Oxide Nanoparticle EUV (ONE) Photoresists: Current Understanding of the Unusual Patterning Mechanism

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In the past few years, industry has made significant progress to deliver a stable high power EUV scanner and a 100 W light source is now being tested on the manufacturing scale. The success of a high power EUV source demands a fast and high resolution EUV resist. However, chemically amplified resists encounter unprecedented challenges beyond the 22 nm node due to resolution, roughness and sensitivity tradeoffs. Unless novel solutions for EUV resists are proposed and further optimized, breakthroughs can hardly be achieved. Oxide nanoparticle EUV (ONE) resists stabilized by organic ligands were originally proposed by Ober et al. Recently this work attracts more and more attention due to its extraordinary EUV sensitivity. This new class of photoresist utilizes ligand cleavage with a ligand exchange mechanism to switch its solubility for dual-tone patterning. Therefore, ligand selection of the nanoparticles is extremely important to its EUV performance.

Keywords: nanoparticle, EUV, photoresist, metal oxide, ligands

1. Introduction

Moore’s law has been the driving force for ongoing innovation in the semiconductor industry for the past few decades. Lithography has made important contributions to the continuous shrinkage in critical circuit dimensions. The evolution of photolithography using shorter wavelength and strategies of immersion and double patterning has greatly pushed the limit of pattern resolution. However, now challenges beyond the 22 nm node using DUV lithography are unprecedented. The EUV wavelength of 13.5 nm is theoretically able to extend the Rayleigh resolution limit to 15 nm half pitch, while ArF double patterning provides only 30-20 nm half-pitch [1]. Recently, the insertion of EUV lithography to high volume manufacturing has become more realistic, as stable 100W EUV light sources become available and are being tested [2-4]. High resolution, low roughness and fast EUV resists are critical to fulfill the theoretical potential of EUV lithography [5].

Oxide nanoparticle EUV (ONE) resists, first reported by Ober et al. in 2011, demonstrated 22 nm negative tone patterns with sensitivity as high as 5mJ/cm² as a non-chemically amplified resist [6]. Although PAG was part of the formulation, it does not serve as catalyst for crosslinking, but as part of a ligand exchange process instead [7]. Previous studies showed the sensitivity of a resist can be varied by changing the binding strength of ligands [8-10]. In this paper, we will continue to discuss EUV performance of ONE resists with new ligands and patterning mechanism in depth.

In this paper we examine the performance of a series of ONE resists with a variety of benzoate ligands, some of which have very low sensitivities. This behavior is important in understanding the mechanism of resist pattern formation. The current understanding of the ONE patterning mechanism will be described.
2. Materials and Methods

2.1. Materials

All reagents as well as PAG (N-hydroxynaphthalimide triflate) were purchased from Sigma Aldrich and used as received. All solvents were reagent grade and purchased from Fisher Science.

2.2. Lithographic Characterization

Nanoparticles were synthesized by the sol-gel technique as described previously [11]. 5wt% of PAG was added to a nanoparticle resist and dissolved in propylene glycol methyl ether acetate (PGMEA). Resist was spun coated onto Si to form 40 nm thick films, followed by a post-apply bake anneal at 110 °C for 60s. EUV lithography was performed using the Berkeley Micro Exposure Tool (BMET) at LBNL.

2.3. Characterization

Particle size was measured by dynamic light scattering (DLS) using a Malvern Zetasizer. Organic content was measured by Thermogravimetric Analysis (TGA, TA Instruments). A Woollam Spectroscopic Ellipsometer was used to measure the film thickness before and after development. The developed images were examined using either a Zeiss Ultra or LEO 1550 FE scanning electron microscope (SEM).

3. Results and Discussion

3.1 Synthesis and characterization of nanoparticles with aromatic ligands

Aromatic ligands with electron withdrawing groups such as bromine or electron donating groups such as methyl groups were chosen to vary the binding strength of benzoic acid in order to study the effects on resist sensitivity (Figure 1). The synthetic protocols are similar to the sol-gel method used previously with some variation of solvents during washing to remove excessive free acid. These amorphous nanoparticles have narrow size distribution around 2-5 nm using dynamic light scattering and have 50% to 60% organic content measured by TGA. DUV lithographic characterization of these nanoparticles with 5 wt. % of NI-tf were performed under 150 mJ/cm² exposure at 248 nm and developed in 4-methyl-2-pentanol. Optimized formulations of these nanoparticle compositions were able to resolve 200 nm lines/space patterns, which were limited by the resolution of the mask used at this wavelength (Figure 2).

