Chemically Amplified Main Chain Scission: New Concept to Reduce Line Edge Roughness and Outgassing

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1. Introduction

According to the ITRS structures down to 65nm have to be resolved for DRAM production until 2007. Coming along with this dimensions the demands on the photoresist raise. One of the first unsolved issues for lithography in the roadmap concerns the 80nm node already in 2004. The maximum line edge roughness must not exceed 4nm (3σ) for the 80nm node and has to be decreased down to 1nm until 2013. Taking the typical dimension of a polymer coil of several nanometer into account, we encounter a serious problem. Within this paper we give a probable solution to this problem by reviving an old resist strategy.

Another critical challenge for upcoming lithography generations is the outgassing issue. This becomes more important as oxygen as cleaning agent for the lense has to be excluded from the exposure process due to its absorption. We believe, that the concept presented in this paper can help to reduce the outgassing of fragments of the resist polymer.

2. Chemically Amplified Main Chain Scission of Polymers

The concept of chemically amplified main chain scission of polymers for photoresist materials was introduced in 1985 by Jean M. J. Fréchet, C. Grant Willson *et al.*[1] This group utilized the acid catalyzed thermal decomposition of polycarbonates to print structures of several microns. The initial work was extended from polycarbonates to polyethers in the following years.[1-9] However, last results in this direction were published in 1992 by Yoshiaki Inaki.[10]

Common chemically amplified DUV photoresists are based on polymers with a backbone consisting of carbon-carbon bonds. To be imageable protection groups are attached pendant to the polymer backbone. After exposure, in a bake step (PEB), the protection groups are cleaved and the polarity and therefore the solubility of the polymer chains in the exposed areas is changed. The size of the polymer coil does not change very much as a result of this treatment. Fig. 1 sketches this correlation.

Fig. 1. Schematic drawing of a common DUV resist with pendant protection groups.

Like common DUV polymers, the protection groups in main chain scission polymer are cleaved by chemical amplification. The difference is that the protection groups are not pendant to, but within the backbone as shown in Fig. 2. As a result, the post exposure bake generates polymer fragments in the exposed areas, that are similar to the monomers. These molecules do not only have a different polarity, like it is the case for the deprotected resist polymer commonly used, but new molecules with completely new properties like size, melting point and vapor pressure, solubility and polarity are generated.

These differences in property can be used to develop the structures printed into the resist.

Fig. 2. Main Chain Scission: The protection groups are in the polymer backbone.

For an initial experiment, we prepared a first polymer having protection groups in the main chain. In Fig. 3 the polymer structure is displayed with the protection groups encircled, including the chemically amplified thermal depolymerization reaction.

Fig. 3 Initial polymer to proof the principles of main chain scission. The protection groups are encircled.

As shown in Fig. 4, utilizing TGA analysis we found the pure polymer to be stable (5% weight loss) up to 175°C.

Fig. 4 Comparison of the thermal decomposition behavior of the polymer, p-toluene sulfonic acid and a mixture of both.

Addition of a strong acid, like p-toluene sulfonic acid, lowered the decomposition temperature by 104°C. From the plot it can be calculated, that the total weight loss of 40% at 150°C corresponds to the loss of CO₂, the diene and parts of the acid. These findings are in good agreement with the results found by the groups of Willson and Fréchet.[1-9]

3. Line Edge Roughness

Upcoming lithographic generations will suffer from new problems like line edge roughness.[11] For 248nm a minor problem, LER becomes significant for lithography at higher resolution starting at 193nm.[12] Several influences on the LER, like image feature size, exposure tool characteristics, resist materials (polymers, photoacid generators, additives), developer and processing conditions have been discussed so far.[13,14] However, only few papers consider the influence of the resist polymer on a molecular level. Lin *et al.* found phase separation of protected and deprotected resist polymers at the line edge to be contributing to the LER.[15] Polymer aggregates with a diameter of 20-30nm in resist films were reported by Yamaguchi *et al.*, who found aggregates remaining at the pattern edge after development cause linewidth fluctuations.[16]

The main chain scission concept is expected to overcome problems occurring from phase separation phenomena and from the size of polymer coils or polymer aggregates. Fig. 5 displays the problems encountered for a common resist.

Fig. 5 Schematic drawing of a common chemical amplified resist before and after exposure, bake and development; "I" stands for insoluble, "S" for soluble groups.

Ideally, during exposure/PEB all protection groups in the polymer are removed and polarity of the whole polymer is changed (Fig. 5, right). However, at the line edge, threshold dose is applied, resulting in an acid gradient and therefore in partly deprotected polymers. If polarity of these polymers is high enough to be dissolved during the development step, cavities will remain in the structure side walls. On the other hand, if polarity is not high enough, polymers with widely deprotected parts are not dissolved and stick out of the side walls due to phase incompatibilities with the protected resist material (Fig. 5, left). Assuming that polymer aggregates are formed in the resist film, the problems become even worse.

In contrast, in the exposed areas polymers with the protection group in the polymer backbone get depolymerized to the size of the monomer units (Fig. 6, right). These units can be dissolved in the developer.

Fig. 6 Schematic drawing of a chemical amplified resist with protection groups in the polymer backbone before and after exposure, bake and development.

Different to the system shown above (Fig. 5), in the line edge region the polymers are not deprotected in parts, but deprotection reactions result in small molecules. Since only these small molecules are dissolved in the development step, no holes or phase separated polymer coils (or aggregates) are remaining in the structure side wall. In consequence the side walls are expected to be smoother, free of roughness coming from molecular influences.

4. Outgassing

Contamination of optical systems during exposure has been recognized as a problem for DUV and 193nm lithography. However, for 157nm

and EUV lithography outgassing can become an important issue, since these techniques have to be performed in the absence of oxygen that acts as cleaning agent during exposure. For common resist materials the outgassing components originate mainly from the photo active component and from the protection groups of the resist.[17] While the contribution of the PAG stays unaffected by the main chain scission concept, outgassing due to the protection groups should be significantly lowered. Fig. 7 sketches the formation of volatile fragments, like 2-methylpropene or ethylvinyl ether, during the exposure of a common resist material. Every protection group that is cleaved generates a volatile fragment, and therefore contributes to the outgassing issue.

Fig. 7 Cleavage of protection groups during exposure results in outgassing of volatile fragments.

Some approaches to overcome this problem have been developed, like e.g. Willson's mass persistent resist or the "MANA" resist possessing high molecular weight leaving groups.[18,19]

During exposure (not PEB!!!) of a resist based on a polymer with the protection groups in the backbone a certain amount of protection groups is cleaved as well.

Fig. 8 Cleavage of protection groups during exposure results in non volatile oligomers.

However, since this are only a few protection groups that are affected, oligomers or polymers reduced in molecular weight are generated. Since these fragments are absolutely non volatile, no polymer related outgassing should occur.

5. Summary

In this paper we present a new concept for chemically amplified resist materials aimed at reduced line edge roughness and reduced outgassing. The concept is based on polymers that can be thermally depolymerized utilizing acid catalysis. The thermal depolymerization leads to small fragments in the exposed areas during the post exposure bake and therefore minimizes the influence of polymer and aggregate size as well as phase incompatibilities on the line edge roughness. On the other hand during exposure itself, if deprotection occurs, non volatile oligomers are generated and therefore polymer related outgassing is reduced.

6. References

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