Studies on resolution with ZEP530A for EUV mask

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ABSTRACT

In this work, Zeon introduces the resolution with ZEP530A without PFAS restriction for dense L/S, iso-space and iso-line patterns on Si wafer by F7000S with VSB type in EB drawing equipment.
Zeon examined litho-performance at dense L/S in changing 3 kinds of developers. The new developer of ZED-K90 (R&D sample) with lower both viscosity and solubility enabled to get lower roughness and enhance the resolution than those of ZED-N60 and N70 on LER although the dose to size was getting higher. There were some pinching defects on the patterns by ZED-N60 due to too strong solubility. On the other hand, ZED-N70 and K90 can be less on them due to the appropriate solubility. Next, litho-performance with ZED-K90 at iso-space and iso-line patterns was evaluated. The resolution was at design CD18nm in iso-line pattern and at design CD12nm in iso-space pattern and it was the best resolution among 3 developers. Additionally, the LER and SER with ZED-90 got lower than those with ZED-N70. It was clarified that the combination of ZEP530A and ZED-N90 had the sufficient potential to both enhance litho-performance including the resolution in EB resists and utilize them for EUV mask.
Keywords: EB lithography; ZEP530A; Main chain scission type resists; PFAS restriction;

1. INTRODUCTION

EUV lithography (EUVL) with NA:0.33 EUV scanner in high volume manufacturing has been used and expanding to several technology nodes [1]. Additionally, EUV scanner with NA:0.55 for high-NA generation will start to utilize several evaluations from 2H 2023 by publishment of ASML. Therefore, masks for EUVL are expected to increase following by expanding the market in EUVL. EUV masks have been required on tighter patterns as the semiconductor's miniaturization is going. So, it is important for EB resists to have the good resolution for kinds of patterns such as dense L/S, iso-line, iso-space and contact holes as well. Alternatively, ZEP520A with main chain scission reaction developed by Zeon has been used in electron beam lithography for years [2] [3] [4] [5], providing for simple composition (polymer and organic solvent), the long shelf life, and then good litho-performance by organic solvents. ZEP530A was developed as maintaining unique characteristics of ZEP520A in order to improve litho-performance further for EB lithography (EBL) in 2019. Additionally, ZEP530A and ZED series for developers are materials which don't get the influence against PFAS restriction because they don't contain any both fluorine elements and functional groups such as -CF3 and -CF2 and so on.

In this work, we introduce the studies on the resolution with ZEP530A and 3 kinds of developers such as ZED-N60, N70 and K90 in EBL. Concretely, Zeon has been evaluating the resolution for dense L/S, Iso-space and Iso-line patterns on Si wafer by F7000S with VSB type in EB drawing equipment (ADVANTEST) in cooperation with imec. Litho-performance was evaluated at the drawing area of 25um x 25um in order to check the effect of back scattering by e-beam.

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1-1. Fundamentals of Zeon Resists

High performance of Zeon resists, positive-tone, is based on a unique polymer, which is designed as a non-CAR, main chain scission type resists. Figure 1 is the polymer structure including ZEP530A for EB lithography product. The polymer is a copolymer of an acrylate monomer and a styrene monomer. Organic solvents are used for Zeon resists, developers and rinsing agents. The benefits of Zeon resists are that first, they have simple composition of just polymer and organic solvent. Polymers and reaction points (X) exist in film uniformly. So, Zeon resists don't have any metals with high EUV absorption. Second, they have long-term stability of films during litho process with delays as the results were indicated at this conference in 2023 [6].

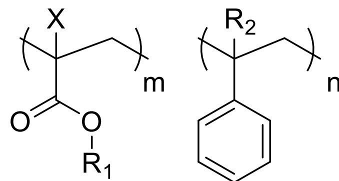


Figure 1 – Fundamental polymer structure on Zeon resists including ZEP530A
Left: Acrylate monomer, Right: Styrene monomer

1-2. Challenges on Resolution of ZEP530A

Figure 2 shows the challenges on ZEP series including ZEP530A. They enable to have good roughness and resolution with relax patterns among dense L/S, iso-line and iso-space patterns due to less effects of back scattering from blanks and Si substrate during e-beam expose. On the other hand, it makes damages larger into unexposed area by back scattering as tighter pitch patterns especially. In the results, the lithography performance including the resolution at dense L/S and iso-line pattern gets worse by reducing film thickness, worse LER and collapsed pattern. In case of iso-space pattern, the resolution got worse due to remained scam and polymers in bottoms.

