

Network properties and acid degradability of epoxy-based SU-8 resists containing reactive gamma-butyrolactone

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Abstract

SU-8 is an octafunctional epoxy-based negative resist supplied with a reactive diluent, gamma-butyrolactone (GBL). This paper characterizes the network properties and acid degradability of cured SU-8 resists with varying GBL monomer content and ultraviolet (UV) irradiation time. The SU-8/GBL network structure was characterized by Fourier transform infrared (FTIR) spectroscopy, ^{13}C nuclear magnetic resonance (NMR) spectroscopy and gas chromatography–mass spectrometry (GC/MS). GBL was found to copolymerize with epoxy to bridge two neighbouring epoxy groups and does not homopolymerize. The maximum GBL:SU-8 molar ratio whereby all GBL fully reacted with available epoxy functionalities in the network was found to be 8:1. Excess GBL beyond the maximum GBL:SU-8 ratio remains in the network as a plasticizer. GBL content and UV irradiation time affect glass transition temperature (T_g), epoxy conversion and molecular weight between cross-links (M_c) which were measured by dynamic mechanical analysis (DMA) and FTIR. The mechanism of cross-linked network acid degradation was found to be surface erosion. Lower epoxy conversion, higher M_c and higher GBL content resulted in a higher dissolution rate, which can be exploited in applications requiring SU-8 removal. A patterned SU-8 grating with relatively high-GBL content (10%) was successfully used as a template for Cu electroforming. © 2008 Elsevier B.V. All rights reserved.

Keywords: SU-8; Acid degradation; Kinetics; Network; Reactive solvent; Gamma-butyrolactone

1. Introduction

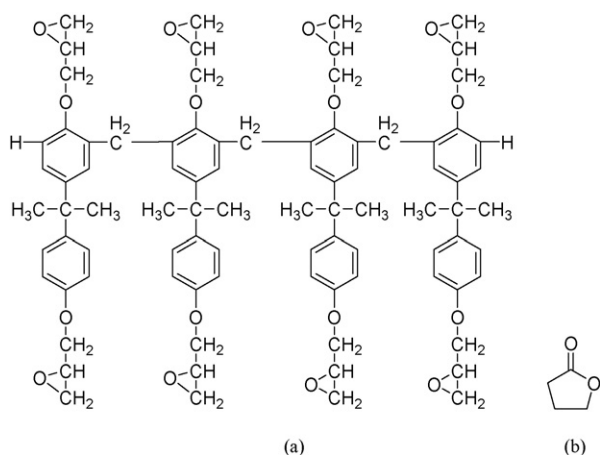
SU-8, now a standard negative resist for very high-aspect-ratio micromachining [1,2], is an octafunctional epoxy-based negative resist supplied with a reactive diluent, gamma-butyrolactone, and a cationic polymerization photoinitiator of triarylsulfonium hexafluoroantimonate salt (Scheme 1). Upon ultra violet (UV) irradiation, the triarylsulfonium hexafluoroantimonate salt decomposes to generate a Lewis acid. The latter acts as a catalyst to initiate the polymerization by opening the epoxy ring in the SU-8 [3,4]. Then chain propagation cross-links the SU-8 resist into a tight network when it is heated to above its T_g (50 °C) [5]. Each epoxy group can react with another epoxy group in the same or other molecules. Mas et al. have reported the copolymerization of diglycidyl ether of bisphenol-A (DGEBA) with GBL and found that spiroorthoester (SOE) intermediates were formed during the cross-linking of epoxy

with lactone [6,7]. Previous studies of SU-8 have reported the thermal, mechanical and viscoelastic [5,8,9] properties of the cured network. The lithographic properties of SU-8 as a function of photoacid generator concentration have also been investigated [10]. The chemical structure of the highly cross-linked SU-8/GBL network has, however, not been studied.

Further, the highly cross-linked SU-8 network is poorly soluble so that its removal remains a great challenge. The ease of SU-8 removal depends on the processing conditions and GBL content. The mechanism(s) of cross-linked SU-8 removal are also not well understood. Removal of SU-8 is needed in many patterning applications such as after Ni or Cu patterned electroforming. Thus, understanding the cross-linking reaction and network properties of cured SU-8/GBL mixture is of interest from the fundamental chemistry and industrial application perspectives. There are, however, no published studies on the effect of gamma-butyrolactone (GBL), on the network properties and acid degradability of cross-linked SU-8.

This article reports our characterization of the properties and acid degradability of the network formed in the curing of SU-8 resist with GBL monomer under conditions of varying GBL

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Scheme 1. Chemical structures of (a) SU-8 and (b) GBL.

content and UV exposure time. The network structure was characterized by Fourier transform infrared (FTIR) spectroscopy, ^{13}C nuclear magnetic resonance (NMR) spectroscopy and gas chromatography–mass spectrometry (GC/MS). The amount of GBL reacted into the network was determined by weighing after vacuum extraction. The effect of GBL content on epoxy conversion, molecular weight between cross-link (M_c) and glass transition temperature (T_g) was measured by Fourier transform infrared (FTIR) spectroscopy and dynamic mechanical analysis (DMA). The effect of epoxy conversion on M_c and T_g of SU-8 with low-GBL content (1 wt.%) was also measured. The acid degradation rate of the cross-linked network was also studied in detail. Control of the network structure to improve acid degradability was demonstrated using a micropatterned SU-8 with a copper template.

