Super High Sensitivity Enhancement by Photo-Sensitized Chemically Amplified Resist (PS-CAR) Process

Seiichi Tagawa*, Satoshi Enomoto, and Akihiro Oshima

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
JST, CREST, c/o Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.
tagawa@sanken.osaka-u.ac.jp

Over the past decade, the low intensity of extreme ultraviolet (EUV) light sources has been the most critical issue in the development of a promising, next-generation, high volume manufacturing (HVM) EUV lithography method. Specifically, enhancing the sensitivity of EUV resists to compensate for this low intensity is one of the most critical challenges for HVM implementations of EUV lithography. However, EUV light source power intensity remains one order less than the required value. Sensitivity enhancement of an EUV resist without any loss in other important properties such as resolution is inadequate to compensate for the low intensity of EUV sources in conventional EUV single exposure. Therefore, we propose a method for increasing the resist sensitivity considerably by combining the lithography of 1st EUV pattern exposure with a 2nd UV flood exposure (PF combination lithography) and a photosensitized chemically amplified resist (PS-CAR). This method achieves high sensitivity enhancement not only with EUV but also with electron-beam, ArF, and other types of pattern exposure. Thus, a sensitivity increase of more than one order without any loss in space resolution was achieved compared with conventional lithography by PF combination lithography of 1st EB pattern exposure with 2nd UV flood exposure and PS-CAR. Differences between EB and EUV resists include energy absorption processes, and the resist sensitivities of EUV can be predicted easily from the exposure results of EB lithography. Therefore, the reaction mechanism of EUV pattern exposure–UV flood exposure combination lithography of PS-CAR can be essentially evaluated with EB pattern exposure–UV flood exposure combination lithography of PS-CAR.

Keyword: Photosensitized Chemically Amplified Resist (PS-CAR), Sensitivity Enhancement, Pattern and Flood Exposure, Combination Lithography, EUV, EB

1. Introduction

1.1 Urgent requirement of sensitivity enhancement in EUV lithography

Lithography is a key technology for high volume manufacturing (HVM). Over the past decade, extreme ultraviolet (EUV) lithography has been the most promising candidate for next-generation lithography (NGL) [1-3]. Electron-beam (EB) lithography has also long been a NGL candidate [3]. However, low throughput (number of wafers per hour) remains the most critical issue with both of these lithography techniques. Throughput is mainly determined by both exposure light intensity and resist sensitivity. EUV light source intensities have not improved substantially in recent years. It should be noted that light source intensity and resist sensitivity complement each other. In other words, it is necessary to increase EUV resist sensitivity to compensate for low EUV light source intensity. However, improving the resist sensitivity is challenging owing to two important issues faced with EUV/EB resists. (1) The most difficult technical requirement with regard to EUV/EB resists is achieving simultaneous improvements in resolution, line width roughness (LWR), and sensitivity (so-called RLS tradeoff) [4]. (2) The reaction mechanisms of pattern formation change dramatically from photochemistry in photoresists to radiation chemistry in EUV/EB resists. The
radiation chemistry of EB/EUV resists must be clarified.

1.2 Chemically amplified resist (CAR) and RLS Trade-off

The first problem can be explained in detail as follows. Nowadays, only chemically amplified resists (CARs) [5, 6] are used for HVM. Such resists were first employed in HVM during the transition of exposure tools from the i line of a Hg lamp to a KrF excimer laser. Ever since, mainstream resist technology has involved the use of CARs in KrF, ArF dry, and ArF immersion lithography, and they are expected to be used for future EUV and EB lithography for HVM. It is generally and widely accepted to be difficult to drastically improve the resist sensitivity, because three important resist properties (resolution, LWR, and sensitivity) have been found to be inversely related (RLS trade-off) [4]. The RLS trade-off was explained clearly through a simulation of acid-catalytic reactions after acid formation, but this simulation did not consider the acid generation processes [4]. Then, simulations that considered the acid generation processes were performed [7, 8]. A critical issue in developing an EUV resist is satisfying the International Technology Roadmap for Semiconductors’ targets [9] of resolution, LWR, and sensitivity simultaneously [10-12].

