Recent EUV Resists toward High Volume Manufacturing

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Extreme ultraviolet lithography (EUVL) has been an attractive method as next generation lithography (NGL) over 20 years, and high-volume manufacturing (HVM) is now going to be realized by great progresses in materials as well as EUV source power enhancement. In this paper, recent reported materials for EUVL are summarized ranging from conventional organic material base resists to novel inorganic material base resists.

Keyword: Extreme ultraviolet lithography, Next generation lithography

1. Introduction

Extreme ultraviolet lithography (EUVL) that extends photolithography to extreme shorter wavelength (13.5 nm) is capable of achieving sub-20 nm half pitch resolution by single exposure [1]. However, owing to challenges which need to be addressed like low source power of EUV light, outgas concern under vacuum condition exposure and Resolution-Line width roughness (LWR) -Sensitivity (RLS) tradeoff, EUVL has not been applied to semiconductor industry yet. Nevertheless, the effort to realize this method is continued by both hardware side and material side, and currently EUVL is estimated to be a viable successor of ArF immersion lithography.

In this review paper, various kinds of recent photoresists designed for EUVL and their feature and capability are discussed briefly.

2. Organic polymer base chemically amplified resists

Among numbers of EUV resists, organic polymer base chemically amplified resists (CAR) have been deeply investigated and look most established at this point. Typically, photo acid generator (PAG) is applied as a source of acid catalyst triggered by EUV exposure. PAG component can be applied as blended form or as incorporated form with resin (polymer bound PAG). In this section, progresses of these materials with various strategies are described.

2.1 PAG blend type
2.1.1 Polymer development

First of all, acid diffusion control studies are summarized. It is believed that higher Tg polymer is favorable to suppress acid diffusion which deteriorates resolution and LWR. Sakai et al. reported that 13% increase of polymer Tg lead LWR improvement from 5.9 nm to 3.9 nm in 22 nm HP [2]. While sensitivity became slightly worse, the total resist performance turned out improved, judged from the Z-factor [3]. Tsubaki et al. investigated the dependency of pinching behavior of 15-18 nm HP with low activation energy (Ea) polymer, revealing that pinching was suppressed when the polymer Tg was 40 °C and over higher than the post exposure bake (PEB) temperature [4]. From the chemical structural point of view, methacrylic terpolymers containing various adamantyl polar units were compared by Tanagi et al. showing that unit with long alkyl connecting group and two hydroxyl groups gave good resist performance in terms of...
resolution and line edge roughness (LER) by EB lithography test. It was assumed that higher proton affinity and long alkyl chain prevented acid diffusion effectively [5].

Relationship of polymer hydrophobicity and resolution limit of positive tone resists was discussed by Tarutani et al. Hydrophobic polymer was found to resolve smaller pitch (down to 20 nm HP) since the pattern collapse caused by capillary force could be suppressed. Since hydrophilicity at film surface seemed required in order to reduce blob defect at the same time, a new additive that only reform only the surface was applied to hydrophobic polymer based resists, realizing both better resolution and defectivity improvement [6].

Negative tone imaging (NTI) EUV resists were also proposed by Tarutani et al. NTI process has a clear advantage on both larger photon density and LWR due to low swelling character of n-butyl acetate (nBA) developer [7, 8]. A new polymer with low Ea was designed containing 2-methyladamantyl-methacrylate (AD-MA) as protected moiety since hydrophobicity change during development process is much larger than that of protected hydroxystyrene which is typically applied for EUV resist polymer unit. As a result, 20 nm isolated trench pattern was achieved as a small dose as 6.25 mJ/cm² by nBA development.

