TOP SURFACE IMAGING SYSTEMS UTILIZING POLY(VINYLBENZOIC ACID) AND ITS ESTER

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Poly(p-vinylbenzoic acid) and its ester are opaque below 300 nm and therefore useful in deep UV top surface imaging (TSI), which is a viable technique to overcome the shallow depth of focus and topography effects. In this paper are described two TSI systems utilizing the benzoic acid derivatives in the chemical amplification scheme. The first system is a single-layer negative TSI based on gas-phase silylation of poly(t-butyl p-vinylbenzoate) resist. The second case is the use of poly(p-vinylbenzoic acid) as a strippable bottom layer in conjunction with a thermally-developable, oxygen RIE barrier resist, which comprises an all-dry bilayer, positive TSI system.

1. Introduction

The performance of integrated circuit devices has been steadily and rapidly improved by increasing the number of components per chip, which has been made possible in turn by reducing the minimum feature size on the chip. The feature size continues to shrink while the resist thickness remains unchanged, demanding higher aspect ratio imaging. As the resolution is proportional to the exposing wavelength and inversely proportional to the numerical aperture (NA) of the lens, the photolithography technology which dominates semiconductor manufacturing today continues to extend its resolution limit by utilizing shorter wavelength radiations (deep UV< 300 nm) or higher NA lenses. Thus, both i-line (365 nm) step-and-repeat lithography with diazonaphtoquinone/novolac resists and KrF (248 nm) excimer laser projection printing with use of chemical amplification resists have demonstrated sub-half-micrometer resolution.
The lithographic resolution depends also on the processing \( k \) constant. The \( k \) constant tends to be larger in manufacturing environments and on reflecting topographic substrates. The shallower depth of focus associated with sub-half-micrometer imaging results in a narrower process latitude. Thus, it is important in the 0.25-\( \mu \)m lithography to eliminate the topography effect and to overcome the shallow depth of focus, which would then reduce the process \( k \) constant and contribute to the higher resolution. The top surface imaging (TSI) technique could play a vital role in achieving the goal [1,2]. The TSI scheme typically employs oxygen reactive ion etching (RIE) in the process and involves silylation after exposure of an opaque single layer resist [3-11], use of bilayer systems employing an imaged organometallic resist as an oxygen RIE mask [12], or silylation of an imaged top resist in a bilayer configuration [13-15].

The silylation TSI scheme employs either generation of a functional group (phenol or carboxylic acid) that can react with silylating reagents [3,4] or photochemically-induced crosslinking of a phenolic resist to limit the diffusion of silylating reagents [5-10]. The acid-catalyzed deprotection chemistry as embodied in IBM's tBOC resist [16] (Scheme I) is very useful in the design of oxygen RIE developable resist systems, providing a high silylation contrast [17]. However, the tBOC resist is designed to be a single layer deep UV system and is transparent in the 250 nm region [18]. Therefore, incorporation of a dye strongly absorbing at the exposing wavelength is required to transform the tBOC resist or methacrylate resists to a TSI system [3,4]. Poly(t-butyl \( p \)-vinylbenzoate) (PTBV) is converted by reaction with a photochemically-generated acid to poly(\( p \)-vinylbenzoic acid) (PVBA, VIBA) (Scheme I) and has been reported as a mid UV [19] and e-beam [20] chemical amplification resist material. Its high opacity below 300 nm precludes its use as a single layer deep UV resist material but has offered an excellent application as a portable conformable mask [19]. In this paper is reported use of the PTBV resist as a deep UV negative TSI system.

Bilayer systems consisting of a thin organometallic resist and a hard-baked novolac resist or cured polyimide as a bottom layer comprise another deep UV TSI scheme as the bottom layer strongly absorbs below 300 nm. A large number of organometallic resists has been reported for use in the bilayer scheme [12]. The top organometallic resists are developed typically with a solvent and used as an oxygen RIE mask. In spite of a large effort directed toward development of oxygen RIE bilayer schemes, however, there has been a reluctance to implement the technique in manufacturing. One disadvantage of the conventional bilayer scheme is an extra coating step. In addition,
wet development of the top resist is prone to adhesion failure and other common problems. In order to alleviate these drawbacks, a new all-dry bilayer scheme has been proposed [21-23], which is based on a thermally-developable oxygen RIE barrier resist (named SPA) consisting of poly(4-trimethylsilylpthalaldehyde) (PSPA) and triphenylsulfonium triflate. The postbake step generally required in chemical amplification resists is actually the development step for the SPA resist, which balances the extra coating step with the absence of the solvent development step and frees the bilayer scheme from the adhesion problem. Another issue which has to be considered in the bilayer lithography is the resist strippability after substrate fabrication. The bottom planarizing layer generally employed is a hard-baked novolac resist or cured polyimide, which is rendered insoluble to avoid interfacial mixing and therefore extremely difficult to remove with a solvent. In this paper is described poly(p-vinylbenzoic acid) as an ideal bottom layer for use in conjunction with the SPA resist in the positive all-dry bilayer TSI scheme.

