Poster

Modeling and Investigation of the ester cleavage in modern Photoresists materials

Pedro Javier Rodríguez Cantó

1. *Department of physical Chemistry, University of Erlangen, Egerlandstrasse 3, D-91058 Erlangen, Germany*
2. *Nanophotonics Technology Center, Camino de Vera s/n, 46022, Valencia, Spain*

pjrodrig@ntc.upv.es

Chemical amplified resists (CAR´s) are widely used in the semiconductor industry very well since its invention in 1980 in terms of high resolution and sensitivity.

Patterning of CAR´s by means of photolithography requires a heating process of 30 - 120 s with a temperature between 110 and 150 ºC between the exposure and the selective development of the polymer to make the polymer soluble.

This process is as follows (Figure 1): a photosensitive molecule (PAG = photo Acid generator) splits off in a strong acid in the exposed areas of the resist. During the post-bake of the resist film (for temperatures higher than 80 ºC) the proton of this acid can react with the t-butyl group of the polymer (inhibitor) at the ester bridge to form the corresponding acid. Isobutene is released as a byproduct. The proton generated upon exposure remains in the formed carbon acid group of the polymer with the subsequent change of solubility in the developer. Simultaneously, a new proton from a methyl group is produced. The course of this catalytic ester cleavage determines, on the one hand, the activation energy (and activation entropy) of the cleavage and on the other hand the diffusivity of the acid in the resist.

Simulation of these processes is very important for the semiconductor industry to minimize time, expenditure and to provide fast analysis and process optimization. Current models for simulation of CAR's (continuum models) are very fast and are often able to accurately simulate photoresist performance for a variety of process conditions. However, they rely heavily upon extensive calibration to expensive lithography experiments, and thus are limited in their predictive capability. Due to the continuum nature of these simulations, they are also limited in their ability to investigate stochastic phenomena such as feature roughness. For this reason, a kinetic molecular model (Figure 2) is presented in this work in which the inhibitor groups (magenta points) form a close meshed grid. As for, the PAG molecules (blue points) are placed into the grid before forming a wide meshed grid. At the exposed areas this grid changes to a partial grid of acid.

During the bake, the proton does not move independently but coupled to the bulky anion, which leads to a limited proton mobility. This has a big influence on the spatial propagation of the ester cleavage. Through the reorientation of the anion, the catalytic proton can react with the majority of the inhibitor groups placed in its surroundings. In order to cleave other inhibitor groups, the bulky anion has to migrate together with the proton. As a result, „virtual holes“ are created around the original location of the PAG, which locally induces a significant change in the networking and dielectric constant of the polymer and hence in the polymer solubility. From this theoretical approach, it can be concluded, that the inhibitor cleavage in the resist takes place spherically. The correlation of the measured kinetic data with the theoretical approach results from a spherical model.

From this approach the specific model parameter **τ** can be defined as the minimal bake time in which the proton (and its anion) cleaves enough inhibitor groups, so that the resist can be develop in this area. This parameter can easly be determined from special experiments varying the exposure time and the bake step. With this model and suitable experiments, we can discriminate between diffusion and reaction. Important data required for simulation can also be determined.

References:

[1] R. Leuschner, G. Pawlowski, *Handbook of semiconductor technology*, Wiley-VCH, (1998).
[2] D. Matiut, A. Erdmann, B. Tollkühn, A. Semmler, Proc. SPIE, **5039**, (2003), 1132-1141.
[3] X. Shi, J. Vac. Sci. Technol., **B 17(2)**, (1999), 350-354.
[4] S. Robertson, *Resist Models: A practical Guide to timely parameter determination and a review of model deficiencies*, 1st IISB Simulation Workshop, Hersbruck (2003).

Figures 1:

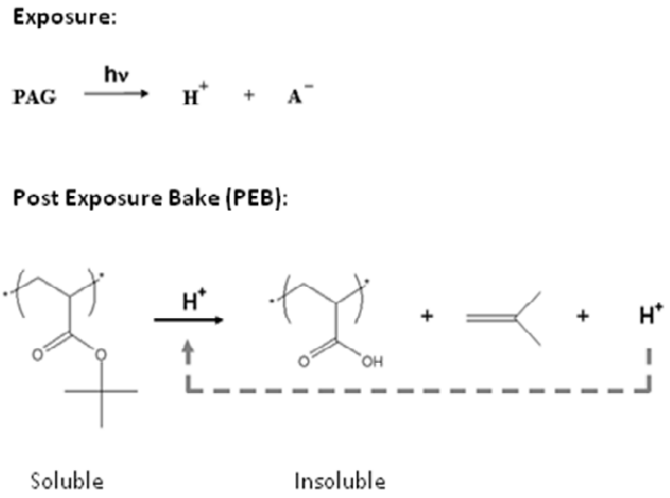

Figure 2:

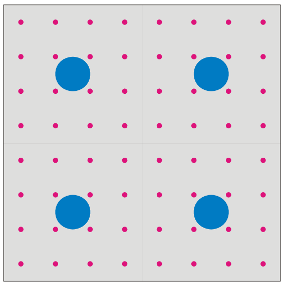

Figure 3: