Density profiles of photoresist thin films by high precision x-ray reflectivity analysis

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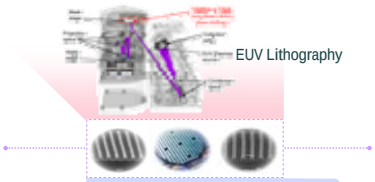
Introduction



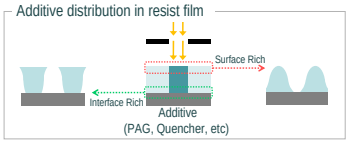
EUV Photoresist
- High resolution
- High sensitivity
- Low LER/LWR

➢ To obtain high resolution and sensitivity and low LER/LWR

➡ Resist film homogeneity!

➢ Resist pattern shape

➡ EUV transmittance, Diffusivity(Acid), Additive distribution



• Objectives

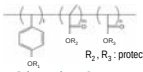
- Homogeneity evaluation of resist film

➡ Density profile of resist film using non-destructive x-ray reflectivity analysis

Experiments

• Material :

➢ Resin :



R_2, R_3 : protecting or adhesion group

➢ PAG : TPS based PAG

➢ Solvent : PGMEA

• Film preparation :

➢ Photoresist solution (PAG - 0, 2, 6, 10, 20wt% relative to resin) 1wt%

➢ Spin-coating(2000rpm, 60s) » Annealing » Reflectivity Analysis

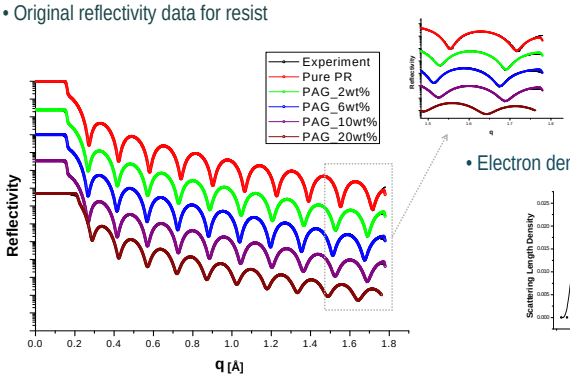
• X-ray reflectivity measurement :

➢ Pohang Accelerator Lab(PAL, 10C1 beam line) in Korea

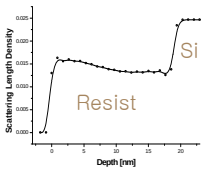
• Fitting : DWBA approach

Result and Discussion

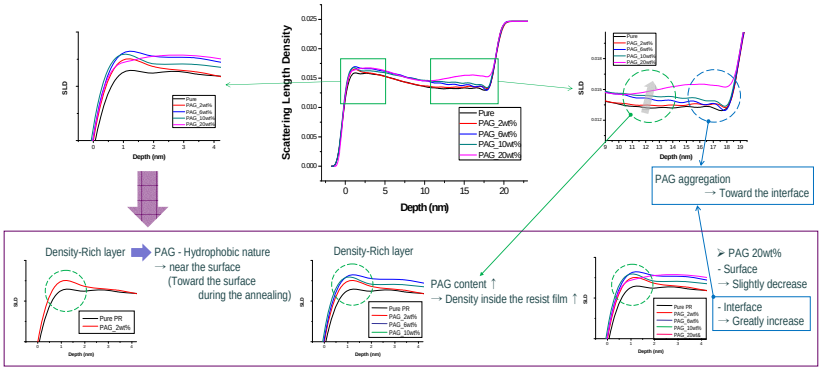
• Original reflectivity data for resist



• Electron density profiles for pure resist



• Electron density profiles for resist containing PAG



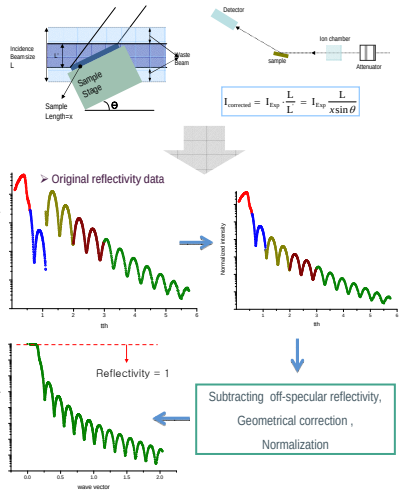
❖ Additional experiment : Element depth profiling → Non-destructive Method : Angle-resolved XPS (On going)
→ Destructive Method : Sputtering XPS

Conclusion

- From x-ray reflectivity analysis, It is confirmed that the PAG of hydrophobic nature is located near the surface.
- As PAG content increase(0-20wt%), the density inside resist film is gradually increased.
- In case of 20wt% PAG content, the density near the interface is greatly increased. It seems to be caused by PAG aggregation.

Details

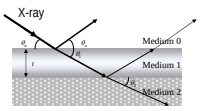
Geometrical Correction of X-ray reflectivity



$$I_{corrected} = I_{Exp} \cdot \frac{L}{L} = I_{Exp} \frac{L}{x \sin\theta}$$

X-ray reflectivity FITTING process

- Mathematical inversion of reflectivity to density is impossible!!
- To get the most approximated density, fitting process is required



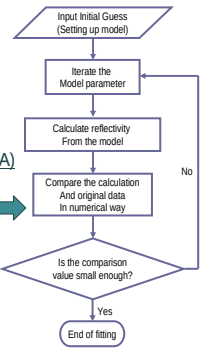
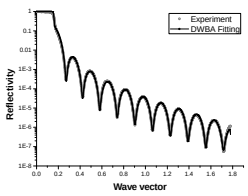
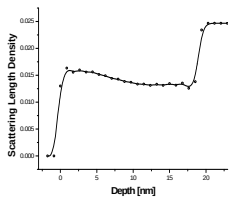
• Set up Model (profile)& fitting with Reflectivity

• Calculation of reflectivity
- Recursive (Parratt) formalism
- Well fitted for thick film/high contrast

$$r_{n-1,n}(k) = \frac{r'_{n-1,n} + r'_{n,n+1}\exp(2id_n k_n)}{1 + r'_{n-1,n} r'_{n,n+1}\exp(2id_n k_n)}$$

• Distorted Wave Born Approx. (DWBA)
- Model independent
- Works for ultra-thin film <400
- Thin virtual slices of ED
- Small density fluctuation

$$R(k) = \left| ir_0(k) + \frac{(2\pi r_e)}{k}\left(a^2(k)\Delta\rho(q_z^2) + b^2(k)\Delta\rho^*(q_z^2)\right)\right|^2$$



Electron Density Profile