Surfactant-Modified Epoxy Resins as Novel Negative-Acting Deep UV Photoresists

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SYNOPSIS

Simple cresol epoxy novolac resins have been modified with hydrophilic chains producing surfactant-modified epoxy resins. They have been formulated with catalytic amounts of photoacid generator and solvent and subsequently exposed to deep UV light. With respect to their photochemistry, they behave as conventional chemically amplified negative acting materials, however, their overall lithography is somewhat more novel. For example, they have high contrast behavior and unexposed regions swell in aqueous base developer and peel-off into solution through an apparent adhesion loss at the wafer–photoresist interface.
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INTRODUCTION

Recently much effort has been invested in achieving the goal of designing high-performance photoresists given the limitations found with current i-line novolac-based materials.[1] It is anticipated that techniques including deep UV exposure, coupled with phase-shifting masks and suitable resists, will enable the production of DRAMs with greater than 64 Mb capacity, employing lithographically fabricated structure of ≤ 0.35 μm. Toward this aim many approaches have been examined,[2] nearly all of which are base-aqueous developable. This commonality results from the need to process with materials with minimal environmental impact; as such, nonorganic developing solutions are desirable.

Applications of epoxy chemistry in microlithographic materials are well known. One of the first commercially successful E-beam-sensitive systems used to write mask blanks was the "COP" resist,[3] which is a copolymer of glycidyl methacrylate and ethyl methacrylate. High-performance E-beam resists based on fractionated epoxy-novolac materials have been investigated.[4] Examples of epoxy-containing materials specifically designed for aqueous developing photoresist applications include copolymers of glycidyl methacrylate and methacrylic acid[5] as well as copolymers of hydroxystyrene and dicyclopentyloxy methacrylate.[6] Similarly, for many years surfactants have been formulated with resists as additives to (1) enhance film formation,[7] hence improving surface structure,[8] (2) improve the efficiency of developing solvents,[9] so-called descumming additives, and (3) minimize adsorption of contaminants, e.g., organic and inorganic bases.[10] In an attempt to utilize these individual characteristics, surfactant-modified cresol epoxy novolac resins (SMCENs) have been synthesized and their performance in a chemically amplified photoresist formulation is reported.

EXPERIMENTAL

SMCEN Preparation

The surfactant employed was prepared *in situ* with the epoxy resin according to a two-step synthesis[11] as described in Figures 1 and 2. Both the anhydride and poly(ethylene glycol) methyl ether were used as supplied by Aldrich Chemical Company, while the epoxy resins were obtained from The Dow Chemical Company.

Introduced to a glass round-bottom flask are 10 g of 2-dodecene-1-yl succinic anhydride (M_w

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Journal of Applied Polymer Science, Vol. 58, 179–183 (1995)
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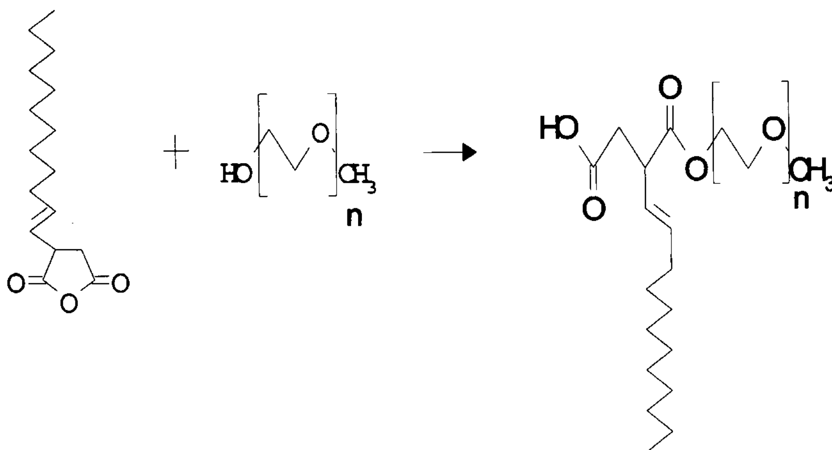

Figure 1 Synthesis of a hydrophilic hemicarboxylic acid ester.

