Effect of Water-Contact on the Roughness of Patterned Photoresist Investigated by AFM Analysis

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ABSTRACT: The effect of water-contact time on the roughness increment of patterned photoresist (AZ5214) was investigated by atomic force microscopy (AFM) analysis and the reason for the roughness increment was studied by the gravimetric experiment and the ellipsometry method. New method for calculating root-mean-square (RMS) line edge roughness from AFM data and the model of immersion lithography for experimentation were established. From the gravimetric experiments, it was confirmed that the diffusion of water into photoresist file is ruled my Fick's law. It was suggested that the amount of the roughness increment during rapid evaporation of water. As a result, the roughness of both the patterned line edge and the surface were proportioned in the root of water-contact time at the initial time and it was the same as the results in previous gravimetric experiments. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2361–2365, 2007

Key words: diffusion; swelling; roughness; AFM

INTRODUCTION

In recent semiconductor research, immersion lithography is one of the most powerful process known for overcoming optical lithography limits.[1,2] In immersion lithography, water or high refractive index fluid is added between the bottom lens and the photoresist on wafer instead of air or empty medium. This fluid increases both the numerical aperture and the depth of focus in optical lithography system.[3] Immersing photoresist in water, however, raises many physical issues by the very nature of diffusion at the interface. One of the most serious problems is the penetration of water into film.[4]

Generally, the diffusion behavior of fluid into thin polymer film on impermeable substrate is explained by Crank's simplified model based on Fick's law. The time-dependant mass increase of polymer film can be expressed as

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{h^2}\right)^{0.5}\left\{\frac{1}{\pi^{0.5}+2}\sum_{n=1}^{\infty}(-1)^n\, i\mathrm{ercf}\left(\frac{nh}{2(Dt)^{0.5}}\right)\right\} \tag{1}$$

and at the initial stage, above eq. (1) can be simplified to

$$\frac{M_t}{M_\infty} = \frac{2}{h}\sqrt{\frac{Dt}{\pi}} \tag{2}$$

where M_t is the time-dependant mass of diffused fluid at time t. h is the initial film thickness and D is the diffusivity of film. The mass gains of film, M_t is usually obtained by quartz crystal microbalance (QCM) measurement.[5,6] The fluid or its vapor uptake accompanies the swelling phenomena with a slower dynamical behavior than diffusion kinetics.[6] Immersion lithography and the existing wet-processes in semiconductor manufacturing are inevitably related with this kind of diffusion dynamics above, and the swelling or fluid-contamination of photoresist can be the reason of line edge roughness (LER), or roughness characteristics of photoresist surface.[7]

In this study, atomic force microscopy (AFM) analysis was carried out after the post exposure bake (PEB) step in the model process of immersion lithography to ascertain the amount of water penetrated into patterned photoresist film. The diffused water into film during time-varied DI water rinse step on immersing process quickly evaporates while the film is heated for PEB step and this evaporation of water can impact the surface of polymer film to increase the surface roughness or LER.[8]

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EXPERIMENT

Material

A positive-tone photoresist AZ5214 (AZ Electronic Materials USA corp.) which is based on NOVOLAC™ resin was spin-coated at 7000 rpm for 60 s on (100) Si wafers, which were sonicated in acetone for 2 min. After soft baking step at 105°C for 1 min, photoresist film were patterned in i-line(Hg–Xe lamp) stepper(Fig. 1). Development was performed using 0.26*N* tetramethylammonium hydroxide (TMAH) for 50 s, and the patterned films were rinsed for 30 s each.

In case of the weighing experiments and the ellipsometry method, the exposing step and the developing step were omitted.

Model process of immersion

To model the water immersion lithography at the laboratory level, a post–soak step was inserted between the rinse step and PEB step and the soaking time was varied from 1 to 150 min for 12 step.[9] DI water was stirred by a magnetic stirrer to maintain the fluidic stream on the patterned photoresist as does the water puddle in an actual immersion system.[10] After the soaking step, each sample was blown out with nitrogen gas for wiping out the wet surface and baked at 120°C for 1 min.

Measurement: Converting AFM raw data into LER profile

AFM data of each sample were obtained by Park Scientific Instruments (PSI's) tapping mode AFM. Both of the planar and the line-edge area of patterns were scanned and the data were analyzed by commercial software. Regarding the planar part of patterned photoresist, root-mean-square (RMS) roughness of the surface can be directly obtained in commercial software from AFM image, but line-edge parts are needed further data handling to get the LER or RMS roughness because the line-edge position cannot be defined by commercial software itself. Therefore, a digitalized method was established to obtain line edge RMS roughness from the AFM raw data (Fig. 2).