Scheme I Acid-catalyzed deprotection for selective silylation.
2. Experimental

Materials

As reported previously [19,20,24], t-butyl p-vinylbenzoate (TBVB) was synthesized by reacting p-vinylbenzoyl chloride, which had been prepared from commercially-available p-vinylbenzoic acid, with potassium t-butoxide and subjected to radical polymerization with \(\alpha,\alpha'\)-azobis(isobutyronitrile) (AIBN) in tetrahydrofuran (THF) at 60 °C (Scheme II). Alternately, TBVB was prepared by treating di-t-butyl dicarbonate with p-vinylphenylmagnesium chloride (Scheme II) [24]. PVBA was obtained by radical polymerization of p-vinylbenzoic acid with AIBN in THF at 60 °C (Scheme II, \(M_n = 6,300\) and \(M_w = 7,600\)).

The syntheses of PSPA [21,22] and triphenylsulfonium hexafluoroarsenate and trifluoromethanesulfonate (triflate) [25,26] have been previously reported. PSPA used in this study had \(M_n\) of 10,600 and \(M_w\) of 16,800. The silylating reagent employed was \(N\)-(dimethylamino)trimethylsilane.

The casting solvents used for the resist formulations were propylene glycol monomethyl ether acetate (PM Acetate) and cyclohexanone for the PTBVB and SPA resists and 2-ethoxyethanol for PVBA.

Scheme II Syntheses of PTBVB and PVBA.
Measurements

NMR spectra were obtained on an IBM Instruments NR-250/AF spectrometer. IR spectra were measured on an IBM IR/32 FT spectrometer using thin (ca. 1 µm thick) polymer films spin-cast on 1-mm thick NaCl substrates. UV spectra were recorded on a Hewlett-Packard Model 8450A UV/VIS spectrometer using thin films cast on quartz plates. Molecular weight determination was made by GPC using a Waters Model 150 chromatograph equipped with 6 µStyragel columns at 30°C in THF. Thermal analyses were performed on a Perkin Elmer TGS-2 at a heating rate of 5 °C/min for thermogravimetric analysis (TGA) and on a Du Pont 910 at 10 °C/min for differential scanning calorimetry (DSC) under an inert atmosphere. Film thickness was measured on a Tencor alpha-step® 200.

Lithographic Evaluation

Spin-cast films were baked at 100-130 °C for 2-10 min prior to UV exposure. Preliminary contact lithography was carried out using an Optical Associate Inc. exposure station, a 254-nm bandpass filter, and a quartz mask. The resists were projection-printed on a Perkin Elmer Micralign 500 in the UV2 mode or on a GCA KrF excimer laser stepper. Postbake was performed at 100-130 °C for 1-2 min.

The gas phase silylation was carried out in a modified Yield Engineering Systems Inc. oven at 105 °C using 220 torr of (dimethylamino)trimethylsilane.

Oxygen RIE was performed on a Plasma Therm etcher at 150 W, 30 mtorr oxygen pressure, 40 sccm oxygen flow, and -240 V bias in the case of the PTBVB TSI. The SPA/VIBA bilayer system was subjected to various oxygen RIE conditions on a Materials Research Co. magnetron etcher MIE 710. Etching of the silicon substrate by CF₄ RIE using the SPA/VIBA bilayer as the mask was carried out on a Plasma Therm etcher at 150 W, 20 mtorr CF₄ pressure, 30 sccm CF₄ flow rate, and -250 V bias for 5.5 min.