There were also various studies about polymer main chain structure. Saccharose cored star block copolymers by Wieberger et al. consisted of GBLMA/MAMA turned out better sensitivity than its star random polymer analogues [9], and an acid cleavable core based star polymer with polyhydroxystyrene (PHS) arms by Iwashita et al. showed better EUV resist performance than its linear polymer in sensitivity and LWR for 30 nm LS [10]. Copolymers of tetrafluoroethylene(TFE)-norbornene derivative by Yamashita et al. [11] and those of trifluoromethacrylate-vinyl ether by Christianson et al. [12] were also reported aiming for high EUV light absorption by fluorine atoms, demonstrating 10 mJ/cm² or better sensitivity for sub-40 nm LS image. Polyesters consisting of BPA/TBE/CM were also proposed by Cardineau et al. since chain-scission behavior was expected to occur on acid generation for higher sensitivity [13].

2.1.2 PAG development

As well as polymer design, PAG design is the key factor to optimize the resist performance for EUV CAR, too. A study by Sugi et al. indicated larger size PAGs with rigid unit as well as polar unit were preferred in order to prevent acid diffusion and they demonstrated sub-30 nm LS resolution [14]. From the electron affinity point of view, linear correlation between the reduction potential of PAG and the acid generation efficiency was found by Tsubaki et al. [15]. Incorporation of trimethylsilylmethyl (TMSM) group onto sulfur atom of arylsulfonium cation was exhibited by Sharma et al., which showed the improved patterning result. The transfer of trimethylsilyl group from PAG to the polymer could be one of benefits [16]. Sulc et al. investigated various aryl sulfonates as neutral PAGs from not only EUVL performance but also PAG decomposition pathway and modeling study of view, and found 4,4’-bistriflate-biphenyl showed 4.8 times improvement compared with control PAG, triphenylsulfonium triflate. They also pointed out that complex generation of both sulfinic and sulfonic acids occurred on decomposition process [17].

Concept of PAG with acid amplifiers (AA) was initially brought by Kruger et al. [18], and continuous development was made, which showed LER improvement [19]. Maruyama et al. developed an AA-PAG which made sensitivity and resolution improvement for 30 nm HP [20]. A novel AA-PAG containing three sulfonfyl groups, initially liberating one sulfonic acid on EUV irradiation which catalyzes consecutive acid generation derived
from the rest of sulfonyl groups was proposed by Joo et al. (Fig. 1) [21].

Figure 1. Decomposition mechanism of AA-PAG proposed by Joo et al.

The idea utilizing photo destructive anion PAG (PDA-PAG) was also demonstrated and showed good EUV performance for 30 nm HP [20]. Since it contains photo destructive unit, the PAG anion part is thought to be decomposed and the size becomes smaller where EUV irradiation is targeted while the size remains large at the periphery area. This means fast acid diffusion can be achieved at the center exposed area but acid diffusion is restricted at the edge of exposed area, which realizes higher sensitivity and excellent LWR at the same time.

2.2 Polymer bound PAG type

The polymer bound PAG (PBP) concept came from acid diffusion control, where larger PAG size is assumed to be preferred but too large size in PAG blend platform can lead to the PAG aggregation which is deleterious to LWR and defect formation. Randomly attaching the PAG moiety to the resist polymer can minimize the concern of the aggregation.

Thackeray et al. reported a good performance EUV resist showing 17 nm HP resolution at a dose of 14.5 mJ/cm² and achieved very low outgassing level by modifying PAG unit monomer ratio and introducing electron rich element in the resist polymer [22]. A dissolution rate study of this class of resists varying the leaving group design was conducted by Ongayi et al. It indicated that lower Ea, hydrophilicity, and larger size of leaving group lead higher sensitivity, however, hydrophobicity seemed required to some extent for the better resolution in order to prevent pattern collapse from capillary force between lines [23]. In another study by Thackeray et al., PBP combined with photo decomposable base (PDB) was demonstrated showing about 20% LWR improvement for 20 nm HP CH [24]. Comparison of PAG blend type and PBP type from blur and swelling point of view was made by Tamaoki et al. and PBP type showed better result and realized 25 nm HP LS with 3.0 nm LWR value by EB lithography [25].