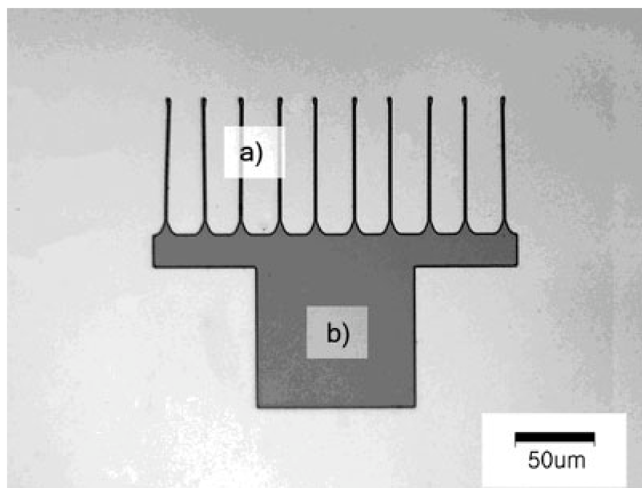

Figure 1 Patterned photoresist on Si wafer. (a) The line edge section and (b) planar section are scanned by AFM.

To locate the line-edge position from the 2D image of AFM data, the definition of line-edge is needed. In case of AFM raw data which contains depth profile with 24 bit data point, it is difficult to define the edge because of the ambiguity of edge slope [Fig. 2(a)]. Consequently, the data should be compressed to a 1 bit image by controlling the contrast of image to more clearly define the edge [Fig. 2(b)]. Data compression obviously means the loss of information, but since each edge slope of scan lines has substantial identity with minor difference, the information loss can be assumed to be minimized. Finally, the location of the line-edge point becomes the summation of 1-bit digital (1 or 0) height information perpendicular direction to line-edge and the RMS of digitalized location is identical to line-edge RMS roughness [Fig. 2(c)]. The original definition of LER is 3σ where σ is the standard deviation of line edge point, but in this work, only σ values are used for the comparison with surface RMS roughness.

Measurement: Mass gain and thickness changes

Mass gain of photoresist film after water-contact was determined by measuring the mass of spin-coated Si wafer before and after water-contact using a microbalance (Metler, XS105) of 10 μg mass resolution. A sealed weighing chamber was filled with humid air before weighing water-contacted photoresists for preventing the evaporation of water during weighing.

Ellipsometry (Rudolph Research, Auto EL) method was used for determining thickness changes in each step and especially *in situ* water-contact and baking system was constructed for accurate experimentation. The thickness of soft-baked photoresist fixed on ellipsometer sample stage was measured in a dry atmosphere, and then the film was immersed in a water puddle. After removing water puddle by suction, film thickness was measured again while the film was exposed by a mild humid air jet. Finally, the sample was hard baked by 120°C dry air and thickness was measured.

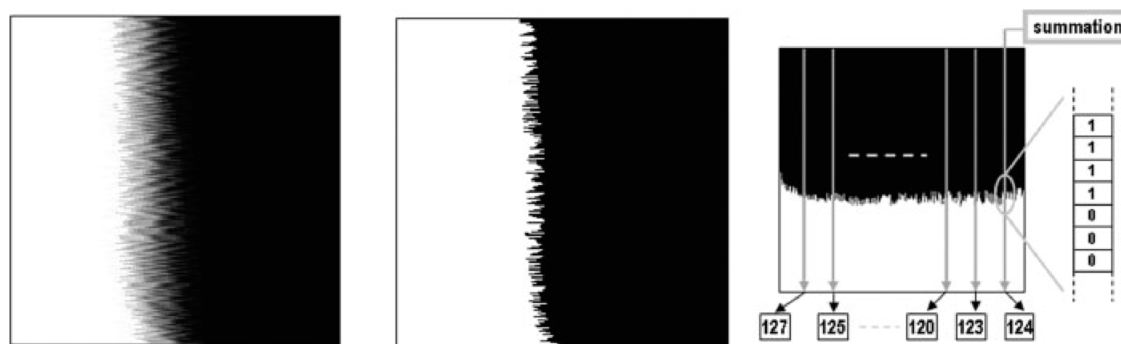

Figure 2 Converting AFM raw data into LER profile. (a) Original AFM image which contains surface morphology related with height profiles. (b) Compressed 1-bit image by controlling the contrast of image (a). (c) Digitizing the location of line edge by the summation of each pixel along the perpendicular direction.

