EUVリソグラフィ用メタルオキサイドフォトレジストの開発

Metal Oxide Photoresists Development for EUV Lithography

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7 nmノード以降の半導体デバイス量産に適用が期待される技術として，極端紫外線（EUV）リソグラフィがある．EUVリソグラフィ技術を量産に適用するためには，高解像度，高感度および低パターンラフネスを満たすフォトレジストの開発が必要となる．フォトレジストとしては現在，高分子材料を主成分に用いる化学増幅型フォトレジストが一般的に知られているが，EUVリソグラフィを含む次世代リソグラフィには，その厳しい要求性能のために，全く新しい材料プラットフォームが求められている．本論文では新規プラットフォームを持つフォトレジストとして，メタルオキサイドフォトレジストの開発状況を報告する．特にメタルオキサイドフォトレジストの現在の課題である微細パターン間のスカムを材料の溶解性制御により改良した検討結果，および、新規メタルコアを適用して改良した結果を紹介する．

EUV (extreme ultraviolet) 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 (line width roughness). 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.

1 Introduction

EUV (extreme ultraviolet) 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 EUV lithography implementation [1]. Regarding photoresists, CAR (chemically amplified resist) is already capable of achieving sub-13 nm half pitch resolution in a single exposure [2]. However, entirely new resist platforms are strongly required to simultaneously satisfy resolution, sensitivity and LWR (line width roughness) requirements of smaller technology nodes.

Recently, several organizations have focused on new EUV organic and inorganic photoresist platform development [3)~6)]. And, 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 (deep ultraviolet), e-beam and EUV exposure. Several advantages of using this system

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compared to polymer type CAR can be considered. For instance, the small size, below 2 nm including an organic ligand, 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 polymer type 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. PAG (photoacid generator) was purchased from Sigma-Aldrich or prepared by JSR Corporation. Metal oxide photoresists were synthesized based on sol-gel techniques.

2.2 Photoresist film formation

For a typical thin film of approximately 40 nm thickness, a resist solution was prepared from a mixture of 60 mg of the synthesized metal oxide, a small amount of photoacid generators and propylene glycol monomethylether acetate as a solvent. 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 QCM (quartz crystal microbalance). DUV exposure studies were performed using a ABM contact aligner at Cornell CNF (Cornell NanoScale Facility). A JEOL JBX9500FS e-beam exposure tool at Cornell CNF was used for e-beam exposure tests. EUV exposure studies were performed at the LBNL (Lawrence Berkeley National Laboratory), IMEC (Interuniversity Microelectronics Centre) and PSI (Paul Scherrer Institute). Negative tone patterns were evaluated after development with organic solvents.

3 Result 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 (soft bake) temperature studies were carried out.

3.1.1 Scum improvement study using higher dissolution rate PAG

In general, PAG structures and properties strongly affect 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 hydrophobic PAG-A is described below. Hydrophobic PAG-A is designed for higher solubility in organic solvents. As shown in Figure 1, a Zr type metal oxide photoresist film with hydrophobic PAG-A showed higher dissolution rate by QCM analysis than that with the reference PAG. PAG-A is a higher dissolution rate PAG based on this

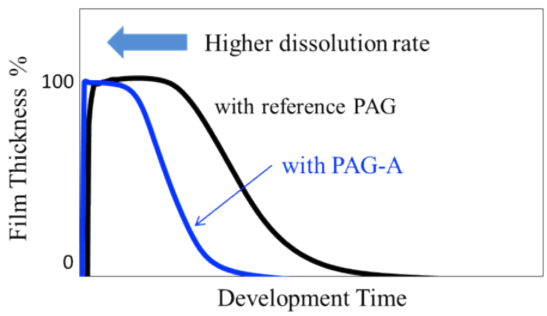

Figure 1 QCM evaluation result of Zr type metal oxide photoresist with reference PAG and PAG-A.

