Sensitizer for EUV Chemically Amplified Resist: Metal versus Halogen

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Extreme Ultraviolet (EUV) lithography utilizes photons of 91.6 eV energy to ionize resists, generating secondary electrons, thus enabling electron-driven reactions. Unlike photolithography, where photons below 7 eV selectively activate photoactive compounds, photons at 91.6 eV ionize all materials, subsequently generating secondary electrons. The energy and the numbers of secondary electrons generated after ionization are determined by the material chemistry. Several metals are reported to have high secondary electron generation capability and high EUV absorption, therefore metals can be one of the solution to deal with the insufficient photon density in resist. Halogen atoms like iodine and fluorine also provide high absorption which would be suitable alternative sensitizer to the metal salts sensitizer. In this work, we study metal salt sensitizers with different cations and anions as well as halogenated sensitizer in both polymer and PAG. Total electron yields are increased with increased resist absorption for both metal and halogen sensitizer. Sensitivity of resists with metal salt sensitizers increase, resulting in increased LCDU. However, halogenated sensitizers do not show positive correlation between sensitivity and electron yield as metal sensitizer. Through this study, we expect to explore materials that enable both high absorption and high photoelectron generation efficiency at 91.6 eV.

Keywords: EUV, Resist, Metal sensitizer, Florine, Iodine

1. Introduction

The ultimate resolution of lithography process is proportional to the wavelength of radiation applied to the photosensitive materials. Extreme Ultraviolet (EUV) lithography with the 13.53 nm wavelength at soft X-ray region is expecting to further push the resolution limit after 193 immersion lithography [1]. Due to the current limit of EUV source power and the throughput requirements for high volume manufacturing, resist sensitivity must be improved for high resolution patterning while maintaining pattern fidelity and uniformity [2].

Control of patterning uniformity such as local CD uniformity (LCDU) at very high-resolution patterning is challenging due to photon shot noise. When the number of photons becomes small, the statistical fluctuation can be appreciable. For EUV lithography, higher energy of each photon reduces the photon density at a given exposure dose; Same exposure dose of EUV lithography renders 14 times less photon density compared to ArF lithography. Furthermore, ultra-thin resist films to prevent pattern collapse result in less than 50% absorption of incident EUV photons [3]. Consequently, high resolution patterns are prone to more severe stochastic challenge.

Another challenge for EUV resists is related to the energy level of EUV radiation. Optical lithography with photon energy less than 7 eV selectively activates certain compounds, like photoacid generator (PAG), to achieve high quantum efficiency. Photon energy of EUV (91.6 eV) exceeds ionization energy of most materials [4], therefore EUV photons ionize any materials encountered including PAGs and resist polymers. Effective reaction catalysts, e.g. acids are not immediately generated after photo-absorption but photoelectrons around 80 eV are first generated. Afterwards, secondary electrons are produced in the cascade due to scattering, until thermalized to low
energy electrons, finally generating acids that are responsible for chemically amplified reactions [5]. Meanwhile, byproducts that consume acids might be generated during ionization as well [6].

Depending on the extinction coefficient and the bonding energy of the materials, the absorption of EUV radiation and efficiency of secondary electron generations are different. Electron generation efficiency is very like to have impacts on the resist sensitivity. Our previous study showed that mixing metal salt sensitizers composing of a metal cation and organic anions into chemical amplified resists (CAR) improved EUV sensitivity [7,8]. These metal salt sensitizers carry high EUV absorption, leading to high photoelectron yield enhanced acid yield [9]. However not only metals have high absorption, halogen atoms like iodine and fluorine also provide high absorption which would be suitable alternative sensitizer to the metal salt sensitizer.

In this work, we study the impacts of metal salt sensitizers and halogenated sensitizers on EUV sensitivity and correlate with their total electron yields. CAR with conventional bounded EUV sensitizer (NXE1816) is chosen as reference due to its capability to achieve sub-20nm half pitch contact hole patterning. Metal salts sensitizers are mixed with the organic reference resist. Halogen sensitizers are chemical modifications of conventional organic sensitizer bounded to resist. To study the impact of halogens, fluorine and iodine are chosen as lower outgassing risk elements compared to chlorine and bromide. Details of samples shown in Table 1 will be discussed in the experiment section.

2. Experimental

EUV resist NXE1816, which contains conventional EUV sensitizers, is chosen as the reference in this study. Metal salt sensitizers are mixed into reference CAR at various loading as shown in Table 1. Metal salt $M^{m+}A^{m-}$ is the same metal sensitizer reported in the author’s previous work. Metal M belongs to the Alkaline earth metal group and $A^{m-}$ is a purely organic anions, similar to the anions found in photoacid generators. To understand the impacts of anion, $A^{m-}$ is replaced with $B^{m-}$ which has higher absorption but similar diffusivity. To understand the impact of cation, metal M is replaced by Y, a lanthanide metal, which has lower absorption but similar atomic number.