3. Results and Discussion

Negative Deep UV TSI by Silylation of PTBVB Resist

As the UV spectra of 1-µm-thick films in Figure 1 indicate, PTBVB is opaque at 248 nm due to extended conjugation, in sharp contrast with
poly(p-t-butoxycarbonyloxy styrene) (PBOCST) which is highly transparent at 248 nm. Thus, PBOCST is suited for single layer deep UV lithography whereas PTBVB is not. The situation is reversed when one considers the deep UV TSI. While PBOCST requires incorporation of a dye absorbing at 248 nm to be usable in the TSI scheme [3,4], the opaque PTBVB is uniquely suited for the technique (Scheme III). PTBVB is converted upon postbake to PVBA, which reacts with a silylating reagent to form a silyl ester in the exposed top portion of the film. The silylation contrast is high because PTBVB in the unexposed regions does not react with the silylating reagent.

Another attractive feature of the PTBVB system is its high thermal stability. In Figure 2 are compared TGA curves of PTBVB and PBOCST. While PBOCST loses as much as 45.5 % of its weight at ca. 190 °C, PTBVB exhibits 27.5 % weight loss at ca. 240 °C. The glass transition temperatures (T_g) of PTBVB and PVBA are observed at 160 °C and 250 °C, respectively, which should be compared with 130 °C of PBOCST and 180 °C of poly(p-hydroxystyrene).

![Fig. 1 UV spectra of 1-μm-thick PTBVB and PBOCST films.](image)

Scheme III Negative deep UV TSI with PTBVB resist.
Figure 3 presents a UV transmittance spectrum of a 0.96-μm-thick film of PTBVB (M_n = 23,800 and M_w = 70,500) containing 9.1 wt% of triphenylsulfonium hexafluoroarsenate. The film is very opaque, transmitting only 0.2% of the 248 nm light. In Figure 4 is exhibited thickness of the resist film measured after postbake at 100 °C for 2 min (●) and after silylation/O_2 RIE (∆) as a function of 254 nm exposure dose. The resist film shrinks upon postbake due to liberation of isobutene (Scheme I). The resist film treated with (dimethylamino)trimethylsilane begins to become resistant to oxygen RIE at <1 mJ/cm² and exhibits maximum retention (75%) of its thickness at ca. 3 mJ/cm² under the silylation and oxygen RIE conditions. As the IR spectra of the PTBVB resist film in Figure 5 indicate, exposure of the PTBVB resist to 3 mJ/cm² of 254 nm radiation followed by postbake at 100 °C for 2 min results in ca. 50% conversion of PTBVB to PVBA as judged by the two carbonyl absorptions of equal intensity.

Figure 3 UV transmittance spectrum of 0.98-μm-thick PTBVB resist containing 9.1 wt% Ph_3S^+-AsF_6.
In Figure 6 is presented a scanning electron micrograph of negative 1-μm line/space images projection-printed on a Perkin Elmer 500 in the deep UV mode. The formulation of the PTBVB resist and its TSI processing conditions were the same as presented in Figure 5, which are far from optimization as evident, for example, from the etch residue on the substrate surface (the TSI image was not treated with a buffered HF solution). However, the scanning electron micrograph presented in Figure 7 demonstrates the high resolution potential of the PTBVB TSI system. Half-micrometer line/space patterns are resolved, although the quality is poor, even on a Perkin Elmer mirror projection scanner with a NA of 0.17, which has never been achieved with any other resist systems in our laboratory.
We are currently optimizing the formulation and processing conditions of the PTBVB TSI resist system to further explore its lithographic capabilities.

All-Dry Positive Bilayer TSI

Acid-catalyzed depolymerization of poly(4-trimethylsilylphthalaldehyde) (PSPA) provides positive relief images simply by heating the resist film after exposure (thermal development), which then function as an oxygen RIE mask for pattern transfer [21-23].
(Scheme IV). The all-dry SPA scheme is the simplest bilayer technique imaginable; the benefit achieved by elimination of a solvent development process overwhelms the drawback introduced by the extra coating step. Figure 8 presents deep UV sensitivity curves for the thermal development of the SPA resist containing 4.8 or 1.2 wt% of triphenylsulfonium triflate. The thermal development was performed at 100 or 130 °C for 1 min. At 4.8 wt% triflate loading, the resist is fully developed to the substrate at ca. 1 mJ/cm² by heating at 100 °C with a contrast (γ) of 1.8. The 1.2 wt% triflate loading offers a high γ of 4.8 and provides full thermal development at ca. 2 and 4 mJ/cm² when the resist film is postbake-developed at 130 and 100 °C, respectively [21-23]. Thus, the thermally-developable SPA resist is highly sensitive.