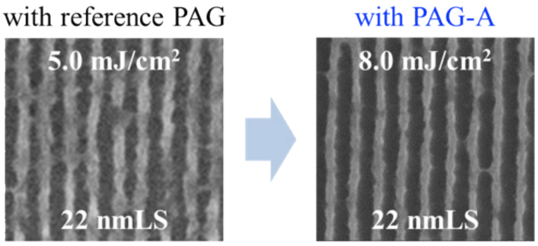

Figure 2　EUV exposure result of Zr type metal oxide photoresist with reference PAG and higher dissolution rate PAG-A.

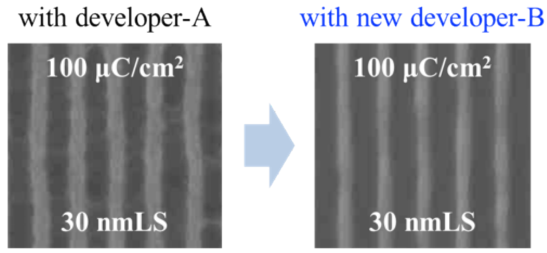

Figure 4　E-beam exposure result with developer-A and higher dissolution rate developer-B.

experiment.

Then, EUV exposure at LBNL B-MET (Berkeley Microfield Exposure Tool) was tested using these two PAGs. As shown in Figure 2, result using the LBNL B-MET shows scum improvement with higher dissolution rate PAG-A with 22 nmLS (line and space) patterning at exposures less than 10 mJ/cm^2. 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. A standard alcohol based developer-A and a new ketone based developer-B were compared by QCM evaluation as shown in Figure 3 and higher dissolution rate of ketone based developer-B was confirmed based on this test. According to previous report, ketone based solvents showed higher solubility than an alcohol based solvent for inorganic-organic hybrid photoresist due to the Hansen solubility parameter [12] This result is in good agreement with the previous work.

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 30 nmLS pattern without scum formation was observed with higher dissolution rate developer-B with retaining e-beam sensitivity, 100 μC/cm^2 (Figure 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 lower SB temperature. Since the crosslinking reaction of a metal oxide film may occur 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 standard process (110 ℃, 60 sec) and lower SB temperature. It was confirmed that lower SB temperature showed higher dissolution rate as we expected.

EUV exposure comparison was carried out at the LBNL B-MET with standard process (110 ℃, 60 sec) and

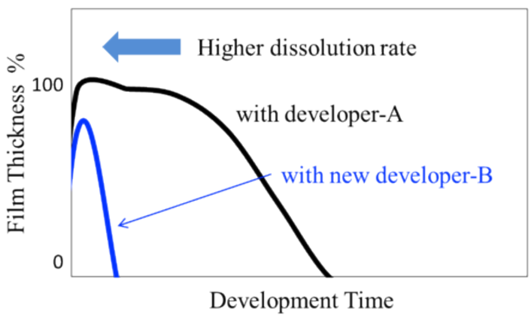

Figure 3　QCM evaluation result of Zr type metal oxide photoresist with developer-A and new developer-B.

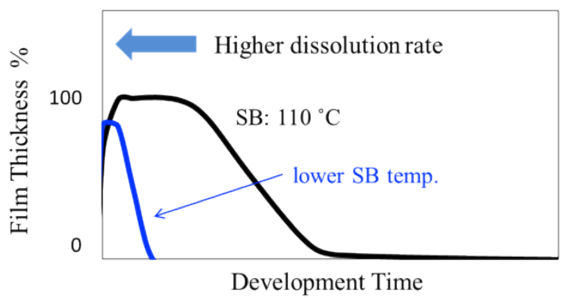

Figure 5　QCM evaluation result of Zr type metal oxide photoresist with lower SB temperature.

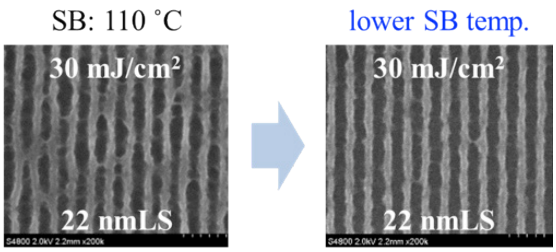

Figure 6 EUV exposure result of Zr type metal oxide photoresist with lower SB temperature.

lower SB temperature. As shown in Figure 6, scum improvement with the same sensitivity was observed with lower SB temperature.

