New resist process improving sensitivity, resolution, roughness and photon shot noise simultaneously

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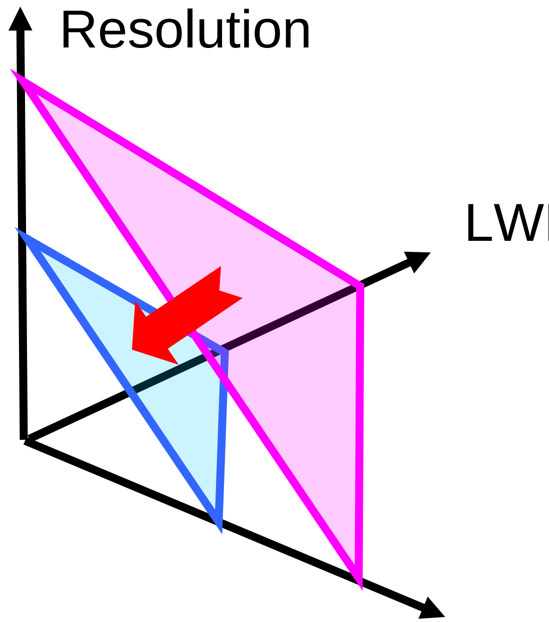
Critical Problems of Next Generation EUV Lithography

1. **The most important critical issue of EUV lithography is the weak intensity of EUV source.**
2. **The resist sensitivity and the exposure light intensity are complimentary. Therefore high sensitization of EUV resists is required.**
3. **However, dramatic enhancement of resist sensitivity is widely confirmed to be difficult due to both RLS trade-off and photon shot noise problems.**



❶ **RLS Trade-off Problem:** *G.M. Gallatin, Proc. SPIE (2005)*, (**Simulations:** no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)

❷ **Photon Shot Noise Problem**: LER and photon hsot noise in intermediate region can be approximated by using chemical gradient for high sensitive CAR.

$LER_{photon\ shot\ noise} \propto \sigma_{photon\ shot\ noise}/dm/dx$

❸ **Change of resist reaction mechanisms from photochemistry to radiation chemistry** (A review paper : Kozawa and Tagawa, 2010)

❸Big Difference Between Reaction Mechanisms of EUV (EB) Resists and Photoresists

・EUV and EB resists（Main process）

Ionization channel

RH ⟿ $RH^{+\cdot}$ + e^- —RH→ RH_2^+ + $R^{\cdot}$ + e^-

Ph_3S^+X —e^-→ Ph_2S + $Ph^{\cdot}$ + X^- —H^+→ Ph_2S + $Ph^{\cdot}$ + H^+X^-

S. Tagawa, et.al. SPIE 3999 (2000) 204.

・Photoresists（Main process）

Excitation channel

$(Ph_3S^+X^-)^*$

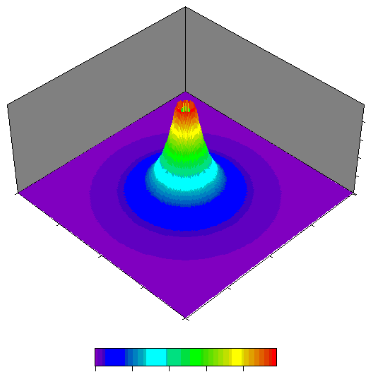
Homolysis → $Ph_2S^{\cdot+}$ + $Ph^{\cdot}$ + X^- (in-cage Reconbination)

- cage-escaped: $Ph_2S^{\cdot+}$ + $Ph^{\cdot}$ + X^- —RH: Solvent→ Ph_2S + $Ph^{\cdot}$ + H^+X^-
- in-cage: → *o*-PhPhSPh + H^+X^-, *m*-PhPhSPh + H^+X^-, *p*-PhPhSPh + H^+X^-

Heterolysis → Ph_2S + Ph^+ + X^- (in-cage)

- cage-escaped: Ph_2S + Ph^+ + X^- —RH→ Ph_2S + PhR + H^+X^-

Acid generation is very fast and mainly produced in nanospace.