Scheme IV All-dry positive bilayer TSI.

Fig. 8 Deep UV sensitivity curves for thermal development of SPA resist.
The bottom planarizing layer for use in the bilayer TSI scheme must (1) be spin-coatable, (2) be resistant to common casting solvents to prevent interfacial mixing, (3) be highly opaque at the exposing wavelength to eliminate the topography effect and to overcome the shallow depth of focus, (4) not be detrimental to the top resist, (5) be etched very rapidly in oxygen plasma, (6) be highly stable thermally, (7) be highly resistant to fluorocarbon plasmas, and (8) be easily stripped after substrate fabrication. The bottom layer materials most commonly employed in the O₂ RIE bilayer systems are hard-baked novolac resists and cured polyimide, which satisfy all the requirements shown above, except (8). To avoid interfacial mixing with the top imaging resist, the bottom layer is rendered insoluble by crosslinking or curing, which increases its thermal stability but tremendously reduces its strippability. We have sought a soluble bottom layer material for ease of stripping to further increase the feasibility of the SPA resist.

Poly(p-vinylbenzoic acid) (PVBA, VIBA) is uniquely suited as a bottom layer for use in conjunction with the SPA resist in the deep UV all-dry bilayer TSI, satisfying all the requirements shown above including the good strippability. VIBA is readily accessible from the commercially-available monomer (Scheme II), soluble in 2-ethoxyethanol and spin-coatable, but resistant to common casting solvents such as PM Acetate and cyclohexanone, precluding interfacial mixing with the SPA layer even without crosslinking. The VIBA film is even more opaque in the 250 nm region (OD = 3.41/µm at 248 nm) than PTBVB. A UV transmittance spectrum of a 0.8-µm-thick film of VIBA is presented in Figure 9. As mentioned earlier, the Tg of VIBA is 250 °C. Thus, VIBA provides an excellent thermal stability and remains soluble even after prolonged heating at 230 °C. In addition, VIBA is resistant to fluorocarbon plasmas due to its aromatic nature but etches rapidly in oxygen plasma due to its organic nature. Its high solubility in aqueous base even after high temperature treatment allows stripping with commonly available tetramethylammonium hydroxide aqueous solution.
In Figure 10 are compared thermally-developed positive images which were transferred to the VIBA layer (a) and a hard-baked novolac resist (b) by magnetron oxygen RIE. The acidic VIBA layer does not induce premature depolymerization of the acid-labile PSPA during prebake (100 °C, 10 min) or postbake. Although the VIBA layer was soft-baked at 130 °C for 10 min and uncrosslinked, no evidence of interfacial mixing was observed, with both VIBA and the hard-baked novolac resist providing clean pattern transfer.

Fig. 9 UV transmittance spectrum of a 0.8-μm-thick VIBA film.

Fig. 10 Positive all-dry bilayer TSI images obtained with SPA resist and VIBA (a) or hard-baked novolac resist (b) as bottom layer.

(a) SPA/VIBA
(b) SPA/hard-baked novolac resist
The oxygen RIE conditions are known to very much affect the quality of images delineated in either silylation or bilayer systems, which is demonstrated in Figure 11 for the SPA/VIBA bilayer configuration. The SPA resist containing 1.2 wt% Ph₃S⁺·OTf was exposed on a Perkin Elmer 500 (UV2, aperture 4, scan speed 3,000) and developed by heating at 130 °C for 3 min. The pattern transfer was performed under different oxygen RIE conditions on a magnetron etcher (1 kW) as demonstrated in Figure 11. Images were subjected to scanning electron microscopic examination without HF treatment to remove residues. A high pressure of 5 mtorr and a high flow rate of 20 sccm resulted in a rough resist surface and a large amount of "grass" on the substrate (Fig. 11a). The reduction of the oxygen pressure and flow to 1 mtorr and 10 sccm improved the surface texture and reduced the grass (Fig. 11b) and a little overetch further reduced the residue in a large area but not in a small space (Fig. 11c). A high flow rate of 20 sccm and a low pressure of 1 mtorr (Fig. 11d) provided the smoothest resist surface and no residues on the substrate. Reduction of the pressure to 0.5 mtorr at the 10 sccm flow rate resulted in grass formation in narrow spaces and clean etching in large open areas (Fig. 11e). The oxygen pressure of 1 mtorr and the flow rate of 20 sccm were chosen to be optimal for the SPA/VIBA system on our magnetron etcher.

