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Photosensitive poly(dimethylsiloxane) materials for microfluidic applications

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Abstract

Poly(dimethylsiloxane) (PDMS) is used as a thermally crosslinked material in microfluidics and Bio-MEMS. Recently photo-patternable materials show increasing interest, as the demand for easy alignment arises for multilayered structures. We present a photopatterning process for PDMS in microfluidics, for two main uses: (a) as a thin (approximately 10 μm) structural layer, and (b) as a very thin (approximately 1 μm) hard mask for oxygen plasma etching of microfluidic polymeric substrates down to several tens of microns. We study the deep-UV and I-line photocrosslinking properties of siloxane copolymers containing vinyl-methyl-siloxane groups as polymerizable units. These materials are sensitive to DUV and can be sensitized to 300–400 nm using free radical initiators. We prove that even thermally curable PDMS (Sylgard 184, base) can become photosensitive in DUV, although its practical use is limited to very thin films, due to its small molecular weight.

Keywords: Poly(dimethylsiloxane); Deep-UV lithography; Photoinitiators; UV curing; Microfluidics

1. Introduction

Silicones are attractive for lithographic applications in multilayer resist schemes. The first use of organosilicon polymers and more specifically of PDMS as thin top imaging resists in bilayer systems was reported by the group of Hatzakis at IBM [1–5]. These bilayer techniques can offer increased resolution and sensitivity, by imaging only a thin radiation sensitive layer, and transferring this pattern to an underlying planarizing polymer layer. While PDMS vinyl copolymers are sensitive to DUV, thin films (<1 μm) of PDMS alone are 193 nm, VUV, and e-beam sensitive and may also be used as resist in bilayer lithography [6,7]. It would thus be useful to develop photopatternable PDMS materials/processes for thicker films sensitive at 254 nm, as well for 300–400 nm radiation, and use these materials in the fabrication of MEMS and microfluidic devices as an alternative to thermally cured PDMS since several labs own DUV or I-line mask aligners. Ideally, one would like to use the same PDMS material for both thermal crosslinking (thermally crosslinkable PDMS contain vinyl groups) and photocuring.

Recently several companies have also commercialized photosensitive silicon containing polymers: WL-5351 and WL-5150 silicones by Dow Corning for electronic packaging applications [8], Cyclotene photosensitive resins from Dow Chemical, (derived from Benzocyclobutene (BCB) monomers) as dielectrics [9], and inorganic–organic hybrid polymers (ORMOCER) [10] for optical applications developed at Fraunhofer Institute and commercialized by Micro Resist. These new materials are however, of different chemical nature and softness compared to the vinyl copolymers or pure PDMS polymers used in lithography thus far.

We present a photopatterning process for PDMS in microfluidics, for two main uses: (a) as a thin (~10 μm) structural layer, and (b) as a thin (~1 μm) hard mask for oxygen plasma etching of polymeric substrates down to several tens of microns. We study the DUV and UV

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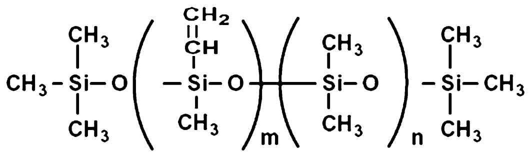
(300–400 nm) photocrosslinking properties of siloxane copolymers. Several PDMS copolymers with vinyl-methyl-siloxane groups as polymerizable units were selected. These copolymers can be sensitized to the 300–400 nm using free radical initiators.

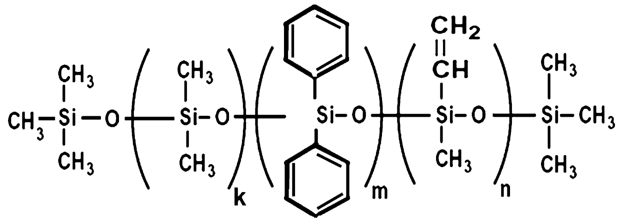
2. Experimental

In this work, two PDMS copolymers, one from ABCR [11] VDT 954, and one from United Chemical Technologies [12] PS 264, were used, as well as the base SYLGARD 184 from Dow Corning; All are shown in Fig. 1. To induce the crosslinking of the material in 300–400 nm region, a suitable free radical photoinitiator has to be introduced into the material. We used three free radical photoinitiators, which are shown in Fig. 2. The optical density of PDMS films with and without photoinitiator was determined with a UV–Vis Lambda 40 Spectrophotometer.