2.3 Up-to-dated polymer CAR materials and beyond

Sakai et al. demonstrated 18 nm CH and 15 nm LS pattern with combination of high Tg polymer and profile control agent. The resist improved not only line profile but also defectivity. The agent was thought to add surface hydrophilicity which is advantageous to reduce defects [2]. Cameron et al. developed RLS balanced PBP type resist with the aid of simulation and achieved 3.2 nm LER at a dose of 16.9 ml/cm² for 22 nm LS and 1.1 nm local CD uniformity (LCDU) at a dose of 26.6 ml/cm² for 20 nm CH [26].

Recently, a novel concept to enhance EUV resist sensitivity, photosensitized chemically amplified resist (PS-CAR) has been brought by Tagawa et al. [27]. In this process, firstly low power pattern exposure which generates acid and photosensitizer (PS) at exposed area. Secondly, intense UV flood exposure is done to the whole wafer which excites PS and encourages more acid generation. The profile after UV flood exposure is the same as first pattern exposure. PS-CAR process with EB lithography was demonstrated and an increase of more than one order in sensitivity without any loss of resolution was achieved.

3. Organic polymer base non-chemically amplified resists

Development of non-chemically amplified resists (non-CAR) sounds retrogression in photoresist history, but getting reconsidered positively because acid diffusion which may limit resolution improvement and worsen LWR for 22 nm HP and beyond does not need to be considered.

Typical examples for non-CAR were based on cross-linking mechanism. Tarutani et al. showed the latest result realizing 3.0 nm LWR at a dose of 14 ml/cm² for 45 nm LS and 18 nm LS at a reasonable dose of 20 ml/cm² [8].
Shirai et al. proposed thiol/ene or thiol/yne radical reaction cross-linking materials consisted of partially allyl or propargyl modified PHS, multifunctional thiol compound, and photoradical generator [28, 29].

Main chain cleavage system materials for positive tone resists were reported by Whittaker et al. Linear polycarbonates, star polyester-block-polymethylmethacrylate and comb polymers with polysulfone backbones were designed based on GC-MS screening, where the sensitivity to fragmentation of various chemical structures was estimated. LS image of c.a. 40 nm were resolved in their preliminary result [30].

Singh et al. investigated homopolymer of 4-(methacryloyloxy)phenyldimethylsulfoniumtriflate (MAPDST) or copolymer of MAPDST and methylmethacrylate. The pendant sulfonium group underwent photoreaction on EUV irradiation to become sulfide group which made the exposed part hydrophobic, giving the negative tone dissolution contrast with alkali developer. These materials realized 25 nm line pattern with LER less than 2.0 nm [31].

4. Organic molecular base resists

Molecular type resists have been of great interest for years since the small size of base matrix material and no dispersion of molecular weight is beneficial to better resolution and lower LWR. Material’s robustness is often discussed like Tg, modulus and adhesion to substrate for these resists.

4.1 Calixarenes

Many of calixarene derivatives have been studied so far aiming for EUV lithography technology. One of them containing 2-methyl-2-adamantyloxycarbonylmethoxy groups as a protecting unit (MGR110P) was developed by Echigo et al. for positive tone CAR and exhibited 40 nm LS resolution at an EB dose of 28 uC/cm² [32]. Similarly, Owada et al. reported that 40 nm HP LS pattern was achieved at a dose of 9.5 ml/cm² with the calixarene of completely regulated protection sites and number of protecting group [33]. As another CAR example, partial acetal protection of hydroxyl-phenyl group of a calixarene with 2-naphthoylethylvinyl ether was carried out by Green et al. and 32 nm LS pattern was available at 30 mJ/cm² dose with the molecule (C3-4NCVE), however, narrower pitch LS was not successfully obtained presumably due to low Young's modulus, high acid diffusion and/or inhomogeneity of resist components in the film [34].

