Metal Organic Cluster Photoresists for EUV Lithography

Kazunori Sakai¹,², Seok Heon Jung¹, Wenyang Pan¹, Emmanuel P. Giannelis¹, and Christopher K. Ober¹*

¹ Materials Science and Engineering, Cornell University, Bard Hall, Ithaca, NY 14853, USA
² JSR Corporation, Fine Electronic Materials Research Laboratories, Lithography Materials Laboratory, 100 Kawajiri-cho, Yokkaichi, Mie 510-8552, Japan
*cko3@cornell.edu

Extreme ultraviolet (EUV) lithography is a prominent candidate for printing under 10nm half pitch patterns. Recently, we have developed metal organic cluster resists possessing higher EUV absorbing elements and controlled molecular size and distribution. Here, we report lithographic performance of zirconium organic cluster and zinc organic cluster resists. EUV exposure results for the zinc organic cluster resists on different underlayers are also discussed.

Keywords: EUV lithography, EUV photoresist, Metal oxide resist, Metal organic cluster photoresist

1. Introduction

Significant effort has been dedicated to the development of extreme ultraviolet (EUV) lithography to achieve the sub-10nm technology node in mass production. Under this circumstance, continuous scaling of pattern size by using EUV lithography has been very attractive. ASML has developed a high-NA tool which has a 0.55 NA value and is able to produce half pitch patterns under 10 nm during a single exposure [1]. Chemically amplified resists, molecular glass resists [2], HSQ resists [3] and metal oxide resists [4,5] are candidates for photoresist printing of less than 10 nm half pitch patterns. We have been developing metal oxide resists since we reported a first example of a hafnium oxide nanoparticle resist in 2010 [6] and recently our main effort has focused on metal organic cluster photoresists [7-9]. Metal organic clusters are inspired by metal-organic framework compounds and this material has potential to meet the material requirements for sub-10nm half pitch patterning, which consists of small molecule size, higher etch resistance and limited acid blur. Here we report the physical properties and lithographic performance of metal organic cluster photoresists and EUV exposure results on underlayers are discussed.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification unless noted otherwise. Metal organic clusters were synthesized from inorganic salts and organic compounds. Photoacid generator (PAG) used was also purchased from Sigma Aldrich.

2.2. Photoresist film formation

A photoresist solution was prepared from a mixture of 60 mg of the synthesized metal organic clusters, photo acid generator and propylene glycol monomethyl ether acetate as a solvent. The total weight of the photoresist solution was 1.5 g. The photoresist solution was purified by filtration using a 0.2 µm syringe filter. The photoresist was spin coated on silicon wafers to obtain a thin and uniform film.

2.3. Characterization

DUV exposure was performed using ASML 300C
DUV Stepper at the Cornell NanoScale Facility (CNF). E-beam exposure was performed using JEOL JBX9500FS at CNF. EUV exposure was performed at Lawrence Berkeley National Laboratory (LBNL) and IMEC.

3. Results and discussion

3.1. Zirconium organic cluster resist

After initial report on Hafnium oxide nanoparticle resist, we have developed zirconium oxide nanoparticle stabilized with carboxylic ligand. While this material showed very high sensitivity with EUV exposure, resolution was limited due to severe bridge and scum formation. To elucidate what makes zirconium oxide nanoparticle resist difficult to print under 30nm half pitch, we have verified the connection between molecular weight of zirconium oxide nanoparticle and EUV lithography performance [10]. Molecular weight of zirconium oxide nanoparticle was measured by using ESI-MS. These results indicated metal oxide resists with lower molecular weight and narrower molecular weight distribution have the potential to produce patterns without scumming. This hypothesis persuaded us to develop zirconium organic cluster with controlled molecular size and distribution [11]. Direct light scattering (DLS) results of zirconium oxide nanoparticle resist and zirconium organic cluster resist are summarized in Fig. 1. While zirconium nanoparticle resists had a particle size of 3.6 nm, the zirconium metal organic cluster resist was 1.7 nm in particle size and had a narrow distribution.

![Zr organic cluster vs Zr oxide nanoparticle](image1)

This difference affected patterning of 500 nm and 250 nm 1:1 line and space patterns with DUV exposure and results are summarized in Fig. 2. While the zirconium oxide nanoparticle resist didn’t give successful patterns for either pattern size, the zirconium organic cluster resist showed clear patterns of both pattern sizes. These results support our hypothesis that narrower molecular size distribution enables better resolution.

![DUV exposure results](image2)

3.2. Zinc organic cluster resist

One of the advantages for using inorganic elements is increased EUV absorption. Materials design mentioned above has been expanded to other metal elements and we have been focusing on zinc organic cluster resist. Two zinc organic cluster resists were exposed with DUV and e-beam and the results are summarized in Fig. 3 and Fig. 4 respectively. Zinc organic cluster resists were different in organic composition. While zinc organic cluster resist gave clear patterns around 500 nm LS to 300 nm LS, some micro-bridge and scum under 35 nm LS were observed in Fig. 3.

![DUV / E-Beam exposure results](image3)

Fig. 2. DUV exposure results of zirconium nanoparticle resist and zirconium organic cluster resist. Reproduced with permission of J. Photopolym. Sci. Technol., 31 (2018) 261. Copyright 2018 The Society of Photopolymer Science and Technology.

Fig. 3. DUV / E-Beam exposure results of conventional zinc organic cluster resist. Reproduced with permission of Chem. Mater., 30 (2018) 4124. Copyright 2018 American Chemical Society.
On the other hand, while there was no real difference between conventional and new zinc organic cluster resists with DUV exposure, new zinc organic cluster resist gave the clear 25 nm LS with no micro-bridge and scum in Fig. 4.

Inspired by this e-beam exposure result, we have evaluated zinc organic cluster resist with EUV and the results are summarized in Fig. 5. Zinc organic cluster worked as EUV photoresist and it gave the under 20 nm half pitch pattern.

Recently, improvement of lithography performance by using underlayer was reported and certain underlayer improved not only sensitivity but also nano-scale defect resistance [12]. A zinc organic cluster resist was evaluated on different underlayer with NXE tool at imec and the results are summarized in Fig. 6. Underlayers also worked with our zinc organic cluster resist and evaluating zinc organic cluster resist on underlayer improved the sensitivity with almost same LWR value. Optimizing underlayers with each zinc organic cluster resists has been investigated.

4. Conclusion
Our analysis study has brought new material design and metal organic cluster possessing controlled molecular size and distribution has been developed. Especially, zinc organic cluster resist gave the 16 nm half pitch pattern with EUV exposure. In addition, combination between zinc organic cluster resist and underlayer improved the lithography performance and has potential to give the narrower pattern size.

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