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Effects of photoacid generator incorporation into the polymer main chain on 193 nm chemically amplified resist behavior and lithographic performance

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The need for chemically amplified resists (CARs) that can resolve sub-65-nm node features with sufficient linewidth roughness (LWR) control and sensitivity to meet the requirements outlined in the International Technology Roadmap for Semiconductors has placed a significant and daunting challenge for the design of resist materials that can achieve these goals. In this article, the ability to improve the performance of CARs designed for 193 nm lithography via the direct bonding of a photoacid generator (PAG) anion into the resist polymer main chain has been investigated. The bound-PAG anion resist is shown to achieve higher sensitivity and resolution with smaller LWR than their blended-PAG resist analog. Binding of the PAG anion provides reduced photoacid diffusivity, higher maximum PAG loadings, and more homogeneous PAG distributions that help achieve these three critical resist requirements. © 2007 American Vacuum Society. [DOI: 10.1116/1.2801868]

I. INTRODUCTION

The dramatic increase in device density and speed in integrated circuit technologies over the past 40 years has been driven principally by advancements in lithography. Currently, a major challenge must be overcome to continue this device density and speed scaling, namely, the development of lithography tools and materials that can provide sub-65-nm feature resolution while also maintaining extremely low feature edge roughness and high wafer throughputs (i.e., high photospeed resists).¹ In terms of lithography tools, 193 nm immersion lithography and extreme ultraviolet lithography are potential tool candidates for the sub-50-nm technology nodes.^{2,3} However, both exposure techniques require a resist material that is capable of translating their radiation patterns into a satisfactory physical relief image.

Chemically amplified resists (CARs) have served for more than 20 years as the high sensitivity, high resolution patterning media for transferring patterns from photomasks to semiconductor substrates. Modern positive-tone CARs are a blend consisting of many components including a protected polymer resin, a photoacid generator (PAG), and usually a base quencher for controlling photoacid diffusion and enhancing the environmental stability of the resist. Blended-PAG CARs have many potential problems that may limit their use for sub-50-nm node devices. These limitations include low PAG solubility in common casting solvents, component aggregation and segregation which cause nonuniform

resist film compositions (e.g., PAG segregation), and photoacid diffusion into nominally unexposed regions.⁴⁻⁸ The low PAG solubility in casting solvents creates a low maximum PAG concentration that can be used in formulating CARs (e.g., typically <5 wt % PAG can be used in blended-PAG CAR formulations). Nonuniform distribution of components in the resist film can lead to nonuniform reaction and development in the film, which can cause poor imaging performance. For example, several studies have linked PAG segregation to increased line edge roughness in CARs.^{9,10} Finally, photoacid diffusion in the resist leads to image blur, loss of resolution, and poor critical dimension (CD) control. These problems ultimately create the trilateral trade-off between achieving high resolution, high sensitivity, and low linewidth roughness through formulation changes in blended-PAG CARs. The design of novel resist materials that can achieve all three characteristics will be critical for the continued success of high resolution patterning in integrated circuit manufacturing.

In order to address this critical resist material design issue, we have recently been investigating a number of routes to overcome these limitations in current CAR designs. One route to improving CAR performance that has been recently developed is the concept of directly incorporating the PAG into the polymer main chain. This simple idea has already been shown to some degree to be one promising route to creating a new generation of high performance CAR materials.^{11,12} This design enables substantially higher PAG loadings than in blended systems while also providing a direct means for limiting photoacid diffusion. In this work, the

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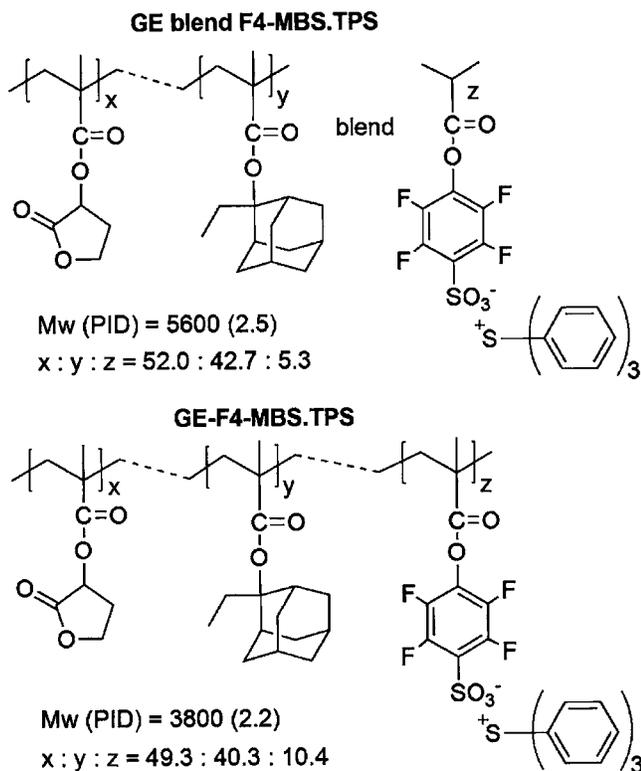


FIG. 1. Structures and compositions of 193 nm polymer-bound PAG and blended-PAG resists.

photosensitivity, resolution, and linewidth roughness (LWR) of a novel polymer-bound PAG CAR designed for 193 nm lithography and its blended-PAG analog have been studied and are compared in detail.

