Fundamental aspects of sensitivity enhancement and RLS trade-off of chemically amplified EUV resist

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Laser-induced plasma produces 13.5 nm (92.5 eV) EUV light.

**EUV Lithography Exposure System**

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 very difficult due to RLS trade-off problem.**
There are two important points in EUV resists

(1) RLS trade off problem
The most difficult technical requirement for EUV resist is simultaneous improvement in resolution, LWR, and sensitivity (RLS).

(2) Change of resist reaction mechanisms
The photon energy of EUV (13.5 nm, 92.5 eV) is much higher than ionization potential of resist materials (~10 eV). Reaction mechanisms change from photochemistry to radiation chemistry. (A review paper : Kozawa and Tagawa, 2010)
There is RLS (Resolution, Line Width Roughness, Sensitivity) Trade-off Problem (1)

1. Around 2000, the limitation of resolution was determined by acid diffusion length around 40-50 nm. EUV resists required less than 40 nm resolution. Easy method for getting high resolution is controlling acid diffusion length by high concentration quenchers.


How to improve RLS trade-off relation in EUV CARs?

1. Exposure (Tool)
2. Interaction of EUV with resists
3. Accumulated energy profile
4. Acid generation
5. Latent acid image
6. Acid diffusion, deprotection reaction
7. Acid catalyzed image (Latent image after PEB)
8. Development
9. Resist pattern formation
10. Other Treatments: Vapor smoothing, Hardbake, Ectching, Ozonation, etc.

Problems have been improved step by step by global efforts.
RLS Trade-off Problem (2)

Simulations: G.M. Gallatin, Proc. SPIE (2005), (Simulations does not contain EUV-induced acid generation mechanism and no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)

Latent Acid Image Distribution: Assumption: rough estimation

But we thought the acid generation mechanisms, especially nano-space reactions (mainly the combination of geminate recombination with dissociative electron attachment) are important and essential for the solution of RLS trade-off problem, because the high acid yield and the small acid space distribution are clearly the best solutions of RLS trade-off problem.

Interaction of EUV with resists

Accumulated energy profile

Acid generation

Latent acid image

Acid catalyzed reaction

Latent acid image

Development

Resist Pattern Formation

A review paper: Kozawa and Tagawa, (2010)
Comparison of products between radiolysis and photolysis of acid generator (Triphenylsulphonium triflate)

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

- **EUV and EB resists (Main process)**
  
  **Ionization channel**

  \[
  \text{RH} \xrightarrow{\text{e}^-} \text{RH}^+ + \text{e}^- \quad \text{RH} \xrightarrow{\text{R}^- + \text{RHH}^+ + \text{e}^-} \]

  \[
  \text{Ph}_3\text{S}^+\text{X} \xrightarrow{\text{e}^-} \text{Ph}_2\text{S} \xrightarrow{\text{R}^-} + \text{Ph}^- + \text{X}^- \quad \text{H}^+ \xrightarrow{\text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+\text{X}^-} \]


- **Photoresists (Main process)**
  
  **Exicitation channel**

  \[
  \text{Ph}_2\text{S}^+ + \text{Ph}^- + \text{X}^- \xrightarrow{\text{cage-escaped}} \text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+\text{X}^- \]

  RH: Solvent

  Homolysis

  \[
  \text{Ph}_2\text{S}^+ + \text{Ph}^- + \text{X}^- \xrightarrow{\text{in-cage Recombination}} \text{Ph}_2\text{S} + \text{Ph}^+ + \text{X}^- \xrightarrow{\text{in-cage}} \text{o} - \text{PhPhSPh} + \text{H}^+\text{X}^- \]

  \[
  \text{Ph}_2\text{S}^+ + \text{Ph}^- + \text{X}^- \xrightarrow{\text{in-cage}} \text{m} - \text{PhPhSPh} + \text{H}^+\text{X}^- \]

  Heterolysis

  \[
  \text{Ph}_2\text{S} + \text{Ph}^+ + \text{X}^- \xrightarrow{\text{cage-escaped}} \text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+\text{X}^- \xrightarrow{\text{RH}} \text{Ph}_2\text{S} + \text{PhR} + \text{H}^+\text{X}^- \]

  Acid generation is very fast and mainly produced in nanospace.
New concept

④ Reconsideration of acid generation mechanisms
Comparison of the new process with the conventional process

(A) Conventional Process  
Radiation chemistry

(B) New Process  
Combination of radiation chemistry with photochemistry

(1st exposure) low power pattern exposure \(\rightarrow\) generation of photosensitizer (PS) and acid

(2nd exposure) high intense UV flood exposure produces huge amount of acid

Photosensitized acid generation reactions at room temperature
Breakthrough of RLS trade-off

The trade-off simulation contains two parts. (Gallatin model)

(1) The aerial image, properly normalized, is taken as the probability distribution for where a photon will be absorbed and cause an acid to be released.

