tert-Butoxycarbonylated novolacs as chemically amplified dual-tone resists

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tert-Butoxycarbonylated, fractionated cresol-formaldehyde novolac (tBOC-N) was investigated as a dual-tone, chemically amplified, deep-u.v. and electron-beam resist. The protected polymer is highly transparent at $\lambda > 240$ nm, and thermally stable up to 170°C. Negative-tone, 75-nm line-and-space patterns were obtained in the tBOC-N-based resist by electron-beam lithography. The deprotected novolac was insoluble in aqueous bases, possibly because of acid-catalysed alkylation reaction.

(Keywords: tert-butoxycarbonylated novolac; chemical amplification; deep-u.v. and electron-beam resist)

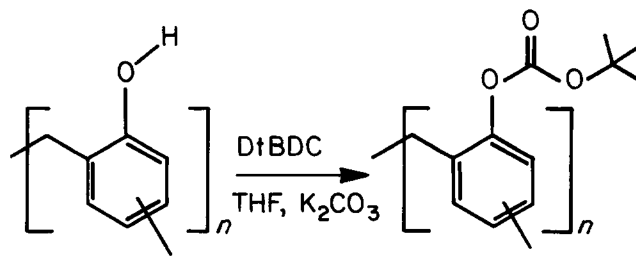
The invention of chemically amplified resists by Ito *et al.*[1] has led to the development of several new families of sensitive imaging materials. Based on the mechanism of image formation, such materials can be divided into two groups: the dual-tone resists, which usually contain hydroxyl groups protected by the tert-butoxycarbonyl[2] (t-BOC) or tert-butyl ester[3] groups, and the negative-tone resists which utilize various acid-catalysed cross-linking reactions[4]. Several groups have reviewed the progress in, and mechanistic aspects of, these materials[5,6].

Poly[(((tert-butoxy)carbonyl)oxy)styrene] (PBOCST)[2] is perhaps the best-known example of a dual-tone imaging polymer, although a number of structurally related polymers have been investigated[7–10]. All chemically amplified resists contain a photoacid generator (PAG), usually in the form of various iodonium and sulphonium salts[11], or *o*-nitrobenzyl esters[12], of strong acids. The PAGs undergo photodecomposition upon exposure to actinic radiation and liberate minute amounts of the strong acid in the matrix. Subsequent short heating of the film at 80–130°C (post-exposure bake, PEB) results in the acid-catalysed deprotection of the t-BOC-protected hydroxyl groups and, consequently, a large polarity change of the exposed polymer.

The majority of currently used photoresists are based on cresol-formaldehyde condensation polymers (novolacs). These resins are not only inexpensive and readily modifiable by a judicious choice of reaction conditions and blendings[13], but due to their polar nature and low molecular weight, novolacs dissolve without substantial swelling. We had hoped that O-substituted novolacs would also exhibit limited swelling, particularly in the negative mode. Although several O-substituted novolacs have previously been used in resist compositions[14,15], we have found only a single reference to a t-BOC-protected novolac (tBOC-N, *Scheme 1*) which was prepared by Houlihan *et al.*[16] in the course of their study on the protection of various hydroxylated compounds by the t-BOC group. However, properties and lithographic applications of tBOC-Ns have not been reported. In this communication, we report selected properties of tBOC-Ns, and the results of an initial lithographic evaluation of chemically amplified resists based on such polymers.

Novolac resins were obtained from Schenectady Chemicals (Schenectady, NY, USA). Sample L was a standard low molecular weight resin ($M_w \simeq 6400$; $M_w/M_n \simeq 4.5$) obtained from a 63:37 mixture of *m*- and *p*-cresols. Sample H was a high molecular weight ($M_w \simeq 60\,500$; polydispersity, $PD = 42$), *m*-cresol novolac. High-molecular weight fractions of polymers H and L, designated as HH and HL, were precipitated with water from novolac solutions in methanol (25 ml water per 100 g of a 20 wt% solution). G.p.c. M_w values for samples HL and HH were 9600 ($PD = 3.6$) and 146 000 ($PD = 28$). t-BOC-protected novolacs were obtained by the method reported by Houlihan *et al.*[16].

The main obstacle to the use of standard novolacs in deep-u.v. resists is their high absorbance at 240–260 nm (0.6–1.2 μm^{-1}). This obstacle does not exist in the case of tBOC-N polymers, since they exhibit a markedly lower optical density in that spectral range (0.15–0.2 μm^{-1}). tBOC-Ns also possess sufficient thermal stability for resist applications, as they exhibit a sharp d.s.c. endotherm at 189–192°C due to the thermally induced decomposition of the t-BOC group. T.g.a. analysis indicated that the tBOC-Ns lose 45.0–45.5% of their



Scheme 1

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weight on heating to 195°C, which is close to the theoretical value. Interestingly, partially substituted novolacs exhibited lower thermal deprotection temperatures (e.g. ~120°C for a 20% substituted novolac) and a correspondingly lower weight loss on heating, thus reflecting the catalytic effect of the acidic phenolic groups on the decomposition of the t-BOC groups[17].