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 20 nmLS using this Zr type metal oxide platform. Therefore, a new metal core study was undertaken and its progress is described 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 [13]. 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 plat-forms have been developed in

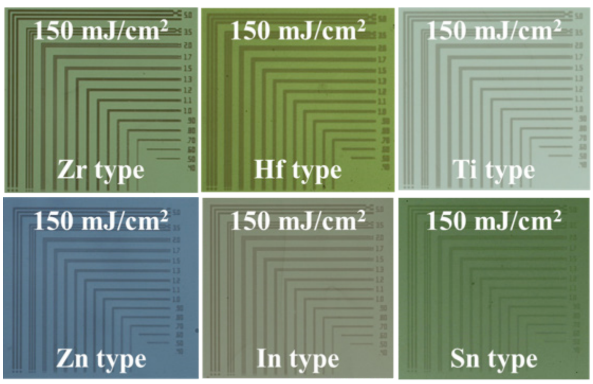

Figure 7 Metal oxide photoresist variation with micro-scale patterning images.

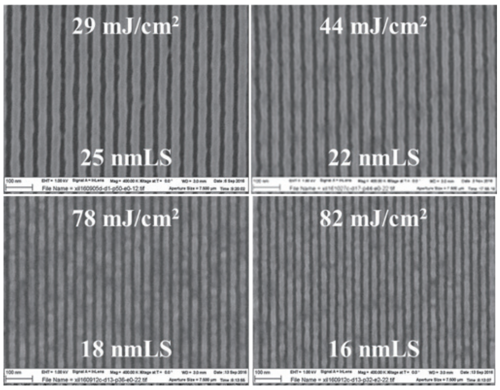

Figure 8 EUV exposure result with new metal core platform at PSI.

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 150 mJ/cm^2 exposure dose, a typical value for 248 nm exposure.

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 PSI. Required exposures of 25 nmLS at 29 mJ/cm^2, 22 nmLS at 44 mJ/cm^2, 18 nmLS at 78 mJ/cm^2 and 16 nmLS at 82 mJ/cm^2 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.

EUV patterning tests at LBNL B-MET were also carried out with a new metal core. 16 nmLS and 15 nmLS patterning was achieved with 124 mJ/cm^2 dose. Furthermore, 14 nmLS and 13 nmLS patterns were achieved with 77 mJ/cm^2 as shown in Figure 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.

Furthermore, this metal oxide photoresist with new metal core was exposed with a NXE scanner with DGL membrane option to protect scanner optics. Then, 19 nmLS at 56 mJ/cm^2 pattern and 18 nmLS at 53 mJ/cm^2 were obtained successfully as shown in Figure 10. No

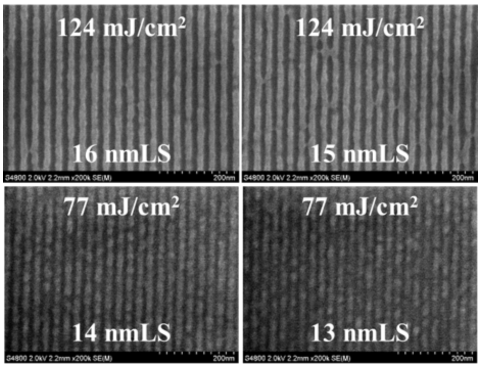

Figure 9 EUV exposure result with new metal core at LBNL B-MET.

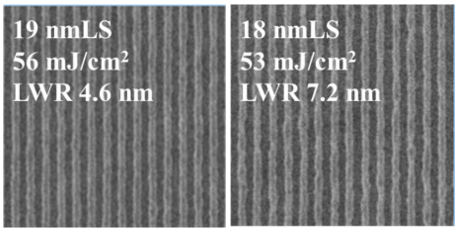

Figure 10 Exposure results from NXE scanner with new metal core.

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.

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 16 nmLS resolution at PSI, 13 nmLS at B-MET and 18 nmLS 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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