= 266.38, 37.54 mmol) and 75.10 g of poly(ethylene glycol) methyl ether (M_w = 2000, 37.55 mmol). Under nitrogen and stirring with a magnetic bar, the reaction was carried out at 140°C for 3 h. Completion was determined by thin-layer chromatography on silica using a mixture of 10% methanol in dichloromethane as eluent (R_f anhydride, 0.93; R_f alcohol, 0.43; R_f acid ester, 0.34). The yield was quantitative.

In a glass round-bottom flask 14 g of cresol epoxy novolac (EEW = 218 ± 5, 64.2 meq) and 6 g of acid ester (M_w = 266.38, 2.65 mmol) are introduced. Under nitrogen and stirring with a magnetic bar, the blend was heated up to 160°C for 2 h. At 90°C, 400 ppm of a 70% solution in methanol of iodide triphenyl phosphonium chloride is added. The completion of the reaction was checked by titration of the epoxide content. Some yellowing was observed. The final epoxy equivalent weight (EEW) value was 307 ± 7; a theoretical value of 315 was expected.

SMCEN Photoresist Formulation

Two different SMCENs with EEWs 307 and 287 were evaluated. The polymer in each case was held in ethylene glycol dimethyl ether as a 75% solids solution. Ethylene glycol dimethyl ether (glyme), diethylene glycol dimethyl ether (diglyme), and propylene glycol methyl ether acetate (PGMEA) were used as solvents in photoresist formulations. Triphenyl sulfonium hexafluoroantimonate was used as a photoacid generator and was obtained from the General Electric Company. Typically, formulations contained 10% polymer when glyme was used, and 10–30% when PGMEA or diglyme was used in the formulations (solvents were analytical grade and used as supplied from Aldrich Chemical Co.). The amount of photoacid generator was 5–7% on solid content.

Lithography and Characterization Equipment

A 500-W Hg-Xe deep UV exposure tool from Oriel was utilized. Narrow band 254- and 248-nm filters were used for wavelength selection. UV spectra of films on quartz substrates were recorded on a Hitachi U-2000 spectrophotometer and film thicknesses measured with a Dektak profilometer.

LITHOGRAPHIC CHARACTERIZATION

SMCEN photoresist formulations act as negative resists, as recorded with the unmodified CENs based compositions.[4] The acid produced by the photocatalyst initiates crosslinking reactions of the epoxy functional groups. The characteristics of these resists are discussed in relation to the specific lithographic processing steps.

Spin Coating

Films (200–1000 nm) on Si wafers of formulations with the three different solvents were spin coated at between 4000 and 5000 rpm. Diglyme gave the best uniformity.

Prebake

The films were baked for 3 min at 90°C in a standard convection oven. It was observed that film defects after spinning are exaggerated during the prebake step and large pin holes are formed. This effect was

