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Research paper

Enhanced mechanical properties of the high-resolution EUVL patterns of hybrid photoresists containing hexafluoroantimonate

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ABSTRACT

The present study investigates the mechanical properties of hybrid photoresists in the context of their pattern-collapse behaviors. The mechanical properties such as the DMT (Derjaguin, Muller, Toropov) modulus and tip-sample adhesion forces of the high-resolution patterns obtained from two hybrid EUV photo-resists, 1.5% & 2.15%-MAPDSA-MAPDST bearing hexafluoroantimonate and triflate counter ion moieties have been investigated using peak force quantitative nano-mechanical mapping (PF-QNM) technique. The mechanical properties of the well resolved high-resolution 90–20 nm (L/5S) line patterns, 20–32 nm (L/2S-L/5S) lines patterns and nano-features such as line-elbow connections have been investigated and analyzed against the differences in their SbF_6^- composition. For the 1.5%- MAPDSA-MAPDST resist case the DMT modulus and tip-sample adhesion forces are found strong dependence on the resist line width and line spacing, as compared to 2.15%- MAPDSA-MAPDST resist. There is a significant improvement in the modulus value of 5 GPa for 2.15%-MAPDSA-MAPDST resist in contrary to the ~2.7 GPa for the 1.5%-MAPDSA-MAPDST resist for the 20 nm (L/2S) Line patterns. Similarly, the tip sample adhesion forces on resist surface are also found dependent on patterns aspect ratio as well as on SbF_6^- content in the resist composition. These studies revealed that an increase of the SbF_6^- content in the resist formulation, imparts cascading effects to the mechanical properties of their high-resolution nanopatterns, which in turns helps to reduce the pattern collapse resulting in superior patterning performances.

1. Introduction

The semiconductor industries over the years have made remarkable progress in the miniaturization and performance enhancement of devices with the advancement of integrated circuit (IC) technology, which helped in reducing the device size promoting higher device density, clock rate, and also transistor switching rate [1–5]. However, the growth of IC technology faces constraints when the feature dimensions reach nanometer regime due to the inherent limitations of various nanofabrication technologies available [5,6]. High-resolution lithographic techniques currently employed for the nano-scale fabrication of devices include deep ultraviolet (DUV), electron beam (e-beam), He ion beam, 193 nm immersion, X-ray and extreme ultraviolet lithography (EUVL) [7–11]. Among these, EUVL, which uses 13.5 nm wavelength for patterning, is a major contender for the next generation sub-10 nm technology node lithography [10,11]. However, the successful implementation of EUVL for nano-scale patterning requires high-end photoresists capable of patterning high-resolution features at high aspect ratios [4,12]. Therefore, semiconductor industry and scientific community have focused their attention on the development of novel EUVL resist materials in recent years [4,10,13–20]. However, the design and development of a high-end photoresist is a formidable task due to a variety of problems observed in high-resolution patterning such as line fracturing, buckling, folding, peel-off and pattern-collapse [21–23]. Especially, the pattern collapse observed for high aspect ratio line patterns (sub-20 nm) is a major challenge in next-generation EUVL applications [21]. Therefore, understanding the factors behind the pattern-collapse behaviors exhibited by resists at higher resolutions is critical in evaluating the resolution limit, particularly for sub-20 nm technology nodes [21,23]. Factors such as capillary forces acting on high-resolution resist patterns during the rinsing or development processes are known to cause pattern collapse [24]. Other factors that may influence the pattern collapse include the feature size, resist thickness, resist modulus, resist adhesion to the substrate and swelling behavior of

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the resist [24]. The minor changes in the developer contact angle significantly affect the capillary forces on the resist side walls and leads to the feature collapsing behaviour at higher resolution nodes [25–28]. Therefore, two main requirements to prevent the pattern collapsing behaviour of the resist is: 1) reducing the surface tension of the developer 2) increasing the resist hardness. However, the contact angle of high resolution resist patterns is very difficult to measure and depends on the forces of adhesion on the surface in contact. Hence the measuring the surface adhesion forces of the patterned resist features is an indirect measure of the contact angle [29]. Therefore, the resist with high modules and high surface adhesion forces can reduce the capillary forces considerably during drying process [24].

Structural engineering is one of the methods to improve the modulus and adhesion properties of the resist. The incorporation of crosslinkers in photoresist materials is known to improve their mechanical strength, resulting in collapse free patterns [24,25,30]. However, the addition of crosslinkers may result in adverse effects like line swelling [24,31–33]. Therefore, alternative methods such as the development of organic-inorganic hybrid resists have been explored toward the development of collapse free patterns at higher resolution nodes [4,15–18]. It has already been shown that the incorporation of inorganic components in the resist formulation helps to improve sensitivity and resolution [23]. In addition, the inorganic components in photoresist formulations are known to increase their optical density by harvesting EUV photons more efficiently leading to superior lithographic performances [4,23]. Therefore, the development of new hybrid n-CARs for high-resolution EUV lithographic applications and investigation of their mechanical properties is extremely important for future semiconductor industries.

