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Ultimate lithography/Lithographie ultime

Photosensitive resists for optical lithography

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Abstract

Optical lithography relies on photosensitive materials to transfer the aerial image into the substrate. These photoresists have been steadily improved to keep up with the innovations in the lithography tools targeting a higher fidelity in the pattern transfer. After describing the resist process and the photolithographic criteria for such materials, this article will focus on the Chemically Amplified Resists (CAR) especially for the 193 nm lithography. The added challenges of the immersion lithography will then be addressed and some perspectives will be given. ***To cite this article: B. Mortini, C. R. Physique 7 (2006).***
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Résumé

Résines photosensibles pour la lithographie optique. La lithographie optique utilise des matériaux photosensibles pour transférer l'image aérienne dans le substrat. Ces photorésines n'ont cessé d'être améliorées pour suivre les innovations des outils de lithographie visant un transfert de motif de meilleure qualité. Après une description du procédé résine et des critères photolithographiques de tels matériaux, cet article se focalisera sur les résines à amplification chimique en particulier pour la lithographie 193 nm. Il traitera ensuite des défis additionnels de la lithographie en immersion avant de donner des perspectives. ***Pour citer cet article : B. Mortini, C. R. Physique 7 (2006).***
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Keywords: Chemically Amplified Resist; Post-exposure bake; Immersion lithography

Mots-clés : Résine à amplification chimique ; Recuit post-exposition ; Lithographie en immersion

1. Introduction

Various lithographic techniques are available to transfer an image onto a silicon substrate. Amongst them, the most common are optical lithography, also called photolithography, which is the industry standard thanks to its high throughput, and electron beam lithography, well known for its high resolution capabilities. Photolithography relies on the image projection of patterns represented on a mask, generally a transparent quartz plate with opaque chromium features, into a photosensitive polymer film. The choice of the exposure wavelength depends on the light source in line with the critical dimension the user wants to achieve. Discharge mercury lamps have been used for years, choosing successively the g-line (436 nm) and i-line (365 nm) wavelengths. Then excimer laser have been selected as deep UV sources, i.e. KrF (248 nm) and ArF (193 nm) lasers, as they were much more powerful than mercury lamps. With

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193 nm lithography, the gain in resolution allowed by the introduction of the immersion lithography, now gives the possibility to extend this technology at least down to about 40 nm critical dimensions.

In order to keep up with the innovations in lithography techniques, photosensitive polymers need to be steadily improved. After describing the resist process and the photolithographic criteria for such a material, this article will focus on the Chemically Amplified Resists (CAR). The principle of such amplification will be described with reference to the early work on the 248 nm resists. Specific issues related to the 193 nm lithography will then be addressed. The introduction of the immersion lithography induces new phenomena, like the interaction between resist and water or the defectivity of such a process, which need more studies.

This article will conclude by looking at potential new showstoppers (e.g. line edge roughness or outgassing of the resist in the next generation of lithography techniques).

2. The lithography process from the resist perspective

2.1. *The resist process*

Two resist categories can then be defined: positive tone resists, for which the exposed areas are dissolved in the developer, leading to resist patterns similar to the image of the mask, and negative tone resists, for which exposed areas become insoluble in the developer and give resist patterns that are the complementary image of the opaque chromium patterns on the mask (Fig. 1).

The lithographic process involves many sequential steps. First, after some substrate pre-treatment in order to enhance the adhesion of the resist (priming step using silane-based adhesion promoter like HMDS (HexaMethyl-DiSilazane)) the resist stack is deposited onto the top of the substrate by spin-coating. Depending on the critical dimensions that have to be achieved, another polymer layer with absorbing properties at the exposure wavelength may have been coated, to avoid light reflection at the bottom of the resist: such layers are called Bottom Anti-Reflective Coating (BARC). In order to avoid compatibility issues and intermixing with the resist layer, BARC systems are based on thermally crosslinked polymer systems. After the BARC deposition a few millilitres of the resist solution is spun during the rotation of the silicon wafer (spin speed around 1500 to 4500 rotations per minute in order to obtain the best uniformity). The fast evaporation of the solvent during this step leads to an expensed polymer film, with a high content of free volume. As a result, a post apply bake step is requested in order to densify the polymer film. Depending on the possibility to perform this bake for few minutes at a temperature higher or lower than the intrinsic glass transition temperature T_g of the resist polymer, the film densification will be partially or fully completed.

