State-of-the-art EUV materials and processes for the 7 nm node and beyond

Elizabeth Buitrago¹, Marieke Meeuwissen², Oktay Yildirim², Rolf Custers², Rik Hoefnagels², Gijsbert Rispens², Michaela Vockenhuber¹, Iacopo Mochi¹, Roberto Fallica¹, Zuhail Tasdemir¹ and Yasin Ekinici¹

¹Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland,

²ASML Netherlands B.V., De Run 6501, 5504 DR Veldhoven, The Netherlands

ABSTRACT

Extreme ultraviolet lithography (EUVL, $\lambda = 13.5$ nm) being the most likely candidate to manufacture electronic devices for future technology nodes is to be introduced in high volume manufacturing (HVM) at the 7 nm logic node, at least at critical lithography levels. With this impending introduction, it is clear that excellent resist performance at ultra-high printing resolutions (below 20 nm line/space L/S) is ever more pressing. Nonetheless, EUVL has faced many technical challenges towards this paradigm shift to a new lithography wavelength platform. Since the inception of chemically amplified resists (CARs) they have been the base upon which state-of-the-art photoresist technology has been developed from. Resist performance as measured in terms of printing resolution (R), line edge roughness (LER), sensitivity (D or exposure dose) and exposure latitude (EL) needs to be improved but there are well known trade-off relationships (LRS trade-off) among these parameters for CARs that hamper their simultaneous enhancement. Here, we present some of the most promising EUVL materials tested by EUV interference lithography (EUV-IL) with the aim of resolving features down to 11 nm half-pitch (HP), while focusing on resist performance at 16 and 13 nm HP as needed for the 7 and 5 nm node, respectively. EUV-IL has enabled the characterization and development of new resist materials before commercial EUV exposure tools become available and is therefore a powerful research and development tool. With EUV-IL, high-resolution periodic images can be printed by the interference of two or more spatially coherent beams through a transmission-diffraction grating mask. For this reason, our experiments have been performed by EUV-IL at Swiss Light Source (SLS) synchrotron facility located at the Paul Scherrer Institute (PSI). Having the opportunity to test hundreds of EUVL materials from vendors and research partners from all over the world, PSI is able to give a global update on some of the most promising materials tested.

Keywords: EUV lithography, CAR, Non-CAR, photoresist, interference lithography, 5nm node, 3nm node

1. INTRODUCTION

As significant progress has been made on the productivity and stability of extreme ultra-violet lithography (EUVL) systems and lithographic performance milestone specifications continue to be met, it is now predicted that EUVL is to be introduced in high volume manufacturing (HVM) for the production of 7 nm node electronic devices by 2020 [1]. High performance EUVL materials to resolve features down to 16 nm and 13 nm HP are needed and intense efforts are made for their development. Moreover, the demonstration of EUVL for printing with a resolution useful for many future technology nodes is furthermore paramount for its successful introduction into the HVM scheme. Therefore, patterning capabilities beyond 13 nm HP is also of significant interest.

Resist performance is characterized by its printing resolution (R), line width roughness (LWR), sensitivity (S) (or best energy (BE), dose to size), and exposure latitude (EL). Nonetheless, it is well known that for chemically amplified resists (CARs), there are trade-off relationships (LRS trade-off) among these that hamper the simultaneous improvement of these parameters. For this reason, different methodologies to enhance EUV resist sensitivity [2, 3], LWR and resolution are being investigated. In the past, the industrial focus has been on the research and development of CARs. At PSI, for instance, we have had the opportunity to test many state-of-the-art CARs from vendors from all around the world and several promising candidates that simultaneously meet sensitivity, LWR and EL high performance requirements for the 7 and 5 nm logic node (16 nm and 13 nm half-pitch HP, respectively) for HVM have been identified for further investigation [2-4]. Although several CARs have been additionally found to be excellent performing down to 13 nm HP and even well resolved down to 12 nm and 11 nm, it has been demonstrated that alternative material solutions for HVM performance for upcoming technology nodes are still needed [2-4]. For that reason, the performance of alternative resist platforms such as Sn-based metal organic resist from Inpria Corp. and a negative tone CAR molecular resist from Irresistible Materials have been previously investigated [5, 6]. A performance update on those materials is presented here. In this paper we focus on alternative materials for 13 nm HP resolution and below and also in here we present different rinse materials that have been able to improve the performance of CARs in terms of sensitivity and LWR for future technology nodes.