RESULT AND ANALYSIS

Absorption measurement by the weighing method

Gravimetric measurement is a typical method used in absorption or diffusion experiments.[5] It is difficult to measure the small quantity of water diffused into polymer film but precise weighing by QCM or other kind of microbalance and weighing large-area films offer alternatives. Figure 3 shows the changes of water uptake in each sample which contacts with water for various times. To confirm the Fickian dynamics of water diffusion at the initial stage, the mass uptake M_t was plotted against the root of water-contact time. Also the diffusion coefficient D at the same region can be calculated where

$$D = \frac{\pi}{4t}\left(\frac{M_t}{M_\infty}h\right)^2 \quad (3)$$

from eq. (2).

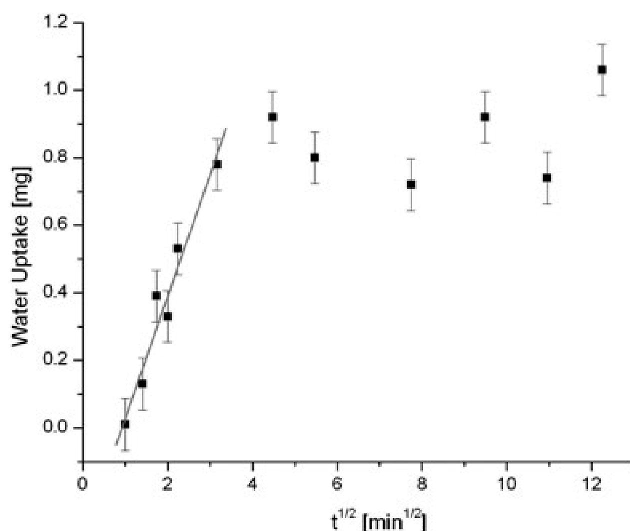

Figure 3 Mass of water uptake in approximately 300 nm thick photoresists. The slope of plot in the initial stage (solid line) is 0.36 mg/min$^{1/2}$ and the diffusion coefficient D is 8.2×10^{-11} cm^2/min from the eq. (3).

For the sake of simplicity, our concern is focused on the initial diffusion mechanism stage which is likely to be due to Fickian behavior even if it has two-stage absorption behavior.[11] And the result shows that a water uptake has linear relation with the square of time and that can be regarded as a good matching with the Fickian model in the initial stage, within 30 min.

Thickness changes by water-contact

Although weighing experiments suggested that the water is diffused into photoresist film during water-contact, the effect of water penetrated inside film on film roughness during PEB has to be understood by swelling dynamics. Morphological changes of film surface are inevitably affected by the expansion and shrinkage of film rather than the diffusion of water itself.

Water molecules penetrated into the free volume of the polymer structure by Fickian dynamics can be regarded as a good solvent for free polymer (photoresist) coil systematically.[6] If a certain amount of water is diffused inside polymer thin film on impermeable wafer, polymer swelling can be saturated at certain time and certain thickness. But since the amount of water increases during the water-contact, the swelling phenomena follow diffusion in similar dynamical way and longer time scale than diffusion.

In Figure 4, triangular symbols indicate the thickness difference between the initial state and the swelled state by water. The diffusion behavior in Figure 3 is very similar but slightly faster than swelling dynamics. Both results show saturation curve and the saturation of swelling occurred a few minutes later.

Film swelling still cannot be the direct reason for surface morphological changes. In PEB step, swollen film shrinks into itself again as the evaporation of water inside film continues. That process is the exact reason for the formation of excess surface roughness.