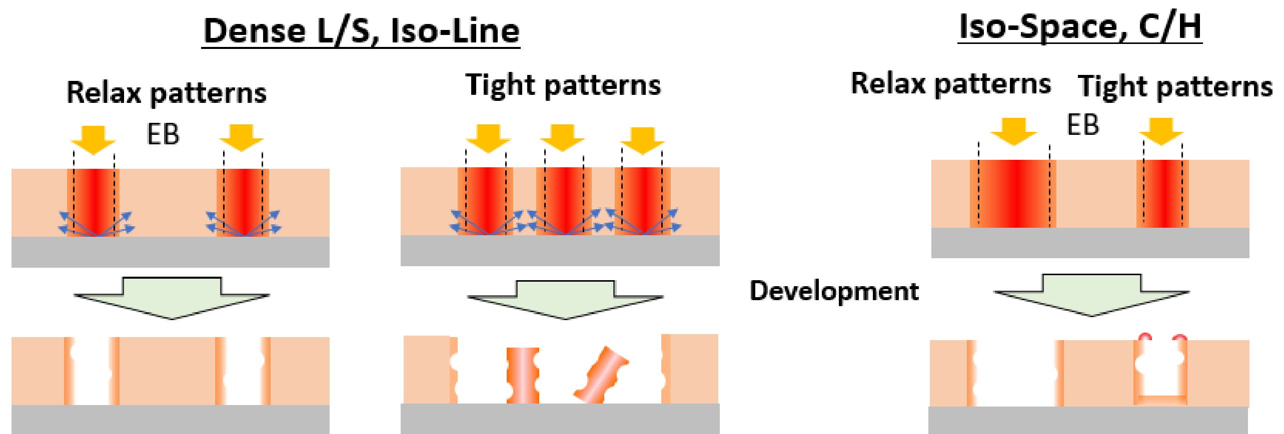


Figure 2 – Assumed causes of worse lithography performance in ZEP series

1-3. Concept to Improve Their Resolution of ZEP Series

In case of low dose on e-beam, polymers in exposed are with ZEP series decompose into their sizes from large to middle. The roughness got worse because they can dissolute into developer as figure 3(a). On the other hand, ZEP series theoretically continuous to degrade down to the monomer level. So, the size of polymers in exposed area gets small and it is expected that the roughness got better using by the low solubility of developer as figure 3(b).

On the other hand, it is maintained generally that CAR has performance limitation such as resolution due to saturation of PAG decomposition. So, Zeon considered that a higher dose leads to an improved LER with developers of low solubility beyond the limitations of CAR.

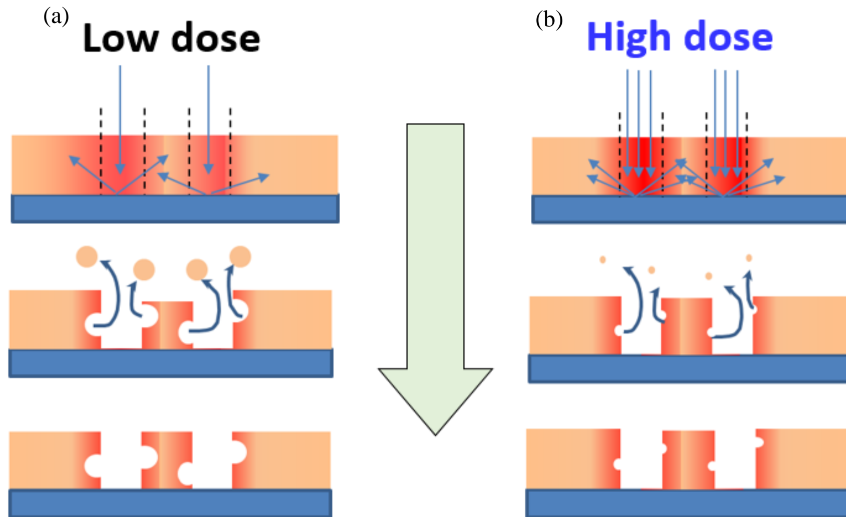


Figure 3 – Concept to improve their resolution of ZEP series

(a) Low dose, (b) High dose,

1-4. Approaches to Enhance the Resolution on ZEP530A

Zeon is conducting both approaches to improve litho-performance on Zeon resists as figure 4 and Table 1. At first, regarding resists for e-beam, Zeon developed the standard EB resists for ZEP520A series, and it is utilized for EBL mainly. On the other hand, it was getting litho-performance insufficient such as the resolution and defects as advancing the generations. Then, Zeon re-develop a new EB resist for ZEP530A series in order to improve them. Concretely, ZEP530A series have higher Mw and narrower Mw distribution on polymer properties than those of ZEP520A series for high resolution.