Fig. 11 Positive all-dry bilayer images delineated in SPA/VIBA under various oxygen RIE conditions (MRC magnetron etcher, 1 kW).
Polyphthalaldehyde derivatives undergo clean thermal depolymerization at ca. 200 °C. Thus, it is interesting to heat the SPA/VIBA bilayer images to this temperature. Figure 12a shows the bilayer images heated at 230 °C for 30 min, demonstrating overall integrity. The images are, however, puffy, which is due to formation of gaseous (at 230 °C) silylphthalaldehyde monomer between the thin skin of the surface silicon oxide and the glassy bottom VIBA layer. If the surface silicon oxide layer has been removed by dipping the wafer in buffered HF, the monomer produced by thermal depolymerization of PSPA is free to escape, leaving only the bottom VIBA layer behind as shown in Figure 12b. In Figure 13 is presented a cross-sectional view of the SPA/VIBA bilayer patterns that were briefly treated with buffered HF and heated at 230 °C for 30 min. What is left and shown in Figure 13 is only the bottom VIBA layer, demonstrating clean removal of the imaging SPA layer by heating and excellent thermal stability of the bottom VIBA layer.

Fig. 12 SPA/VIBA bilayer images heated at 230 °C for 30 min right after etching (a) and after HF treatment (b).
The SPA/VIBA bilayer system was subjected to further processing conditions. The silicon substrate was etched by CF$_4$ RIE using the patterned SPA/VIBA bilayer as the mask (Figure 14a) and then the resist film was stripped with neat MF 312 (aqueous tetramethylammonium hydroxide). The resist system maintained its integrity during CF$_4$ RIE and the stripping was cleanly completed within 10 min at room temperature without vigorous agitation or sonication (Figure 14b). Organic solvents such as N-methylpyrrolidinone (NMP) can be also used as a stripper.

The VIBA bottom layer cannot be used along with a top resist that requires aqueous base development but can be used in conjunction with organometallic resists such as polysilanes and others that employ rather nonpolar organic developers.

Fig. 13 SPA/VIBA bilayer images heated at 230 °C for 30 min after HF treatment (the surface silicon oxide layer removed by HF dipping and the SPA resist layer by thermal depolymerization, leaving only the bottom VIBA layer).

Fig. 14 Scanning electron micrographs of positive images etched into silicon substrate by CF$_4$ RIE using SPA/BIVA bilayer as the mask. (a) after CF$_4$ RIE and (b) after stripping the resist film with MF 312 (10 min).
Figure 15 demonstrates the high resolution capability of the all-dry bilayer TSI system. The top SPA resist containing 1.2 wt% of Ph3S-OTf was exposed on a GCA KrF excimer laser stepper (NA = 0.35), thermally developed by postbake at 120 °C for 60 sec, and used as the oxygen RIE mask for pattern transfer on a MRC magnetron etcher (1 kW, 1 mtorr, 20 sccm, 1.3 min). The all-dry bilayer system is capable of generating clean sub-half-micrometer images.

Fig. 15 Sub-half-micrometer positive images delineated in all-dry bilayer system by KrF excimer laser exposure, thermal development, and O2 RIE pattern transfer.

4. Summary

The top surface imaging technique can alleviate the detrimental effects of the shallow depth of focus and the substrate surface variations on the resolution and the line width control and therefore is likely to play a vital role in sub-half-micrometer photolithography. Poly(p-vinylbenzoic acid) and its ester, opaque below 300 nm, find excellent applications in the deep UV TSI scheme.

(1) Acid-catalyzed deprotection of poly(t-butyl p-vinylbenzoate) can be used to design a negative TSI system involving silylation and oxygen RIE development.

(2) Poly(p-vinylbenzoic acid) possesses all the necessary properties as a bottom layer for the bilayer TSI scheme. Its solubility in aqueous base or some organic solvents even after high temperature treatment (230 °C) provides ease of stripping. The material is particularly attractive when used in conjunction with a thermally developable top resist, comprising all-dry positive bilayer TSI.
Acknowledgment

The author thanks L. A. Pederson for his assistance in magnetron oxygen RIE studies. Exposures of the resists on a Perkin Elmer 500 were carried out by N. J. Clecak, whose help is gratefully acknowledged. L. Doane's assistance in exposing the SPA resist on a GCA KrF excimer laser stepper is also deeply appreciated. Special thanks also go to W. P. England who synthesized PTBVB.

References


