

Deep UV Photoresists : Dissolution Inhibitor

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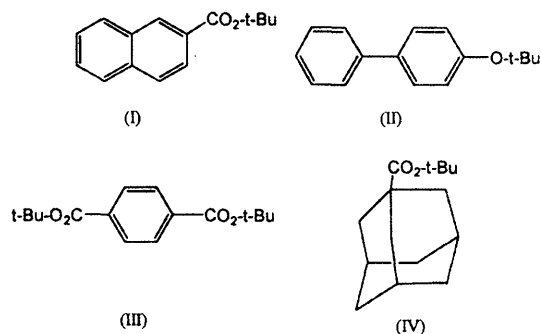
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Abstract : A new class of deep UV photoresist based on the principles of chemical amplification was developed. This photoresist consists of three basic elements: a copolymer, blocked tetrabromobisphenol-A as a dissolution inhibitor and a photosensitive onium salt as a photoacid generator. On irradiation followed by a post exposure bake, tert-butoxycarbonyloxy phenyl group is converted to phenol group. Thus the initially base insoluble resin is converted under UV irradiation to a base soluble resin which may be preferentially removed by dissolution. This new photoresist display high sensitivity, 10 mJ/cm².

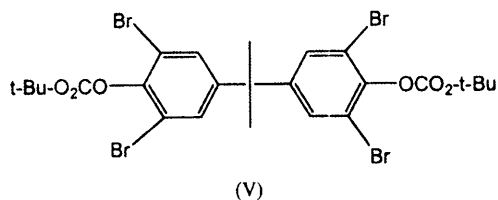
1. INTRODUCTION

Photolithography is a key technology for very large scale integration(VLSI) and the fabrication of sub-micron devices.^{1, 2)} The basic principle of photolithography is based on the radiation-induced structural degradation, or alternation of highly specialized photosensitive polymeric films, called photoresists.³⁻⁵⁾ In this article, we describe a new class of dissolution inhibitor which can be used to produce novel photoresists that operate using the principle of chemically amplification. Generally, three component chemically amplified resist (CAR) systems consist of a base soluble resin, a dissolution inhibitor and a photoacid generator (PAG).^{6, 7)} A base soluble resin based on the poly(4-hydroxystyrene-co-styrene) has been prepared and shown to possess good etching resistance and a low deep-UV absorbance. Dissolution inhibitors have mainly been employed which consist of a base soluble carboxylic acid protected by tert-butyl group that is labile in the presence of a strong acid. A considerable number of photoacid generators also have been tested including a number of aromatic onium salts having both inorganic and organic counterions.^{8, 9)} The dissolution inhibitors having tert-butyl groups (I~IV) have been reported.^{10, 11)}

All of these compounds worked in experimental



resist formulations and in that regard were useful in demonstrating the feasibility of using this chemistry. However, for a variety of reasons cited below, it was found that many of them would not fit into a practical system. 1) All the aromatic dissolution inhibitors had strong absorption in the deep UV. 2) Poor quality films due to incomplete miscibility of the base resin and the dissolution inhibitor. 3) Irreproducible results due to volatility of dissolution inhibitor. 4) Poor resolution due to low thermal stability (low melting point) of dissolution inhibitor. Thus, we introduce tetrabromobisphenol-A protected by tert-butoxycarbonyl group (V) as a dissolution inhibitor which solves many of these problems. This paper deals with the preparation and preliminary tests on photoresist formulations based on this chemistry.



2. EXPERIMENTAL

Materials and Measurements :

Tetrabromobisphenol-A, potassium tert-butoxide, di-tert-butylidicarbonate were purchased Aldrich Chemical Co. and used as received. (8:2) Poly(4-hydroxystyrene-co-styrene) (M_w = 12,000g/mol, M_w/M_n = 1.1) was used as received from the Shin-Etsu Company. (4-Decyloxyphenyl) diphenylsulfonium hexafluoroantimonate was prepared as described in a previous report.¹²⁾

¹H-NMR data was obtained in CDCl₃ with a Varian Model XL 200 Spectrometer equipped with a Fourier Transform Accessory. UV spectra were recorded on a Hitachi U-2000 Spectrophotometer. Molecular weight and molecular weight dispersity were measured using a Hewlett Packard 1047A Gel Permeation Chromatography.

Instruments for Lithographic Evaluation :

The photoresist solutions were purified by filtration through 0.2m filters (Scientific Resources Inc.) and a Solitech Model 1110 Headway Spin Coater was used for spin coating. Film thicknesses and refractive indices were measured on a Nanometrics Co. (Nanospec/AFT) and Rudolph Auto EL-II Ellipsometer. UV irradiation from a GE H3T7 450W medium pressure mercury-arc lamp, was used without a filter, in air, for preliminary test. Deep UV irradiations were carried out with a 248nm KrF excimer laser system (N.A = 0.45) at Rochester Institute of Technology(RIT).