❶RLS Trade-off Problem in Standard CAR

① Exposure (Tool)

② Interaction of EUV with resists

③ Accumulated energy profile

④ Acid generation

⑤ Latent acid image

⑥ Acid diffusion, Solubility change

⑦Acid catalyzed image (Latent image after PEB)

⑧ Development

⑨Resist pattern formation

⑩ Other Treatments: Rinse, Vapor smoothing, Hardbake, Ectching, Ozonation, etc.

Resist Pattern Formation Processes of EUV CARs

A review paper: Kozawa and Tagawa, (2010)

Based on the standard resist pattern formation model of EUV CARs including radiation chemistry, the RLS trade-off has been improved steadily by worldwide efforts such as high absorption materials②③, metal resists ②③, ⑩, radiation chemistry②③④⑤、high Tg⑥⑦, NTI⑧⑨,DDR⑧⑨⑩. This approach is now reaching near physical limit of the model. **Therefore, novel processes and materials of overcoming RLS trade-off must be necessary for EUVL HVM.**

Reconsideration of ④、⑤ for the high yield & the small space distribution of acids.

Simulations of CAR: *G.M. Gallatin, Proc. SPIE (2005)*, (no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)

One of best solutions of ❶RLS trade-off and ❷PSN problems is PSCAR

A new high resist sseniitzation process by the combination lithography of EUV or EB pattern exposure with UV flood exposure of *Photosensitized ChemicalAly plmified Resist*™ (PSCAR™) was proposed at Osaka University in 2013.

(S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013)

EUV/EB Pattern exposure + thermal reaction ➡ (EUV/EB Pattern + UV flood) exposure + thermal reaction

CAR **PSCAR**

One of Solutions of ❶RLS Trade-off Problem is PSCAR

A high resist sensitization process by the combination lithography of EUV or EB pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist*™ (PSCAR™) was proposed at Osaka University in 2013.

(S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013))

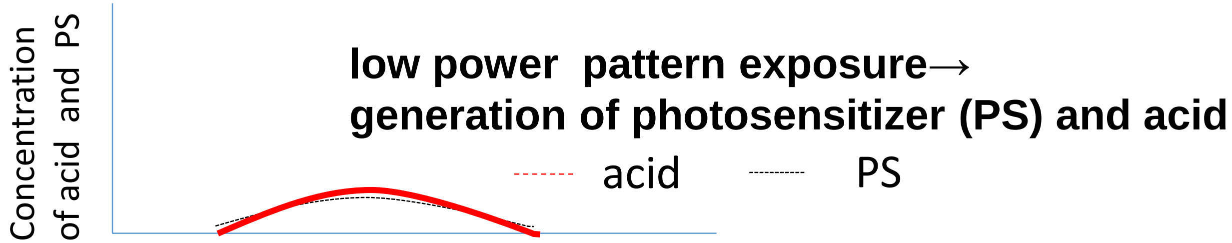
1. The first EUV pattern exposure produces photosensitizers (PSs).

2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.

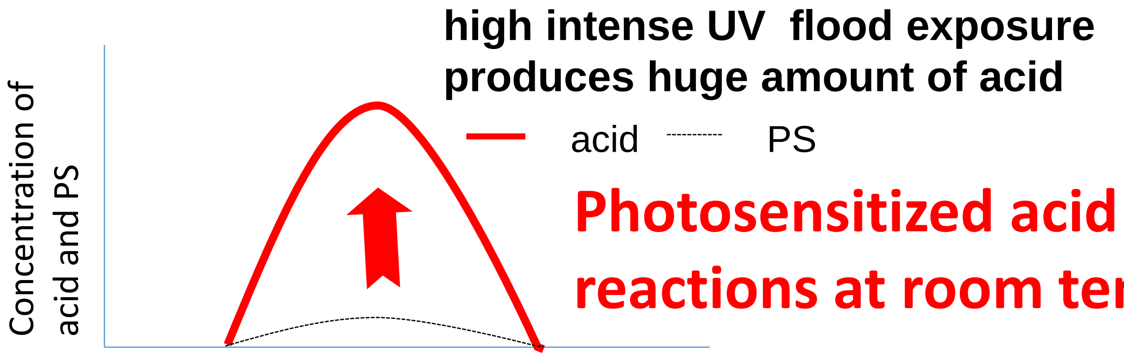
3. Only PSs have absorption bands at the second flood exposure wavelength. Sensitivity enhancement occurs by excitation of PSs.