However, the mechanical properties such as the modulus and adhesion are relatively hard to evaluate at nano-scale regime where the bulk properties disappear and various interface contributions start to dominate [34]. There are only a few reports on the evaluation of modulus of a photoresist material with respect to its pattern collapse behaviors [23,24,35]. Winroth et al. extracted the intrinsic stress of the exposed resist patterns by calculating the lateral force required to break the resist lines by using AFM technique [34]. However, these methods are tedious, time-consuming and also result in the destruction of the resist patterns. The Peak Force Quantitative Nano-mechanical Mapping (PF-QNM) method is a non-destructive technique capable of quantifying DMT (Derjaguin, Muller, Toropov) modulus and tip-sample adhesion forces with high spatial resolution [36,37].

Considering the above facts, the present study demonstrates the effect of varying concentrations of an inorganic moiety, hexafluoroantimonate (SbF_6^-), in hybrid resist formulations on the mechanical properties such as modulus and adhesion of their patterns. To accomplish this, we have developed two different hybrid copolymer resists 1.5% -& 2.15%-MAPDSA-MAPDST (where MAPDSA = (4-(methacryloyloxy)phenyl)dimethylsulfonium hexaflouroantimonate and MAPDST = (4-(methacryloyloxy)phenyl)dimethylsulfonium triflate) containing different percentages of SbF_6^- counter ion moiety for higher resolution EUVL applications (1.5% and 2.15% resists hereafter). We included MAPDST in the hybrid resist because it is known to undergo polarity change on EUV exposure by the conversion of hydrophilic sulfonium triflates into hydrophobic sulfide functionality during the lithography process. Our earlier studies have also shown that the introduction of SbF_6^- moiety in the formulation helps to improve the sensitivity of the photo-resist [38]. Consequently; the obtained nanofeatures were subjected to mechanical studies by using non-destructive PF-QNM technique. Furthermore, the effect of the aspect ratio on mechanical properties of high-resolution line patterns has also been studied by a quantitative mapping of the variations in modulus and tip-sample adhesion force values.

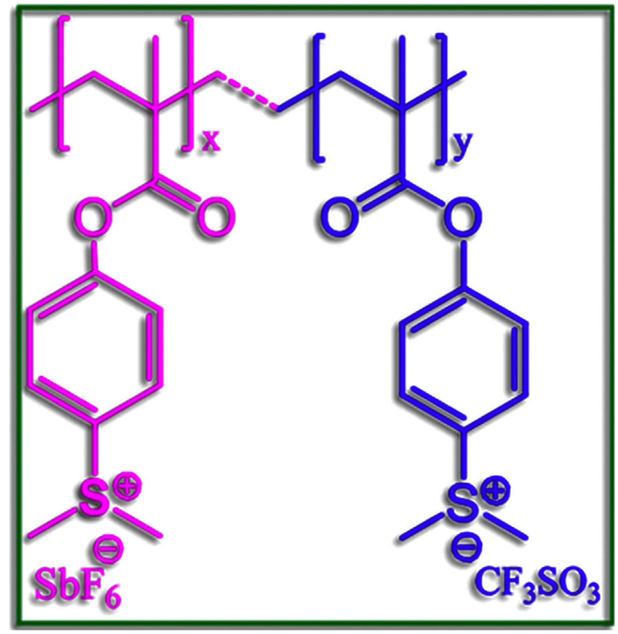

Fig. 1. Chemical structures of the MAPDSA-MAPDST copolymer resist.

2. Material and methods

2.1. Materials

The hybrid copolymer resists 1.5%- & 2.15%- MAPDSA-MAPDST (1.5% and 2.15% resists) with a chemical structure shown in Fig. 1 were synthesized and characterized according to our published procedure [38,39]. The FT-IR profiles for 1.5% and 2.15% resists were given in the Supplementary material (see, Figs. S1 and S2).

2.2. Thin film preparation, and EUV exposure

Resist solutions were prepared by dissolving solid 1.5% and 2.15% resists (3 wt%) in acetonitrile followed by filtration through 0.2 μm Teflon filters. Smooth resist thin films of ∼ 45 nm thickness were achieved by spin coating the resist solutions onto 4″, p-type silicon substrates at 4500 rpm for 60 Sec. Thereafter, thin films were subjected to pre-exposure bake at 60 °C for 60 s. EUV exposures on the resist films were performed by using a micro-exposure tool (MET) at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory (LBNL) using ALS MET Standard low flare bright-field R4C3 Mask IMO228775. A post exposure bake was applied on the EUV exposed resist films at 65 °C for 60 s. Thereafter, resist films were developed with 0.02 N tetramethylammonium hydroxide (TMAH) solution for 15 s, followed by DI water rinsing for 10 s. Due to the over development of resist nanofeatures in industrial standard 0.26 TMAH, we used dilute 0.02 N TMAH as the developer in the present study. The calculated center dose and sizing dose values for 1.5% and 2.15% resists were 41 & 96 mJ/cm^2 and 11 & 33 mJ/cm^2, respectively [34].

2.3. FE-SEM and AFM characterization details

Field Emission Scanning Electron Microscope (FE-SEM Carl Zeiss, Ultra Plus) and Atomic Force Microscopy (AFM-Dimension Icon, Bruker) were utilized for investigating the critical dimensions (CD) of the line and other nano-patterns obtained from the 1.5% and 2.15% resists.