Design of Protective Topcoats for Immersion Lithography

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Interactions of water and 193nm resists are described and detailed. Leaching of PAGs is experimentally verified, and the influence of PAG structure on leaching rate is determined. The mode of action of immersion topcoats is described. The influence of the topcoat/resist interaction is assessed. Finally, the design evolution of immersion topcoats with desirable properties is discussed.

Keywords: immersion lithography, topcoats, PAG extraction, leaching, fluoropolymers

1. Introduction

Immersion Lithography has become a major focus for advanced 193nm lithography at the 65nm node (and below). The most immediate interest is in sub-1.0 numerical aperture imaging for rapid introduction of water immersion lithography into high volume manufacturing given the demonstrated potential for improvements in process window [1]. From a materials perspective, the safety of lithographic tooling is a paramount consideration. Water in contact with resist materials has been shown to result in several measurable phenomena [2]:

1. Water can permeate into the resist.
2. Water can extract resist components from the film
3. Particles and/or bubbles can form in the water and generate defects

The material/water interactions we focus on are permeation of water into the resist (or topcoat) material, extraction (by/into water) of PAGs out of the resist film, and the resist (or topcoat) interfacial properties.

This paper attempts to answer the following questions:

1. What is the most important function of topcoats in immersion lithography?

2. Is a topcoat-free immersion resist desirable?
3. What structural factors impact PAG extractability (by water) in immersion lithography?
4. What polymer structural factors are important in the design of high performance topcoats?

2. Experimental

2.1. Materials

All polymers used in this study were low-to-medium molecular weight methacrylate polymers (unless otherwise indicated) prepared by standard free radical solution polymerization techniques using azo initiators. Photoacid generators (PAGs) and other resist components were obtained through commercial sources.

2.2. Methods

Resist baking studies: We vary the bake temperature on each wafer using an IBM designed and built thermal gradient plate (TGP) [3].

Resist/Topcoat Dissolution studies: We use a combination of quartz crystal microbalance (QCM) to investigate the complex dissolution behavior of 193nm resists and topcoats. QCM has been used for many years for aqueous base dissolution rate

and dissolution behavior determination. Our system is modified to evaluate very rapid dissolution rates and to also obtain film mechanical information through a resistance circuit [4].

Extraction studies: We have devised a simple apparatus for the controlled “exposure” of resist films to water. This tooling, built in IBM Almaden Research Center, is known as WEXA (Water Extraction Apparatus). Two types of WEXA are in use: WEXA-1 (see Figure 1), used by IBM in Albany Nanotech, is used to screen resists prior to use on an immersion lithography scanner. WEXA-2, used in IBM Almaden Research Center, contains a quartz window for 193nm exposure, so extraction coupled with exposure experiments can be conducted. The extractate flows into a clean sample bottle for analysis at Exygen Corporation (State College, PA) using LC/MS/MS. The sensitivity of this technique is approximately 1.0 ppb for perfluoroalkyl sulfonate anions found in most 193nm PAGs.

Lithography Experiments: Dry 193nm lithography was performed at IBM Almaden Research Center using an Ultratech 193nm Microstep (0.6 NA). Immersion experiments discussed below were performed at RIT on the Amphibian Interference Stepper.

3.Results and Discussion

3.1. Topcoat Function

It is important to establish the important roles for topcoats so that rational topcoat design can be undertaken. Immersion lithography at 193nm is in its infancy, especially considerations important to volume production. First and foremost, protection of the immersion lithographic tooling from chemical interaction with resist components (PAG, photoacid, other low molecular weight water soluble compounds) is presumably achieved through the use of protective topcoats. The resist process, having notorious sensitivity to airborne base contamination, could be substantially improved upon through the use of protective topcoating. The liquid/solid interface (surface energy) may be exquisitely tailored through the separation of function of resist and protective topcoat. This may be important for high speed scanning in water immersion lithography. Other (presumably lesser) considerations like reflectivity control may be important to maximize process window in the coming era of extreme low-k manufacturing.

Our initial hypothesis that the topcoat was “blocking” penetration of water into the resist has proven to be incorrect [2]. Water penetration studies on hydrophilic materials coated with topcoats show that water permeates through the topcoat very rapidly. It is unclear if the topcoat density is low (high free volume) or if channels exist through the topcoat. This is a topic of current research.