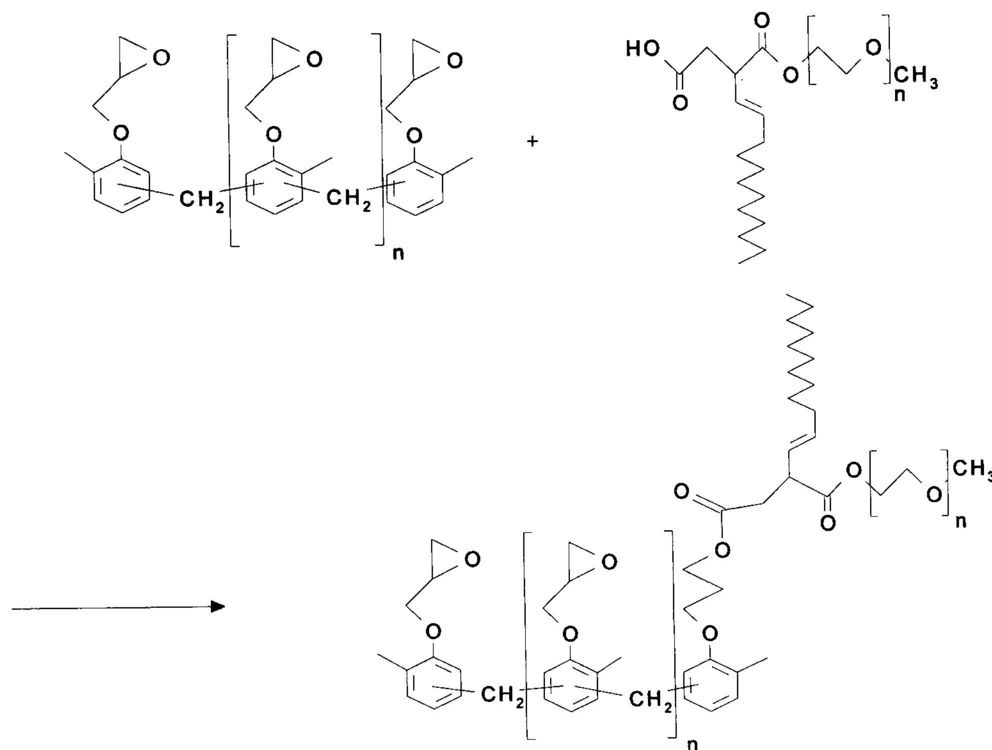

Figure 2 Synthesis of the surfactant modified epoxy.

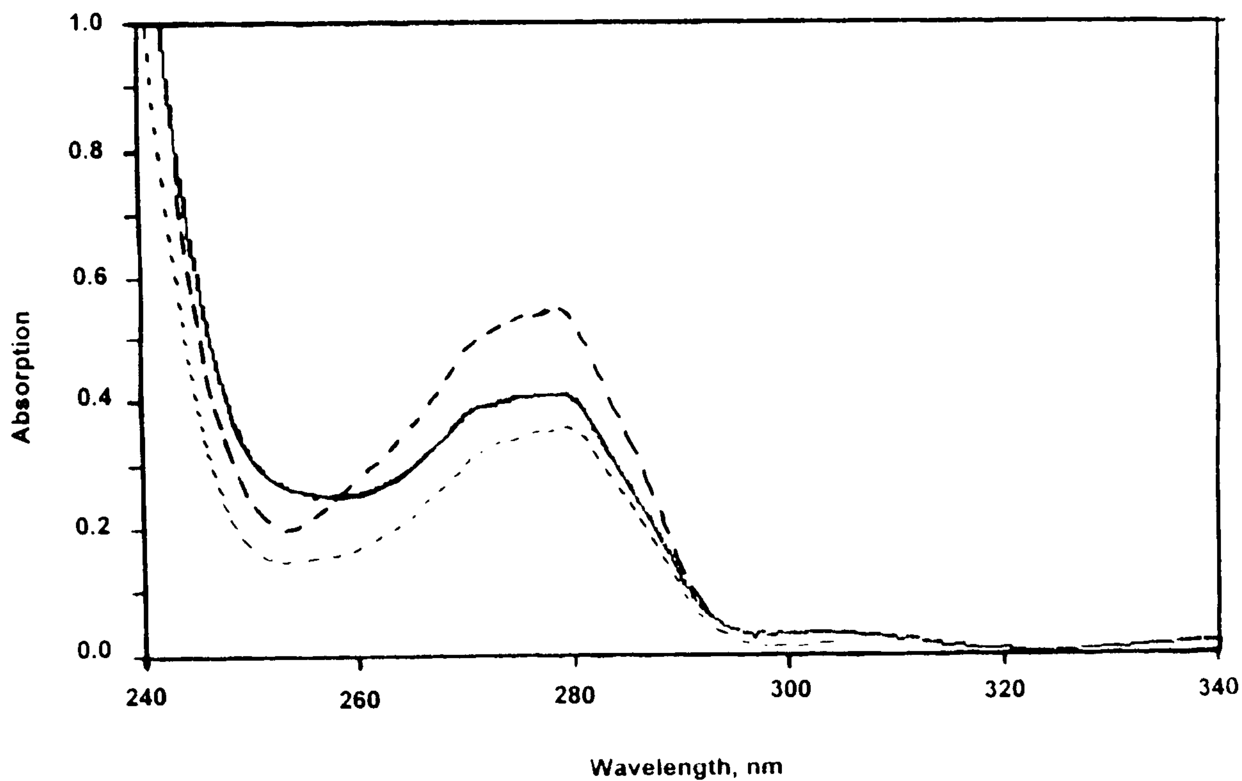

Figure 3 UV absorption spectra for original CEN (thick dashed line), SMCEN (light dashed line), and SMCEN with 5 wt % photoacid generator (solid line).