We have evaluated the efficacy of several PAGs, namely, triphenylsulphonium trifluoromethanesulphonate (TPS-OTf), triphenylsulphonium hexafluoroantimonate (TPS-SbF_6), a mixed sulphonium-SbF_6 salt (Cyracure UV-6974, Union Carbide), and 2,6-dinitrobenzyl tosylate, in deprotecting the tBOC-N matrix. TPS-OTf turned out to be the most efficient PAG on a per weight basis, thus subsequent, more detailed lithographic studies were limited to that compound. The deep-u.v. and electron-beam sensitivity of the tBOC-N/TPS-OTf resists was very high. For example, the deep-u.v. sensitivity was 4 and 10 mJ cm^{-2} at TPS-OTf concentrations of 4 and 0.5 wt%, respectively. The i.r. and u.v. spectra of films deprotected under such conditions indicated that >95% of the t-BOC groups were decomposed after heating for 3 min at 120°C.

All novolac samples studied in the present work were readily soluble in aqueous bases and C_1–C_6 alcohols. However, the solubility of the starting novolacs, their tBOC-N derivatives and the deprotected novolacs in organic solvents strongly depended on their molecular weight, polydispersity and the degree of functionalization. It was also clearly related to the presence of oligomers in polymer samples because of their high solubility in a wide variety of solvents. For example, the starting novolac L was partially soluble in anisole and xylene (~30%), and the tBOC-N(L) was partially soluble (>30%) in isopropyl alcohol (IPA). In contrast, the 'fractionated' polymers tBOC-N(HH) and tBOC-N(HL) were completely insoluble in IPA.

The most significant difference between the starting and deprotected novolacs concerns their solubility in aqueous bases. In contrast to the deprotected PBOCST (i.e. PHOST)[7–10], the deprotected novolac films were always hydrophobic and insoluble in aqueous base solutions*. Since the starting novolac films containing the same PAG concentration were fully soluble in such solutions, the well-known dissolution inhibition effect of many onium salt-type PAGs[19] cannot be responsible for the observed behaviour. The deprotected novolac dissolved slowly and non-uniformly at KOH concentrations >0.3–0.4 N by a pitting process reminiscent of corrosion.

Comparison of the i.r. spectra of the original and deprotected novolac films of the same thickness indicated that the intensity of the ν_{OH} band (3200–3600 cm^{-1}) in the latter is 10–20% lower than in the former. In addition, the intensity of the ν_{C-H} band of the t-butyl band at 2980–2850 cm^{-1} was significantly stronger in the deprotected novolac than that expected from the intensity of the $\nu_{C=O}$ band at 1755 cm^{-1} (the residual t-BOC groups). These results suggest an excessive amount of t-butyl groups in the deprotected polymer, probably due to the acid-catalysed alkylation of the otherwise crosslinking-prone novolac. Putative reactive sites include the *ortho* ring positions, the activated methylene bridges between the aromatic moieties or the phenolic oxygens (O-alkylation). Although such reactions do not result in crosslinking (g.p.c. curves of the starting and deprotected novolacs are superimposable), the alkylated polymer would be expected to exhibit lower solubility in aqueous bases because of its lower polarity and the lower concentration of the ionizable OH groups.

The possibility of the previously reported neutralization of the photogenerated acid by airborne amines[20,21] was eliminated by reducing the time delay between the exposure and the heating step to <15 s, as well as by removing the top 100 nm of the deprotected film in an oxygen plasma. Thus, in contrast to other dual-tone chemical amplification resists, positive-tone images in tBOC-N-based resists can only be obtained by using non-aqueous, alcohol-based developers.

Three deep-u.v. lithographic sensitivity curves for the tBOC-N(HL) film containing 4 wt% of TPS-OTf are shown in *Figure 1*. Curve A traces a decrease in film thickness as a function of the deep-u.v. dose (PEB: 3 min at 120°C). Curve B indicates that the exposed and baked tBOC-N film remains insoluble in IPA until one-third of the t-BOC groups is deprotected, at which point its solubility rapidly increases. A similarly abrupt solubility change was observed during the negative-mode development in several alkylated aromatic solvents, such as *p*-diethylbenzene, n-butylbenzene and tetrahydronaphthalene (curve C). Such a rapid solubility change with polymer composition is equivalent to a high lithographic contrast which, in turn, determines the resist's resolution. The calculated contrast values for curves B and C are $\gamma_p = 4.0$ and $\gamma_n = 7.6$, respectively.