3.2 PAG Leaching

WEXA testing done on a variety of resists (both commercial and model systems) has shown that resist components were easily extracted into the water. The extent and kinetics is a strong function of chemical (in this case PAG) structure. We conducted a leaching experiment where a methacrylate resist polymer was used to formulate three different model resists using three different triphenyl sulfonium (TPS) salts (with molar equivalent loadings). The salts featured different fluorosulfonate anions, trifluoromethyl- (TFM), perfluorobutyl- (PFBuS), and perfluorooctyl sulfonate (PFOS). We ran WEXA extraction experiments at three different contact times, 5.5 sec, 60 sec and 300 sec. The data is shown in Table 1.

Figure 1. WEXA (Water Extraction Apparatus). Left side is fluid-filled syringe pump, center is WEXA head on 300mm wafer, right is collection vial.

Table 1: Triphenylsulfonium anion structure vs extraction time for model 193nm resist. Data tabulated in ppb anion found in water.

PAG Anion	5.5 sec	60 sec	300 sec
TFM	4	7	12
PFBuS	8	10	12
PFOS	18	11	17

The data indicates that the triflate-containing resist exhibits gradual PAG leaching. During

very short contact times presumably found in an immersion scanner, relatively small amounts (ca. 4 ppb) of triflate are found in the water. Very different behavior is found using a resist formulated with a PFOS PAG. We see an immediate leaching behavior of this PAG. In fact, all the PAG apparently extracts in the first few seconds with no new PAG extracted, even at long times. This near-volcanic eruption behavior is due presumably to the high surface segregation property of PFOS PAGs [5]. Short-time leaching results are important as this simulates real behavior (in an immersion scanner). These results are most likely dominated by near-interfacial concentration of PAG in the resist. Interestingly, the perfluorobutane sulfonate (PFBuS) anion shows intermediate behavior, with relatively high immediate extraction of PAG, followed by systematic increase of leaching at longer times.

We next studied the impact of topcoats and 193nm exposure on the leaching of PAGs from resists. For this experiment, we used a PFOS-containing commercial 193nm resist (a worst case). The data are found in Table 2.

Table 2: Extraction data for 60 sec leach time (ppb PFOS anion) from a PFOS-containing resist and same resist with topcoat, before and after exposure to 193nm light.

	No Topcoat	Topcoat
unexposed	45	3
Exposed	55	4

Note that the overall extractable load is quite high, due to the PFOS PAG in this resist. This is the highest leaching from resist we have seen thus far. Shorter leaching times would presumably yield similar, high leaching amount. Also note that the impact of exposure is relatively small, with about 20% increase in leaching amount. Quite surprisingly, the topcoat did not completely eliminate PFOS leaching from this commercial resist (although it substantially suppressed the amount of PFOS leached into the water).

PFOS-containing resists are not well suited for immersion lithography. In addition to the "volcanic" leaching mentioned above, the PFOS anion tends to persist in the WEXA equipment (possibly because of the same molecular property that causes environmental persistence) and this property could possibly exist in use (i.e., in an immersion scanner). Our results indicate that the PFOS-based PAGs are poor choices for immersion lithography applications. The surface-active quality that assists in resist profile control [5] is the

same property that precludes use in immersion applications.

It is unclear at what limit the resist extraction/leaching could cause harm to tooling (or loss of process control). Our results indicate that PAG anion structure exerts a strong influence on extractability from resist films. It may be possible in the future to formulate resists with very low extractables that would be safe for immersion tooling and also robust in imaging properties. Still, topcoat/resist process has an intrinsic advantage: decoupling the resist from important considerations of surface energetics (with water).

Figure 2: Chemical structure of HFA-based methacrylate terpolymer used in Version 1 topcoat.

3.3. Topcoat design

We have explored several families of topcoats with the following properties: development in aqueous base (TMAH), solubility in solvents which are not solvents for photoresists, and relatively high transparency at 193nm. These materials contain HFA acidic functional groups attached through alkyl (or cycloalkyl) spacers to a methacrylate group. We have developed both positive and negative 193nm photoresists with these monomers/polymers [6]. The negative resist polymer (shown in Figure 2) works as a protective topcoat, known as Version 1 Topcoat.