New Process: Combination of radiation chemistry with photochemistry

(1st exposure)

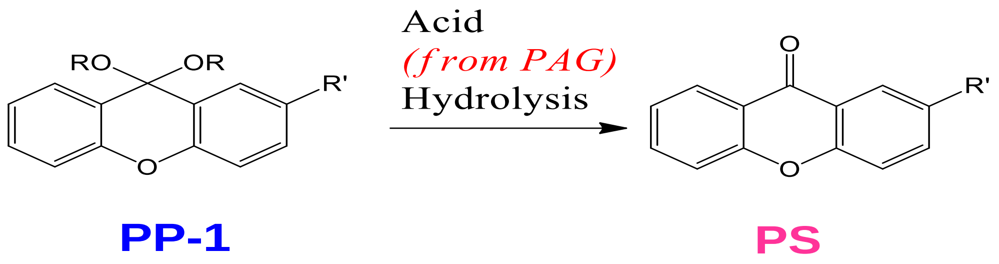


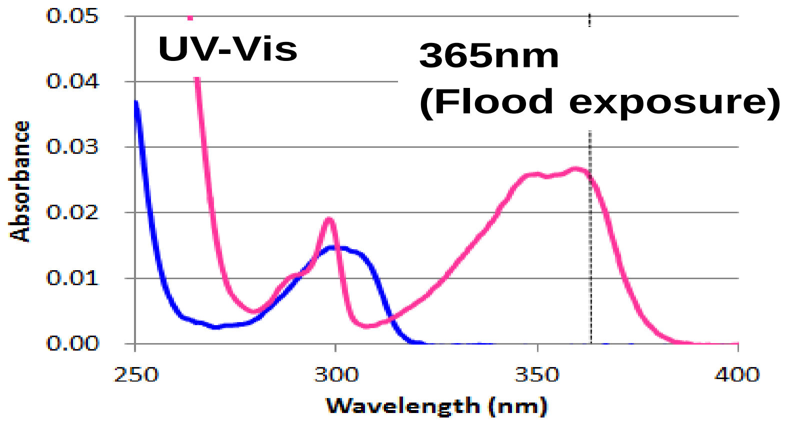
(2nd exposure)



