Recent Progress in EUV Metal Oxide Photoresists

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EUV lithography is a promising candidate for the manufacturing of semiconductor devices for the 7 nm node and beyond. The success of any lithography depends on the availability of a suitable resist with high resolution, sensitivity and low LWR. Though polymer type CAR (chemically amplified resist) is the current standard photoresist, entirely new resist platforms are required due to the performance targets of smaller process nodes. To meet this target, metal oxide photoresists have been designed and lithographic properties have been studied. In this paper, scum elimination studies with dissolution rate acceleration concepts and new metal core applications are described.

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

1. Introduction
EUV lithography is the most promising candidate for continuation of Moore’s law. But the complexity of the scanner source technology and the need to realize high enough power for throughput concerns, has delayed EUVL implementation [1]. Regarding photoresists, CAR is already capable of achieving sub-13nm half pitch resolution in a single exposure [2]. However, entirely new resist platforms are strongly required to simultaneously satisfy resolution, LWR and sensitivity requirements of smaller technology nodes.

Recently, several organizations have focused on new EUV organic and inorganic photoresist platform development [3-6]. A metal oxide photoresist system which comprises an inorganic core and an organic ligand has been developed at Cornell University [7,8]. These metal oxide photoresists show promising lithographic performance using DUV, e-beam and EUV exposure. Several advantages of using this system compared to polymer type CAR can be considered. For instance, the small size, below 2nm including ligands, is a clear advantage for ultimate resolution of the patterning step. A second aspect is that metal oxide photoresists generally show higher etch resistance than CAR. In this paper, recent progress in metal oxide photoresists is discussed. Lithographic performance improvement studies, especially scum elimination, using the dissolution rate acceleration concept and new metal core applications are described.

2. Experimental
2.1. Material
For Zr type metal oxide photoresist, zirconium isopropoxide and reagent grade solvents were purchased from Sigma-Aldrich and used as received. Photoacid generators were purchased from Sigma-Aldrich or prepared by JSR Corporation. Silicon wafers were purchased from WRS materials. Metal oxide photoresists were synthesized based on sol-gel techniques.

2.2. Photoresist film formation
For a typical thin film of approximately 40nm thickness, a resist solution was prepared from a mixture of 60 mg of the synthesized metal oxide, a small amount of photoacid generators and PGMEA. The total weight of the resist solution was 1.2 g. The resist 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
Dissolution rate studies were carried out using a quartz crystal microbalance (QCM). DUV exposure studies were performed using an ABM contact aligner at Cornell CNF. A JEOL JBX9500FS e-beam exposure tool at Cornell CNF was used for e-beam exposure. EUV exposure studies were performed at the LBNL B-MET, IMEC and PSI. Negative tone patterns were evaluated after development with organic solvents.

3. Results and discussion

3.1. Scum improvement study with a Zr type metal oxide photoresist

A recent challenge for Zr type metal oxide photoresist has been scum improvement for dense patterns. Patterning performance of a semi-dense line pattern seems to be promising as reported previously [9]. However, severe scum in the unexposed area was observed when a 1:1 dense pattern was checked. Various improvement studies were attempted at IMEC [10] but continuous improvement was required to achieve better resolution with dense patterns using Zr type metal oxide photoresists. For scum improvement, the dissolution rate acceleration concept was tested at this time for scum removal from unexposed areas. Higher dissolution rate PAG, higher dissolution rate developer and lower SB temperature application studies were carried out.

3.1.1. Scum improvement study using higher dissolution rate PAG

In general, PAG structures and properties strongly affect to the lithographic performance of CAR resists. PAG design for a metal oxide photoresist is also important for lithographic performance based on our previous studies [11]. Comparison between reference PAG (N-hydroxynaphthalimide triflate) and PAG-A is described below. As shown in Figure 1, a Zr-type metal oxide photoresist with PAG-A showed higher dissolution rate by QCM analysis than with the reference PAG. PAG-A is a higher dissolution rate PAG based on this experiment. Then, EUV exposure at LBNL B-MET was tested using these two PAGs. As shown in Fig. 2, results using the LBNL B-MET shows scum improvement with higher dissolution rate PAG-A with 22nmLS patterning at exposures less than 10 mJ/cm². This result indicates the dissolution rate acceleration concept works for scum improvement.