2. METHODS

In this study, EUV-IL exposures were performed over a period of several months in 2016 in which different state-of-the-art resists and rinse materials for sensitivity and pattern collapse improvement from different vendors all around the world were tested. Two state-of-the-art alternative resist platforms (Sn-based metal organic resist from Inpria Corp. and a negative tone CAR molecular resist from Irresistible Materials) were furthermore investigated as follow up from previous results. The naming convention is consistent (*i.e.*, UL1 = underlayer 1, R1 = resist 1). Different underlayer formulations from different vendors may also have been used. The type of resist or underlayer and process conditions (resist and underlayer thickness, post-exposure bake (PEB), post-apply bake (PAB) temperature and process time) were determined by the different resist suppliers. CAR development was performed in a semiautomatic tool (SUSS Microtech) that includes a 30 second 2.38% TMAH dispense step, different rinse materials were furthermore investigated. Reference exposures using our reference resist and underlayer material R1UL1 were regularly performed.

SEM images of the resist patterns were obtained using a SEM Carl Zeiss SUPRA 55VP. The in-lens detector with a scanning speed of 10 seconds was used. The acceleration voltage and aperture size was set to 1 kV and 7.5 μ respectively to minimize electron beam damage and get surface information. The magnification and working distance are both kept constant at 400000 and ~ 3 mm, respectively. The CD and LER values are obtained from the analysis performed with commercially available modeling software (SuMMIT $\text{\textregistered}$).

The performance of the different materials was evaluated using EUV interference lithography (EUV-IL) at the Swiss Light synchrotron facility located at the Paul Scherrer Institute [7]. The technique has been previously described in detail elsewhere [8]. EUV-IL uses a mask with transmission-diffraction gratings that is illuminated by a spatially coherent beam of EUV light ($\lambda = 13.5$ nm) [4, 9]. Periodic images are produced by the interference of two or more diffracted beams with first-order diffracted beams overlapping at a certain distance from the mask. The aerial image has a period P that is given as (Eq. 1):

$$P = \frac{\lambda}{2 \sin \theta_m} = \frac{P_g}{2m} \quad (\text{Equation 1})$$

where θ_m denotes the diffraction angles and m the diffraction order, and P_g is mask grating period, that is half of the mask grating period P_g when a pair of first-order ($m = 1$) diffraction interference beams are used. The interference lithography masks used here consist of SiO_x (from HSQ, hydrogen silsesquioxane) gratings fabricated on 100-nm-thick Si_3N_4 membranes and a gold photon-stop covering all areas around the gratings to absorb the zeroth-order beam just as described elsewhere [4, 10]. Dose-on-mask (mJ/cm^2) is determined from the measured flux (mW/cm^2 , measured before and after the exposure) and exposure time (s). The corrected dose-on-wafer values are calculated based on predetermined

tool-factors (ratio between the dose-on-mask and dose-on-wafer) proportional to the mask efficiency as previously described [11].

A major strength of the present study is the fact that all the exposures are performed with the same tool and all the analysis is carried out with the same SEM tool and images are processed with the same software and its parameters. This approach makes a sound assessment and comparison of different resists possible. We note that in particular LWR values are very sensitive to the tool and analysis parameters and our consistent approach is the only way to judge on the relative performance of different resists.