4.2 NORIA

A new ladder cyclic oligomer “NORIA” (water wheel in Latin) was invented by Nishikubo et al. and its derivatives have been attractive as novel organic molecular resist candidates owing to its rigid structure with relatively high Tg, moderate molecular size for nano patterning and ease of protection [35].

For positive tone development approach, Kudo et al. proposed NORIA derivatives protected by both methoxy group and adamantyl ester group which improved sensitivity for 32 nm LS patterning from analogues protected by only adamantyl ester group [36]. Maruyama et al. demonstrated 22 nm HP LS resolution with a protected NORIA material [20]. Blending of NORIA containing oxetane cross-linker and methyladamantyl protected NORIA was examined by Kulshreshtha et al., showing good negative tone resist performance with nBA development as narrow ultimate resolution as 20 nm LS and improved LER compared with the reference without cross-linker derivative [37].

4.3 Other molecules

Fullerene has also been investigated as a core unit for molecular resist, and its derivatives were intensively studied by Frommhold et al.
For positive tone CAR, \(t\)-butylacetate (tBAC) protected methanofullerene with SbF\(_6\) PAG gave isolated lines as small as 20 nm by EB lithography [38]. On the other hand, fullerene derivatives with PAG and epoxy cross-linker provided negative tone CAR, and found to resolve 22 nm HP with 4-5 nm LER at EUV dose of 25-30 mJ/cm\(^2\) [39, 40]. Independently, Oizumi et al. reported a fullerene derivative with methyladamantanyl ester protecting group worked for a positive tone resist resolving 32 nm LS HP with an LWR of 5.7 nm at an EUV dose of 18.1 mJ/cm\(^2\) [41].

A derivative of xanthendiol was designed by Sato et al. and studied for negative tone resist. Its Tg was as high as 152 °C, and resolved 20 nm HP when applied with PAG and cross-linker materials [42].

5. Inorganic material base resists

In the early stage of EUV resist development, silicon compounds/polymer base materials attracted much more attention since its low absorbing character to EUV light were thought to be advantageous similar to KrF or ArF resists design [43]. However, as many of these materials contained Si-H bonds for cross-linking or Si-Si backbone for higher transparency to EUV light wavelength (13.5nm), stability at ambient condition was not sufficient. In addition, as the importance of resist film absorbing character to EUV light was getting realized due to low source power of EUV light, silicon material investigation for EUV resist became shrunk. Instead, resists containing metal element with high EUV absorption property for excellent sensitivity are now gaining interest. These materials are also expected to have better robustness and good etching selectivity to neighboring layer(s) like organic or silicon base materials. All resists described here were non-chemically amplified type.

5.1 Hydrosilsesquioxanes (HSQ)

Even though silicon base resists have not been regarded as hot materials in EUV lithography like in year of 2000 and around, hydrosilsesquioxanes (HSQ) resist is noteworthy. Ekinci et al. reported that ultimate resolution limit of HSQ material has marked the world record as narrow as 7nm HP LS although high energy EUV dose was required [44]. Dinh et al. noticed that film quality after coating was of great concern [45], but HSQ resist still attracts researchers’ attention.

5.2 Hafnium oxide sulfate (HfSOx)

One of the most advanced metal resists for nanolithography is hafnium oxide sulfate material containing peroxy group attached to hafnium atoms. This novel type resist, developed by researchers at Inpria Co. [46], realized 8 nm HP at an EUV dose of 160-200 mJ/cm\(^2\) [44].

Hafnium element was chosen since high EUV absorption cross section relative to many other metals. As seen in Fig. 2, it was noted that peroxy group hinders network formation by capping small inorganic clusters until the EUV exposure, followed by breaking peroxy bonds with secondary electrons triggered by EUV photons leading decomposition and polymerization which makes the exposed area insoluble to TMAH developer and works as a negative tone resist. According to Oleksak and Herman, the presence of sulfur is needed for patternability since films containing no sulfate are not soluble in basic solutions [47].

