t-BOC MALEIMIDE COPOLYMERS FOR THERMALLY STABLE DEEP UV RESISTS BY CHEMICAL AMPLIFICATION

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Four kinds of new t-BOC protected maleimide copolymers P(t-BOCMI/St), P(t-BOCMI/SiSt), P(t-BOCMI/t-BOCSt) and P(t-BOCOPMI/SiSt) were investigated as thermally stable, deep UV resists in high sensitivity. The resist polymers are composed of N-(t-butyloxycarbonyl)maleimide (t-BOCMI) or N-[p-(t-butyloxycarbonyloxy)phenyl]maleimide (t-BOCOPMI) and styrene derivatives (X-St) such as styrene (St), p-(t-butoxycarbonyloxy)styrene (t-BOCSt) and p-trimethylsilylstyrene (SiSt). The t-BOC protected copolymers have alternating structures and are readily deprotected by thermolysis and acidolysis to the corresponding polar maleimide (MI) and phenolic OH functions from t-BOCMI and t-BOC-oxypheyl, respectively. The deprotected polymers P(MI/St), P(MI/SiSt), P(MI/HOSt) and P(HOPMI/SiSt) exhibit quite high T_g 's above 245°C and high oxygen RIE resistance. In particular, the both silicon containing polymers P(MI/SiSt) and P(HOPMI/SiSt) are superior to a novolac photoresist in oxygen RIE resistance. The RIE resistance of the resist polymers in Cl_2/He and CHF_3/C_2F_6 gases are found to be comparable to the novolac resist. The three t-BOCMI copolymers have very low absorbance no more than 0.2 per μm at 248 nm wavelength. The polymers P(t-BOCMI/St), P(t-BOCMI/SiSt), P(t-BOCMI/t-BOCSt) and P(t-BOCOPMI/SiSt) were compounded with 10 wt % of triphenylsulfonium hexafluoroantimonate as a photoacid generator and the resists are named as MIST, MISIX, BMIST and PMISIX, respectively. The resists films were exposed to deep UV or KrF excimer laser and post-exposure baked at 100°C followed by development with aqueous alkaline solutions for positive image-making to get sub-micron patterns. In the case of MISIX and PMISIX resists only negative tone images were possible by organic developing. Thus the t-BOC protected maleimide copolymers combine capability of high resolution with high sensitivity in deep UV region and thermal stability above 200°C along with high oxygen RIE resistance.

INTRODUCTION

High resolution resist materials are becoming more essential in microlithography for fabricating a sub-half micron minimum feature size. The resist community places high resolution with high sensitivity, high resistance to dry etching and thermal stability as today's main targets imposed on polymeric resist materials [1]. Based on the concept of "chemical amplification", there have been derived a number of new resist polymers which provide novel imaging systems to achieve very high sensitivities along with high resolution in short wavelength deep UV or KrF excimer laser lithography [2].

Among the various chemically amplified resist systems, the polymer side-chain deprotection system has attracted much attention because of their high resolution capability with high sensitivity even retaining main-chain integrity. Such examples are poly(p-t-butoxycarbonyloxystyrene) (PBOCSt), poly(t-butyl p-vinylbenzoate) (PTBVB), and certain polymethacrylates, which are easily converted upon thermolysis to poly(p-hydroxystyrene) (PHOST), poly(p-vinylbenzoic acid) (PVBA), and poly(methacrylic acid), respectively [3, 4]. The protected polymers bring remarkable change in polarity after deprotection of the side-chains. Among the various protecting groups, the t-butyloxycarbonyl (t-BOC) group is most successfully utilized in chemical amplification resist systems, providing highest sensitivity.

One of the required properties placed on resist polymers is thermal stability of patterned resist images after deprotection. Resist polymers which have high glass transition temperature (T_g) above 200°C are preferred for advanced lithographic processes. One of the common synthetic techniques to improve thermal stability is incorporating a maleimide unit into copolymers [5]. Therefore, the novel resist design concept has been applied to imaging of high temperature polymers such as a maleimide-styrene copolymer [6] and a N-(p-hydroxyphenyl)maleimide-styrene copolymer [7]. The t-BOC group was introduced to protect imide NH in the former and phenolic OH in the latter copolymer through post-reactions on the both maleimide copolymers. Several types of protected maleimides were also studied in an effort to increase the thermal deprotection temperatures [8]. All of the reported maleimide copolymers were found to have high T_g above 200°C after deprotection of the side-chains.