3.1.2. Scum improvement study using higher dissolution rate developer

A second approach for scum improvement is a higher dissolution rate developer. For negative tone patterning of metal oxide photoresists, organic solvents are mainly used as developers. The standard developer-A and the new developer-B were compared by QCM evaluation as shown in Fig. 3 and higher dissolution rate of developer-B was confirmed based on this test. Then e-beam lithography was tested on the Zr type metal oxide photoresist using developer-A and higher dissolution rate developer-B. As a result, good 30nmLS pattern without scum formation was observed with higher dissolution rate developer-B with retaining e-beam sensitivity, 100 µC/cm² (Fig. 4). Dissolution rate of the developer appears to be one of several key items for scum improvement.
3.1.3. Scum improvement study using lower SB temperature

A third approach for scum improvement is a lower SB temperature. Since the crosslinking reaction of a metal oxide film is expected during the bake process, lower SB temperature is expected to suppress the crosslinking reaction. Therefore higher dissolution rate should be observed with lower SB temperature. Figure 5 shows the film dissolution rate comparison between a reference temperature and lower SB temperature. As we expected lower SB temperature showed higher dissolution rate.

In this section, three dissolution rate acceleration approaches, higher dissolution rate PAG use, higher dissolution rate developer use and lower SB temperature, were investigated and all approaches worked for scum improvement. However, patterning resolution is more than 20nmLS using this Zr type metal oxide platform. Therefore, a new metal core study was undertaken and is described the progress in the next section.

3.2. New metal core study

3.2.1. Metal oxide photoresist variation

We have mainly focused on metal oxide photoresist development using Zr and Hf cores in recent years. However, Zr and Hf are relatively low EUV absorbing metals [12]. At this time, a hypothesis that lithographic performance can be further improved by using higher absorbance metals was investigated. New metal oxide photoresists with selected metal cores were designed. Figure 7 shows our metal oxide photoresist platform tests. So far 4 new platforms have been developed in addition to Zr and Hf cores. Good contrast of micro-scale patterning was observed with Zr, Hf, Ti, Zn, In and Sn type metal oxide photoresists using 150mJ/cm² exposure dose, a typical value for 248 nm exposure.

EUV exposure with lower SB temperature was carried out at the LBNL B-MET. As shown in Fig. 6, scum improvement with the same sensitivity was observed at lower SB temperature.

3.2.2. EUV exposure results using a new metal core

Since new metal core platforms have been developed, EUV exposure tests have also been studied. Figure 8 shows EUV exposure results at the Paul Scherer Institute (PSI). Required exposures of 25nmLS at 29.06 mJ/cm², 22nmLS at 43.55 mJ/cm², 18nmLS at 78.37 mJ/cm² and 16nmLS at 82.35 mJ/cm² were achieved with new metal core platforms. No scum was observed between patterns and this tendency is totally different from Zr type metal oxide photoresist as described above. Higher EUV absorbance and smaller particle size than Zr type
metal oxide photoresist are considered to be among the reasons for this lithography performance improvement.

Fig. 8. EUV exposure result with new metal core platform at PSI.

EUV patterning tests at LBNL B-MET were also carried out with a new metal core. 16nmLS and 15nmLS patterning was achieved with 124 mJ/cm² dose. Furthermore, 14nmLS and 13nmLS patterns were achieved with 77 mJ/cm² as shown in Fig. 9. Further sensitivity and resolution improvement seems to be possible after further changes, for example a new ligand, are made and lithography process optimization is carried out with this material.

Fig. 9. EUV exposure result with new metal core at LBNL B-MET.

Furthermore, this metal oxide photoresist with new metal core was exposed with a NXE scanner with DGL membrane option to protect scanner optics. Then, 22nmLS and 19nmL37nmP at 54 mJ/cm² pattern were obtained successfully as shown in Fig. 10. No scum was observed between patterns, and further resolution improvement is promising with additional process condition optimization since these results are just coming from preliminary tests.

Fig. 10. First exposure results from NXE scanner with new metal core.

4. Summary and outlook

In this paper, metal oxide photoresist lithographic performance improvement studies, especially related to scum improvement were described. From PAG, developer and SB temperature studies, a dissolution rate acceleration concept works for scum improvement. Furthermore, new metal cores were investigated and finally 16nmLS resolution at PSI, 13nmLS at B-MET and 19nmL37nmP with NXE scanner were achieved without scum. Further resolution improvement would be anticipated since these results are just coming from preliminary tests with new metal cores.

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