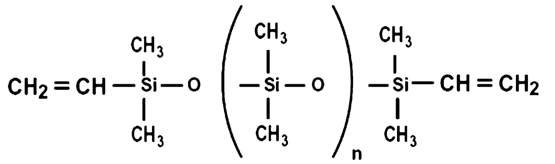
The photosensitive PDMS materials were dissolved in methyl isobutyl ketone (MIBK) or in toluene and the films were spin-coated either on Si or on PMMA substrates, (after priming with HMDS solution in toluene), and then baked at 50 °C for 1 min. The films were then exposed to DUV light broadband 254 nm (usually without photoinitiator) or to UV light broadband 365 nm (always with photoinitiator). After the UV exposure, the samples were thermally treated on a hotplate at 120 °C for 5 min, to induce crosslinking of the film. Subsequently, the layers were developed for approximately ~3 min using a mixture of methyl isobutyl ketone and 2-propanol (1:1). The thickness of the films was measured by a M2000 Woolam spectroscopic ellipsometer (245–1000 nm, 470 wavelengths).



(a) VDT 954

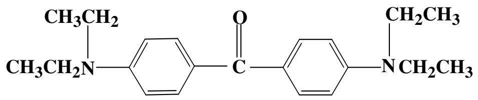


(b) PS 264

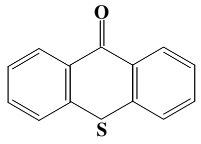


(c) Sylgard 184 Base

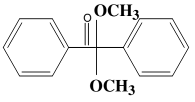
Fig. 1. PDMS materials used in this work: (a) vinyl-containing poly(dimethylsiloxane) [(VDT 954), vinylmethylsiloxane-dimethylsiloxane-trimethylsiloxy terminated copolymer, 300,000–500,000 cST (vinyl amount 11.0–13.0%)], (b) PS 264, Poly(dimethylsiloxane) – (5%) – (diphenylsiloxane) (0.1–0.3%) (methylvinylsiloxane) copolymer, $M_n = 450{,}000$ and $M_w = 990{,}000$, Gum, and (c) vinyl terminated poly(dimethylsiloxane) (SYLGARD 184 Base, MW ~60,000).



(a) Photoinitiator A



(b) Photoinitiator B



(c) Photoinitiator C

Fig. 2. Photoinitiators used in this work: (a) 4, 4'-*bis*(diethylamino)benzophenone, 99+% (A(365) = 1 for concentration 0.0008%, in acetonitrile), (b) thioxathen-9-one, 98% (A(365) = 0.15 for concentration 0.0005%, in acetonitrile) and (c) Igracure 651 (2,2-dimethoxy-2-phenyl acetophenone), (A(254) = 0.5 for concentration 0.001% in acetonitrile), used by Shaw et al. [5] for DUV. A is used for thin films ~1 μm, B for thicker films ~10 μm, C is used for DUV exposures.

3. Results and Discussion

Fig. 3 shows the absorption spectrum of PDMS films (PS 264) without and with 4% photoinitiator A (see Fig. 2a). As can be seen, the PDMS material without photoinitiator only absorbs in the DUV region, which is attributed to phenyl groups of PS 264. Therefore, it is not necessary to add photoinitiator for DUV, although

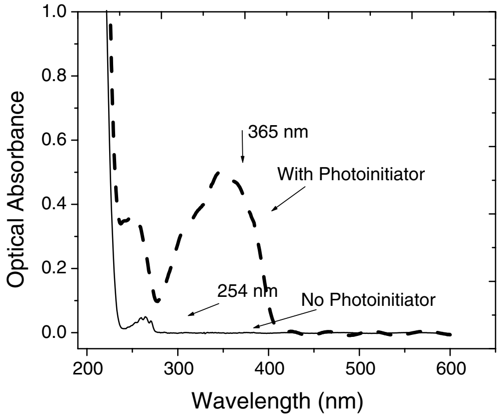


Fig. 3. Optical absorption of 1.2 μm thick PDMS (PS 264 copolymer) without and with 4% photoinitiator A (Fig. 2a). [$\alpha = 0.026\ \mu m^{-1}$ at 248 nm and $\alpha = 0.38\ \mu m^{-1}$ at 365 nm, respectively].