1.3 Difference of radiation chemistry and photochemistry of resists

The second problem can be further explained as follows. This problem involves the very dramatic changes in the pattern formation reaction mechanisms from photochemistry in photoresists to radiation chemistry in EUV/EB resists. The first systematic study of resists’ radiation chemistry was conducted for clarifying the unusually high sensitivity and high resolution of chlorinated polystyrene–type EB non-chemically amplified resists (non-CARs) with pulse radiolysis based on the direct measurement of reactive intermediates in solid films and solutions of resists [13-15]. In addition, these studies clarified the differences between the reaction mechanisms of photoresists and EB resists [14, 15]. Photoresist reactions mainly occur owing to the excited states of photoactive compounds (PAC) via direct excitation. Energy deposition in EB resists is nonselective and proportional to the electron density of the EB resist materials. Pulse radiolysis studies of solid films and solutions of EB resists showed that the highly sensitive reactions of dissociative electron attachment of electrons with chlorinated compounds produce anions (Cl−) and radicals (R1) [13-15]. These are similar to the anions (X−) and radicals produced in the dissociative electron attachment of electrons with acid generators in chemically amplified resists (CARs) [16-18] and are important for sensitizing EB resists. These pulse radiolysis studies also showed the importance of the geminate ion recombination (nano-space reaction) of Cl− and positively charged sites for preparing EB resists with high space resolution that produce radical (R3) and acid (HCl) through CT complex with strong, broad absorption around 500 nm [13-15]. This is similar to the production of acid (HX) in the geminate ion recombination of X− with protonated compounds in chemically amplified resists (CARs) [16-18]. However, direct time-resolved observations of nano-space reactions such as the geminate recombination of solute radical ions [19, 20] and that of electrons and positive holes [21, 22] have already been confirmed with picosecond pulse radiolysis.

The very dramatic change in the reaction mechanism of acid generation from photochemistry to radiation chemistry was also confirmed experimentally in EB chemically amplified resists (EB CARs) as similar to EB non-CARs [17]. Especially, the acid generation mechanism changes markedly above the ionization potential of resist materials [16, 17, 18]. Below the ionization potential, acid generators are mainly decomposed from their excited states via direct excitation [23]. The differences in the acid generation mechanisms based on radiation chemistry and photochemistry were clarified with time-resolved spectroscopy and product analysis [17]. In depositing the energy of ionizing radiation into EB CARs, direct electronic excitation and ionization of acid generators are generally ineffective because the energy deposition mechanism is nonselective [16, 17]. Effective charge and energy migration/transfer from energy absorption sites to reaction sites, effective dissociative electron attachment, and geminate recombination (nanospace reaction)–as similar to EUV/EB non-CARs as described above are also important for achieving EUV/EB CARs with high sensitivity and high space resolution [17,18].

2. Sensitivity Enhancement Methods

The intensities of light sources remains only ~10
W in semiconductor companies/ research consortia sites. Separately, several hour continuous operation at 40-55 W in the prepulse mode for use as an internal test light sources at light source vendor site has been achieved in 2013. However, these intensities are much lower than the required EUV power of 250 W for achieving a 100 wafer per hour scanner throughput assuming photosensitive sensitivity of 15 mJ/cm² [24].

The sensitization of EUV resists to compensate for lower power of EUV light sources is one of the most critical challenges for HVM implementations of EUV lithography. The present paper describes the process of increasing the sensitivity of EUV/EB resists by one order without any loss in space resolution.

The conventional method of EUV/EB resist sensitization involves enhancing the pattern formation efficiency of EUV/EB CARs by clarifying the pattern formation mechanism of EUV/EB CARs. This is because the material design of CARs for ionizing radiation requires different knowledge based not on photochemistry but on radiation chemistry [17, 18]. The pattern formation efficiency is determined by the incident energy absorption efficiency, quantum yield of acids, and catalytic chain reaction efficiency. However, the energy absorption efficiency is limited by sidewall degradation [25, 26]. The quantum yield is limited by the secondary electron emission efficiency unless the catalytic chain reaction is incorporated into the acid generation process [27]. The efficiency of the catalytic chain reaction is limited by the diffusion-controlled rate of the chemical reaction [28, 29]. Therefore, for developing next-generation resists, pattern formation efficiency should be increased to a value close to the physical limit [18]. Following this approach, the performance of EUV resists has improved steadily year on year owing to global efforts [10-12, 30-32]. However, this orthodox approach is inadequate to compensate for the one order lower intensity of EUV light sources than the desired intensity.