II. EXPERIMENT

A. Material preparation

Structures and compositions of resist materials used in this study are shown in Fig. 1. The PAG and polymers were synthesized and prepared as described previously.¹² The polymer-bound PAG terpolymer was composed of 2-ethyl-2-adamantyl-methacrylate (EAMA), γ -butyrolactone methacrylate (GBLMA), and triphenylsulfonium salt 4-(methacryloxy)-2,3,5,6-tetrafluorobenzenesulfonate (F4-MBS-TPS). The blended-PAG analog resist was prepared by blending triphenylsulfonium salt 4-(isobutyloxy)-2,3,5,6-tetrafluorobenzenesulfonate (F4-IBBS-TPS) with GBLMA-co-EAMA copolymers of similar GBLMA:EAMA monomer ratios as used in the polymer-bound PAG resist. Resist solutions were made by dissolving 4 wt % solids (including polymer resin and PAG) in cyclohexanone (Sigma Aldrich) and filtered through 0.2 μm Teflon syringe filters. Prime grade 4 in. silicon wafers were used as the substrate for deep ultraviolet (DUV) exposure. A freestanding silicon nitride membrane was prepared as described in previous work and used as the substrate for ultrahigh aerial image contrast electron-beam patterning.¹³ Both substrates were primed with a solution containing 20 vol % 1,1,3,3,3-hexamethyl-

disilazane (ICN Biomedicals) and 80 vol % propylene glycol-1-monomethylether-2-acetate (Sigma Aldrich). Resist films (~ 134 nm) were prepared by spin coating the resist solutions onto the primed substrates (3000 rpm, 60 s) and baking the resulting film at 100 $^{\circ}\text{C}$ for 90 s.

B. DUV exposure and photoacid concentration determination

The resist films for collecting DUV contrast curves were exposed with incremental doses using an Oriel Instruments exposure source (model No. 87530-1000, Hg-Xe arc lamp) equipped with a 248 nm bandpass filter (bandwidth ~ 11 nm, full width at half maximum). The intensity of the lamp source was measured to be 1.01 mW/cm^2 using a Moletron PM3 power probe and EPM2000 energy meter. After exposure, the resist film was post-exposure baked at 100 $^{\circ}\text{C}$ for 90 s, developed with standard 0.26N tetramethylammonium hydroxide solution (TMAH) (AZ Electronic Materials) for 15 s, and rinsed with de-ionized water. The remaining film thickness in the exposed region was measured using a variable angle spectroscopic ellipsometer (J. A. Woollam Inc.) by fitting the ellipsometry data with a Cauchy model for the resist film in the low absorbance wavelength region (400–1000 nm). The photoacid concentration generated in the resist film upon exposure was quantified by an on-wafer acid-sensitive dye method.¹⁴

C. Ultrahigh aerial image contrast electron-beam patterning

Resist films for electron-beam patterning were exposed using a JEOL JBX-9300FS electron-beam lithography system (100 kV, 2 nA) with a beam spot size of 8 nm. Isolated spaces were patterned via single pixel wide electron-beam exposures, and 1:1 line/space arrays were patterned with various pitch sizes. The patterned resist films were post-exposure baked at 100 $^{\circ}\text{C}$ for 90 s, developed in 0.26N TMAH solution for 15 s, and rinsed with de-ionized water. The resulting relief patterns were top-down imaged using a LEO 1530 thermally assisted field emission scanning electron microscope (SEM) (3 kV, 100 000 magnification). The intrinsic resolution of these positive-tone resists was determined by the width of the minimum isolated space that could be resolved. The half-pitch resolution and LWR were determined using offline image analysis of SEM images, and final resist CD and LWR values were taken as the average from five different lines with a 1.5 μm inspection length.