Synthesis of 4,4' - Isopropylidenebis(2,6-dibromo-1-tert-butoxycarbonyloxy benzene) (B-BPA) : A solution of 10g (0.018mol) tetrabromobisphenol-A in dry THF was treated with 4.03g (0.036mol) of potassium tert-butoxide

under a nitrogen atmosphere. After stirring for a few minutes at room temperature, 8.72g (0.04 mol) of di-tert-butylidicarbonate was added and the mixture was stirred for 2 hours at room temperature. After reaction, the mixture was poured into ice water. The product was extracted with ethyl acetate, washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 5g (37%) of a product which was purified by recrystallization from ethanol:

Calculated: C, 40.32; H, 3.76. Found: C, 40.90; H, 3.86.

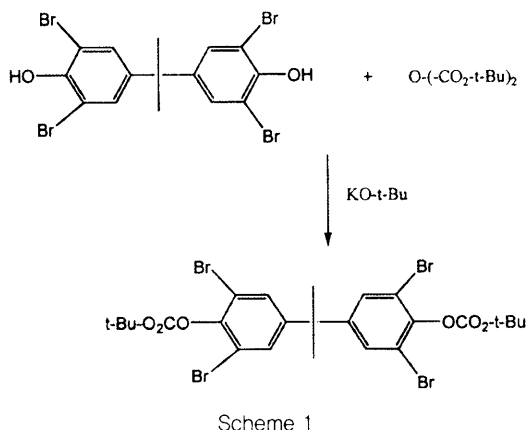
¹H-NMR (2°C00MHz, CDCl₃): 7.4 ~ 7.3 (s, 4H), 1.7 ~ 1.5 ppm (d, 24H).

UV Studies : A solution was prepared by dissolving 0.7g of (8:2) poly(4-hydroxystyrene-co-styrene) with 0.3g of 4,4' -Isopropylidene bis(2,6-dibromo-1-tert-butoxycarbonyloxybenzene) (B-BPA) containing 0.015g (5wt% on the basis of B-BPA) (4-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate in chlorobenzene. Photoresist films spin coated from the above solution on a quartz substrate were soft baked at 80 oC for 30 min and then irradiated with a 450W medium pressure mercury arc lamp to generate acid. The UV spectra was recorded before and after exposure. Next, the substrates were heated at 100 oC for 5 min. Again, the UV spectrum was recorded.

Lithographic Evaluation : A solution was prepared by dissolving 1.4g of (8:2) poly(4-hydroxystyrene-co-styrene) with 0.6g of B-BPA containing 0.03g (5wt% on the basis of B-BPA) (4-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate in chlorobenzene (solid content : 15 wt%). The photoresist films were spin coated to a thickness of 0.5m onto silicon wafers and soft baked at 80°C for 30min. The resist films were exposed using a 248nm KrF excimer laser stepper. After post-exposure bake(PEB) at different temperatures and times, the photoresist films were developed in an aqueous base developer (MF-312 from shipley Co.; 0.54N). The remaining film thickness was measured using a Nanospec/AFT instrument.

3. RESULTS AND DISCUSSION

Synthesis of B-BPA : B-BPA was synthesized by the reaction of tetrabromobisphenol-A and di-tert-butylidicarbonate in the presence of potassium tert-butoxide and purified by recrystallization from ethyl alcohol (Scheme 1).



Characterization of B-BPA and Photoresist

B-BPA has a high melting point (m.p = 165 °C) and shows good miscibility with poly(4-hydroxystyrene-co-styrene). In addition, the UV absorption coefficient of B-BPA was low (1938) at 248nm. Figure 1 shows the UV absorption spectra of the 0.5 m resist film before, after exposure and after PEE. The combined absorbance of the photoresist film is 0.248 before exposure. Thus this photoresist system has a low

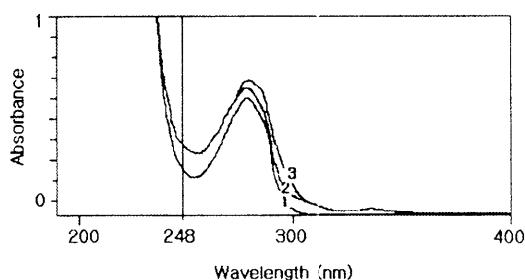


Figure 1. UV absorption spectra of 0.5 m thick photoresist consisting of copolymer/B-BPA/PAG (70/30/1.5 wt ratio) (1) before, (2) after UV exposure, and (3) after PEB at 100 °C for 5 min.

absorbance at 248nm.