Unexpectedly gratifying results were obtained when tBOC-N(HL) or -(HH) films containing 8 wt% TPS-OTf were patternwise exposed with a highly focused 50 kV electron beam. For example, well-resolved, negative-tone line-and-space patterns (gratings) having a pitch of <150 nm were obtained at an electron-beam line dose of only 0.065 nC cm^{-1} (4.3 μC cm^{-2}) (*Figure 2*). We believe these are the most dense periodic patterns ever reported in a high-sensitivity, negative-tone resist.

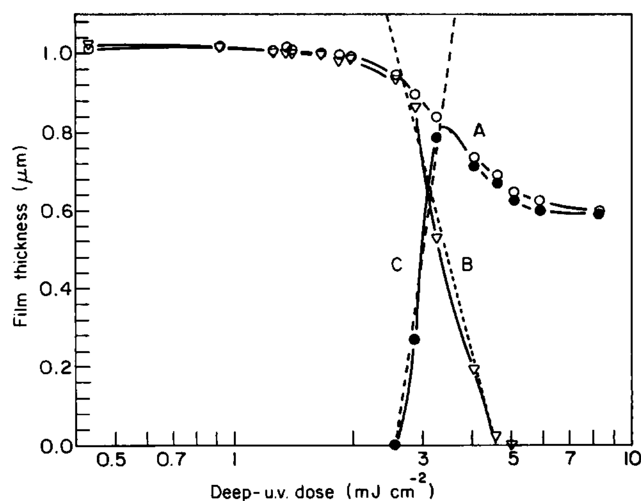

Figure 1 Lithographic contrast curves for tBOC-N(HH) (1 μm thick film, 4 wt% TPS-OTf) as a function of the deep-u.v. dose after PEB (3 min at 120°C, curve A), and after subsequent development in 2-propanol (1 min at 21°C, curve B) and tetrahydronaphthalene (1.5 min at 15°C, curve C)

*Similar behaviour was recently reported for an acid-deprotected tetrahydropyranyl derivative of poly(hydroxystyrene)[18]

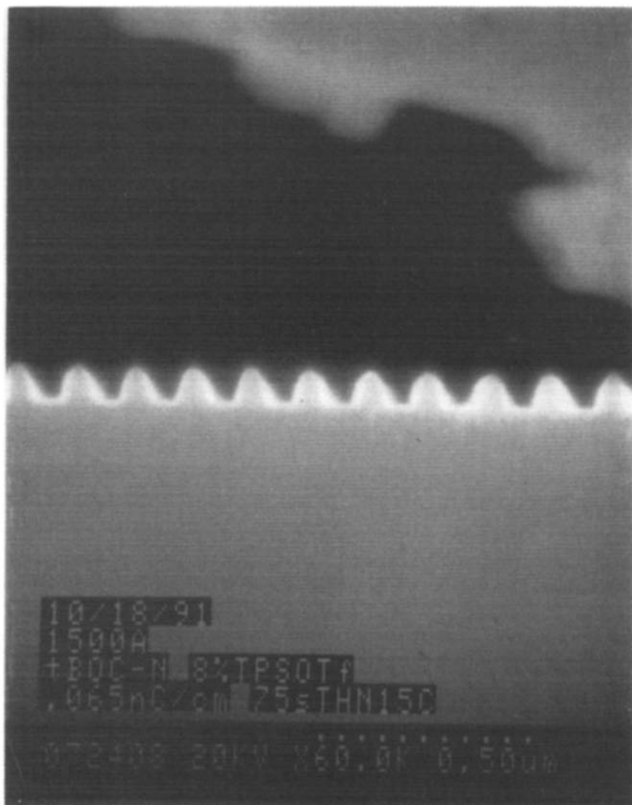

Figure 2 An array of 75-nm lines and spaces delineated with a 50 kV electron beam in a 150-nm-thick film of tBOC-N(HH) containing 8 wt% TPS-OTf (line dose = 0.065 nC cm^{-1}; PEB: 3 min at 120°C; developed for 20 s in tetrahydronaphthalene at 15°C)

In summary, partially fractionated (or extracted) t-BOC-protected novolacs are promising, inexpensive matrix resins for chemically amplified resists. Detailed lithographic evaluation of such materials, including partially protected polymers and various molecular weight fractions, is in progress. We are also investigating, by a variety of spectroscopic techniques, the puzzling dissolution behaviour of the deprotected tBOC-N films and will report the results in a forthcoming publication.

Note added in proof

After this paper was submitted for publication, Brunsvold *et al.*[22] reported the use of t-BOC-protected novolacs for surface imaging applications and Ban *et al.*[23] reported the use of t-BOC-blocked novolacs as dissolution inhibitors for novolac-based resists.

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