![Figure 2. DUV patterning of ZrO₂ nanoparticles with aromatic benzoate ligands. A) ZrO₂-o-BrBA b) ZrO₂-o-TA c) ZrO₂-p-TA](image)

3.2 EUV results of nanoparticles with aromatic ligands

ZrO₂-p-toluic acid showed the best DUV performance, thus chosen for EUV studies. ZrO₂-p-toluic acid resists compositions were formulated containing 5 wt-% of a nonionic photoacid generator (PAG) as per protocols mentioned in earlier studies [12]. The resist formulation was spin coated onto silicon wafers at 4000 rpm for 40 nm films. Delays between post-apply bake and exposure and then between exposure and development should be minimized to avoid sensitivity changes. Clearing dose E₀ of the ZrO₂-p-toluic resist developed in 4M2P is shown in Figure 3. E₀ of ZrO₂-p-TA was larger than 40 mJ/cm², higher compared to nanoparticles with benzoate ligands and other aliphatic ligands.

EUV patterns of ZrO₂-p-toluic acid were imaged by SEM and their CD and LER values were calculated from these SEM images by Summit™ software. ZrO₂-p-toluic acid only resolved 60 nm half pitch at a dose of 42.4
mJ/cm² and 40 nm half pitch at a dose of 100 mJ/cm² with 12 nm LER. Z factors were 9.22*10⁻⁶, calculated using the following equation

$$Z \text{ factor} = (\text{resolution})^3 \times (\text{min LER})^2 \times \text{Esize}.$$  

This value is much lower than our previously studied aliphatic ligands and benzoic acid, although its binding strength is similar or lower compared to benzoic acid [8]. Therefore, EUV performance of ZrO₂-p-TA reveals that sensitivity of a nanoparticles resist is not only related to strength of ligands but its chemical composition.

3.2 Solubility comparison of nanoparticles with aromatic ligands and aliphatic ligands.

Besides exposure which enables the ligand exchange process, the development process in organic solvents also plays an important role in pattern formation. Very often PGMEA, 4-methyl-2-pentanol or their mixture at different ratios are utilized as developer, while isopropanol, 2-butanone and butyl acetate could also be used. Nanoparticles with different ligands have huge solubility differences in these solvents. Solubility of ZrO₂-p-toluic acid and ZrO₂-methacrylic acid with and without exposure in 15 different solvents were studied and plotted in a triangular Hansen 3D solubility parameter graph. ZrO₂-methacrylic acid has more significant changes after exposure. Its solubility in isopropanol, 4-methyl-2pentanol, MIBK, MEK or butyl acetate changed from fast dissolution rate (<10 s) to medium dissolution rate (10-30s). However, for ZrO₂-p-toluic acid still dissolved readily within 3 seconds after exposure to 150 mJ/cm². The lower sensitivity of ZrO₂-p-toluic acid might therefore be due to a less significant dissolution rate change between the nanoparticles before and after exposure and the subsequent ligand exchange. Furthermore, this is also indicative of the low contrast that we currently observe with our present generation of nanoparticle photoresists.

4. Conclusion

This paper studies nanoparticles with aromatic ligands which includes a broad range of pKa values. ZrO₂ nanoparticles with bromobenzoic acid, o-toluic acid and p-toluic acid were successfully synthesized and characterized using DUV lithography. Among them, ZrO₂-p-toluic acid was chosen for EUV studies. Although p-toluic acid is a weaker ligand compared to benzoic acid, it only resolved 60 nm patterns with a much higher dose, which suggest nanoparticle sensitivity is not just related to the ligand binding strength. Our solubility studies of p-toluic acid compared to methacrylic acid in 15 different ligands showed that the less significant solubility difference of ZrO₂-p-toluic acid before and after exposure might have a strong influence on its sensitivity. Therefore, further investigation of ligand structure and their solubility change will provide insight to improve nanoparticle design and developer choice.

Acknowledgements

The authors gratefully acknowledge SEMATECH for funding, as well as the Cornell Nanoscale Science and Technology Facility (CNF), Cornell Center of Materials Research.
(CCMR), the KAUST-Cornell Center of Energy and Sustainability (KAUST_CU) and Lawrence Berkeley National Lab (LBNL) for use of their facilities.

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