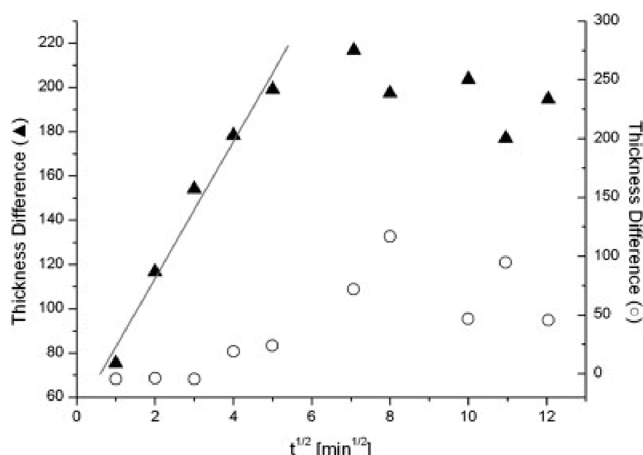

Figure 4 Thickness increase (▲) after water-contact and thickness changes (○) after whole process including PEB step using 120°C dry air with various time. Solid line indicates linear fit at initial stage.

Open circles in Figure 4 represent total thickness changes for the entire process including the PEB step. In the initial stage, thickness differences have near-zero values which means expanded polymer film shrinks reversibly, while shrinking process turns into an irreversible process when the water-contact time is getting longer. Figure 5 also shows that the recovery percentage drops to 40–50% where the recovery percentage is defined by the shrinkage of thickness over the expansion.

This irreversibility is assumed to result from rapid evaporation of diffused water. When the film is baked at high temperature to eliminate water inside film, diffused water molecule escape quickly and this process can create many voids previously occupied by water molecules. It gets harder to recover original position of polymer chains as the amount of diffused water gets larger because of those hole-formations above. Therefore, film thicknesses get harder to return to original thickness.

Causality between the roughness and the water absorption

From the previous experiments, it was confirmed that the diffusion mechanism of water into photoresist films are governed by Fick's law and the diffusion accompanies the swelling of film at the same time. The swelled film containing water inside film goes back to the original state with the fast evaporation of water during the postexposure bake step. In the process, surface morphology can be influenced by the shrinkage of film itself to recover from the swelled state and the abundance of hole-formations inside film resulted from fast evaporation. When the evaporating of water is assumed to directly affect the surface morphology of film,[8] the roughness changes over water-contact time will show a similar tendency with the water-uptake of film over water-contact time.

The RMS roughness in both the Figures 6(a,b) were plotted against the square root of water-contact time. In both cases, the roughness changes have a linear relationship with the square root of time within 1 h. Compared with eq. (2), it can be rationalized that the roughness increment is originated only by the evaporation of water, i.e. the roughness increment represents the amount of water penetrated into photoresist film since all system was controlled to be under same condition at each processing step except for the water-contact time. The linear relationship between the evaporation rate and film roughness was reported and since the amount of water represents the evaporation rate at instant evaporation, the causality between the roughness and the water absorption can be rationalized. Therefore, the slopes of linear fit in Figure 6 are proportioned to $\sqrt{D}/h$, where D is the water diffusivity into film and h is film thickness. The slope in case of LER is approximately four times bigger than that of the surface RMS roughness, and is related to the line edges are more exposed to water when compared with its volume than the planar surfaces. According to AFM image analysis, the thickness of the planar section of pattern is much thicker than twice of line height, and from this fact, the diffusivity of the line edge section is calculated to be approximately three times bigger than that of planar section of pattern. This fact quite well matches the fact that the line edge part has three times the water-contact surface area per volume than the planar surface which has only one-dimensional diffusion along the depth of film.

In the meantime, as the water-contact time decrease to 0, each RMS roughness converse on positive non-

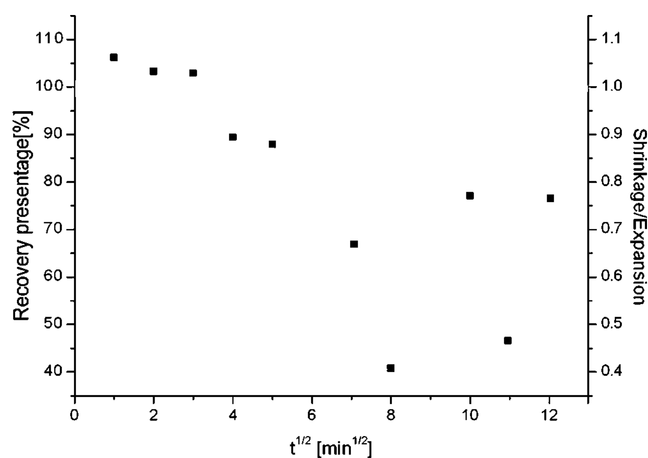

Figure 5 Black dots indicate the recovery percentage of photoresist film. At each point, thickness change during baking process (film shrinkage) is divided by thickness change during water-contact (film expansion) and that defines the recovery percentage.

