Materials and Process Parameters on ArF Immersion Defectivity Study

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The immersion-specific watermark defect is discussed in its formation mechanism and in the influence of materials and exposure process. The non-topcoat approach was the basis of the work, where the properties of resist surface itself played the key role. Water droplets left on the resist surface were considered to induce the watermark defect in two possible ways; (1) the droplet is carried over to PEB process and impact the resist properties under the heat, (2) the droplet already evaporates before the PEB leaving some residue on the surface. A notable reduction in the resist dissolution rate was observed in the former case, which could be due to either physical or chemical change in the resist materials triggered by the water, and thereby would result in an unavoidable patterning failure. Therefore it is essential not to leave any water droplets on the surface in preventing the watermark formation. A very much hydrophobic materials design was proven effective in achieving this. The watermark formation was correlated to the scanning speed of immersion showerhead and the defectivity was evaluated in this perspective. The receding contact angle of the resist surface was found to well correlate to the “allowable” scanning speed, and was concluded that the higher was the better. A resist material was newly designed by using a hydrophobic polymer on this basis and the resist demonstrated a promising results not only in the watermark defectivity but also in lithographic performance.

Keywords: watermark, defectivity, non-topcoat, immersion lithography

1. Introduction

The Immersion lithography at the wavelength of 193nm is expected to be the most promising lithography for producing features smaller than 65nm. Remarkable progresses continuously made during the last few years in this technology field are apparently bringing this cutting-edge technology to the front of practical application of such device production. However, a further work is still necessary in order to get a certain level of maturity of the resist and associated materials if we want actually implement this technology in the device production. The biggest challenge in such materials development is how to avoid the “watermark” defects, which is immersion specific and most critical.

Some groups have already reported on this “watermark” defects issues from several different aspects. In preventing this defects, the most common approach discussed so far were an introduction of cover coating materials (topcoat) onto the resist film. This sounds to make sense because the topcoat can simply separate off the resist and water, and therefore will shut off the interaction between the

resist film and water. However the present authors believe that such topcoat system does not provide satisfactory solution to the issues. This is for mainly 3 reasons [1]. In some topcoat systems, water can penetrate through the topcoat film and would eventually touch the resist layer [2]. Another defect due to the resist-topcoat interaction can be induced [3]. Generally speaking, topcoat approach requires a more complicated process and therefore not preferable from CoO perspective.

On the other hand, study on the non-topcoat system from the viewpoint of defectivity has not much reported so far. Obviously the system will need a more sophisticated materials design and is regarded more challenging. In this paper, we will discuss our technical approach to realize the non-topcoat system thorough the study of watermark formation mechanism and the materials approach to reduce it.

1. Experimental

2.1 Materials

Adamanthane-based alicyclic methacrylate

copolymers having an acid-decomposable group were used for the resist base resin in this study. A model resist, which we consider a representative ArF composition for the dry-exposure use, was prepared by using this base resin and a triphenyl sulfonium nonaflate PAG and a tertiary amine quencher. The solvent was PGMEA/PGME. To study the influence of the film surface hydrophobicity on the scanning speed, hydrophobic monomers were further copolymerized quantitatively to control the film surface hydrophobicity.

2.2 Lithographic Characterization

The resist solution was filtered and spin-coated on silicon wafer that was coated with a bottom anti-reflection coating (BARC), and prebaked at either 110 °C or 120 °C for 60 seconds to give a film thickness of around 200 nm. A commercially available product was used for the BARC. The imaging exposure was performed with ArF dry scanner (0.75NA, 2/3 Ann.) and also with ArF immersion scanner (0.85NA, C-quad). After the exposure, post exposure bake (PEB) was applied at around 120 °C for 60 seconds and the resist image was developed in 2.38% aqueous TMAH solution for 60 seconds unless otherwise specified.

2.3 QCM Analysis

QCM(Quartz Crystal Microbalance) was used to

analyze the dissolution rate of the film or to monitor dissolution behaviors, e.g., swelling, by the oscillation frequency change of the substrate. The resist film was casted onto a quartz substrate and then baked at 120 °C for 60 sec. The coated substrate was dipped into 2.38% aqueous TMAH solution and oscillation frequency of the substrate was measured throughout the development time by using the resist development analyzer (RDA-Qz3, Lithotech Japan).

2.4 Contact angle measurement

Fig.1 illustrates our measurement methods of the static and dynamic contact angles. The static contact angle is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas and solid phase intersects. The dynamic contact angle is defined for a moving three-phase contact line. There are several different criteria for the dynamic contact angle definition, which primarily depends on the measurement methodology. The dynamic contact angles we examined were "advancing contact angle" and "receding contact angle", each measured in the following manner.

