Investigation of the Effects of Base Additives in Molecular Glass Photoresist Films

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Abstract:

Advances in the semiconductor industry are spurred by the need for higher resolution. To accomplish this, molecular glasses are used as photoresists in this project; they are potentially capable of higher resolution than traditional polymeric resists. Acid diffusion in the post exposure bake step leads to blur and widening of lines. This undesirable effect is counteracted by introducing a small concentration of base in the resist mixture. This project examines new base molecules with larger cores as opposed to commonly used base additives.

Introduction:

Molecular glasses possess several desirable qualities such as smaller molecule size and disordered arrangement, but enough cohesion to not be liquid [1]. A good resist has structural features that promote steric hindrance, such as a bulky, asymmetrical configuration. These properties also increase the glass transition temperature (Tg) [2]. The desired Tg is > 80°C because if it is too low, resist reflow will occur, and this decreases feature sharpness. Figure 1 shows the molecules that were studied.

These molecular glasses belong to the category of chemically amplified resists. They require a photoacid generator (PAG): a molecule added to the resist mixture which releases strong acid after exposure and post-exposure bake. In addition, some of the resist's free hydroxyl groups are protected with *tert*-butoxycarbonyl (*t*-BOC). Deprotection occurs when the *t*-BOC group is in the presence of acid, increasing solubility in the developer.

Some acid diffusion is desirable, as that is what creates the pattern in the exposed area of the wafer, where the PAG is activated by UV and post-exposure bake. However, too much acid diffusion in the unexposed area will adversely affect resolution [3]. Some acid will migrate into the unexposed area. Hence the focus of this project: introducing base additives to counteract acid diffusion in the unexposed area. Base additives are not expected to affect the exposed area of the wafer, as there is so much more acid in that area. However, in the unexposed area the base will have more of an effect on a small amount of stray acid.

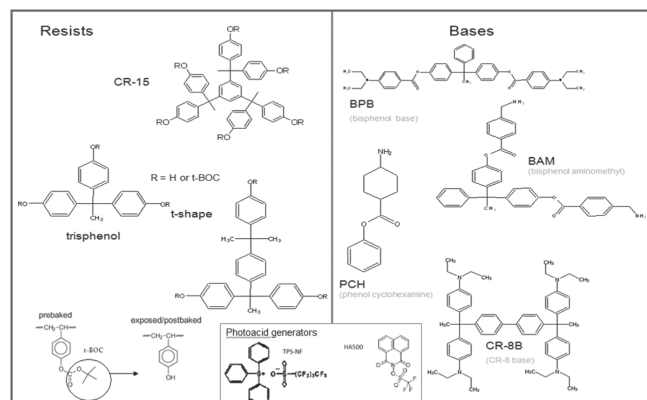

Figure 1: Resists, bases, and photoacid generators.

Experimental Procedure:

The resist mixture consisted of 57 mg resist, 5% photoacid generator with respect to resist, and 0.3% base additive with respect to resist. This was solvated with ethyl lactate to make a 5% solution. Wafers were spun for one minute at 2000 rpm with an acceleration of 1000 rpm/sec, followed by baking at 115°C for one minute. Exposure arrays were done using the Autostep AS200 365-nm stepper as well as the ASML PAS 5500 deep-UV stepper. Post-exposure bake was 80°C for one minute, then wafers were developed using dilutions of 0.26 N tetramethylammonium hydroxide. The amount of time and the strength of dilution were varied.

Contrast curves were constructed using the ABM contact aligner with a 254 nm mirror. The sensitivity was the exposure dose required to clear 50% of the resist, while the dose to clear was the exposure dose required to clear all the resist [1].

Etch rate studies were performed in order to further characterize the behavior of resist/base systems. Three etch gases were tested: trifluoromethane (CHF_3), tetrafluoromethane (CF_4), and sulfur hexafluoride (SF_6). Figure 4 shows the etch conditions, as well as the etch results.

Results and Discussion:

Exposure arrays were done on the AutoStep i-Line stepper for combinations of the resists and bases shown in Figure 1, as well as control wafers of resist without base. Neither trisphenol resist nor BPB base produced any image and were eliminated from consideration. The remaining combinations were redone on the ASML deep-UV stepper, and we found that the consistently best-performing base was the BAM base, which gave the smallest lines as well as the best quality.

Figure 3 shows 254 nm contrast curves for all resist/base systems. It is found that in general, base additives are seen to increase sensitivity. The etch rate studies, shown in Figure 4, show that BAM base increases etch resistance in all etch gases. In addition, an Ohnishi number and ring parameter were calculated for each resist/base system; a small Ohnishi number or large ring parameter should correspond to a low etch rate, i.e., high etch resistance [4]. The measured data were found to deviate from the predictions, however this can be accounted for by the fact that the models were originally developed for polymers and hence are inadequate for molecular glasses.

Future Work:

Since BAM base has consistently shown to be the best-performing base, further studies on it are warranted, such as testing it on higher-resolution equipment. In addition, it would be useful to expand the study to even more base additives for comparison purposes, such as aminosulfonate onium salts.