Second, regarding developers, Zeon has 4 kinds of developers as obeying usage applications. Their characteristics are as Table 1. ZED-N50 has so high solubility that sensitivity is very fast. But the resolution is not good because it is easy to generate bridges and pinching defects and so on the patterns. Basically, their viscosity is getting higher as the number of developer's name is increased. On the hand, ZED-K90, one of new developers, has low viscosity and solubility for ZEP530A series. Zeon conducted dissolution rate measurement (DRM) with EUV light at 20mJ/cm^2_dose by NXE3300B at imec (Figure 5). It was showed that the dissolution rate with ZED-N70 was at 31.7% and it with ZED-K90 was at 2.1% in case it with ZED-N60 at 100%.

By both effects on both polymer's properties of ZEP530A and lower solubility as ZED-K90, their gamma values on those contrast curves were enhanced as Figure 6 although their Eth got slower dose.

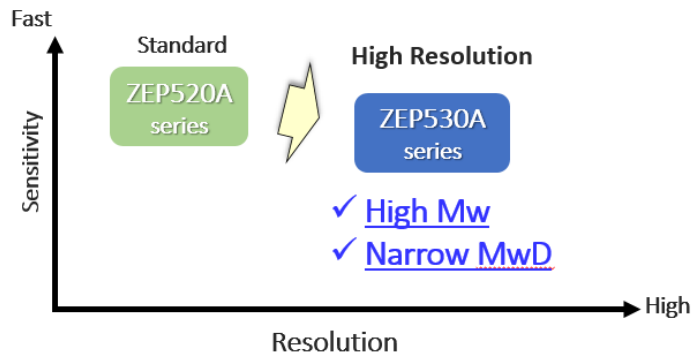


Figure 4 – Approaches to improve resolution on ZEP series

Table 1 – Developers for ZEP series

	Name	Status	Viscosity	Solubility
	ZED-N50	Commercial	81%	High
Examined	ZED-N60	Commercial	100%	
	ZED-N70	R&D	124%	
	ZED-K90	R&D	78%	Low

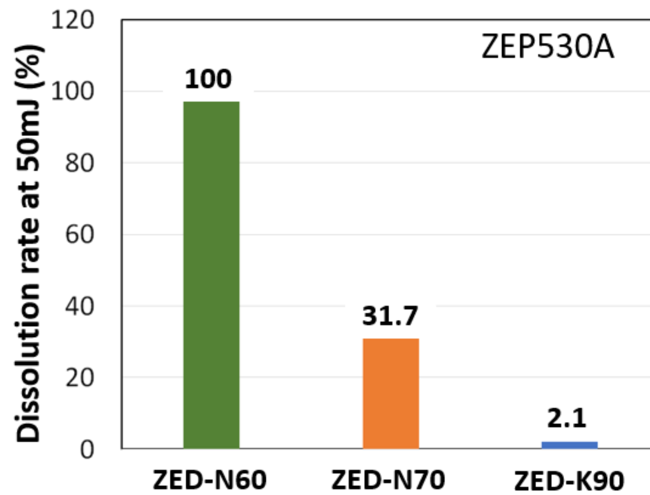


Figure 5 – Dissolution rates with ZEP530A and each developer by EUV in NXE3300B.

(Each rate was indicated the ratio in case of the rate with ZED-N60 at 100%)