Then the resist layer is selectively exposed at the desired wavelength or with an e-beam to generate what is called a ‘latent image’. This latent image has to be converted into a change of the polymer chemistry, and thus a change in the dissolution speed in the developer: this is obtained through the post exposure bake step. Finally, the resist layer is developed in a TetraMethylAmmonium Hydroxide (TMAH) at 0.26 N (2.38 wt%).

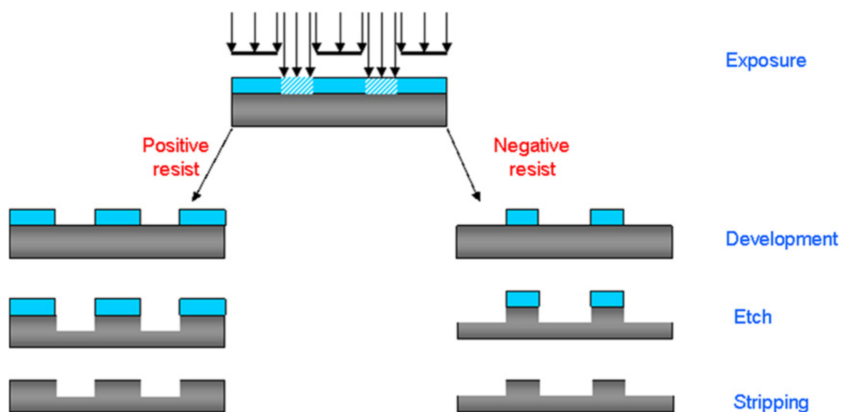

Fig. 1. Positive tone versus negative tone resists.

2.2. Process criteria for a resist material

As already mentioned, each wavelength change has requested some new photosensitive materials.
However, photoresist formulation should always fulfil the same main requirements:

- *Transparency*—The photoresist film should be transparent enough in order to provide good patterning properties, as the aerial image should be transferred through the whole film thickness. This corresponds more or less to an absorbency below 0.2 μm^{-1}.
- *Development contrast*—A sufficient dissolution contrast between exposed and unexposed areas of the resist layer is required in order to generate precise patterns during the development step. During the past 15 years, chemically amplified systems have demonstrated their competitive properties on this specific requirement.
- *Material stability during the integration step*—This means two main conditions: first, the resist material should have a sufficient thermal stability to withstand such an integration process. Secondly, the chemical composition has to be selected to provide the best chemical resistance to the integration process. In the past, novolac resists have shown very stable behaviour during the integration process (etch or implant steps). This has become not so obvious with chemically amplified chemistries and more especially with polymer platforms for the 193 nm lithography. The empirical law, known as the Ohnishi parameter that is usually referred to, indicates that the higher the carbon atom content is in the resist versus other atoms such as oxygen, the more robust will be the resist during the etch steps.
- Finally, a photosensitive resist must have *excellent film properties*, no segregation of its different compounds should take place during the spin coating step or later and the remaining layer has to be stripped under wet or dry treatments without defectivity issues.

3. Chemically Amplified Resists (CAR)

3.1. Early developments

For now 20 years, the most advanced resists have all been based on the chemical amplification mechanism introduced by IBM research teams [1]. This concept is presented in Fig. 2, where most of these resists are positive tone chemically amplified systems.

The first step of the reaction chain in Chemically Amplified Resists is the photogeneration of an acid by the sensitization of a photoacid generator (PAG) compound, such as onium salts (Fig. 3).

Then, during the Post Exposure Bake (PEB) step, an acid catalysis deprotection reaction occurs in the exposed areas (Fig. 4), removing some dissolution inhibitor functionalities which have been grafted onto the polymer chain and thus making it soluble in a basic developer. This reaction proceeds in a catalytic way in that the H^+ ion involved in the chemical reaction is regenerated at the end of the reaction.

The relative temperature of the post-apply bake (or softbake) with respect to the intrinsic glass transition temperature T_g has been shown to strongly impact the performance of Chemically Amplified Resist, as the residual solvent content and the free volume amount in the resist layer strongly impact the acid diffusion length as well as the diffusion of contaminant species in the resist.

For 248 nm chemically amplified resists, it leads to two resist categories: non-annealing resists, with T_g superior to the bake temperature, and annealing type resists, with a post apply bake step performed at a temperature superior to T_g.

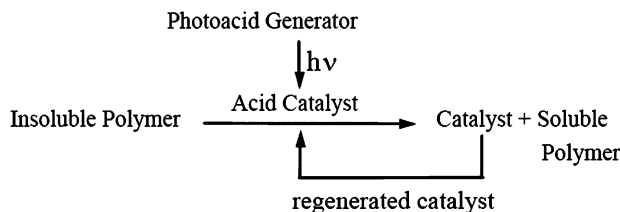

Fig. 2. Principles of the chemically amplified photoresist concept.