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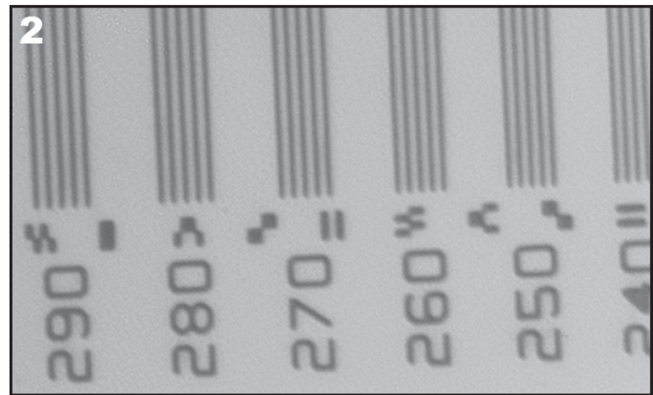
References:

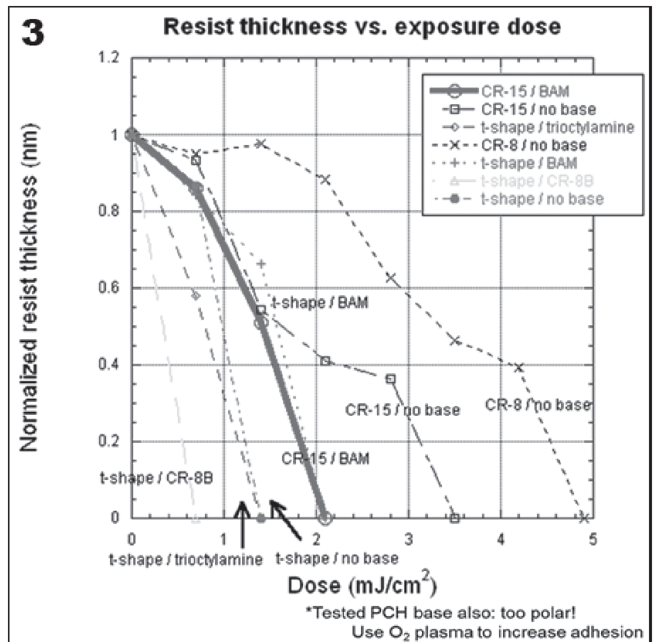
[1] Ito, H. Chemical amplification resists for microlithography. Adv Polym Sci, 172, 37-245. (2005).

[2] De Silva, A., Lee, J.K., Andre, X., Felix, N.M., Cao, H.B., Deng, H., and Ober, C.K. Study of the Structure-Properties Relationship of Phenolic Molecular Glass Resists for Next Generation Photolithography. Chem Mater, 20 (4), 1606–1613. (2008).

[3] Pawloski, A.R., and Nealey, P.F. The Multifunctional Role of Base Quenchers in Chemically Amplified Photoresists. Chem Mater, 14 (10), 4192–4201. (2002).

[4] Gogolides, E., Argitis, P., Couladouros, E.A., Vidali, V.P., Vasilopoulou, M., Cordoyiannis, G., Diakoumakos, C.D., and Tserepi, A. Photoresist etch resistance enhancement using novel polycarbocyclic derivatives as additives. J Vac Sci Technol B, 21(1), 141-147. (2003).





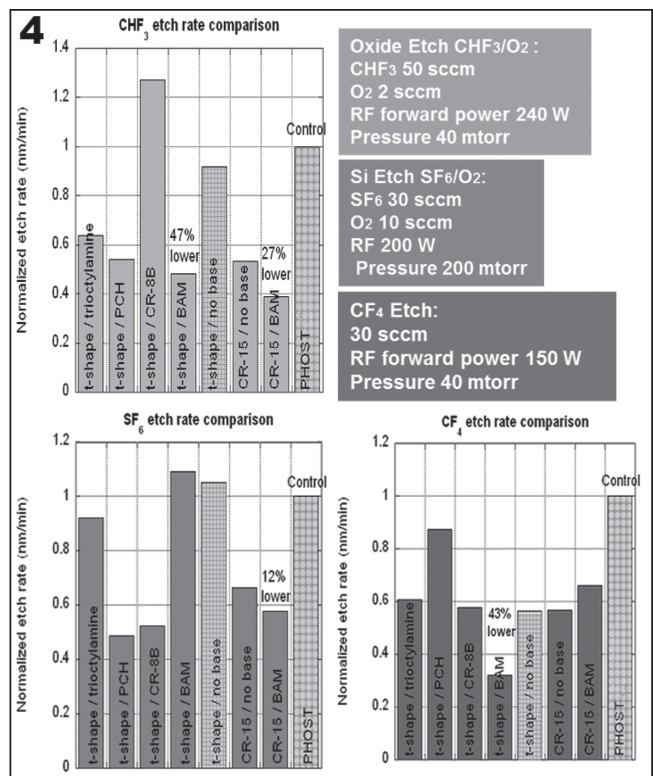


Figure 2, top: Representative ASML lines with t-shape resist and BAM base.

Figure 3, middle: 254-nm contrast curves.

Figure 4, bottom: Etch rate studies.