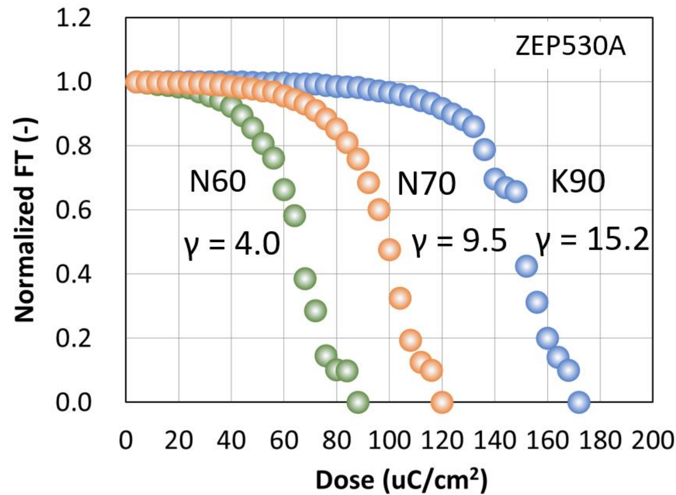


Figure 6 – Contrast curves with ZEP530A and each developer such as ZED-N60, N70 and K90 by e-beam

2. TEST CONDITIONS FOR EVALUATION ON EBL AT IMEC

Zeon evaluated lithography performance by e-bem as Table 2. Concretely, Zeon used the substrate with Si wafers of 300mm for the evaluation on the resolution because imec didn't have any equipment for blanks substrate for EBL. Resist was used by ZEP530A and the film thickness was adjusted at 60nm with at 130 deg.C for 3 minutes for prebaking process.

Zeon utilized F7000S with VSB type and accelerating voltage at 50 kV which was made by ADVANTEST at imec. Drawing field are decided by 25um x 25um as we can evaluate litho-performance with the effect of backscattering. Patterns was evaluated at dense L/S, iso space and iso line as Table 2. Zeon resists including ZEP530A don't need PEB process basically. Developers used ZED-N60, N70 and K90 as explained at previous section. Rinse agent was used by IPA (Isopropyl Alcohol).

Table 2 – Test conditions for evaluation on EB lithography at imec

Process	Conditions
Substrate	300mm Si wafer
Resist	ZEP530A (FT: 60nm)
Prebaking	130 deg C, 3 min., Hot Plate
EB exposure	**F7000S (VSB, ADVANTEST) at imec** Drawing Field : 25 um x 25 um Accelerating Voltage : 50 kV
Patterns (nm)	Dense L/S : P200-20 Iso Space : CD100-10 Iso Line : CD100-10
PEB	w/o
Development	Developers : ZED-N60, ZED-N70, ZED-K90
Rinse	Rinse Agent : IPA (Isopropyl Alcohol)

3. LITHO-PERFORMANCE BY EB AT DENSE L/S IN CHANGING DEVELOPERS

3-1. Lithography Performance at Dense L/S in Changing Developers

Table 3 and Figure 7 show litho-performance with ZER530A in varying developers such as ZED-N60, ZED-N70 and ZED-K90. Collars in sells of each space CD means that blue is normal without both collapsed patterns and defects such as bridges and pinching. Orange is with bridges and yellow is with collapsed patterns in each CDSEM.

In case of ZED-N60 and N70, their minimum resolution was at 20nm design HP. On the other hand, it with ZED-K90 was at 18nm design HP. Zeon figures that the effect with low viscosity with ZED-K90 to prevent the collapsed patterns. Then, the higher dose is, the lower LER is as Zeon aimed by the concept.

Table 3 - Lithography performance in varying both developers and pattern designs

No pattern / Bridge / Normal / Collapse

Design HP	Dose (μC/cm²)	ZED-N60 140	ZED-N60 150	ZED-N60 160	ZED-N70 180	ZED-N70 190	ZED-N70 200	ZED-K90 260	ZED-K90 275	ZED-K90 290
24nm	Space CD (nm)	21.93	24.11	25.67	22.76	24.12	25.63	21.1	23.26	24.71
	LER (nm)	3.03	2.77	2.84	2.84	2.62	2.67	2.64	2.44	2.41
	SEM									
22nm	Space CD (nm)	19.14	21.64	23.4	20.27	21.62	23.26	18.41	20.87	22.47
	LER (nm)	3.5	2.96	2.93	2.94	2.6	2.64	3.14	2.48	2.54
	SEM									
20nm	Space CD (nm)	16.85	19.14	21.38	17.76	19.11	24.01	16.31	18.52	20.76
	LER (nm)	4	3.25	4.23	3.35	2.75	5.49	3.56	2.55	4.23
	SEM									
18nm	Space CD (nm)	14.85	16.42	18.97	14.85	16.42	18.97	14.28	15.73	
	LER (nm)	4.32	4.04	5.61	4.32	3.65	0	3.99	3.28	
	SEM									