Imaging with these topcoats on 193nm resists leads to varied results, however. We often see resist profile changes that are highly dependent on topcoat material using the same resist process. Typically, some topcoat compositions lead to t-topping in the photoresist, some topcoats even lead to top-skin formation, while others generate a rounded profile. The resist formulator and lithographer often attempt to control the resist profile through the complex interplay between

polymer, PAG, base, process temperature and optical considerations (mask, illumination, etc.). Our results indicate that use of protective topcoat leads to added complications in profile control.

We sought to answer the question of why does the topcoat change the resist profile. Dissolution properties of the topcoat and resist were studied. Quartz crystal microbalance of a prototype topcoat with resist (after exposure) suggests an interfacial layer of lower dissolution rate than in the resist by itself. Interrupted development of the topcoat/resist shows strong induction phenomena at the topcoat/resist interface, with a pronounced "breakthrough effect" clearly visible. Figure 3 shows an SEM micrograph of a resist topcoat that has been allowed to develop past the topcoat "endpoint" showing that the resist has developed a pronounced skin. We believe that this phenomena accounts for the top-skinning of many resist/topcoat compositions.

After evaluation of many topcoat compositions, we find that topcoat glass transition temperature is one important design variable. The Version 1 topcoat polymer has a glass transition temperature close to 110C. Thus, the resist PEB temperature is typically greater than the topcoat Tg. This presumably helps drive the PAG diffusion from resist to topcoat. Materials with higher glass transition temperatures tend to perform better. Adjusting the glass transition temperature of the topcoat composition while maintaining the other

Figure 3: SEM image of resist/topcoat after 4.75 seconds of development. Topcoat breakthrough time is 3.5 seconds. Non-uniform development is noted. Clean development is observed after 6 seconds.

important properties (dissolution in developer, solubility in alcohols), is a significant challenge. Polymers with high Tg tend to have slower dissolution rates in this class of materials. One monomer very useful for combining high Tg with

high dissolution rate is bis-hexafluoroalcohol cyclohexyl methacrylate (Bis-HFA CHMA). Polymers based on this monomer (see Figure 4) have Tg in the 150C range and very high dissolution rates. Ito and coworkers have used this type of monomer before [7].

Resist materials processed in immersion lithography give excellent imaging results when a high Tg topcoat of this type (known as Version 2 topcoat) is applied. There is no detectable interfacial induction and image quality is excellent. Figure 5 shows results from interference imaging at 90nm pitch (45nm lines/spaces) with a high Tg topcoat based on polymers described in Figure 4 on top of a commercial 193nm resist (JSR AR-1682J).

Figure 4: Chemical structure of bis-HFA cyclohexyl methacrylate polymer. This class of materials combines high Tg and high dissolution rate. This material is known in this paper as Version 2 Topcoat.

Figure 5: SEM micrograph of 45nm lines/spaces printed in JSR AR-1682J using high Tg Version 2 topcoat. Interference Exposures on Amphibian immersion stepper.

Figure 6: 45nm l/s images printed using V2 topcoat (top) and V1 topcoat (bottom) in amine contaminated environment. Interference immersion exposures.

A dramatic example of the impact of different topcoats on resist profile and resolution is shown in Figure 6. This resist was processed in a laboratory with contaminated air (no amine filtration) using interference lithography. A low Tg topcoat which tends toward t-topping (via interfacial induction presumably due to PAG migration) (see section 3.2 above) produces massive "skin" formation and no useful imaging, while the high Tg topcoat is a robust barrier to environmental contamination and is able to produce 45nm lines/spaces in a poor environment.

4. Summary

PAG extraction by water from 193nm resists has been quantified using WEXA apparatus.

TPS-PFOS PAG was shown to be the worst case in terms of extractability, both in amount and kinetics. The PFOS anion showed rapid extraction, while other PAG anions gave far different behavior. The aqueous topcoats reduced but did not eliminate PAG leaching. High Tg topcoats (where Tg is above process temperatures) gave better lithography results than topcoats with Tg below the process temperature. Enhanced environmental stability was noted with the high Tg topcoat.

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