In our laboratory, a new monomer N-(t-butyloxycarbonyl)maleimide, t-BOCMI was successfully prepared and copolymerized with various styrene derivatives [9]. The monomer t-BOCMI is quite readily copolymerized with electron-rich styrene derivatives X-St in alternating structures as described in Fig.1. To bring high dry etching resistance t-BOCMI was copolymerized with p-trimethylsilylstyrene SiSt to give an alternating copolymer P(t-BOCMI/SiSt). It is a well known technique to incorporate silicon moieties for enhancing oxygen reactive-ion etching (RIE) [10].

In this work, the t-BOC protected maleimide copolymers were studied to bring high resolution capability with high sensitivity in deep UV region by chemical amplification as well as thermal stability with high T_g 's above 200°C and high RIE resistance comparable to a novolac resist.

EXPERIMENTAL

Instruments

Proton and C-13 NMR spectra were taken on a varian Gemini 300 MHz spectrometer and infrared spectra were recorded on an Alpha-Centauri FT-IR spectrophotometer of Mattson Co. UV absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Thermal analyses were carried out with a DuPont Model 910 DSC and Model 951 TGA at a heating rate of 10°C/min under nitrogen atmosphere. Film thickness of resists was measured by an Alpha-step 200 of Tencor or Talysurf-10 of Taylor-Hobson Co.

Polymers

The t-BOCMI monomer was radically copolymerized with styrene monomers X-St such as styrene (St), p-trimethylsilylstyrene (SiSt) and p-(t-butoxycarbonyloxy)styrene (t-BOCSt) to obtain alternating P(t-BOCMI/X-St) in high conversion above 80 % [9]. The t-BOCMI copolymers P(t-BOCMI/X-St) were found to have alternating structure. Another maleimide monomer, N-[p-(t-butoxycarbonyloxy)phenyl]maleimide, t-BOCOPMI was prepared and it was copolymerized with SiSt to give alternating P(t-BOCOPMI/SiSt) [7].

Resist Evaluation

A resist solution was prepared by dissolving 10 wt % of a copolymer in cyclohexanone or chlorobenzene. As a photoacid generator (PAG) triphenylsulfonium hexafluoroantimonate (TPSHFA) was used 10 wt % to a copolymer. The resist solution was spin-coated at 1000 to 3000 rpm with a Headway spinner on silicon wafers, quartz wafers or salt plates to render around 1 µm thickness after soft baking at 100°C for 5 min in a convection oven. The resist films were exposed to 260 nm light through a quartz mask by contact mode with an OAI Hybralign Series 400 Exposure System equipped with a deep UV, 500 W short arc lamp which is mounted with a narrow-band 260 nm filter. Then the exposed resist film underwent post-exposure bake (PEB) at 100°C for 5 min. After the PEB the film was developed with aqueous alkaline solutions such as NMD-3 (2.38 wt % tetramethylammonium hydroxide) and AZ-351 (4 wt % NaOH) developer for positive image-making or organic solvents such as anisole, toluene, dichloromethane, etc. for negative image-making.

RIE Resistance

The reactive-ion etch (RIE) resistance were carried out by using oxygen, Cl₂/He and CHF₃/C₂F₆ with a DRYTEK QUARD 484 etcher. In the RIE test process, the resists were coated with a TARGE TRACK coater at 1500 rpm on 5" silicon wafers and were baked in a convection oven under nitrogen flow. The resist film thickness was measured with a Litz MDV-SP.

RESULTS AND DISCUSSION

Resist Polymers

The t-BOC protected resist polymers were prepared by copolymerization of N-(t-butyloxycarbonyl)maleimide, t-BOCMI with styrene derivatives (X-St) such as styrene (St), p-trimethylsilylstyrene (SiSt) and P-(t-butyloxycarbonyloxy)styrene (t-BOCSt)

(Fig. 1.) [9]. Another t-BOC protected maleimide monomer, N-[p-(t-butyloxycarbonyloxy)phenyl]maleimide (t-BOCOPMI) was also copolymerized with SiSt [7]. The silicon containing styrene SiSt was chosen for enhancing dry etching resistance [10]. The characteristics of the resist polymers are summarized in Table I along with thermal properties. All the maleimide (MI) copolymers were found to have 1 to 1 alternating structures and the resists are named as follows: MIST for P(t-BOCMI/St), MISIX for P(t-BOCMI/SiSt), BMIST for P(t-BOCMI/t-BOCSt) and PMISIX for P(t-BOCOPMI/SiSt).