III. RESULTS AND DISCUSSION

A. Photosensitivity and resist contrast

The DUV photosensitivity and resist contrast of both the polymer-bound PAG and blended-PAG resists are shown in Fig. 2(a). The corresponding photoacid concentration upon DUV exposure is also shown in Fig. 2(b). The polymer-bound PAG resist showed significantly improved photospeed (15.0 mJ/cm^2) and resist contrast (8.9) as compared to its blended-PAG analog (20.0 mJ/cm^2 and 5.5). Looking at the

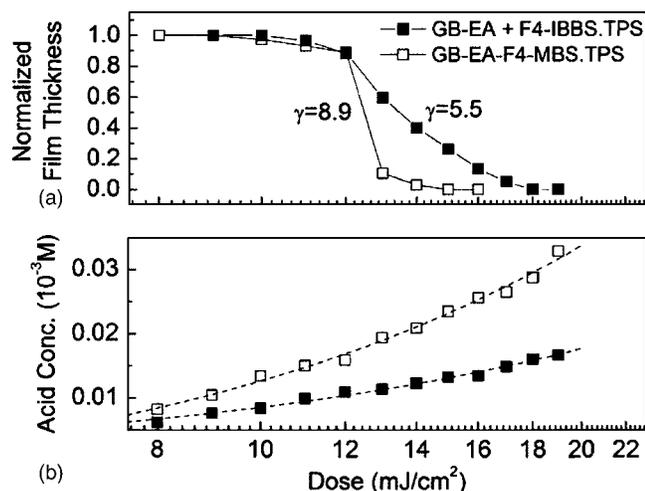


Fig. 2. (a) Contrast curves and (b) the corresponding acid concentrations for the polymer-bound PAG and blended-PAG resists using DUV (248 nm) exposure.

combination of Figs. 2(a) and 2(b), it is possible to draw some comparisons about the relative photoacid diffusion and photoacid catalytic deprotection chain lengths in the polymer-bound PAG and blended-PAG resists. For example, it is observed at the condition where both resists generate $0.015 \times 10^{-3}M$ photoacid concentration, that approximately 10% film thickness loss for the polymer-bound PAG resist and 95% film thickness loss for the blended-PAG resist occurs during development. Since both resists have approximately the same composition, it is expected that their dissolution properties should be similar which would allow differences in developed film thickness loss to be attributed mainly to differences in resist deprotection level after exposure and post-exposure bake. In this case, the observed film thickness losses during development for identical photoacid concentrations in the two resists would indicate that the extent of deprotection in the polymer-bound PAG resist is significantly lower than in the blended-PAG resist. This supports the idea that the photoacid diffusivity and catalytic deprotection chain length are significantly smaller for the polymer-bound photoacid in the case of the polymer-bound PAG resist as compared to the free acid made in the blended-PAG resist. By looking at the same resist thickness loss (50%) in Fig. 2(a), the corresponding acid concentration [$0.018 \times 10^{-3}M$] in the polymer-bound PAG resist is significantly higher than that [$0.012 \times 10^{-3}M$] in the blended-PAG resist. Although the bonding of the PAG anion to the polymer chain may reduce the photoacid diffusivity and thus decrease the catalytic chain length of the photoacid, the ability to incorporate much higher PAG loadings in the polymer-bound PAG material can enable generation of substantially higher photoacid concentrations in the polymer-bound PAG material under the same exposure dose that can compensate for the reduced catalytic chain length. The end result is that it can be possible to produce higher photospeed materials in the polymer-bound PAG resists as compared to blended-PAG resists even with the reduced photoacid diffusion. Further-

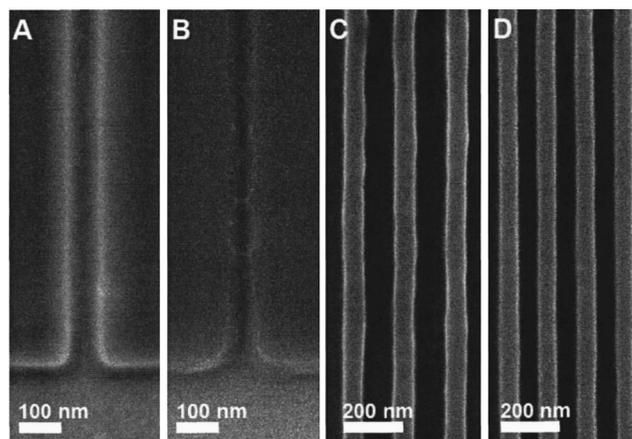


Fig. 3. SEM images of patterned resist films: minimum isolated space pattern achieved on (A) GE blend F4-IBBS.TPS and (B) GE-F4-MBS.TPS, and minimum 1:1 line-space patterns achieved on (C) GE blend F4-IBBS.TPS and (D) GE-F4-MBS.TPS.

more, the photolysis of the PAG and the resulting photoacid anion formed on the polymer may serve to further increase the degree of the polarity change in the polymer between the exposed and unexposed materials that can act in concert with the deprotection reaction to increase the development contrast in the case of the polymer-bound PAG materials.