Resist Evaluation

Sensitivity Dependence on the Concentration of B-BPA : The photoresist sensitivity was measured with varying B-BPA concentration. As shown in Figure 2, the sensitivity increased with an increase in B-BPA concentration. When the resist thickness was normalized, the sensitivity was 10mJ/cm².

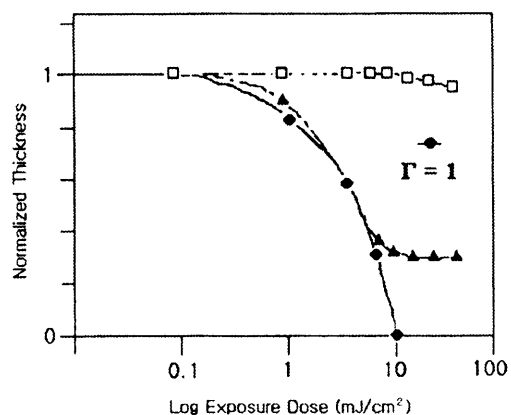
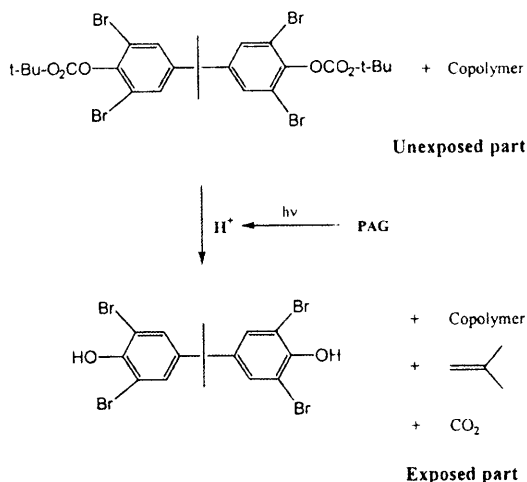


Figure 2. Characteristic exposure curves for the photoresist consisting of copolymer/B-BPA/PAG (70/30/1.5wt ratio) PEB conditions: (●) 100°C /10min, (▲) 100/5min, copolymer/B-BPA/PAG (80/20/1wt ratio) PEB conditions: (□) 100°C /10min.

The Effects of Basicity and Development

Time : The resist films can be developed in the exposed areas with aqueous base because of the acidity of the phenolic functionality, whereas the unexposed area is insoluble in aqueous base. Consequently, development in aqueous base solvents generates a positive image of the mask (Scheme 2).

As shown in Figure 3, the sensitivity of the photoresist system strongly depends on the basicity of the developer. When an aqueous base is used, a concentration as high as 0.54N is needed to develop the exposed areas. However, in this case, the film thickness loss in the unexposed areas was large. This phenomenon may be due



Scheme 2

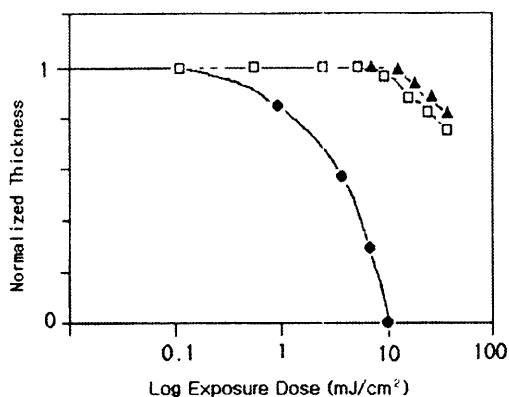


Figure 3. The effect of basicity and development for the photoresist consisting of copolymer/B-BPA/PAG (70/30/1.5wt ratio). PEB condition: 100°C/ 10 min.
 (—●—) MF-312 (0.54N), 30 sec; (1:1) MF-312: H₂O (0.27N),
 (—▲—) 1min, (—□—) 3min

to the poor solubility of the deblocked B-BPA dissolution inhibitor in an aqueous base after post-exposure baking (PEB) probably due to the bulky bromine groups in the positions flanking the phenol group.

4. CONCLUSIONS

In this paper, we described the development of

new positive photoresist based on the chemical amplification and dissolution inhibition. This photoresist was composed of an alkali soluble hydroxystyrene resin, an alkali insoluble compound containing an acid labile blocking group which acts as a dissolution inhibitor, and a photosensitive onium salt. B-BPA was designed and synthesized as a dissolution inhibitor and then evaluated after formulation. Preliminary lithographic experiments have shown this resist to be sensitive, particularly at 248nm. The sensitivity was 10mJ/cm².

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