Photosensitized acid generation reactions at room temperature

One simple example of PSCAR: precursor(PP) of PS and PS

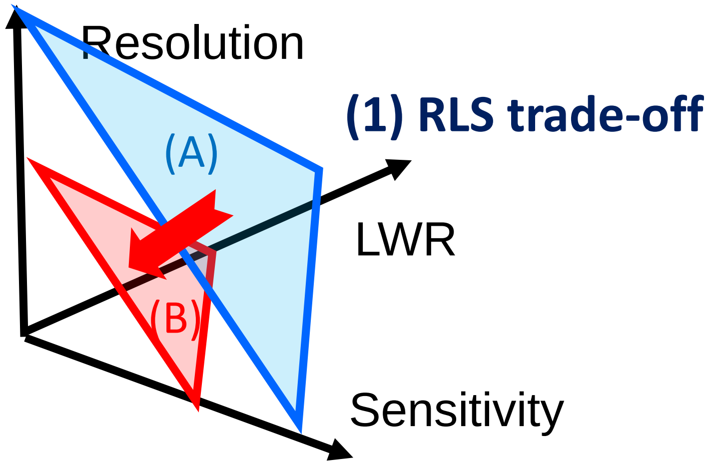


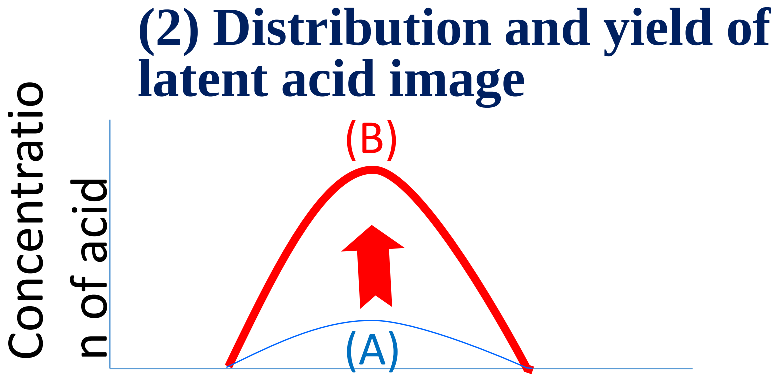


One example of PP and PS and their reaction and UV-Vis spectra

1. The first EUV pattern exposure produces photosensitizers (PSs).
2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.
3. Only PSs have absorption bands at the second flood exposure wavelength. Sensitivity enhancement occurs by excitation of PSs.

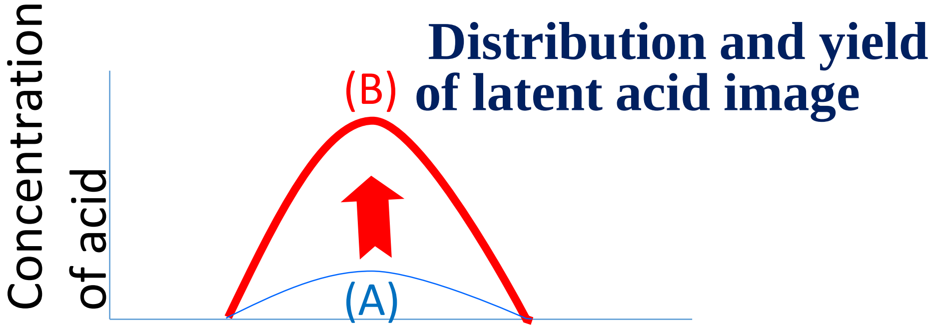
❶ Breakthrough of RLS trade-off

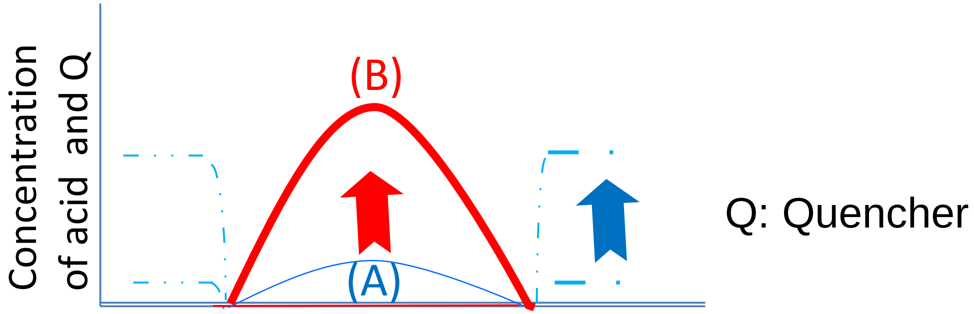




Schematic drawing of (1) RLS trade-off (2) initial distributions and yields of acid. If initial acid yield increases from (A) to (B) with the same distribution, RLS trade-off is improved from (A) to (B). (S. Tagawa, SPIE Newsroom, 13 March 2014)

Breakthrough of ❷Photon Shot Noise Problem





Schematic drawing of acid generation processes of PSCAR by the combination of 1st EB or EUV pattern exposure with 2nd photon flood exposure. The resolution is controlled by ratio of acid to quencher. Therefore, the higher chemical gradient (dm/dx) can be obtained in PSCAR comparing standard CAR.

LER due to photon shot noise can be approximated by using chemical gradient for CAR/PSCAR.

$$LER_{\text{photon shot noise}} \propto \sigma_{\text{photon shot noise}} / dm/dx$$

CAR

EUV Pattern exposure + thermal reaction

Acid generation(AG) ➡ acid catalyzed reaction (ACR)

➡

PSCAR

(EUV Pattern + UV flood) exposure + thermal reaction

AG + PS eneration+g ➡ spherical acid cluster generation ➡ ACR

dm/dx of PSCAR is larger than dm/dx of standard CAR.

$\sigma_{\text{photon shot noise}}$ of PSCAR is smaller than $\sigma_{\text{photon shot noise}}$ of standard CAR.