(2) The acid catalyzed deprotection reactions and resist development process.

The change of the first part is a key for the 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).
I-215 clean room (Class 1000) 80 m²

Elionix ELS-100T (125 keV)

Pattern exposure (EBL)

Flood exposure (UV)

Sample 4 inch wafer

UV light source
20 nm dense CH pattern formation, PS-CAR (S1)
125 keV EB pattern exposure + UV flood exposure

(b) EB only  D:480 μC/cm²
CH20nm P40nm

c) EB D:400 μC/cm², 1 min 2nd UV
flood exposure, CH20nm P40nm

(d) EB D: 320 μC/cm², 3 min 2nd UV
flood exposure, CH20nm P40nm

e) EB D: 220 μC/cm², 5 min 2nd UV
flood exposure, CH20nm P40nm
PSCAR Papers in SPIE Advanced Lithography Conference

- **Challenge toward breakage of RLS trade-off by new resists and processes for EUV lithography** 22 Feb. 2016 • 4:00 - 4:30 PM
  Seiji Nagahara, Michael A. Carcasi, Gosuke Shiraishi, Yuichi Terashita, Yukie Minekawa, Kosuke Yoshihara, Masaru Tomono, Hironori Mizoguchi, Hideo Nakashima, Seiichi Tagawa, Akihiro Oshima, Hisashi Nakagawa, Takehiko Naruoka, Tomoki Nagai, Elizabeth Buitrago, Michaela Vockenhuber, Yasin Ekinci, Oktay Yildirim, Marieke Meeuwissen, Coen Verspaget, Rik Hoefnagels, Gijsbert Rispens, Raymond Maas

- **Fundamental aspects of a new process of high-resist sensitization by the combination lithography of EB/EUV pattern exposure with UV flood exposure of photosensitized CAR and non-CAR** 22 Feb. 2016 • 4:30 - 4:50 PM
  Seiichi Tagawa, Akihiro Oshima, Cong Que Dinh, Shigehiro Nishijima

- **Novel high-sensitivity EUV photoresist for sub-7nm node** 22 Feb. 2016 • 5:10 - 5:30 PM
  Tomoki Nagai, Hisashi Nakagawa, Takehiko Naruoka, Seiichi Tagawa, Akihiro Oshima, Seiji Nagahara, Gosuke Shiraishi, Yukie Minekawa, Yuichi Terashita, Kosuke Yoshihara, Elizabeth Buitrago, Michaela Vockenhuber, Yasin Ekinci, Oktay Yildirim, Marieke Meeuwissen, Rik Hoefnagels, Gijsbert Rispens, Coen Verspaget, Raymond Maas

- **Sensitivity enhancement of chemically amplified resist and evaluation using EUV interference lithography** 24 Feb. 2016 • 9:30 - 9:50 AM
  Elizabeth Buitrago, Seiji Nagahara, Oktay Yildirim, Hisashi Nakagawa, Seiichi Tagawa, Marieke Meeuwissen, Tomoki Nagai, Takehiko Naruoka, Coen Verspaget, Rik Hoefnagels, Gijsbert Rispens, Gosuke Shiraishi, Yuichi Terashita, Yukie Minekawa, Kosuke Yoshihara, Akihiro Oshima, Michaela Vockenhuber, Yasin Ekinci

- **The reaction mechanism and patterning of photosensitized chemically amplified resists** 24 February 2016 • 10:40 - 11:00 AM
  Seiichi Tagawa, Akihiro Oshima, Cong Que Dinh, Shigehiro Nishijima, Seiji nagahara, Michael Carcasi, Gosuke Shiraishi, Yuichi Terashita, Yukie Minekawa, Kosuke Yoshihara, Hisashi Nakagawa, Takehiko Naruoka, Tomoki Nagai
Important Points of New Process

- The first EUV pattern exposure produces photosensitizers.
- Resist has no absorption band of the second flood exposure light wavelength region. Therefore, no reaction of resist occurs if only the second flood exposure is carried out.
- Only photosensitizer has absorption band of the second flood exposure light wavelength region.
- **New method coexisting together with most of other global efforts overcoming RLS Trade-off**