Impacts of halogens are studied by chemically modifications of conventional EUV sensitizers bounded to resist. C-3 contains a modified sensitizer with 12 fluorine atoms and C-4 with 6 fluorine atoms in each sensitizer monomer. EUV sensitizer chemical structural can usually be modified by only 1 iodine atom. Therefore, sensitizer half modified by iodine C-6 or fully modified by iodine C-7 are prepared. Literatures also suggest the different chemistries of halogenated sensitizer can potentially leads either increase or decrease acid yield [10,11]. Therefore, C-5 is prepared in the form of iodonium PAG to understand the impact of sensitizer chemistry at similar absorption level.

EUV exposures were performed in Imec using ASML NXE: 3300B and standard quasar illumination condition. TEL CLEAN TRACKTM LITHIUS Pro™ Z-EUV tool was used. 35 nm resist films were freshly coated on AL412 20 nm underlayer on Si and soft baked at 105 °C for 60 s. OPD262 static 30 s development and SPC683 rinse were applied after PEB. The target feature for this study is 20 nm orthogonal CH at 40 nm pitch with 20% reticle bias. LCDU is the averaged 3 sigma variation of 81 contacts holes of 9 exposed fields. SEM were performed on the HITACHI CG-5000 at 500 V and 8 pA. Dissolution rate are measured by dissolution rate monitor.

| Sample | EUV Sensitizer | Metal salts sensitizers | Metal salts loading mol/g resist |
|--------|---------------|-------------------------|---------------------------------|
| Ref    | Conventional  | NA                      | 0                               |
| CM-1   | Conventional  | $M^{m+}A^{m-}$          | $8.8\pm0.1\times10^{-5}$        |
| CM-2   | Conventional  | $M^{m+}B^{m-}$          | $8.8\pm0.1\times10^{-5}$        |
| CM-4   | Conventional  | $M^{m+}B^{m-}$          | $17.6\pm0.1\times10^{-5}$       |
| CY-1   | Conventional  | $Y^{m+A}^{m-}$          | $8.8\pm0.1\times10^{-5}$        |
| CY-2   | Conventional  | $Y^{m+A}^{m-}$          | $17.6\pm0.1\times10^{-5}$       |
| CY-3   | Conventional  | $Y^{m+A}^{m-}$          | $26.4\pm0.1\times10^{-5}$       |
| C-3    | Fluorinated   | (12)                    | NA                              |
| C-4    | Fluorinated   | (6)                     | NA                              |
| C-5    | Iodinated PAG | NA                      | 0                               |
| C-6    | 50% Iodinated | 50% conventional        | NA                              |

Table 1. Metal and halogen sensitizers for EUV patterning and total electron yield (TEY).
during exposure to EUV light. This quantity is normalized to the incident power and the detail can be found in reference. The absorption coefficient of the samples was measured/calculated by using the tabulated data from known literature.

3. Results and discussion

3.1. Impacts of metal sensitizer anions

As shown in Fig. 1, by mixing the metal sensitizer in C-1, sensitivity of CM-1 increased by 8%, similar to the sensitivity improvement of metal sensitizer in the high quencher loading resists platform in reference [7]. With high absorption anion B\textsuperscript{m-}, sensitivity of CM-2 further increased by 15% from reference CAR, given that the metal specie and the sensitizer loading remained the same. Higher absorption of anions increased the density of photons absorbed in resist film, resulting in the increase of second electron yield as shown in Fig. 2. 1% and 4% of absorption increase by CM-1 and CM-2 lead to 2% and 9% electron yield increase per incident photon and 8% and 15% sensitivity improvement. The similar secondary electron generation efficiency of CM-1 and CM-2 suggests that anions are likely only contribute to photon absorption but do not impact the secondary electrons generation efficiency.

3.2. Impacts of cation

To study the impacts of cations of metal salt sensitizers on the EUV resists sensitivity, cation of CM-1 is substituted by metal Y which has similar atomic number, but less EUV absorption. CY-1 contains the same anions and molar percent of metal as CM-1, so the calculated absorption coefficient is slight less than CM-1. As shown in Fig. 1, CY-1 showed greater sensitivity improvement than CM-1 at the same metal loading despite lower absorption.

CY-1 also showed a faster sensitivity enhancement with increasing metal loading. Such sensitivity enhancement is a result of higher secondary electron yield by the new metal introduced in this work. CY-1 showed 39% higher secondary electron yield than reference, while CM-1 showed 9% increase. On the other hand, the double and triple metal sensitizer loadings only slight increase secondary electron yields, similar to the result as reference [7], suggesting sensitivity of metal sensitized resist is not proportional to secondary electron yield. It is worth notice that for CM-4, 29% dose reduction results 5% LCDU increase, while for CY-2, 32% dose reduction results resulted in 29% LCDU increase. Although LCDU always trades off with sensitivity improvement, such huge increase in LCDU for CY type of metal is not merely due to the shot noise caused by lower dose. More investigations are needed to study film property change and electron blur behaviors.