Fig. 1. Alternating copolymerizations of t-BOCMI and styrene derivatives X-St.

Table I. Thermal Properties of t-BOC Protected Maleimide Polymers

Resist	Polymer ^a	Inherent Viscosity ^b	T _{dp} ^c °C	Weight Loss ^d , %	Deprotected Polymer ^e	T _g ^f °C	T _{dc} ^g °C
MIST	P(t-BOCMI/St)	0.94	152	33	P(MI/St)	245	370
BMIST	P(t-BOCMI/t-BOCSt)	0.69	170	48	P(MI/HOSt)	280	400
MISIX	P(t-BOCMI/SiSt)	0.77	166	26	P(MI/SiSt)	260	370
PMISIX	P(t-BOCOPMI/SiSt)	0.94	183	21	P(HOPMI/SiSt)	260	370
	P(MI/St)	0.96				245	370

^aThe structures of the copolymers are alternating: St, styrene; t-BOCSt, p-(t-butoxycarbonyloxy)styrene; SiSt, p-trimethylsilylstyrene; t-BOCOPMI, N-[p-(t-butoxycarbonyloxy)phenyl]maleimide; MI, maleimide. ^bInherent viscosities in dl/g were measured at a concentration of 0.20 g/dl in dioxane at 25°C. ^cThe deprotection temperature T_{dp} was measured in the first run of DSC. ^dWeight loss of the protected copolymers was measured by TGA at T_{ap}. ^eUpon deprotection of the copolymers t-BOCMI and t-BOCOPMI units are converted into maleimide (MI) and N-(p-hydroxyphenyl)maleimide (HOPMI), respectively. ^fThe glass transition temperature T_g of the deprotected polymer was measured in the second run of DSC. ^gThe onset decomposition temperature T_{dc} was measured by TGA.

Thermal Properties

Thermal deprotection of *t*-BOC protecting groups of phenolic functions is verified with precipitous weight loss and a strong endotherm observed at a temperature of around 160°C [7]. The characteristic thermal behaviors of the *t*-BOC protected maleimide polymers are summarized in Table I in terms of a deprotection temperature T_{dp} and the amount of weight loss of the original *t*-BOC protected polymers, and a glass transition temperature T_g and an onset decomposition temperature T_{dc} of the deprotected polymers. In thermogravimetric analysis P(*t*-BOCMI/SiSt) was estimated to lose 26 % of the original mass between 150°C and 180°C, then a plateau followed by eventual decomposition (T_{dc}) at 370°C as shown in Fig. 2. The weight loss in the TGA thermogram agrees well with the calculated amount 26.8 % for evolution of carbon dioxide and isobutene during deprotection of alternating P(*t*-BOCMI/SiSt). The plateau is correspond to the deprotected polymer P(MI/SiSt) which has a high T_g at 260°C measured in a second run of DSC analysis. In a DSC thermogram of P(*t*-BOCMI/SiSt) thermal deprotection of *t*-BOC groups is observed at 166°C during a first run as shown in Fig.2. The second run was measured with the same polymer sample which was deprotected and heated up to 220°C during the first run then cooled down to a room temperature.

The similar thermal behaviors of the alternating P(*t*-BOCOPMI/SiSt) are shown in Fig. 3, which means somewhat higher deprotection temperature of 183°C and mass loss of 21 wt %. Then the deprotected polymer becomes the copolymer of *N*-(*p*-hydroxyphenyl)maleimide (HOPMI) and styrene, P(HOPMI/St) which has high T_g of 260°C. In Fig. 4 the chemical transformations of the *t*-BOC protected maleimide copolymers either in thermolysis or in acidolysis are described. The observed amounts of weight loss of the polymers generally agree well with the calculated values. In the case of the alternating P(*t*-BOCMI/*t*-BOCSt) the both *t*-BOC monomer units contribute to weight loss as much as 48 % of the original mass. Upon thermal deprotection of the alternating *t*-BOC maleimide copolymers P(*t*-BOCMI/X-St) at 150 to 180°C they convert to maleimide structures as P(MI/X-St) providing quite high T_g 's above 245°C (Table I, Fig. 4). For comparison, poly(maleimide-alt-styrene), P(MI/St) was also prepared from a copolymerization of maleimide and styrene in 1 to 1 molar feed ratio and the resulting P(MI/St) shows the same T_g and decomposition temperature as the deprotected polymer obtained from P(*t*-BOCMI/St). Therefore generated resist images from the polymers P(*t*-BOCMI/X-St) are expected to withstand in harsh lithographic processes above 200°C.