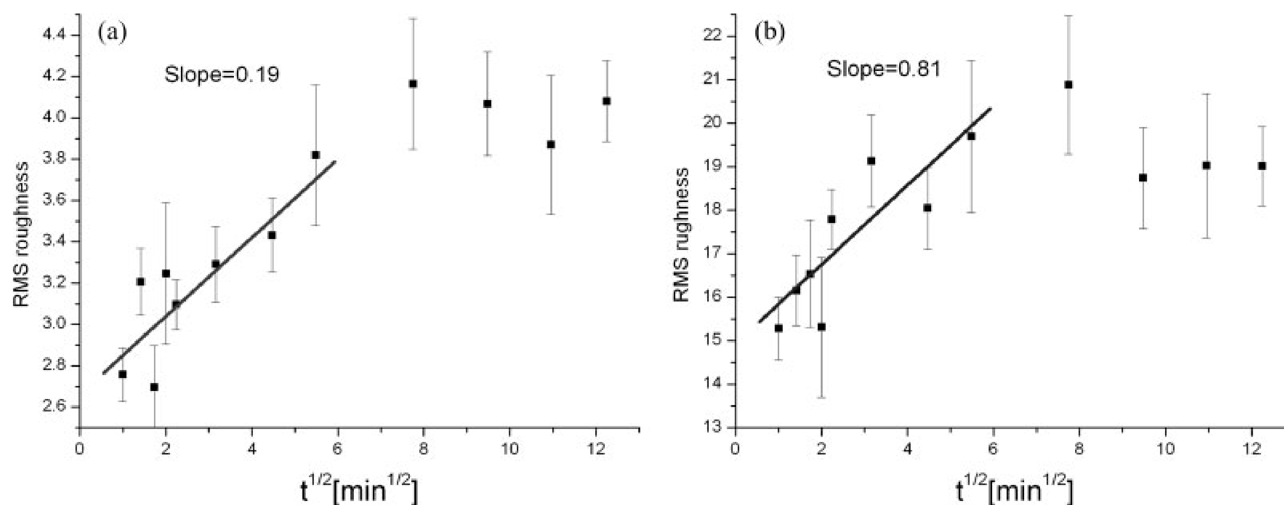

Figure 6 (a) Surface RMS roughness of patterned photoresist versus the root of water-contact time. Note that RMS roughness has a linear relation to the root of water-contact time at the initial stage. (b) RMS line edge roughness versus the root of water-contact time. This shows almost same trend with (a). Solid lines are fitted at the initial stage of diffusion.

zero values since the roughness of film has intrinsic value even though there is no water. But note that there is certain difference between the intrinsic roughness of planar part and line edge part of film. The reason of higher roughness values of line edge is usually due to the acid diffusion near the line edge during the exposing step.[12] The diffusion of acid from photo acid generator (PAG) during the exposing step breaks the molecular bonding of photoresist and after the developing step that wipes out the exposed part of the photoresist by UV and the acid and the roughness of line edge section is determined by the diffusion of acid, molecular size, etc.

SUMMARY AND CONCLUSION

The effect of water-contact on the roughness of patterned photoresist was investigated by AFM analysis, gravimetric measurement, and the ellipsometry method. In addition, a new method for calculating RMS line edge roughness from AFM raw data was established.

In consideration of the short water-contact time in the actual immersion process, our concern concentrated on the initial stage of diffusion dynamics. From the results of our gravimetric experiment, it was confirmed that the diffusion of water into photoresist film is ruled by Fick's law. The diffused water inside film can swell the film and cause the surface morphological changes during the PEB process followed by fast evaporation of water inside the film. Therefore, it was supposed that the roughness after water-contact and the post-baking process represents the amount of water which penetrates into polymer film. The roughness of both the patterned line edge and the surface were proportioned in the root of water-contact time at the initial time and it was the same as the results in previous gravimetric experiments. Also, the scale of the diffusivities of line edge part and planar part was quite well fitted with the state of things. In conclusion, the roughness of film can represent the amount of water uptake before the PEB process. Therefore, measuring the roughness of polymer film after PEB process can be the nondestructive way for photoresist film which gives monitoring information about water diffusion into film such as the amount of water diffused in real time.

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