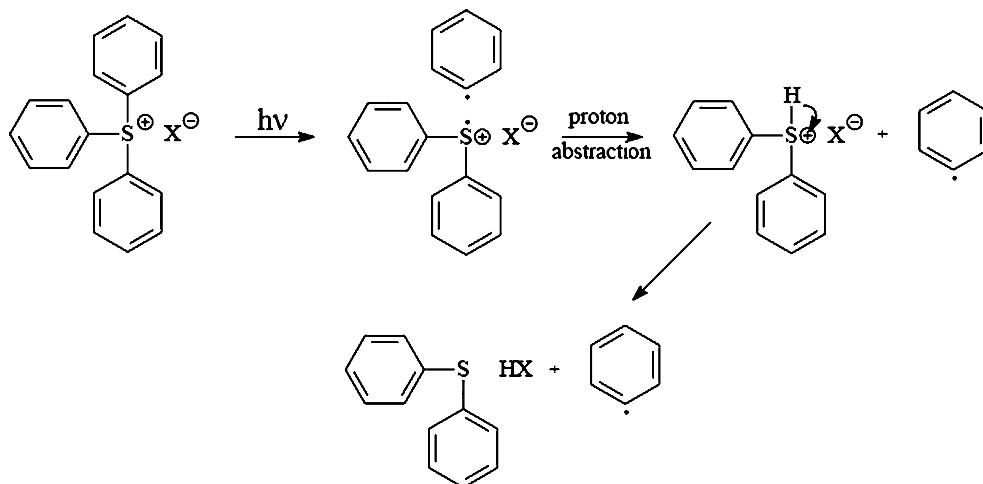

Fig. 3. Acid generation under UV radiation for onium salts in Chemically Amplified Resists.

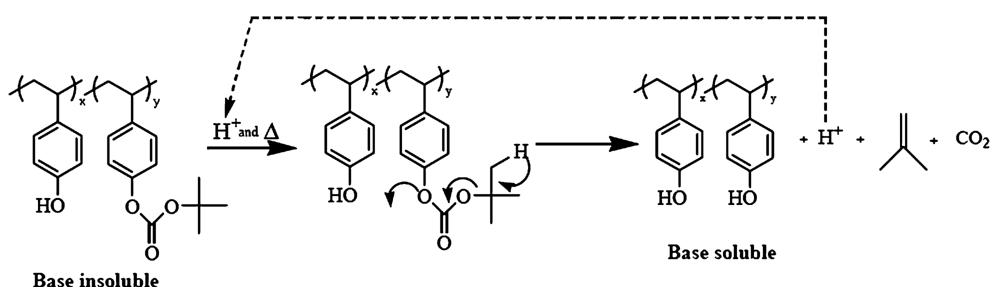

Fig. 4. Acid catalysed deprotection of a t-ButylOxyCarbonyl (t-BOC) carbonate protected poly4-hydroxystyrene, a typical polymer matrix for 248 nm chemically amplified resists.

From the chemical point of view, non-annealing type resists are often low-activation or moderate activation energy resists, having protecting groups such as acetal groups. These groups, which control the dissolution properties of the photoresist film, can be removed from the polymer backbone by thermal activation for bake temperatures lower than the polymer T_g. On the other hand, high activation energy protecting groups, such as t-butyl groups, can withstand higher temperatures and thus post apply bake above the resist polymer T_g (around 130 °C for poly-hydroxystyrene polymers) can be performed. As a consequence, annealing-type resists are less sensitive to contamination and delay time issues.

3.2. 193 nm resists

This concept has been kept for the development of 193 nm photoresists but the polymer backbone has been changed from poly-hydroxystyrene to mainly acrylate chemistry in order to keep a sufficient transparency at this wavelength. However, compared to 248 nm chemistries, 193 nm resists often request more functionalities grafted on the polymer backbone to achieve all the lithographic specifications. As a example, alicyclic units such as norbornane and adamantane have then been introduced in order to achieve a high C:H ratio and maintaining a sufficient etch resistance (Fig. 5). As the complexity of the polymer chemistry has increased with 193 nm resists, the control of the polymer composition and monomer arrangements can play a role in the final lithographic performance, especially on line edge roughness.

For 193 nm resists, the glass transition temperature of the backbone polymers is generally higher (around 150–170 °C) than with 248 nm resists. As a result, the majority of the 193 nm chemically amplified resists has to be considered as non-annealing resist film. As residual solvent and extra-free volume may remain in the resist film after the post-apply bake step, diffusion control of the small active species such as the photogenerated acid or external contaminant will be more difficult, having some impact on the process window stability of such products.