B. Intrinsic and half-pitch resolution

The polymer-bound PAG resist showed the capability to resolve higher resolution features than the analogous blended-PAG resist, as illustrated in Fig. 3. The minimum isolated space width resolved for the polymer-bound PAG resist was 39.3 nm, which was significantly smaller than the 76.2 nm minimum feature size resolved for the blended-PAG material. The fact that these isolated space features were patterned using single pixel wide electron-beam exposures on a low-backscatter substrate allows one to determine a crude estimate of the corresponding photoacid diffusion lengths in these materials. One measure of photoacid diffusion length that can be used to compare the materials is the minimum resist half space width produced from the single pixel wide exposure minus the approximate half single pixel electron-beam diameter, which we will refer to here as the photoacid diffusion length. Since the single pixel electron-beam diameter is 8 nm, the photoacid diffusion lengths in this work were calculated for the polymer-bound PAG and blended-PAG resists to be 15.6 and 34.1 nm, respectively, under identical pre- and post-exposure processings. This result supports our hypothesis that incorporating the PAG anion into the polymer chain significantly reduces photoacid diffusion and can dramatically reduce photoacid diffusion induced image blur. The half-pitch resolution achieved by the polymer-bound PAG resist was also superior to that of the blended-PAG resist. Finally, the blended-PAG resist showed much more significant linewidth slimming (12.7 nm smaller than the smallest 1:1 nominal 80 nm feature that was obtained for that resist, or an approximately 16% CD error) than that of

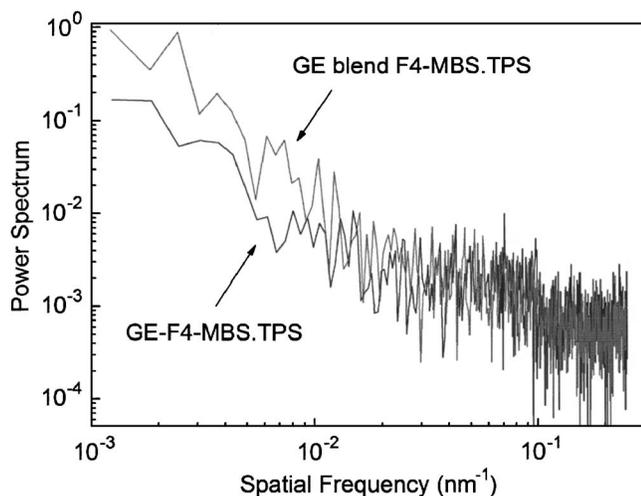


FIG. 4. Power spectrum of the minimum half-pitch patterns of GE-F4-MBS.TPS (60 nm) and GE blend F4-IBBS.TPS (80 nm).

the polymer-bound PAG resist (3.3 nm smaller than the nominal resist CD of 60 nm, the highest resolution 1:1 line-space feature obtained for that resist, or an approximately 5% CD error).

C. Linewidth roughness

The blended-PAG resist showed obvious linewidth fluctuations as compared to the polymer-bound PAG material. The half-pitch SEM images shown in Fig. 3 are one clear example of this dramatic difference. The power spectrum of both resists at the best half-pitch resolution is shown in Fig. 4. The major improvement of LWR is in the low spatial frequency region. This region is approximately the length scale at which the roughness might be expected to become dominated by photoacid diffusion and inhomogeneous PAG distribution effects. The 3σ LWRs of polymer-bound PAG and blended-PAG resists are calculated to be 6.0 and 11.3 nm, respectively. As compared to the blended-PAG resist, the reduced photoacid diffusion in polymer-bound PAG resist couples with the higher PAG loading to lead to more uniform photoacid distribution after exposure and thus we believe leads to the observed reduction in LWR. In essence, binding of the PAG anion to the polymer and incorporation of a higher PAG loading produces a higher density of overlapping but smaller deprotection volumes created by each single photoacid molecule as compared to the blended-PAG system at the deprotection front. These smaller overlapping deprotection volumes result in a smoother edge transition at the developed feature edge and lower LWR.

IV. CONCLUSIONS

The impact on resist performance of binding the PAG anion to the resist polymer main chain has been studied for a

193 nm chemically amplified photoresist. The polymer-bound PAG resist exhibits higher photosensitivity, improved resolution, and lower LWR than its blended-PAG analog. The improved lithographic performance of the polymer-bound PAG resist is due to a combination of factors including the higher PAG loading possible in the polymer-bound PAG resins, the reduced photoacid diffusivity due to binding of the photoacid anion, and the elimination of the inhomogeneous distribution of PAG. These results suggest that the design of polymeric resist resins containing polymer-bound PAG anions can break out of the perceived limitations and trade-offs between resolution, LWR, and photospeed in traditional multicomponent blended-PAG CARs. Using this new material design paradigm, it may be possible to develop resist material solutions without sacrificing any of the three critical characteristics (i.e., photospeed, resolution, or edge roughness). This work also validates that our basic design, which makes possible a single-component resist material, is a promising route to achieving resist materials with superior performance for future lithography generations.

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