An alternative method of EUV/EB resist sensitization is as follows. The use of acid amplifiers to increase acid generation by orders of magnitude has been suggested [33] but not yet applied to HVM. Recently, the application of acid amplification to EUV CARs was proposed [34]. An EUV resist loaded with an acid amplifier showed 25% higher sensitivity than the original formulation [35]. The first detailed and systematic study of the role of acid amplifiers in the two acid-generation steps of EB/EUV CARs loaded with acid amplifiers, i.e., initial acid generation by EB/EUV exposure and acid amplification reaction, employed both time-resolved pulse radiolysis and spectrophotometric titration methods [36]. Many factors have been found to disturb acid amplification [36]. Moreover, it was recently found experimentally that thermal diffusion in acid amplification leads to a problem similar to RLS trade-off [37]. Therefore, a new acid amplification reaction induced by non-thermal diffusion is required, as discussed later.

Given the shortcomings of the above methods, a third method of EUV/EB resist sensitization without loss in other important properties such as resolution and LER must be developed. Therefore, we propose a new process involving the combination of a novel lithography technique with a new type of resist. We employ a novel multi-exposure lithography technique involving at least one pattern exposure (EUV/EB/ArF) and one ultraviolet (UV) flood exposure. Here, we employ the combination lithography of EB pattern exposure with UV flood exposure (PF combination lithography) technique and photosensitized chemically amplified resist (PS-CAR), a new type of resist. We develop new sensitization enhancement mechanisms, including acid amplification by non-thermal diffusion at room temperature.

3. Experiment, Results, and Discussion

Figure 1 shows a comparison of (a) the conventional lithography process for HVM with (b) the new process. The new process involves the combination lithography of 1st pattern exposure and 2nd UV flood exposure (PF combination lithography) of a PS-CAR. The conventional and new processes are without and with, respectively, the 2nd UV flood exposure.
Figure 2 shows schematic drawing of (A) the acid generation in the chemically amplified resist (CAR) by the conventional pattern exposure and (B) the new acid generation process of PS-CAR by PF combination lithography. The new acid generation process of PS-CAR by PF combination lithography produces photosensitizer (PS) and acid by 1st low power pattern exposure. Acid amplification occurs owing to the 2nd intense UV flood exposure. After the 1st pattern exposure, the 2nd UV flood exposure induces acid only in the 1st pattern’s exposure area because PS-CAR has no absorption in the UV flood exposure wavelength region. This acid amplification is induced by the 2nd UV flood excitation of PS and non-thermal diffusion process at room temperature. The profile of the acid generated by the 2nd UV flood exposure is identical to the profile of the PS generated by the 1st pattern exposure.