2. Experimental details

2.1. Materials and characterization

NANOTM SU-8 100 and SU-8 developer provided by Microchem Corp (Newton, Massachusetts) and gamma-butyrolactone (GBL) from Sigma–Aldrich Chemie GmbH (Germany) were used. The melting and boiling points of GBL are -45 and 204 °C respectively, and the vapour pressure at 20 °C is 0.2 kPa. The molecular structures of SU-8 and GBL are shown in Scheme 1. Silicon wafers were used as the substrates and were pre-cleaned as described in the literature [11]. Ultraviolet (UV) exposures were performed with a SUSS MA6 mask aligner equipped with a mercury (Hg) lamp. The lamp was used without a filter and the measured intensity at 365 nm was 10 mW/cm².

2.2. Sample preparation

Three groups of samples (denoted Sample Groups A, B and C) were prepared. In Group A, 100 μm thick SU-8 films were prepared whilst in Groups B and C, both 100 and 400 μm thick SU-8 films were prepared. The 100 - μm -thick SU-8 films were used for Fourier transform infra red spectroscopy (FTIR) and

gas chromatography coupled with mass spectroscopy (GC/MS) characterization. The 400 - μm -thick SU-8 films were used for dynamic mechanical analysis (DMA) characterization. Group A samples were used to investigate the curing reaction of SU-8 in the presence of GBL. Group B samples were used to investigate the effect of epoxy conversion on the network properties of SU-8 samples with 1% GBL by varying UV exposure time. Group C samples were used to investigate the effect of varying amount of GBL content on the network properties of cured SU-8. Table 1 summarizes the objectives and processing conditions of the samples.

For Group A samples, 100 μm thick SU-8 100 was coated onto Si wafers by spin coating at 3000 rpm for 30 s. Group A contained one sample coated with SU-8 with zero GBL content (denoted A1) and another (denoted A2) coated with as received SU-8 100 (27 wt.% GBL). Since SU-8, as supplied, contains GBL, it was necessary to partially or fully remove the GBL for experiments in which GBL content was varied below the as-supplied proportion; this was accomplished by pre-exposure vacuum extraction of those samples. The GBL extraction softbake for Sample A1 was 3 h at 95 °C on a hotplate followed by 65 °C for 4 days (96 h) under vacuum condition (<0.01 atm). Both samples were exposed to UV light for 70 s. Post Exposure Bake (PEB) was done at 65 °C for 3 min and 95 °C for 10 min, using a hotplate. The processed SU-8 films were then delaminated from the substrates by quick cooling from 95 °C to -85 °C using a SANYO MDF-U50V ultra low-temperature refrigerator.

Group B samples had constant GBL content of 1 ± 0.2 wt.% (determined by FTIR and described as 1% hereafter) and varying epoxy conversions ranging from 0 to 95% ; the variable conversion was produced by varying UV exposure from 0 s to 500 s. 100 μm (denoted B1) and 400 μm (denoted B2) thick SU-8 100 films were prepared on silicon wafers by spin coating at 3000 rpm for 30 s and 500 rpm for 60 s, respectively. Samples B1 were softbaked at 65 °C and then 95 °C for 10 and 30 min, respectively. Samples B2 were softbaked at 65 °C and then 95 °C for 30 and 200 min, respectively. All softbaking was done using a hotplate.

Group C samples had varying GBL content ranging from 1% to 80% (wt.%). 100 μm thick (Samples C1) and 400 μm thick (Samples C2) SU-8 films were prepared. For GBL content lower than 30% , the coating was done by spin coating. In this subgroup, GBL weight percentage contents of 1% , 3.9% , 4.1% , 6.9% , 15.7% and 27% were prepared. These samples were softbaked at 95 °C for varied times to yield the variable GBL contents. For samples with GBL content of 30% or higher (i.e. 30% , 32% , 35% , 40% , 50% , 70% and 80%), diluted SU-8 was coated onto Si wafers using a mold/spacer made of polyester film (specifically Melinex[®] 454 film from DuPont Company). The high-GBL content formulations had very low viscosity and easily filled the mold/spacers, with the excess flowing over the edges of the spacers. The diluted SU-8 samples were exposed to UV (70 s) without any softbake.

After UV exposure and PEB (Table 1), all samples (Groups A–C) were kept in a vacuum oven at 65 °C under vacuum condition (<0.01 atm) for at least 6 days. This was to extract excess unreacted GBL in the cured SU-8 resist. The Group C samples

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