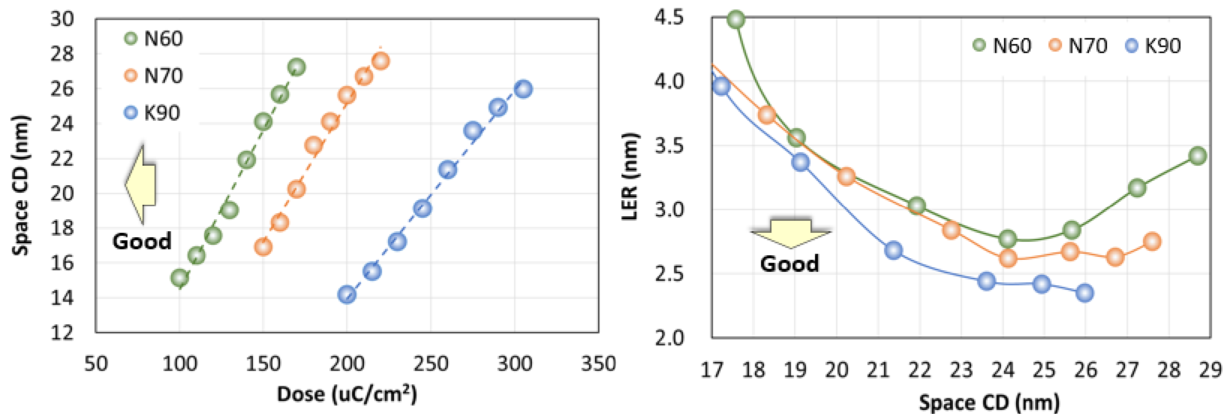


Figure 7: Lithography performance in changing developers at design hp24nm dense L/S

3-2. Process Window at Dense L/S between ZED-N70 and ZED-K90

Table 4 shows the process window with ZEP530A, ZED-N70 and ZED-K90 at dense L/S. Collars in sells of each space CD means that blue is normal without both collapsed patterns and defects such as bridges and pinching. White is no patterns. Orange is with bridges and yellow is with collapsed patterns in each CDSEM. Process window with ZED-K90 which had normal patterns got wider than that of ZED-N70. The minimal resolution with ZED-N70 was at 17.8nm and it with ZED-K90 was at 15.7nm. Therefore, the resolution with ZEP530A enabled to be enhanced using by high dose, low solubility and viscosity at dense L/S patterns.

Table 4 – Process window of dense L/S with ZED-N70 and ZED-K90

Legend: No pattern / Bridge / Normal / Collapse

ZED-N70

	Designed Space CD											
uC/cm^2	10	12	14	16	18	20	22	24	30	40	50	100
150					12.9	14.2	15.3	16.9	21.4	30.2	39.8	84.7
160					13.4	14.9	16.4	18.3	24.3	34.9	44.8	91.7
170					14.3	15.9	17.8	20.2	27.3	37.7	47.5	95.3
180					15.2	17.8	20.3	22.8	29.3	39.5	49.5	98.0
190					16.9	19.1	21.6	24.1	30.5	40.8	50.9	99.7
200						24.0	23.3	25.6	31.8	42.1	52.0	100.9
210							25.9	26.7	32.9	43.3	53.2	102.1
220							28.6	27.6	34.2	44.4	54.3	103.5
230								30.4	35.2	45.8	55.6	104.7

ZED-K90

	Designed Space CD (nm)											
uC/cm^2	10	12	14	16	18	20	22	24	30	40	50	100
200					13.6	13.8	13.5	14.3				
215					12.2	13.0	14.3	15.6	19.6	26.7	34.5	74.9
230					13.2	13.8	15.5	17.3	22.1	32.6	42.2	88.0
245					13.3	14.9	16.9	18.8	25.6	37.0	45.9	93.9
260					14.3	16.3	18.4	21.1	27.2	27.9	47.5	96.2
275					15.7	18.5	20.9	23.3	29.4	39.5	50.7	98.1
290						20.8	22.5	24.7	30.7	40.8	52.0	99.7
305							23.7	26.0	31.9	42.2	53.4	100.8
320								26.9	33.3	43.5	53.4	102.3

4. LITHO-PERFORMANCE BY EB AT ISO LINE AND SPACE IN CHANGING DEVELOPERS

4-1. Lithography Performance at Iso Line and Iso Space with ZEP530A and ZED-K90

Table 5 and figure 8 show the litho-performance with ZER530A in varying developers such as ZED-N60, ZED-N70 and ZED-K90. Collars in sells of each space CD means that blue is normal without both collapsed patterns and defects such as bridges and pinching. Orange is with bridges and yellow is with collapsed patterns in each CDSEM. the minimum resolution at iso-line was at 20nm design CD and the minimum resolution at iso-space was at 12nm design CD. Their roughness on LER and SER with ZED-K90 was lower than that of ZED-N70.