3. CAR EVALUATION AND COMPARISON AT 16 AND 13 NM RESOLUTION AND BEYOND

Different state-of-the-art positive tone CARs have been evaluated by EUV-IL with the aim of resolving (L/S) patterns down to 16 nm and 13 nm HP for HVM and below for future technology nodes. The graphs presented in Fig. 1 show the CD and LWR vs. dose of a two selected CARs with different processing conditions. Dose-to-size values (best energy, BE) for 1:1 L/S patterns were determined at 16 nm HP for two highly performing resists; our reference R1, and R2 when treated with two different rinse materials after development. In Fig. 2 we can see the corresponding line/space SEM images as the dose increases for two highly performing CARs when treated with a new rinse material for LWR and sensitivity improvement. R2 is a chemically amplified resist that has a similar performance in comparison to the reference. UL1R2 was, in fact, selected to be tested with this new highly interesting rinse material because it shows a particularly low LWR (<4 nm) at 16 nm in comparison to R1. It is clear that when processing this resist using this new rinse after development, both the LWR and the best energy are furthermore reduced while maintaining a relatively high exposure latitude. This was observed for a wide range of CARs tested. We also tested these materials down to 11 nm HP. We have observed well-resolved patterning down to 12 nm HP with some pattern collapse and pinching in all cases. Furthermore, this highly performing resists R2 is interesting down to 13 nm HP when the standard rinse material is used as it also shows a relatively high exposure latitude as seen in Table 1 for this HP as well as low LWR values even though the BE is still higher in comparison to the reference resist. This material with the new rinse is also interesting down to 14 nm HP due to the extra low LWR values found but no exposure latitude was found unfortunately at 13 nm HP and below.

Figure 1. Average CD vs. dose (left) and average LWR vs. dose (right) graphs for two high performing resists (R1 and R2) as processed with different rinse materials.

Figure 2. SEM (L/S) images as the dose increases for two highly performing CARs when treated with a new rinse material for LWR and sensitivity improvement at 16 nm HP resolution. UL1R1 is the reference resist.

Table 1. BE, EL, LER and Z-factors for the high performing resists (R1 and R2) as processed with different rinse materials at HP = 16 nm. The same UL material was used. UL1R1 is the reference resist process.

Name	BE (mJ/cm ²)	EL (%)	LWR (nm)	Z-factor
UL1R1-std rinse (Ref)	38.5±6.3	22.6±5.2	6.5±1.3	2.9E-08
UL1R2-std rinse	44.7	30	3.7	1.3E-08
UL1R2-new rinse	40.1	24	2.9	6.8E-09

We have also investigated negative tone chemically amplified molecular resists from Irresistible materials. They consist of a molecular resin, a cross-linker, a photoacid generator, and a quencher. In comparison to Fullerene-based resists, which have also been shown to be promising candidates for EUV lithography, it is possible to synthesize such materials with a cleaner and easier formulation process while still maintaining many of the same interesting properties and high resist performance characteristics. We had the opportunity to test three different molecular resist formulations; two of them differ in the quencher concentration (xMT) used and the a third ExMT was designed for enhanced crosslinking and increased sensitivity. The number of functional groups on the resin molecule xMT molecule is doubled and by doing so, the number of cross-linking sites (on the molecular resin molecule) is increased to improve the sensitivity of the material. The xMT materials have been previously investigated [5, 6] by EUV IL. The LWR and CD vs. BE values obtained from these Irresistible Materials are shown in Fig. 4 from well resolved patterns at 16 nm HP.

Figure 4. Average CD vs. dose and average LWR vs. dose graphs for the high performing resists (R1 and R2) as processed with different rinse materials.

Figure 5 shows the corresponding line/space SEM images as the dose increases when using the different molecular resist formulations down to 16 nm HP. We have well resolved patterning down to 16 nm HP. The resist performance improved from last year results (xMT-0801: BE < 30 mJ/cm², LWR < 6.5 nm and EL > 15%) [3]. Especially these two different resist formulations were found to be very interesting due to their extremely low best energy values and high exposure latitudes down to 14 nm HP as can be seen in Table 2.