A 6 μ L water droplet was gently placed from the dispensing tube onto the resist surface. The droplet volume was controlled to increase by 6 μ l per second. Contact angle at the three-phase

Fig.1 Contact Angle measurement

Fig.2 Maximum Scan Speed vs. Contact Angles

boundary was measured while the contact lines were advancing, which gave the advanced contact angle. In a similar way, the shape of the liquid–solid interface was measured while they were receding, which gave the receding contact angle. In this measurement, the dynamics among the elements reached a sort of equilibrium after a few seconds, and thereby the contact angle came to a steady number.

3. Results and Discussion

3.1 Influence of Surface Hydrophobicity to the Number of Residual Water Droplets

As the water droplets remaining on the wafer must directly or indirectly be the cause of the watermark formation, water droplets should not be left on the wafer after the immersion shower head goes through the resist surface. To that end, one reasonable approach for minimizing this would be to optimize the surface hydrophobicity of the resist layer itself or, if applicable, of the topcoat layer. In this paper, resist materials with the non-topcoat application are primarily discussed unless otherwise specified.

To examine the quantitative correlation in depth, we prepared a group of experimental resist films having different surface hydrophobicity by using a variety of resist component materials as described in the next section. The surface hydrophobicity of samples was evaluated with the two dynamic contact angles for the measure. The samples were then evaluated for their “allowable” maximum scan speed of the immersion head. The allowable maximum scan speed is defined as the highest scanning velocity of the optical element to allow the water to move without leaving any droplet behind. The results are plotted in Fig. 2.

The results teach that hydrophobic films give

Fig.3 Newly developed hydrophobic materials

higher maximum scan speed as expected, and therefore hydrophobic materials are preferable in reducing the water droplet formation. Between the two different dynamic contact angle measures, the receding contact angle better correlated to the maximum scan speed. This would make sense, because the receding angles is the parameter to describe the de-wetting characteristics and is therefore expected to well fit the water droplet formation mechanics after the scanning.

3.1.2 Hydrophobic resist materials design

We newly designed a number of hydrophobic resist component materials to obtain the desired resist surface properties. By using those, we prepared a group of resist samples with varying surface hydrophobicity. In Fig. 3 the receding contact angles of such resist films are plotted as a function of the static contact angles. When looking at the dry resist as a reference, which was the adamantyl acrylate terpolymer-based resist, the contact angle was 62 degree for the static, and 46 degree for the receding. All of the resist samples shown here gave higher contact angles than this reference. The most hydrophobic sample we have designed gave 79 degree for the receding, which was outstandingly high.

One of the concerns of these hydrophobic materials design is the degradation of the lithographic performance, as materials-hydrophobicity may affect the acid diffusion length during PEB process or penetration rate of the developer during development process. We believe that this is a subject for the other materials parameter optimization and thereby manageable without losing the hydrophobicity advantage. To verify this, lithographic performance was compared between the two resist samples made respectively with a

Fig.4 Feasibility of Hydrophobic Polymer (Dry exposure)

Fig.5 Contact Angles both to water and developer

hydrophobic polymer and a hydrophilic polymer (Fig. 4). The results show that there were no lithographic disadvantages with the hydrophobic sample in terms of its sensitivity, exposure latitude and LWR. Regarding the depth of focus, even a better result was demonstrated.

The “post-development” defect, which is a defect possibly induced during development and/or rinse process, is another big concern. This is because such hydrophobic surface would probably suffer from lack of wettability to developer and rinse water, which could induce another type of watermark defect after the development and/or rinse.

This is a contradictory requirement because the surface has to be hydrophobic at the exposure step whereas the surface needs to be hydrophilic at the time of development step. It is essential to meet this difficult requirement when we want to design a “defect-free” non-topcoat resist. One of the ways to

Fig.6 SEM photo of the watermark

satisfy this contradictory requirement is to switch the film surface hydrophobicity from hydrophobic to hydrophilic during the development process. We developed a unique polymer that actually had such desired switching function. Fig.5 shows the contact angles both to water and developer measured for the polymer we developed. The conventional ArF dry polymer, which was the reference, showed almost the same contact angles both to water and developer. On the other hand, the newly designed polymer showed very high contact angle to water, while giving almost equivalent value to the reference when measured with developer. The result indicates that a certain class of polymers actually shows “hydrophobicity switching”. The lithographic properties obtainable with this new polymer look promising so far, but will be reported for its detail elsewhere.

Fig.7 Schematic representation of the droplets drying behavior

Fig.8 Profile change of the droplets

Fig.9 Water uptake measurement

3.2 “Watermark” Mechanism: Evaporation of Water Droplet

As the watermark defects were supposed to form by the action of the remaining water droplets on the resist films, we studied how the remaining droplets interact with the film to form the watermark defect.