The new processes can be applied to not only EB/EUV/ArF pattern exposure but also to other types of pattern exposure. However, EUV lithography technology requires this new sensitivity enhancement method very urgently, as described in 1.1. But 300 mm wafer EUV exposure experiment as 1st pattern exposure is not available for the first experiment of this kind of the essentially revolutionary method rising from laboratory curiosity. Both EB and immersion ArF are available, but EB is more widely available. The reaction mechanisms of EUV and Immersion ArF CARs are different, as described in 1.3. The differences between EB and EUV resists lie in their energy absorption processes: the energy absorption of EB and EUV resists are proportional to the electron density and linear absorption coefficients of resist materials, respectively. The difference in the acid yield of ionization between EB and EUV was simulated [18, 38]. Recently it was found that the resist sensitivity in the EUV/soft x-ray region can be evaluated from the exposure results at any wavelength in this region [39]. Furthermore, the difference between EB and EUV resists lie in their energy absorption processes: the energy absorption of EB and EUV resists are proportional to electron density and linear absorption coefficients of resist materials respectively. The resist sensitivities of EUV can be predicted easily from the exposure results of EB lithography [40]. Therefore, the reaction mechanism of the EUV pattern exposure–UV flood exposure combination lithography of PS-CAR can essentially be evaluated by EB pattern exposure–UV flood exposure combination lithography and PS-CAR. However, there are many technical differences and problems such as reduction projection and non-reduction projection exposure with and without mask.
The first high-sensitivity enhancement experiments were carried out with the 1\textsuperscript{st} EB pattern exposure–2\textsuperscript{nd} UV flood exposure combination (PF combination lithography) of a photosensitized chemically amplified resist (PS-CAR). The dependence of $E_0$ on UV flood exposure time is shown in Fig. 3. The sensitivity of the PS-CAR was improved by PF combination lithography. EB pattern exposure was performed using a 30 keV JSM-6500F EB exposure system (JEOL, beam current: 12.5 and 28 pA, <1E-4 Pa) with Beam Draw (Tokyo Technology). After the 1\textsuperscript{st} EB pattern exposure, the 2\textsuperscript{nd} flood UV exposures were performed at room temperature. The resulting sensitivity is more than 10 times higher compared with that of single EB exposure.

Sensitivity curves, and line and space patterns were observed using an atomic force microscope (AFM, Nano Navi II / SPA-300HV, Hitachi High-Tech Science). Two AFM pictures of the 75 nm line and the space pattern shown in Fig.4 were measured under identical positive tone PS-CAR, spin coat, prebake, PEB temperature and time, and development conditions. The difference lay in the dose of the 1\textsuperscript{st} EB pattern exposure and the presence or absence of the 2\textsuperscript{nd} UV flood exposure. Resist sensitivities were 77 and 8.8 μC/cm\textsuperscript{2} for single EB pattern exposure and PF combination lithography, respectively. This implies an about 9 times higher sensitivity without any loss of space resolution was achieved with PF combination lithography of PS-CAR than that with conventional EB single exposure lithography. The sensitivity and the resolution of the CARs share a tradeoff relationship, because a longer acid diffusion length is required to induce the necessary amount of chemical reactions when the acid concentration is reduced. This trade-off relation was simulated by different models [4, 41] and confirmed experimentally [10-12, 41]. The experimental results of high sensitization without any loss in resolution cannot be explained by the models based on the conventional single EB exposure processes [4, 41], but can be explained by the new process (PF combination lithography of PS-CAR).

4. Conclusion

An increase of more than one order in sensitivity without any loss of space resolution was achieved with PF combination lithography of PS-CAR than that with conventional single EB exposure lithography. The difference between EB and EUV resists lies in their energy absorption processes. The resist sensitivities of EUV can be predicted easily from the exposure results of EB lithography [40]. Therefore, the reaction mechanism of combination lithography of PS-CAR can be essentially evaluated with EB pattern exposure–UV flood exposure combination lithography and PS-CAR.

Sensitization of the EUV resist reduces the required EUV intensity and, in turn, the EUV source development cost, EUV exposure system price, radiation damages of EUV optical components, and production cost of semiconductor devices. This is despite the fact that the required EUV power will be achieved after some more years. The new sensitivity enhancement processes can be applied not only to EB/EUV/ArF pattern exposure but also to other types of pattern exposure. If the initial acid yield drastically increases with the same acid distribution at the present experiment, the RLS trade-off is dramatically improved according to excellent RLS simulation model given by Gallatin [4]. The PF...
combination lithography of PS-CAR will improve not only sensitivity and RLS trade-off but also resolution and line edge roughness including photon shot noise, in the near future in combination with sophisticated new scientific ideas.

Acknowledgements
This work was partially supported by “Nanotechnology Platform Project (NOF in Osaka Univ.)” [F-13-OS-0001, S-13-OS-0001] of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The authors are grateful to Dr. T. G. Oyama for her valuable assistance and discussions, and to Mr. D. N. Tuan and Mr. C. Q. Dinh for their valuable assistance.

References
37. S. Tagawa, D. N. Tuan, C. Q. Dinh, S. Enomoto, unpublished data.