Therefore $LER_{\text{photon shot noise}}$ of PSCAR is smaller than $LER_{\text{photon shot noise}}$ of CAR.

Now EUV-IL exposure results in SPIE Advanced Lithography 2016

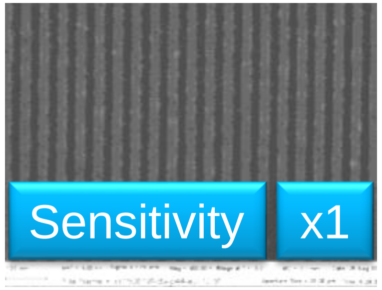
Sensitivity Enhancement by PSCAR2 with Flood Exposure

PSCAR by JSR

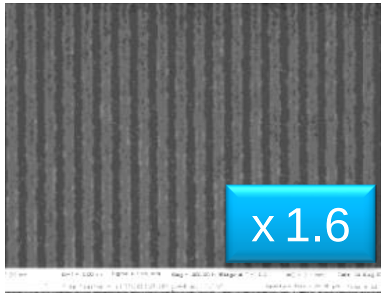
EUV Interference Lithography by ASML PAUL SCHERRER INSTITUT PSI

22 nm HP

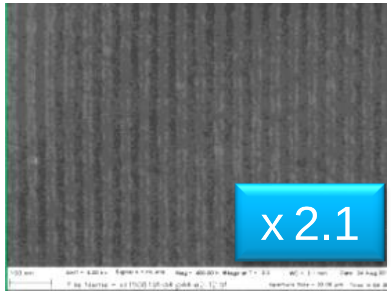
UV Flood Dose 0 J/cm^2
EUV Dose 32.1 mJ/cm^2



UV Flood Dose 0.75 J/cm^2
EUV Dose 20.1 mJ/cm^2

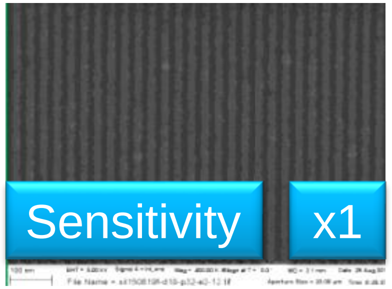


UV Flood Dose 1.0 J/cm^2
EUV Dose 15.6 mJ/cm^2

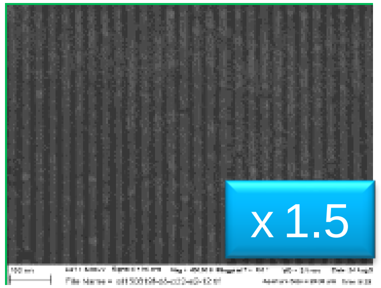


16 nm HP

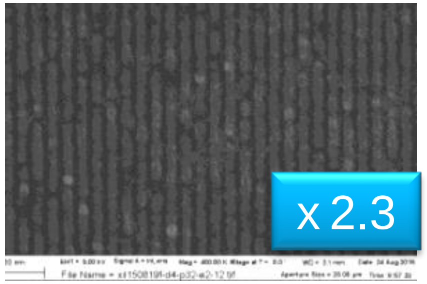
UV Flood Dose 0 J/cm^2
EUV Dose 40.3 mJ/cm^2



UV Flood Dose 0.75 J/cm^2
EUV Dose 27.6 mJ/cm^2



UV Flood Dose 1.0 J/cm^2
EUV Dose 17.9 mJ/cm^2



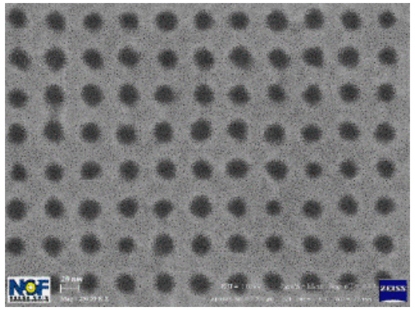
PSCAR will improve EUV exposure throughput
by sensitivity enhancement with adding flood exposure step

