POSITIVE CHEMICAL AMPLIFICATION RESIST FOR DEEP UV LITHOGRAPHY

Hideo Kikuchi, Nobuyuki Kurata and Keiichi Hayashi

Research Laboratory, Toyo Gosei Kogyo Co., Ltd.
563 Komegasaki, Funabashi, Chiba 273 JAPAN

The chemical amplification concept proposed in 1982 to support high resolution short wavelength lithographic technologies is based on acid-catalyzed crosslinking, deprotection, and depolymerization reactions¹⁾.

This paper reports the chemical amplification resist system which is based on the acid-catalyzed deprotection reactions of methacrylic ester copolymers with styrenic monomer. Resolution capability of these resist systems for KrF excimer laser lithography is demonstrated.

POLYMERS AND ACID PHOTOGENERATORS

The copolymers of 1a-c containing acid labile protecting groups of carboxylic acid as shown in Figure 1 were prepared.

Figure 1. Copolymers of styrenic monomers and methacrylic esters containing acid labile protecting groups

Figure 2. Acid Photogenerators

Photoresist solutions were prepared by dissolving polymers 1a-c and various acid photogenerators (3.0 wt.% relative to the polymer) as shown in Figure 2 into diethylene glycol dimethyl ether (DEGDME).

The resist solutions were filtered through 0.2 μm filters. Spin coated resist films on a NaCl plate were baked at 85°C for 30 min., were exposed through a 254 nm and were postbaked at 105°C for 10 min. Using AG-1, AG-2, AG-3, AG-4 and AG-5 as a acid photogenerator, methoxymethyl carboxylate or 2-tetrahydropyranyl carboxylate was converted to carboxylic acid. These reactions were found by IR spectroscopic studies. On the contrary, using AG-6 and AG-7, a significant amount of absorption due to carboxylic acid was not observed.

OPTICAL PROPERTIES

The transmittance of the resist film composed of polymer 1a ($x=0.5$) containing 5wt.% of AG-1 was 47% at 248 nm and did not significantly change with exposure. The transmittance of 3 wt.% AG-1 was 58%.

LITHOGRAPHIC PERFORMANCE

Each resist solution which consist of polymer 1a ($x=0.5$) and AG-1 (3wt.% or 5wt.% relative to the polymer) dissolved in DEGDME or 1-acetoxy-2-methoxyethane (AME) were spin-coated on a silicon wafer, which was then prebaked on a hot plate at 85°C for 1 min, respectively. Lithographic imaging was performed using a KrF excimer laser stepper

(Canon FPA-4500, NA=0.37). The irradiated resist films were baked on a hot plate at 60°C or 70°C for 1 min: and then developed in 0.08N TMAH.

Figure 3 shows the effects of the acid photogenerator concentration, post exposure bake (PEB) temperature and solvent on the contrast curves. Figure 4 shows their effects on the pattern profile.

Figure 3. Effects of acid photogenerator concentration, PEB temperature and solvent on contrast curves

solvent		DEGDME	AME	
AG-1		5 wt %	5 wt %	3 wt %
PEB temp.	60°C			
	70°C			

Figure 4. Effects of acid photogenerator concentration, PEB temperature and solvent on pattern profile (0.4 um 1/s pattern)

Using DEGDME as a solvent, the resist showed a very high sensitivity of 7 mJ/cm² (Eth), however, its pattern profile showed reverse taper profiles. These results suggest that the solvent remains in the resist film even after the prebake and an acid generated upon exposure rapidly migrates within the resist film during the post exposure bake.

Figure 3 also shows that post exposure bake temperature has little effect on the sensitivity. This phenomenon might be due to the high reactivity of the protective groups of the polymer with acid.

Figure 5 shows line and space patterns (l/s) in a 0.96 micron thick film with vertical sidewalls. A 0.32 micron l/s pairs resolution was easily achieved with no critical thickness loss.

Figure 5. SEM micrographs of 0.35um and 0.32um l/s pairs in 0.96um thick film of the resist composed of the polymer 1a and 3 wt% AG-1 exposed on the Canon FPA-4500 excimer laser stepper (NA=0.37). Prebaked at 85°C/1 min.; exposure at 36 mJ/cm²; post exposure bake at 70°C/1 min.; 1 min. development in 0.08N TMAH

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