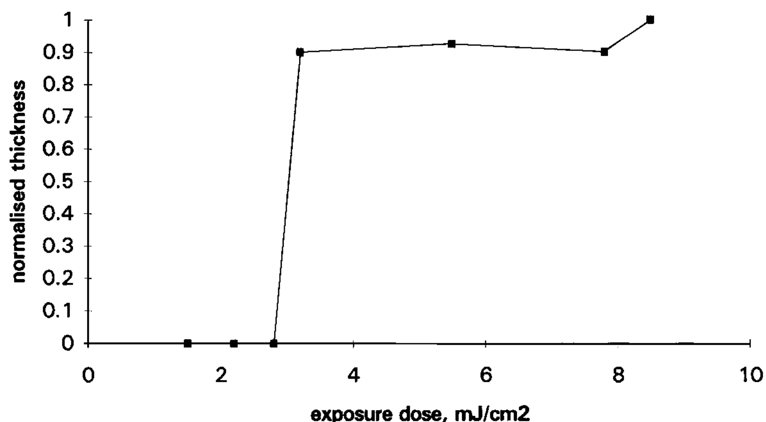

Figure 4 Exposure curve obtained using SMCEM with 5 wt % photoacid generator using 248 nm radiation.

dramatically reduced by filtering solution before preparing the films and also processing in a clean environment. The presence of the surfactant chains, possibly causing particle formation, may be responsible for this behavior. It was also observed that the films are very soft; for example, their thickness cannot be measured with the Dektak instrument. To measure thickness it was necessary to expose and postbake the films.

Exposure

UV spectra of films were similar to the original CENs (see Fig. 3). The presence of the surfactant does not substantially change the spectrum and the film remains reasonably transparent in deep UV light (A_{254} = 0.327 and A_{248} = 0.506 for a 1-μm film containing 5% photoacid generator in SMCEN of EEW = 307). Using the Oriel exposure tool, bulk sensitivity for a 90% thickness retention was approximately 12 mJ cm^{-2} with 254 nm source in a 1-μm film. Thinner (0.6–0.7 μm) films with the same catalyst content exposed at 248 nm show bulk sensitivities close to 5 mJ cm^{-2}.

Postbake

The time and temperature were chosen to be similar to previous work with the original CEN compounds (90°C for 3 min). After the postbake, latent images were clearly visible when exposure doses were higher than the threshold limit. The exposed areas appear as if they were mechanically separated from the unexposed regions. Further, it was found that delays between exposure and post bake severely change the lithography, i.e., resulted in sensitivity loss. Exposed features also became thinner with increasing delay.

Development

Standard AZ type developers (e.g., AZ 500-27, primarily a 2.5 wt % tetramethyl ammonium hydroxide (TMAH) solution) at 45°C gave the best results. Development of the photoresist time varied between 5 and 30 min. The unexposed/postbaked SMCEN material did not develop by dissolution of polymer into the aqueous phase, and selectivity occurred through adhesion loss. The chemistry of this process is not clear, although it appeared that developer enters the unexposed regions, diffuses through the bulk, swelling the material, and when it reaches the wafer–photoresist interface causes adhesion loss. As such, material was peeled-off into the aqueous phase. In the case of the SMCEN with higher EEW (i.e., greater surfactant modification) development was quicker. This was also noted with poorer quality films, indicating that the adhesion loss was dependent on developer penetration rate. Additionally, water alone, even at temperatures up to 50°C, did not develop the resist and the presence of ionics, from the TMEH solution, was necessary to develop patterned structure. An exposure curve, typical of results obtained with the SMCEN-containing resists studied to date, is shown in Figure 4. The very high contrast for this system (i.e., the tangent to the curve) highlights the peeling action and is not typical for negative acting systems.

Further experiments are required to determine if this resist is suitable for fine line lithography and also to understand the process details, particularly the development stage, of this novel negative acting photoresist.

The authors would like to express their gratitude to the Dow Europe Discovery Research Fund for financial assistance and also Roman Streck, Dow Deutschland Inc., for assistance with the relevant analytical chemistry.

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Received April 1, 1995
Accepted April 21, 1995