Figure 5. SEM (L/S) images showing the different Irresistible Materials tested at 16 nm HP resolution.

Table 2. BE, EL, LWR and Z-factors for the high performing molecular resists materials tested at HP = 14 and 16 nm.

Name	HP	BE (mJ/cm ²)	LWR (nm)	Z-factor
EX1-213-010-25nm	16	20.5	4.5	1.4E-08
EX1-213-010-25nm	14	21.3	4.3	8.7E-09
xMT-213-200-25nm (5% Quencher)	16	34.8	3.0	1.1E-08
xMT-213-200-25nm (5% Quencher)	14	32.9	2.9	7.7E-09
xMT-213-210-25nm (2% Quencher)	16	24.2	3.7	9.8E-09
xMT-213-210-25nm (2% Quencher)	14	22.7	4.1	7.3E-09

We have also tested Sn-based metal-organic resists from Inpria, where its performance has been reported previously [3-5, 12]. This is a negative tone resist that forms a stable oxide after exposure. This is a high resolution resist that features high absorbance in the EUV range and high etch resistance into an organic layer. These Sn-based metal organic resist have already been shown to achieve every high exposure latitude values of over 30% at 16 nm. In here, we investigated two different formulations of the Inpria resist, YA and YF. YA was furthermore investigated with and without an underlayer. The underlayer exposure was repeated as we were missing the lower dose range, unfortunately we went too low and we missed the middle part, so we had to estimate our results. Nonetheless, it is clear from the SEM images and the calculated values that these resists are highly performing with very high exposure latitudes and very low LWR values. YA in particular, with and without the use of an underlayer was found to have best energy (BE) values now comparable to those of our chemically amplified reference resist. Then we tested these materials down to 11 nm HP. And in fact we find that again both materials are highly performing down to 12 nm HP with high Exposure latitude for such high resolutions of over 10% and low LWR values below 3 nm. YA with an underlayer has the lowest BE down to 12 nm HP and we even find an exposure latitude down to 11 nm of around 9% for this material. This is the very first time that we find such high ELs down to 11 nm HP.

Figure 6. Average CD vs. dose and average LWR vs. dose graphs for Inpria materials tested down to 12 nm HP.

Figure 7. SEM (L/S) images showing Inpria materials tested down to 11 nm HP.

Table 3. BE, EL, LWR and Z-factors for Inpria materials tested down to 12 nm HP.

Name	HP	BE (mJ/cm2)	EL (%)	LWR (nm)	Z-value
YF-18nm	13	64.0	25	2.0	4.2E-09
YF-18nm	12	80.1	15	2.5	5.5E-09
YA-18nm	13	64.6	19	1.8	3.3E-09
YA-18nm	12	67.2	11	1.7	2.6E-09
YA-18nm	11	71.0	8	3.4	7.4E-09
UL3-YA-18nm	13	55.6	13	2.4	4.2E-09
UL3-YA-18nm	12	57.6	14	3.9	7.5E-09

4. CONCLUSIONS

In this study we have identified several promising candidates that meet high performance characteristics down to 16 nm HP (7 nm node). It is clear that alternative processes, materials are needed for the 5 nm and beyond. In particular, new rinse materials were shown to improve BE and LWR for CARs down to 14 nm HP (for UL1R2). Further improvements are needed for the extendibility of CARs at sub 16nm HP. Promising molecular resists materials EX1-213-010 and xMT-213-210 that have very low BE < 25 mJ/cm² and apparent high EL > 20% down 16 nm HP were also investigated. It is observed that LWR improved in subsequent tests. Finally, both Sn-based resist formulations (YA and YF, 18 nm thickness) tested were found to be highly performing with extremely high EL >45%, low LWR values ~ 2.3 nm and sensitivities comparable to CARs ~ 40 mJ/cm² at 16 nm HP. Sn-based resists highly performing down to 11 nm HP. YA has high EL ~ 8% down to 11 nm HP, LWR ~ 4.2 nm and BE ~ 70 mJ/cm². In comparison, last year it was shown that Sn-based resist (25 nm thickness) at 13 nm HP had already high EL ~ 11.8%, LWR ~ 3.3 nm, BE > 75 mJ/cm².