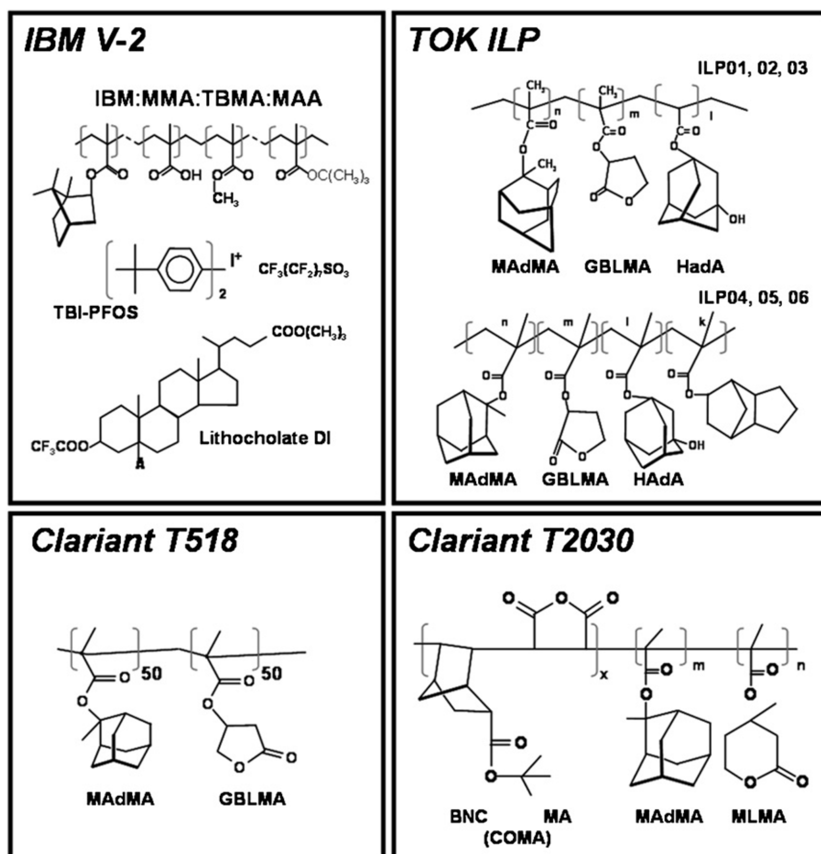

Fig. 5. Examples of various positive tone 193 nm chemically amplified resists published in the literature (from [2]).

4. Challenges in 193 nm immersion lithography

Going to higher index media than the air allows transferring a better image within the photoresist layer. As a result, immersion lithography with water or even higher index fluids between the bottom lens of the lithography tool and the resist layer is under development to reach dimensions below 50 nm. 193 nm chemically amplified resists have been successfully used at the beginning using some conventional 193 nm formulations and adding at the top of the resist a developer developable top coat material (Fig. 6).

Indeed, a specificity of immersion lithography lies in the interactions between resist and water. For example, it has been shown that PAG contained in the resist can leach into water [3]. This leaching can have important consequences such as damaging the lens system of the scanner or modifying the resist performance, for example by creating T-topping. 193 nm resists developed for conventional exposure in the air show high leaching values for the photoacid compounds, which have been reported as the main species involved in the leaching phenomenon. PAG amounts in water have been measured around 3×10^{-11} mol/cm^2: such values are above the upper value specifications recommended by scanner vendors. Such leaching values can be decreased to 5×10^{-13} mol/cm^2 with the use of a top-coat, meeting scanner recommendations (as an example, ASML has proposed a first leaching specification a 1.6 E-12 mol/cm^2/s) and thus allowing the use of the same resist for dry and immersion lithography. Dedicated 193 nm resists for immersion have been developed. By adding specific additives, resist suppliers have modified the surface properties of the resist film, limiting PAG leaching (Fig. 7).

However, such behaviour corresponds to a material hydrophobicity which may affect the acid diffusion during the PEB process or the penetration rate of the developer during development process, and at least induces defectivity after development [4].