Fig. 4. Thermal and acidolytic deprotection of the alternating P(*t*-BOCMI/X-St) to P(MI/X-St): (a) X = H, P(*t*-BOCMI/St) to P(MI/St); (b) X = Si(CH₃)₃, P(*t*-BOCMI/SiSt) to P(MI/SiSt); (c) X = OCO₂-Bu-*t* to OH, P(*t*-BOCMI/*t*-BOCSt) to P(MI/HOSt).

Fig. 2. Thermal analysis of the alternating P(t-BOCMI/SiSt): (a) a TGA thermogram; (b) DSC thermograms in the first run for deprotection and the second run for the deprotected polymers.

Fig. 3. Thermal analysis of the alternating P(t-BOCOPMI/SiSt): (a) a TGA thermogram; (b) DSC thermograms in the first run for deprotection and the second run for the deprotected polymers.

Resist Evaluation

For applications in the deep UV lithography, the resist polymers should have low absorption characteristic in this region. Three t-BOCMI copolymers P(t-BOCMI/St), P(t-BOCMI/SiSt) and P(t-BOCMI/t-BOCSt) were found to have very low absorbance in film less than 0.2 for 1 μm thickness, i.e., 0.13/ μm for MIST, 0.14/ μm for MISIX and 0.13/ μm for BMIST at 248 nm wavelength. The UV absorption spectra of P(t-BOCMI/St) and P(t-BOCMI/SiSt) are shown in Fig. 5 and Fig. 6, respectively. The absorption intensities are not varied appreciably after deprotection of the both polymers. However P(t-BOCOPMI/SiSt) exhibits somewhat higher absorbance of 0.66/ μm at 248 nm.

All the t-BOC protected polymers are very soluble in common organic solvents and insoluble in aqueous alkaline solutions. The deprotected polymers P(MI/St) and P(MI/HOSt) are very soluble in aqueous base but insoluble in organic solvents. However, the SiSt-containing polymers P(t-BOCMI/SiSt) and P(t-BOCOPMI/SiSt) are also insoluble in aqueous alkaline solutions even after deprotection. As deprotected polymers P(MI/SiSt) and P(HOPMI/SiSt) are generally become less soluble and only soluble in some selected organic solvents.

Imaging studies of the t-BOC protected copolymers were done with the resist solutions containing triphenylsulfonium hexafluoroantimonate (TPSHFA) as a photoacid generator (PAG). The photoacidolysis of resist polymers containing 10 wt % of TPHFA were confirmed with IR spectral change as shown in Fig. 7 and Fig. 8 for MISIX and PMISIX, respectively. The resist films on salt plates were exposed to deep UV without any appreciable change in IR absorption spectra. However, by doing the PEB at 100°C for 5 min the characteristic carbonyl absorption bands around 1760 cm^{-1} are disappeared due to deprotection of the t-BOC groups. The MIST films spin-coated on silicon wafers were exposed to deep UV or KrF excimer laser, then post-exposure baked at 100°C for 5 min and developed with NMD-3 for 1 min dip. Thus the positive tone images with sub-micron resolution were obtained at exposure energy less than 20 mJ/cm^2 . In the case of MISIX, the negative tone images were generated by developing with toluene.

RIE Resistance

The RIE resistance of the four t-BOC protected maleimide resists MIST, BMIST, MISIX and PMISIX was carried out after deprotecting the t-BOC groups. Because the images of the deprotected resists are thermally stable and more practical in lithography. All the resist films without PAG were spin-coated on silicon wafers to obtain around 1 μm thickness film. Then the deprotection of the t-BOC groups were performed in a convection oven at 200°C for 10 min under nitrogen. The RIE resistance of the deprotected copolymers was investigated as the structures of P(MI/St) for MIST, P(MI/HOSt) for BMIST, P(MI/SiSt) for PMISIX and P(HOPMI/SiSt) for PMISIX. The RIE resistance was compared with an AZ1512 novolac photoresist which was postbaked at 120°C for 30 min. The results of the RIE resistance in oxygen, $\text{CHF}_3/\text{C}_2\text{F}_6$ (50/25) and Cl_2/He (30/30) were summarized in Table II.