5. ACKNOWLEDGEMENTS

We would like to acknowledge Markus Kropf, and Daniel Fan for their technical expertise and assistance. We thank our various materials suppliers greatly. Part of this work was performed at the Swiss Light Source in the Paul Scherrer Institute.

REFERENCES

- [1] C. Smeets, "EUV Lithography Industrialization Progress," in *EUVL Symposium*, Hiroshima, 2016.
- [2] T. Nagai, H. Nakagawa, T. Naruoka, S. Tagawa, A. Oshima, S. Nagahara, *et al.*, "Novel high sensitivity EUV photoresist for sub-7nm node," 2016, pp. 977908-977908-7.
- [3] E. Buitrago, S. Nagahara, O. Yildirim, H. Nakagawa, S. Tagawa, M. Meeuwissen, *et al.*, "Sensitivity enhancement of chemically amplified resists and performance study using EUV interference lithography," 2016, pp. 97760Z-97760Z-15.
- [4] E. Buitrago, O. Yildirim, C. Verspaget, N. Tsugama, R. Hoefnagels, G. Rispen, *et al.*, "Evaluation of EUV Resist Performance Using Interference Lithography," in *SPIE Advanced Lithography*, 2015, pp. 94221S-94221S-13.
- [5] E. Buitrago, O. Yildirim, R. Fallica, A. Frommhold, C. Verspaget, N. Tsugama, *et al.*, "The road towards single digit nanometer resolution patterning in mass production: State-of-the-art EUV resists platforms compared," in *EUVL Symposium*, Maastricht, The Netherlands, 2015.
- [6] A. Frommhold, A. G. Brown, R. E. Palmer, T. Lada, and A. P. Robinson, "Organic hard masks utilizing fullerene derivatives," in *SPIE Advanced Lithography*, San Jose, 2015, pp. 94250L-94250L-8.
- [7] Y. Ekinici, M. Vockenhuber, M. Hojeij, L. Wang, and N. M. Mojarad, "Evaluation of EUV resist Performance with Interference Lithography Towards 11 nm Half-Pitch and Beyond," in *SPIE Advanced Lithography*, San Jose, 2013, pp. 867910-867910-11.
- [8] E. Buitrago, T. S. Kulmala, R. Fallica, and Y. Ekinici, "Chapter 4 - EUV lithography process challenges," in *Frontiers of Nanoscience*. vol. Volume 11, R. Alex and L. Richard, Eds., ed: Elsevier, 2016, pp. 135-176.
- [9] N. Mojarad, D. Fan, J. Gobrecht, and Y. Ekinici, "Broadband Interference Lithography at Extreme Ultraviolet and Soft X-ray Wavelengths," *Optics Letters*, vol. 39, pp. 2286-2289, 2014.
- [10] E. Buitrago, R. Fallica, D. Fan, T. S. Kulmala, M. Vockenhuber, and Y. Ekinici, "SnOx high-efficiency EUV interference lithography gratings towards the ultimate resolution in photolithography," *Microelectronic Engineering*, vol. 155, pp. 44-49, 2016.
- [11] Y. Ekinici, M. Vockenhuber, B. Terhalle, M. Hojeij, L. Wang, and T. R. Younkin, "Evaluation of resist performance with EUV interference lithography for sub-22-nm patterning," in *SPIE Advanced Lithography*, 2012, pp. 83220W-83220W-11.
- [12] R. Fallica, J. K. Stowers, A. Grenville, A. Frommhold, A. P. G. Robinson, and Y. Ekinici, "Dynamic absorption coefficients of chemically amplified resists and nonchemically amplified resists at extreme ultraviolet," *Journal of Micro/Nanolithography, MEMS, and MOEMS*, vol. 15, pp. 033506-033506, 2016.