Summary of PSCAR in SPIE Advanced Lithography 2016

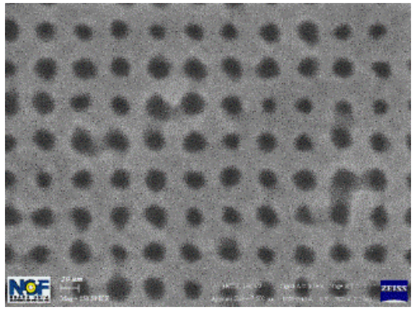
- In SPIE Advanced Lithography 2016, papers on PSCAR showed good EUVL and EB experimental results of uv sensitization of PSCAR, metal resists, NTI etc..
- EUV-IL experiments showed EUV PSCAR processes work well for 16 nm HP LS.
- PSCAR samples exposed by EUV-IL were investigated by EB exposure experiments. The status of PSCAR exposed by EUV-IL at SPIE 2016 for three important definitions of PSCAR is shown as described below.

1. The first EUV pattern exposure produces photosensitizers (PSs).	**yes**
2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.	**Need improvement**
3. Only PSs have absorption bands at the second flood exposure wavelength. Sensitivity enhancement occurs by excitation of PSs.	**Need improvement**

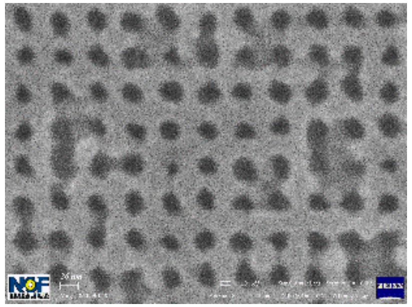
PSCAR PP-2
PSCAR exposed by EUV-IL



(a) EB only
D:400 μC/cm2

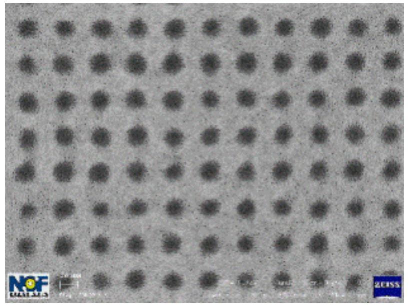


(b) EB D: 260 μC/cm2, 2nd UV flood exposure 1.2 J/cm2

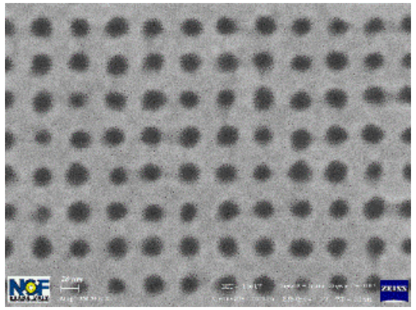


(c) EB D: 220 μC/cm2, 2nd UV flood exposure 1.8 J/cm2

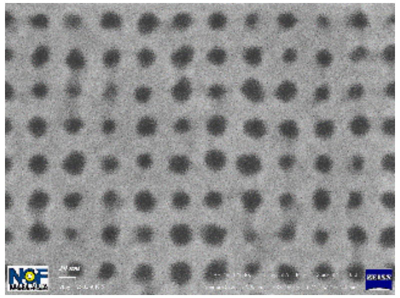
New PSCAR
PP-5



(a) EB only
D: 440 μC/cm2



(b) EB: 260μC/cm2, 2nd UV flood exposure 6 J/cm2



(c) EB:200μC/cm2, 2nd UV flood exposure 8.4 J/cm2

Dense 20 nm hp CH, 125 keV EB pattern exposure, PSCAR is the same except for PP, UV flood (365 nm, 40mW/cm2)

(2^{nd} uv flood exposure done in air, not in line process)

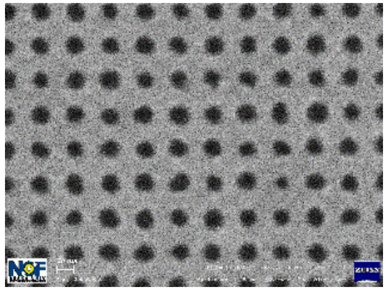
Optimization of PSCAR needs a little more time than standard CAR.

