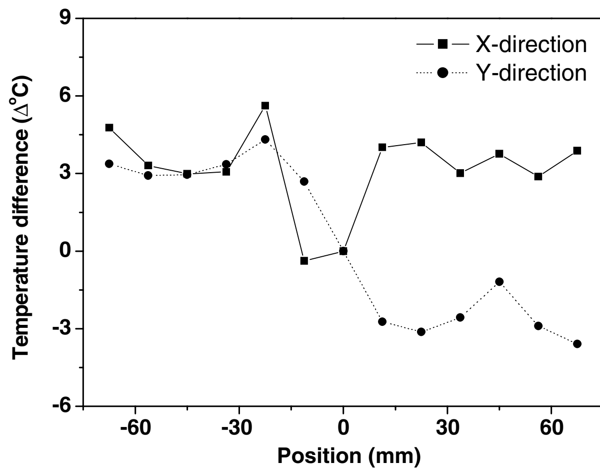

Fig. 7. The temperature variation monitor on the 6-inch wafer with the developed fluorescence probe technique.

is worst temperature uniformity. In addition, high pressure compression has a synergetic effect on temperature bias and alters the imprint depth in different areas. Based on the criteria, the development of the temperature measurement methods is a very important issue for ensuring the reliability of imprint process.

4. Conclusions

We have already established the resist film temperature measurement method based on the thermal sensitive fluorescence dye to measure the resist film after the imprint. This fluorescence technique is a simple and sensitive method for temperature measurement. Aside from the conventional thermal couple method, fluorescence probe is a non contact measurement method and will reduce contamination during sensing processes. This technique is a non contact method and can be extended to in situ temperature characterization in the future. The real temperature in the resist during imprint will be recorded by the developed fluorescence probe technique.

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