The SiSt-containing resist polymers MISIX and PMISIX reveal much higher oxygen RIE resistance than the novolac resist. The deprotected maleimide copolymers of MIST and BMIST even exhibit high oxygen RIE resistance comparable to the novolac resist. In Cl/He and CF RIE treatments all the deprotected polymers also resulted in high resistance

Fig. 5. UV absorption spectra of the alternating P(t-BOCMI/St), before (solid line) and after (broken line) deprotection of t-BOC groups (film thickness, 0.9 μm)

Fig. 6. UV absorption spectra of the alternating P(t-BOCMI/SiSt), before (solid line) and after (broken line) deprotection of t-BOC groups (film thickness, 0.7 μm).

Fig. 7. Infrared spectral change of the MISIX resist containing 10 wt % TPSHFA casted on a salt plate, (a) prebaking at 100°C and (b) after PEB at 100°C for 5 min.

Fig. 8. Infrared spectral change of the PMISIX resist containing 10 wt % TPSHFA casted on a salt plate, (a) prebake at 100°C and (b) after PEB at 100°C for 5 min.

comparable to the novolac resist. For enhancing the oxygen RIE, incorporation of silicon moieties into polymer-chains is a well known synthetic technique and the higher contents of silicon more than 10 wt % are required for effectiveness. This effect is verified in MISIX and PMISIX resists. The silicon contents are 7.5 % for P(t-BOCMI/St) and 10.3 % for deprotected polymer P(MI/SiSt), and 6.0 % for P(t-BOCOPMI/SiSt) and 7.7 % for the deprotected polymer P(HOPMI/SiSt). The deprotected polymer P(MI/SiSt) with high silicon contents achieved the highest oxygen RIE resistance among the tested resists.

Table II. RIE resistance of the deprotected polymers

Resist	Thickness ^a , Å		RIE Rate, Å/min		
	Prebaking	Deprotection	O ₂ ^b	CF ^c	Cl/He ^d
MIST	11410	7490	2870	440	1560
BMIST	10480	5420	2860	620	1830
MISIX	10480	7990	890	480	1960
PMISIX	15900	12710	1300	580	1640
AZ1512	12510 ^e		2960	460	1320

^aThe resists were spin-coated at 1500 rpm for 50 sec on 5 inch silicon wafers and prebaked at 110°C for 60 sec. The deprotection of t-BOC groups from the prebaked resists was done at 200°C for 10 min in a convection oven. ^bO₂ RIE: oxygen flow, 50sccm; RF power, 400 mW/cm²; pressure, 200 mtorr. ^cCF RIE: CHF₃/C₂F₆ flow, 50sccm/25sccm; RF power, 400 mW/cm²; pressure, 600 mtorr; cf, SiO₂ etch rate=2500 Å/min. ^dCl/He RIE: Cl₂/He flow, 30sccm/30sccm; RF power, 400 mW/cm²; pressure, 150 mtorr; cf, polysilicon etch rate=3500 Å/min. ^eThe film thickness measured after postbaking at 120°C for 30 min.

CONCLUSIONS

Three t-BOCMI copolymers P(t-BOCMI/St), P(t-BOCMI/SiSt) and P(t-BOCMI/t-BOCSt) exhibit promising characteristics for applications in deep UV lithography as follows: low absorbance less than 0.2/μm at 248 nm, high sensitivity, high thermal stability of generated image patterns above 200°C and high oxygen RIE resistance. Deprotection of t-BOC groups occurs 150 to 200°C and eventual T_g's are very high up to 250°C. The polymers were formulated with TPSHFA as a photoacid generator. The resists were spin-coated and exposed to deep UV then underwent PEB at 100°C. The resists, MIST and BMIST gave sub-micron positive tone images with aqueous alkaline development in high sensitivity by chemical amplification. The resists, MISIX and PMISIX only generated negative tone images with organic development.

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