To simulate the phenomenon, we first observed microscopically the drying behavior of a water droplet that was left under the air at room temperature. A 1 μ L of water droplet was manually placed onto a resist surface. As shown in the Fig. 8, the original droplet placed on the resist film continued to evaporate at room temperature and finally disappeared. In this sequence, the volume of the droplet continued to shrink while keeping the radius of the contact zone steady for the first 300 seconds. When the height of the droplet came to almost 350 μ m, the contact angle reached 35 degree, which corresponded to the receding angle of the film. Beyond this, the radius of the droplet began to decrease to keep the contact angle steady at this receding angle. After a lapse of almost 600 sec, when the droplet diameter was around 100 μ m, the diameter didn't shrink any further but the height continued to decrease and the droplet finally disappeared from the film surface in microscope view.

After the droplet evaporate, the physical appearance of the resist film surface was observed using SEM. An obvious local abnormality of the surface as shown in Fig.6 was observed, which looked like some film inflated defects with the size ranging from 10 μ m to 1 μ m or less

Dissolution rates are lowered at the water dropped region

Fig.10 Dissolution rate comparison

distributed in the circular area of 100 μ m radius. The size of the area corresponds to the diameter of the droplets at the 3rd phase, which was just before the droplet disappeared. Assuming that this circular abnormality would end up with a circular imaging defect in actual lithography, the result implies that the circular defects like watermark(WM) may be formed not by the original droplet before the shrinking but by the final stage of the evaporation, where a water penetration into the film is supposed to occur. This is considered one of the possible schemes for the watermark formation.

3.2.2 “Watermark” Mechanism: Influence of Water Droplet in PEB Process

There is another possible scheme for the watermark formation, which is related to the PEB process. In the real immersion process, the water droplets are likely carried over to the PEB step. This is because, as shown above, a relatively large-volume droplets (around 1 mL) could take 100 sec-ordered time to disappear at room temperature. We therefore tried to find out what would happen if the droplets present on the film during PEB process.

Water uptake behavior of the film was analyzed using QCM method. The resist-coated quartz substrates were dipped into water under different temperatures (Fig. 9). A larger frequency change was observed when measured in a hot water in comparison to that measured in a water at room temperature. The result indicated that the water penetrated more into the resist film when the temperature was raised. Therefore, the remaining

water-droplets on the film will readily penetrate into the film under a higher temperature in PEB step. It will, of course, compete with the evaporation from the surface under such high temperature.

We ran a resist PEB process by artificially placing a water droplet on the resist surface to know its influence on the resist dissolution properties. Fig.10 shows a comparison of the dissolution rate of the film in developer each measured for the water droplet region and reference region respectively. We clearly saw a decrease in the dissolution rate at the water droplet region (colored in green). This is interesting because the water presence somehow impacted irreversibly the resist development rate despite the water itself was no more there after the PEB. Several interpretations would be feasible to explain why this happened. For example, physical changes in the polymer structure like higher-order polymer architecture change or a structural conformation change, each can be triggered by the presence of water under the heat. Another possible mechanism would be a damage in the deblocking efficiency caused by a local temperature drop by the heat of water evaporation.

Fig.11 Effect of scan velocity on the actual Immersion defect counts

3.3 Defectivity Performance of the Resist made with a Hydrophobic Polymer

Fig.11 shows the effect of scan speed on the actual watermark defect counts evaluated by using a realistic immersion scanner. In this experiment, two resists that have different contact angles were evaluated. One was a new hydrophobic polymer-based resist developed under this guideline and the other was a reference resist made with a

relatively hydrophilic conventional polymer. Apparently faster scan generated more defects for both materials, which must be explained that the faster scan will have more chance to leave water droplet on the film after the scanning. It is clear that hydrophobic polymer-based resist were better in terms of the defect counts under the same scan speed, which in turn means preferred in achieving a faster scan speed.

Fig.13 is the defect number from a realistic immersion exposure tool obtained for a non-topcoat resist. The watermark defect counts found were greatly reduced with hydrophobic materials thus developed.

4. Conclusions

The formation mechanism of the watermark in immersion process was studied. Two schemes were considered depending on whether the water droplets evaporate during PEB or already before the PEB. When the droplets evaporate before the PEB, some microscopic abnormality in the appearance, like residue at the surface, was observed after the droplet evaporation. Possibly a nano-scale water uptake may have caused this and ended up with a imaging failure. When the water droplets evaporate during PEB, an influence in dissolution rate reduction was observed, which could be explained either by a polymer physical structure change or a de-blocking reaction suppression possibly caused by the presence of water at high temperature.

In order to avoid the watermark formation, the most basic approach is not to leave any water droplets after immersion shower head goes away from the resist surface. This requires a very much hydrophobic surface design. However, in non-topcoat resist design, such hydrophobic surface has to be provided by the resist itself, and therefore may suffer from a larger risk of watermark defect formation not by immersion itself but by the following development process. To overcome this contradictory requirement, the "hydrophobicity switching" approach is proposed. A new resist material was designed by using a hydrophobic polymer, which demonstrated promising lithographic results and good defectivity.

Fig.12 water-induced defect images

Fig.13 defect counts

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