Nanoparticle photoresists from HfO₂ and ZrO₂ for EUV patterning

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Performance requirements for EUV resists will demand the development of entirely new resist platforms. A challenge in designing these new HfO₂ and ZrO₂ nanoparticle resists is the selection of molecular structures that will provide both superior performance in imaging and etch resistance while maintaining optimal absorbance at EUV wavelengths. We have previously described the use of inorganic nanoparticle photoresists for 193 nm and e-beam lithography. These inorganic photoresists are made of oxide nanoparticles and have shown etch resistance that is 25 times higher than polymer resists. The high etch resistance of these materials allow the processing of very thin films (< 40 nm) and will help push the resolution limits below 20 nm without pattern collapse. Additionally, the small size of the nanoparticles (< 5 nm) leads to low LER. In this presentation we show that these inorganic resists can be applied to EUV lithography. We have successfully achieved high resolution patterning (<30 nm) with very high sensitivity and low LER.

Keyword: EUV lithography, inorganic photoresist, hafnium oxide, zirconium oxide, nanoparticles, etch resistance

1. Introduction

Currently, extreme ultraviolet (EUV) lithography is considered the upcoming next generation patterning system [1]. Despite remaining challenges with the EUV system, alternative lithographic techniques, such as double patterning, nanoimprint and self-assembly, either cannot achieve the required resolution or have other issues that limit their applicability. As a result, EUV lithography and improved photoresists for this patterning technology are important goals in the ITRS roadmap.

The desired performance characteristics of EUV photoresists will require the development of entirely new photoresist platforms. As pattern sizes reach the sub-20 nm range, it is necessary to use thinner films to prevent pattern collapse from high aspect ratios. An aspect ratio of 2:1 would require films within the 30-40 nm range. However, photoresist films that are comprised of organic

materials cannot sufficiently resist the etch process as thinner films [2]. Therefore, extremely high etch resistant structures must be studied and developed to allow pattern transfer to the underlying substrate.

Given the relatively low intensity of current EUV sources, the next generation photoresists will need to demonstrate high sensitivity and optimum absorbance. At 13.5 nm which is the wavelength used in EUV lithography, the absorption of all materials is very strong and only dependent on their atomic composition and density [3]. For example, elements that are commonly used in photoresists at other wavelengths, such as fluorine, are highly absorbing at 13.5 nm making them problematic for EUV applications. Other elements including carbon, silicon, zirconium or hafnium have very high transmission. A challenge in designing new photoresists for EUV lithography is

the selection of molecular structures that have optimum absorbance.

In order to fulfill the requirements that were mentioned above, in this study we present a next generation photoresist material based on hybrid organic/inorganic nanoparticles. The nanoparticles are comprised of a hafnium oxide or zirconium oxide core that is surrounded by organic ligands. Previous work at Cornell University has studied the application of these inorganic photoresists in DUV, 193 and e-beam lithography [4]. These studies also revealed that the nanoparticle films exhibit exceptionally high etch resistance due to their thermal and chemical stability [5]. Additionally, the hybrid nature of the nanoparticle films enables the control of the film absorbance in order to optimize their lithographic performance. By controlling the ratio of the organic and inorganic content of the films it is possible to regulate the film density and therefore its absorbance. Additionally, Hf and Zr have different absorption coefficients at 13.5 nm wavelength and this gives additional flexibility in the photoresist formulation in order to fine-tune film absorbance.

2. Experimental

2.1 Materials

All chemicals were purchased from Sigma Aldrich unless otherwise indicated, and used without further purification. All solvents were reagent grade and similarly purchased from Sigma Aldrich unless noted otherwise.

2.2 Synthesis of Nanoparticles

Hafnium oxide nanoparticles stabilized with carboxylic acid ligands were prepared by a controlled hydrolysis reaction. Hafnium isopropoxide was dissolved in an excess of carboxylic acid solvent at 65°C followed by the slow addition of a water/carboxylic acid mixture. After stirring for 21 h the product was precipitated by addition of water. This precipitate was centrifuged at 8,000 g for 5 min and then dissolved in acetone and reprecipitated twice with water. The final product, a white powder, was obtained after drying under vacuum. The same approach was used to prepare zirconium oxide nanoparticles starting from zirconium isopropoxide as a precursor.

2.3 Photoresist formulation and thin film preparation

Photoresist solutions were prepared by adding controlled amounts of the nanoparticle powder to PGMEA followed by the addition of the selected photoactive compound and any other required additives. Any aggregates or dust were removed by filtration using a 0.2 µm filter membrane. To prepare thin films for lithography experiments the photoresist solution was spin coated directly on unprimed Si wafers and then baked to remove any excess solvent.

2.4 Lithographic processing

EUV experiments were carried out at Lawrence Berkeley National Laboratory using the SEMATECH BMET. After exposure the films were developed manually using a custom-made organic developer. DUV (254 nm) testing was carried out at the Cornell Nanoscale Science and Technology Facility (CNF), using an ABM contact aligner equipped with a mercury lamp UV source. For pattern transfer experiments a PlasmaTherm PT72 etcher was used.