3.3. Impacts of fluorine

Halogens are possible to be incorporated to resist compositions at multiple destinations, such as PAG, polymer backbone, or any functional units in the polymer chains. In order to better understand impacts of the micro chemical environment where these fluorine atoms attach, we modified the conventional EUV sensitizer with 12 fluorine atoms (C-3) and 6 fluorine atoms (C-4) and molar ratio the same as reference CAR. Absorption of resists increased with increasing number of fluorine atoms in the sensitizer unit as shown in Fig. 3. Higher EUV absorption by fluorine resulted in the increase of total electron yield as shown in Fig. 2. Yet, compared to the metal sensitizer CM-2 which has EUV absorption of 5.60 \(\mu m^{-1}\), C-3 has higher absorption of 5.94 \(\mu m^{-1}\), but the electron yield is almost the same. This result suggested that the total electron yield caused by

![Fig. 1. Impacts of metal sensitizer absorption on resists sensitivity.](image)

![Fig. 2. Total electron yield of metal sensitizer resists and halogen sensitizer resists.](image)
metal sensitizer is not only due to its high absorption, but also due to the capability of higher secondary electron generation in the chemical environment of the selected metal. Once electrons are generated, the efficiencies of converting electron to reactions are similar. 9% of higher electron yield of CM-2 and C-3 resulted in approximately 14% sensitivity improvement (~25 mJ/cm²) and 5% LCDU increase (4 nm) (Fig. 4).

Fig. 3. Impacts of halogen sensitizer absorption on resists sensitivity.

Unlike metal salt sensitizers, the higher electron yield of C-4 that contains 6 fluorine atoms resulted in no difference in EUV sensitivity yet better LCDU. While the higher electron yield of C-3 with 12 fluorine resulted in improved sensitivity, but slight worse LCDU. The higher absorption of C-4 at the same dose level, might be one of the keys to reduce photon shot noise and LCDU improvement. 6 fluorine modification seems to lower the secondary electron efficiency due to the byproduct of fluorine ions [6]. However, it is unclear why C-3 with almost same hydrocarbon chemistry but only different numbers of fluorine showed improved sensitivity.

Yet, the chemical ambient where fluorine atoms attached could lead to different response to higher absorption.

3.4. Impacts of iodine

Iodine has much higher EUV absorption even comparing to metal, however, the effects of iodine is controversial in the literature [11,13,14]. Iodine anion PAGs or iodine in PAG anions were generally shown to have higher acid yield, while poly(4-iodostyrene) shows only 14.2% acid yield compared to poly(4-hydroxystyrene). In this work, iodine is incorporated in either PAG (C-5) or polymer-bound sensitizer unit (C-6, C-7). As a result of halogen incorporation, EUV absorption of C-5, C-6 and C-7 increase by 6%, 24% and 46% respectively (Fig. 3) and total electron yield increase by 10%, 40% and 30% respectively (Fig. 2) in comparison to C-1. Although C-3 and C-4 have slightly higher absorption than C-5, the electron yield is lower, suggesting that iodine is more effective of inducing extra secondary electrons than fluorine.

However, the higher electron yield by iodine does not always yield in higher EUV sensitivity or better LCDU (Fig. 6). When half of the EUV sensitizer unit is replaced by iodine sensitizer, although absorption is increased by 24% and electron yield is increased by 40%, sensitivity is even decreased by 7%. The extra electron generated is very likely consumed by iodine ions cleaved from sensitizer [10,13]. If all EUV sensitizer is bound with iodine, its capability of electron generation is further harmed by eliminating original sensitizer, therefore the total electron yield is even less than C-6. As more sensitizer is bound with iodine, more iodine ions can be generated after ionization and consumed more acid, therefore both sensitivity and LCDU are greatly harmed.

Fig. 5. Impacts of LCDU values on resists sensitivity.
3.5. Impacts on dissolution

In previous study, both maximum dissolution rate and minimum dissolution rate increase with the addition of metal sensitizer [7]. To confirm the impacts of metal sensitizer on dissolution, the same metal sensitizer as previous M-1 is used but added to another resist platform. With a different resist platform, the same metal sensitizer lower both the $R_{\text{max}}$ and $R_{\text{min}}$ of CM-1 from reference CAR instead (Fig. 7). Therefore, the impact of metal sensitizer on dissolution behavior is resist dependent.

On the other hand, both fluorine and iodine compounds are always considered as dissolution inhibitor. As shown in Fig. 6, dissolution contrast of C-4, C-6 and C-7 are indeed lower than reference CAR. However, the lower dissolution contrast does not limit the LCDU performance of C-4. Such improvement is again thanks to it is higher EUV absorption, moderate decrease of reaction efficiency.

4. Conclusion

In this work, we studied metal sensitizers in EUV chemically amplified resist with different cations and anions as well as fluorine and iodine sensitizer bound to PAG or resist polymer. Metal sensitizer improved both EUV photon absorption, electron yield and resulted higher sensitivity. Higher absorption of anions increase electron yield by merely higher absorption but has limited impacts on electron generation efficiency, however cations of metal sensitizer dictates electron generation efficiency. Sensitivity improvement by metal sensitizer comes with a price in LCDU and cations has dominating effects on LCDU.

Fluorine and iodine sensitizer also help with electron generation with their higher absorption. However, higher electron yield does not always translate to higher sensitizer for all halogen sensitizer. The chemical ambient where these halogens are attached have huge impact on the sensitivity.

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