As a consequence, developer developable top-coat layers, are, for the time being, the best intermediate solution. Top-coat layer acts as a barrier layer, preventing PAG leaching into water, and modifying the surface properties of

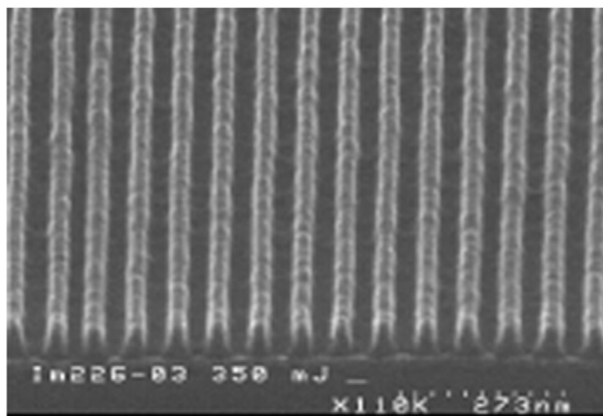

Fig. 6. 35 nm dense lines and spaces in a 60 nm film of a 193 nm chemically amplified resist (1.38 NA, immersion liquid: water). A developer developable top coat (90 nm film thickness) has been applied on the top of the resist to limit the chemical interactions with water.

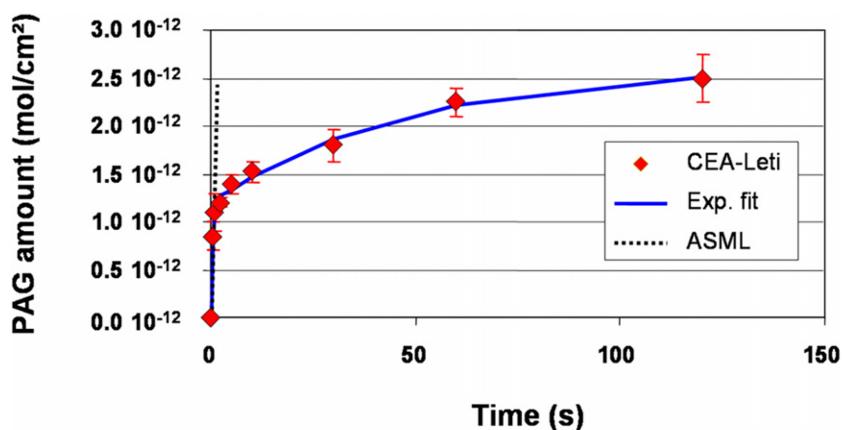

Fig. 7. Monitoring of the leaching kinetics for a 193 nm immersion dedicated resist.

the film in contact with water without impacting the resist dissolution rate in the developer. By adjusting the chemical formulation, the dynamic contact angles (advancing angle and receding angle) of the water meniscus can be tuned. Advancing contact angle values impact the air bubble trapped into water. High receding angles limit the generation of water droplet formation and immersion defects such as watermarks [5]. This new type of defect is still not well understood. It corresponds to an inhibition of the resist film where some water droplets have been left. However several hypotheses are still under discussion to explain this effect. As a result, immersion lithography is still at the early stage for the resist material development, giving some opportunities for the introduction of new chemistries.

5. Perspectives

As optical lithography progresses, new problems which were negligible in the past, become critical. Line Edge Roughness and resist outgassing are among the new issues which resist development will have to face in the near future.

Chemically amplified resists are based on a diffusion/reaction mechanism: one molecule of photoacid is able to react with several hundred to few thousands of blocking groups. This diffusion concept starts to be a concern below 90 nm and with the higher complexity of resist polymers (at least three different functionalities in 193 nm resists, and some bulky protecting groups). Indeed, this induces some roughness in the pattern definition, called Line Edge Roughness (LER), as the quantization of the photochemical reaction produces variation in the line geometry. There is a trade-off between high sensitivity resists, requiring low exposure dose and low line edge roughness. Limiting the line

edge roughness requires shorter diffusion length, which impacts negatively the resist sensitivity. New chemistries use several PAG in their resist formulations to achieve the best compromise (using both bulky PAG with limited diffusion length and small PAG molecule to boost the resist sensitivity). In addition, process conditions can have a strong impact on LER. Depending on resist film thickness or the solvent of the resist solutions, different LER can be observed in the patterns. Further understanding of this phenomenon will need to study more in detail the physics of the resist film formation by spin-coating.

Moving to EUV lithography also brings the potential problem of resist outgassing. In irradiating the resist with a 13.5 nm light under high vacuum, by-products of the photon/material interactions are outgassed and contaminate the optics. Research teams are now focusing on this topic that can dramatically change the conception of future resist chemistries.

In summary, advances in the chemical formulation of photoresists along with the fine tuning of the chemical amplification were able to cope with the technical progress of the optical lithography. Although more issues now have to be addressed and solved there is no fundamental reason to expect hard showstoppers in the optical resists.

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