Table 5 – Lithography performance with ZEP530A and ZED-K90 at iso-line and iso-space patterns

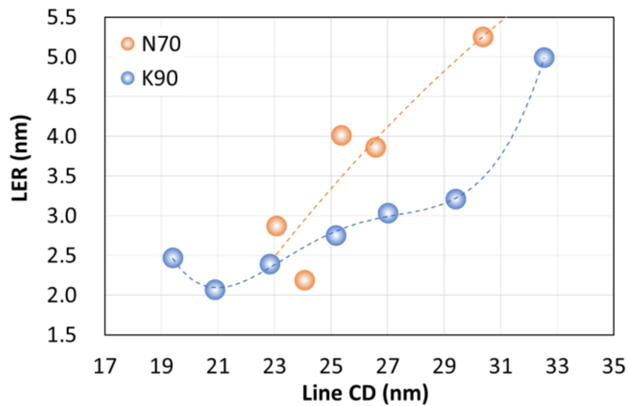
ZED-K90

Iso-Line (FT: 60nm)

Design CD	Dose (µC/cm^2)	230	240	250	260
24nm	Line CD (nm)	25.18	22.83	20.89	19.4
	LER (nm)	2.75	2.39	2.07	2.47
	SEM				
22nm	Line CD (nm)	23.49	20.99	19.24	46.23
	LER (nm)	3.25	2.2		
	SEM				
20nm	Line CD (nm)	21.45	19.37		
	LER (nm)	2.79	2.84		
	SEM				
18nm	Line CD (nm)	19.24	44.02		
	LER (nm)	2.96			
	SEM				

Iso-Space (FT: 60nm)

Design CD	Dose (µC/cm^2)	375	400	425	450	475
16nm	Space CD (nm)	13.63	14.56	15.94	16.94	17.6
	SER (nm)	2.81	2.21	1.97	1.84	1.66
	SEM					
14nm	Space CD (nm)		12.61	13.44	14.64	15.58
	SER (nm)		2.8	2.26	2.01	1.96
	SEM					
12nm	Space CD (nm)		13.02	13.35	14.43	15.42
	SER (nm)		2.72	1.87	1.88	1.87
	SEM					
10nm	Space CD (nm)					
	SER (nm)					
	SEM					



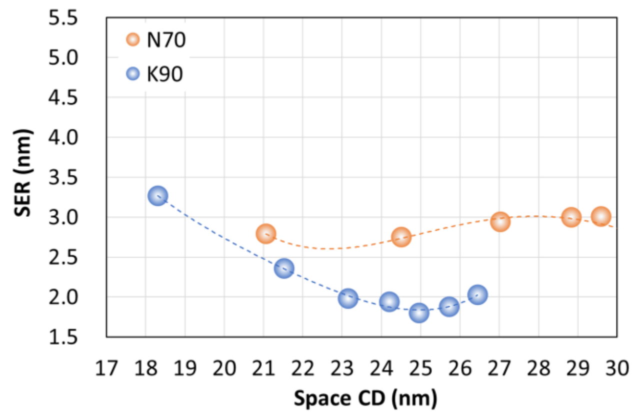


Figure 8: Lithography performance with ZEP530A, ZED-N70 and ZED-K90 at hp24nm of iso-line and iso-space

4-2. Process Window with ZEP530A and ZED-K90 at Iso-Line and Iso-Space

Table 6 shows the process window with ZEP530A and ZED-K90 at iso-line and iso-space. Collars means as same as section 3. Process window which had normal patterns at iso-space got very wider especially. The minimal resolution with iso-line was at 19.2nm and it at iso-space was at 14.4nm. Therefore, the resolution with ZEP530A enabled to be enhanced using by high dose, low solubility and viscosity as ZED-90 as same as dense L/S patterns.

As the below process window of iso-space, the combination with ZEP530A and ZED-K90 is good at iso-space, especially. Therefore, it can be utilized at iso-space specially for good litho-performance if we could separate the litho-process between L/S, iso-line and iso-space pattern.