3. Results and Discussion

Our prior work with inorganic photoresists has focused on the hafnium oxide system with methacrylic acid as the organic ligand (HfMAA). Using this system and with the addition of a photoradical initiator, we were able to demonstrate high resolution negative tone patterns. The same films can also be patterned in positive tone when an additional PEB step is added and aqueous TMAH is used as the developer. To expand the potential of the inorganic photoresists, ZrMAA films were also tested for both positive and negative tone patterning under DUV exposure. Furthermore, both positive and negative tone patterns were obtained from HfMAA and ZrMAA films using a PAG as a photoactive compound. These results are demonstrated in Figure 1.

The dual tone capability of the inorganic nanoparticle films and the various formulations that give high quality patterns demonstrate the flexibility of this versatile inorganic photoresist. In fact, any combination of Hf or Zr nanoparticles with a photoradical initiator or a PAG will give both positive and negative tone patterns. The same system is patternable under DUV, 193, e-beam and EUV exposure.

Figure 1. Positive and negative tone DUV patterns using the inorganic photoresist with a PAG additive: A) HfMAA, positive tone, B) HfMAA, negative tone, C) ZrMAA, positive tone and D) ZrMAA, negative tone.

The same resist formulations that were patterned using DUV at Cornell were then tested under EUV exposure at the LBNL. Those that showed the best performance were the ZrMAA

Figure 2. Negative tone patterns after EUV exposure of the ZrMAA photoresist with a PAG additive: A) 32 nm lines at 5.6 mJ/cm² and B) 26 nm lines at 4.2 mJ/cm².

nanoparticles with PAG. Figure 2 shows two representative SEM images of negative tone patterns that were printed with this system. Image analysis was carried out using the SuMMIT software which showed that the patterns on Figure 2A are 32 nm wide with a LER = 5.9 nm while the patterns on Figure 2B are 26 nm with LER = 3.8 nm.

These results demonstrate the high-resolution capabilities of the inorganic photoresist but what is even more remarkable is the photoresist's sensitivity. The patterns shown on Figure 2 were created after exposure at 5.6 mJ/cm² and 4.2 mJ/cm² respectively. That is the highest reported sensitivity to date of any EUV resist that has been tested. Given the relatively low intensity of current EUV sources, the sensitivity of the photoresist is very important so that the whole EUV processing can be cost effective.

To obtain the high-resolution patterns shown in Figure 2 the film thickness of the photoresist had to be reduced to 40 nm. Even thinner films, around 30 nm thick, are required in order to

improve the resolution below 20 nm half-pitch. As a result the etch resistance of the photoresist material has to be exceptionally high to allow pattern transfer. Figure 3 demonstrates the etch rate of the HfMAA film compared to poly hydroxystyrene (PHOST). Both films were etched using a SF_6/O_2 mixture while the HfMAA film was also initially treated with O_2 plasma for 30 sec to remove the organic ligands. As a result the etch rate of the hafnium film is 0.17 nm/sec or 10.2 nm/min which is 25 times slower than the etch rate of the PHOST film under the same conditions.

The etching of patterned films was also studied in order to examine the pattern transfer into the Si substrate. Figure 3 shows an SEM cross-section image of the transferred patterns after SF_6/O_2 etching. A small layer of remaining HfMAA film is still present while the pattern has been deeply etched into the Si substrate. Before etching with SF_6/O_2 , the film was treated with O_2 plasma in order to increase its inorganic content and improve its etch resistance. Thermal treatment was also studied as an alternative but the quality of the patterns was affected and as a result the pattern transfer was not successful. On the other hand, the successful pattern transfer that is demonstrated on Figure 3 means that the O_2 plasma treatment does not affect the quality of the patterns.

4. Conclusions

This paper reports ongoing studies building from our previous work on inorganic photoresists by applying them to EUV lithography. The HfMAA and ZrMAA nanoparticles described in this study can be used to form versatile photoresists that have dual tone capability and work with either radical photoinitiators or PAG additives. These photoresists have been previously applied to DUV, 193 and e-beam lithography and this study also shows their potential as EUV resists. The ZrMAA films were patterned at negative tone using a dose of 4.2 mJ/cm^2 , the lowest reported to date for a EUV photoresist. The inorganic photoresists have also shown superior etch resistance than polymer photoresists and successful pattern transfer was demonstrated using SF_6/O_2 . Further studies are now underway in order to improve the patterning resolution and optimize the positive tone patterning under EUV exposure.

5. Acknowledgement

The authors gratefully acknowledge

Figure 3. Top: SEM cross-section image showing the transferred pattern in the Si substrate. Bottom: Film thickness versus etching time for HfMAA and PHOST films. Remaining film thickness was measured after various time intervals during etching with SF_6/O_2 .

SEMATECH for funding, as well as The Cornell Nanoscale Science and Technology Facility (CNF), Cornell Center of Materials Research (CCMR) and the Center of X-Ray Optics (CXRO) at the Lawrence Berkeley National Laboratory for use of their facilities.

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