![Derivative of xanthendiol](image)

![Figure 2. Simplified exposure mechanism of HfSOx resist](image)
5.3 Metal oxide nanoparticles (NP)
Ober’s group has intensively studied metal oxide nanoparticles (NP) with very high sensitivity for EUV lithography application [48]. Starting from alkoxides of zirconium or hafnium, controlled hydrolysis was carried out in an excess of carboxylic acid followed by precipitation treatments to give ZrO$_2$-NP or HfO$_2$-NP with organic ligands. Size of NP was controlled below 3 nm which is suitable sub-20 nm lithography. Combined with photoradical initiator or PAG, these NP gave both positive and negative tone patterns. The best result was obtained from methacryl acid (MAA) or trans-2, 3-dimethylacrylic acid (DMA) ligated ZrO$_2$-NP with PAG enabling sub 30 nm line patterns at an EUV dose below 5 mJ/cm$^2$, showing one of the best EUV sensitivity results ever reported.

![Figure 3. Schematic representation of the ligand exchange mechanism](image)

It was assumed that ligand exchange from weaker acid (MAA, DMA) to stronger acid from PAG (benzoic acid, sulfonic acid etc.) is the main driving force to give the dissolution contrast (Fig. 3), but ligand ejection by EUV photons followed by aggregation between NP was also possible mechanism to exhibit the contrast [49]. The advantage of utilizing metallic compound was proved in etch resistivity [48a], however, the effect of EUV absorption with these transition metals is ambiguous.

5.4 Molecular Organometallic Resists for EUV (MORE)
Brainard’s group proposed the concept of Molecular Organometallic Resists for EUV (MORE), which are comprised of molecular organometallic compounds. The MORE approach utilizes high EUV optical density metals to increase the photon absorbance of thin resist films [50]. The advantage of single molecule is also expected similar to organic molecular base resists mentioned above.

One of the promising results was exhibited from an oxalate complex of cobalt. The negative tone image was obtained on EUV irradiation and 22 nm HP LS pattern with LER of 4.0 nm was realized at a dose of 30 mJ/cm$^2$. Regarding the mechanism of dissolution contrast, both cross-linking between cobalt after decomposition of oxalate group to carbon dioxide and reduction of metal center to zero-valent on EUV irradiation were considered for increasing insolubility to developer.

Tin cluster materials containing organic substituents on tin atoms were also of the group interest since tin is expected to one of the best elements to gain EUV photons. It was found that coupling between tin atoms after radical scission of C-Sn bond is the mechanism for solubility change. Down to 18 nm HP pattern was available, but requirement of hundreds of mJ/cm$^2$ EUV dose was the problematic [50, 51].

5.5 Other materials
Bismuth-phenyl oligomers were also studied at Brainard’s group. Oxidation by sulfuryl chloride of bismuth-phenyl oligomer gave oxidation state of +V with two Cl atoms on bismuth, which provided negative tone resist enabling 21 nm line resolution while replacement of two chlorides with two acetates gave another resist with sensitivity of 30 mJ/cm$^2$. But overall resist performance was not remarkable at this point [52].

Mixing of metal-containing additive with organic material base resist was proposed. Singh et al. reported EB lithography test with polymethylmethacrylate (PMMA) with molybdenum or tungsten polyoxometalates (POMs) which acted as positive tone resists with improved resolution limit compared with reference PMMA. In this case, POMs were assumed to work as not only electron harvesters but also oxidizing agent which encouraged polymer decomposition [53].
6. Conclusion

Numbers of research groups have been developing EUV materials from various approaches. Organic material base resists, especially chemically amplified resists are getting matured in terms of resist performances as well as feasibility to HVM. On the other hand, inorganic material base resists are growing rapidly and demonstrating remarkable property from a specific point of view. Many of inorganic resists are now mainly investigated by academic institutes, but the collaboration of industry-government-academia research group will be realized and materials innovation of these novel resists should be achieved. Although what type of materials to be applied is uncertain yet, we strongly believe that implementation of EUVL comes in a few years.

References

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