Table 6 – Process window with ZEP530A and ZED-K90 between iso-line and iso-space

Legend: No pattern / Bridge / Normal / Collapse

Iso-Line

Dose	Designed Line CD (nm)											
uC/cm^2	10	12	14	16	18	20	22	24	30	40	60	100
190	21.6	24.2	26.3	29.8	31.9	34.1		39.0	43.7	50.4	75.7	
200		20.1	22.1	24.7	27.0	29.1	31.0	32.5	39.4	49.3	70.6	
210			19.5	21.7	22.9	25.3	27.7	29.4	35.1	45.2	66.2	130.4
220				18.9	20.5	23.5	25.6	27.0			62.6	116.8
230				28.4	19.2	21.5	23.5	25.2	30.8	40.7	61.0	105.6
240					44.0	19.4	21.0	22.9	28.9	38.7	58.8	99.2
250							19.2	20.9	27.8	37.1	57.0	95.0
260							46.2	19.4	32.2	35.1	55.0	91.4
270								33.6	44.0	41.3	53.4	88.3

Iso-Space

Dose	Designed Space CD (nm)											
uC/cm^2	10	12	14	16	18	20	22	24	30	40	50	100
350					14.1	15.4	17.6	20.6		38.8	56.5	95.5
375				13.6	14.9	17.8	20.2	22.3	28.2	38.0	58.1	96.8
400		13.0	12.6	14.6	17.0	19.2	21.5	23.6	28.9	39.2	58.9	98.0
425		13.4	13.4	15.9	18.2	20.3	22.5	24.4	29.9	38.8	59.6	99.0
450		14.4	14.6	16.9	18.8	21.1	22.9	24.9	30.7	40.5	60.3	99.4
475		15.4	15.6	17.6	19.7	21.8	23.6	25.6	31.1	41.2	60.9	100.2
500		16.2	16.2	18.2	20.3	22.3	24.1	26.4	31.8	41.7	61.5	100.8
525		16.7	16.8	18.7	20.7	22.8	24.7	26.7	32.3	42.3	61.9	101.3
550		17.1	17.2	19.1	21.2	23.1	25.2	27.4	32.8	42.6	62.7	102.2

5. CONCLUSIONS

In this work, Zeon studied the lithography performance including the resolution with ZEP530A in changing developers on Si wafers. Developer, ZED-K90 with low solubility and viscosity, has demonstrated better LER and resolution margin due to less collapsed patterns than those of ZED-N60 and ZED-N70 like Zeon's concept. It was clarified that the combination of ZEP530A and ZED-N90 had the sufficient potential to both enhance litho-performance including the resolution in EB resists and utilize them for EUV mask.

6. REFERENCES

[1] R.-H. R. Kim, "EUV insertion strategy into logic technology on the horizon of scaling paradigm change", Proc. SPIE **10957**, 1095706 (2019); doi: 10.1117/12.2516524

[2] K. Koshelev, M. A. Mohammad, T. Fito, K. L. Westra, S. K. Dew and M. Stepanovaa, "Comparison between ZEP and PMMA resists for nanoscale electron beam lithography experimentally and by numerical modeling," J. Vac. Sci. Technol. B **29**, 06F306 (2011); doi: 10.1116/1.3640794

[3] Nakajima A., Kozawa T., Hoshino M., Hashimoto M. , "Material design for the improvement of ZEP520A performance," PHOTOMASK TECHNOLOGY 2018 **10810**

[4] Ayako Nakajima, Manabu Hoshino, Masakazu Hashimoto, Takahiro Kozawa, "Effects of molecular weight and dispersity on performance of main-chain-scission-type resist," Japanese Journal of Applied Physics **58(2)** 020909-1-020909-4

[5] R. Fallica, D. Kazazis, R. Kirchner, A. Voigt, I. Mochi, H. Schift and Y. Ekinci, "Lithographic performance of ZEP520A and mr-PosEBR resists exposed by electron beam and extreme ultraviolet lithography", J. Vac. Sci. Technol. B **35**, 061603 (2017); doi: 10.1116/1.5003476

[6] Akihide Shirotori, Manabu Hoshino, Makoto Fujimura, Sin Fu Yeh , Hyo Seon Suh, Danilo De Simone, Geert Vandenberghe, Hideaki Sanuki
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