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Improved properties of epoxy nanocomposites for specific applications in the field of MEMS/NEMS

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Abstract

Increasing interest in specific applications in the field of micro- and nano-electromechanical systems (MEMS and NEMS) has raised the request for new functional polymeric materials. Hybrid materials consisting of inorganic nanoparticles in polymer matrices represent a novel class of materials for lithographic patterning with unique properties, which arise from the synergism between the properties of both components [N. Damean, B.A. Parviz, J.N Lee, T. Odom, G.M Whitesides, J. Micromech. Microeng. 15 (29) (2005)]. We demonstrate the miscibility of epoxy resin surface-modified SiO_2 nanoparticles into epoxy photomaterial to create a patternable material with new properties, such as reduced refractive index for waveguiding applications. The lithographic, optical and mechanical properties of the silica-doped epoxy materials were investigated depending on the silica content in the photomaterial. Up to 60 μm thick layers were processed using UV lithography.

Keywords: Epoxy nanocomposites; Hybrid material; Silica; SiO_2 nanoparticle; MEMS

1. Introduction

Increasing interest in specific applications in the field of MEMS and NEMS has raised the request for new functional polymeric materials. Epoxy based photoresists are being broadly used for the fabrication of micromechanical devices [2]. SU-8, the well known thick photoresist with superior lithographic properties over a wide range of thicknesses, has made a tremendous impact on the development in this field by simple fabrication of permanent plastics elements with vertical sidewalls and a high aspect ratio [3]. For new low cost applications, organic materials are required which can be lithographically patterned and exhibit properties comparable to inorganic materials, such as high hardness, magnetism or conductivity. Another interesting application is the definition of polymer waveguides, which requires materials with lithographic capabilities comparable to the original organic materials, but with sufficient difference in the refractive index between core and clad material.

Hybrid materials consisting of inorganic nanoparticles in polymer matrices represent a novel class of materials for lithographic nanopatterning with unique properties, which arise from the synergism between the properties of both components [1]. The use of nanoparticles is often limited by their low solubility in most organic solvents which leads to phase separation or sedimentation of the particles from the matrix or by the poor miscibility of all components. There are several ways to overcome the low solubility of the nanoparticles and to increase the chemical compatibility between the single components: (i) by in situ formation of the nanoparticles in a prepolymeric matrix [4], (ii) by adding ligands to form core/shell like nanoparticles or (iii) by polymeric particle coating [5–8]. It is known that the particle size is an important factor as well as the interface region between filler and matrix

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for the macro or micro optical and mechanical or other new properties of the formulated composites. Since the mechanical properties of the interface region may be different from that of the matrix, the formation of the interface region will affect the bulk properties.

A variety of nanoparticles-polymer mixtures for special applications are described, e.g., magnetic nanoparticles (iron oxides usually Fe_2O_3 or Fe_3O_4) to add magnetism to polymers, luminescent core/shell nanoparticles (e.g., CdSe/ZnS), nickel, or conductive silver, copper and single or multi walled carbon nanotubes e.g., for electrochemical sensing [5,9]. The addition of pure silica particles of different sizes (50 nm up to 4 μm) into alkali-curable epoxy materials and the influence on the material's mechanical properties of the resulting material depending on the silica content are described elsewhere in the literature e.g., [6,10,11].

Jiguet et al. [12] described the admixture of pure silica particles into SU-8 resists. With 27 ppm/°C the silica-doped material exhibited a lower coefficient of thermal expansion (CTE) than pure SU-8 with 50 ppm/°C. No specification about the particle size, particle content and processable layer thicknesses were given.

In this study, we demonstrate the miscibility of epoxy resin surface modified SiO_2 nanoparticles into the epoxy photomaterial to create a patternable material with new properties. The lithographic, optical and mechanical properties of the formulated materials were investigated. Layers up to 60 μm were lithographically processed.

2. Experimental

2.1. Materials

A high viscosity solution of epoxy resin coated silica nanoparticles with a filler content of 40 wt% silica (Nanopox XP) provided by Hanse Chemie AG, Germany was used. Nanopox product is a colloidal silica sol in a resin matrix, consisting of surface-modified spherically shaped synthetic SiO_2 nanoparticles of small size (average diameter of 20 nm) with an extremely narrow particle size distribution of 5–6 nm. Due to the chemical synthesis and the chemical modification of the surface of the silica nanoparticles, their distribution is homogeneous and agglomerate-free in the epoxy resin matrix.

The epoxy equivalent of the silica reinforced resin was determined and is about 261 g/eq and is slightly higher than that of the SU-8 resin which allows a cationic polymerisation analogous to the resin of the SU-8 resist. The chemical bonding both covalent and non-covalent, between filler and polymer matrix should improve the compatibility of the materials.

The silica reinforced resin was mixed with an epoxy resin and photoacid generator, whereas the amount of silica reinforced resin was varied from 0 to 100 wt% of the resin solid content (SiO_2-0-, SiO_2-25-, SiO_2-50-, SiO_2-75-, SiO_2-100-). The obtained photosensitive mixtures with a solid content of up to 67 wt% were clear, homogeneous and long-term stable.

2.2. Measurements

Lithographic evaluation was carried out using a RC 5 spin coater system (Suss MicroTec, Germany) without a cover and a vacuum contact Suss mask aligner MA 56 (UV 400) with an intensity of about 10 mW/cm^2 at 365 nm. UV spectra of the resist films were measured on quartz substrates using UV–vis/NIR spectrophotometer Lambda 19 (Perkin–Elmer). The Cauchy coefficients of the silica-doped photosensitive layers were determined using an elipsometer SENTECH SE 850 in the spectral range of 480–900 nm and 480–1700 nm. The Cauchy coefficients are material constants. The refractive index of the resist films depending on the wavelength can be calculated from the Cauchy equation. The hardness of the resist layers was measured using a TriboScope (HYSITRON, USA).

3. Results and discussion

3.1. Lithographic properties

The resist layers of the composites doped with different amount of silica resin were clear, homogeneous and non-sticky. Typical process parameters were: prebake (PB): 50 °C/90 °C for 5 min/20 min, dose: 500 to 800 mJ/ cm^2, post exposure bake (PEB): 50 °C/ 90 °C for 5 min/ 10 min, develop: mr-Dev 600/IPA: 2 min/2 min.

Experimental results confirm that the lithographic properties of this modified resists remain unaltered by the presence of the synthetic SiO_2 nanospheres. Only the exposure dose is slightly increased by increasing the silica amount, from 500 mJ/cm^2 to 800 mJ/cm^2 for a 55–60 μm thick resist layer. It should be pointed out that cracks and stress, which sometimes can occur in this type of epoxy resists, is effectively reduced with increasing amount of silica. After developing the materials with higher amounts of silica (e.g., SiO_2-75- and SiO_2-100-) a thin insoluble residue layer is observed. This could be a thin layer of silica. Resolutions of up to 7 μm at a film thickness of 60 μm were obtained. Due to the size of the silica nano particles of around 20 nm the resolution of thinner layers is limited (see Fig. 1).

3.2. Optical properties

Due to the low refractive index of silica of 1.49 down to 1.46 at wavelengths of 400 to 1550 nm silica nanoparticles are promising candidates for decreasing the refractive index of a silica-doped composite material. The refractive index of the resist solutions with different silica content [n_D^{25}: 1.5409 (SiO_2-0-) > 1.5359 (SiO_2-25-) > 1.5291 (SiO_2-50-) > 1.5230 (SiO_2-75-) > 1.5159 (SiO_2-100-)] and the refractive index of the uncured and the crosslinked