CAR: EUV/EB Pattern exposure (radiation chemistry) + acid catalyzed reaction (thermal reaction)

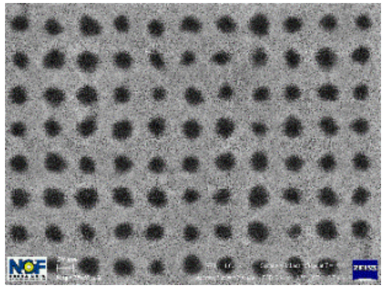
PSCAR: EUV/EB Pattern exposure + UV flood exposure(electron/energy transfer) + acid catalyzed reaction

One example: Not best optimization of PSCR material components and processes and also poor experimental condition (2^{nd} uv flood exposure done in air, not in line process)

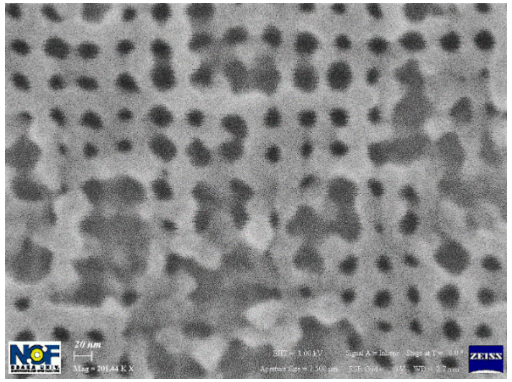
(A)



(a)EB only
D:520 µC/cm2

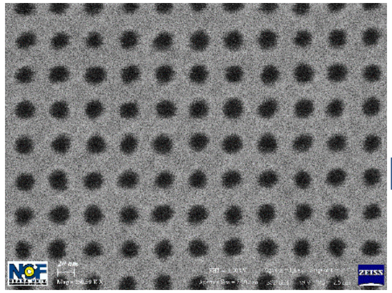


(b) EB : 280µC/cm2,
2nd UV flood exposure 3.6 J/cm2

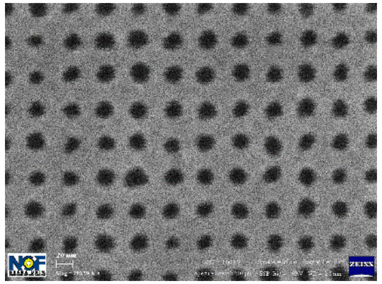


(c) EB : 240µC/cm2, 2nd UV flood exposure 4.8 J/cm2

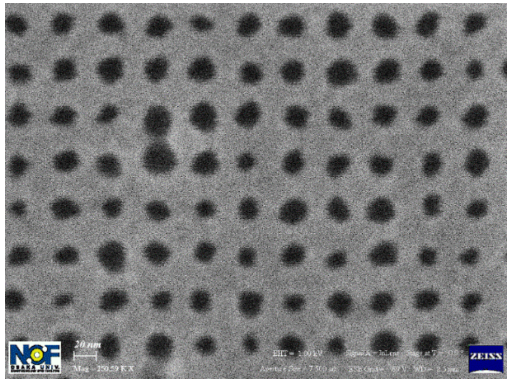
(B)



(a) EB only
D:520 µC/cm2



(b) EB : 280µC/cm2,
2nd UV flood exposure 3.6 J/cm2



(c) EB : 240µC/cm2 (2nd UV flood exposure 4.8 J/cm2

Dense 20 nm hp CH, the same PSCAR (PP-5,Q3, the same 125 keV EB pattern exposure and UV flood (365 nm, 40mW/cm^2), a little bit of different PEB conditions

Summary

- Fundamental aspects of RLS trade-off and photon shot noise problems of CAR and PSCAR have been explained.

  RLS trade-off is improved in PSCAR comparing with standard CAR.

  $LER_{\text{photon shot noise}}$ of PSCAR is much smaller than $LER_{\text{photon shot noise}}$ of standard CAR for the same sensitivity.

- Progress in PSCAR materials and processes has been made since SPIE Advanced Lithography 2016.
- Remarkble improvement is expected with optimization of PSCAR material components and processes.

Acknowledgments

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Thank you for your kind attention.