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Siloxane-based polymer epoxies for optical waveguides

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ABSTRACT

We introduce a new class of siloxane-based epoxy polymers for thin film optical waveguide applications. The thickness of spun-on films can be controlled by varying either spin speed or viscosity using solvents. Cured films exhibit excellent adhesion to silicon oxide and Al and excellent thermal and chemical stability. Waveguides of ~ 2 micron thickness on silicon oxide exhibit <0.2 dB/cm loss at 830 nm. We demonstrate the formation of a 45° vertical mirror using reactive ion etching slope transfer from photoresist to epoxy polymer film.

Keywords: siloxane, polymer, epoxy, optical waveguide, loss, thin film

INTRODUCTION

Optical communications have been making inroads into shorter distance applications as the capabilities of processors and the consequent need for higher speed data links increase. The connection and routing of fiber to chips can be a demanding and cost-limiting fabrication task. Materials that can be processed as complementary metal-oxide semiconductor (CMOS)-compatible thin films as well as larger fiber-optic components may be of great utility because inexpensive semiconductor lithographic processing could be used for many components while ensuring compatibility with polymer optical technology. Desirable materials should exhibit the following properties: 1) good adhesion to CMOS materials, including silicon oxide, copper, and aluminum; 2) good thermal stability at CMOS back end processing temperatures; 3) a useful range of index of refraction with loss <0.5 dB/cm at the application wavelength (630-830, or 1550 nm); and 4) a capability of being processed into waveguides and couplers using lithographic techniques that are compatible with silicon chip processing. We describe here the processing and properties of alkoxy-siloxane-based polymer epoxies that are competitive in this application.

CHEMICAL AND PHYSICAL PROPERTIES

The siloxane polymers in the current study are based on an –Si-O-Si- backbone with epoxy functional groups. A preparation method is described by Crivello and collaborators [1]. Molecular weights prior to curing range from 1500 to 10000 grams/mole with between 5 and 60 –Si-O-Si- units in a chain. Similar siloxane-based epoxy polymers are available as PC2000 and PC 2003 from Polyset Inc., Mechanicville, New York. Additional details on properties and processing can be found in references [2] and [3]. A closely related epoxy polymer, also produced by Polyset Inc., has been used to form microlens arrays by molding [4].

The siloxane resin has a viscosity of 20,000 cps at 25°C. It can be thinned with a variety of solvents including alcohols, acetates, ketones, aromatics, or aliphatics. For the present study the liquid siloxane resin was typically thinned to 20% solids in a methylethyl ketone (MEK)/1-methoxy-2-propanol acetate (PMA) solvent in order to spin films onto a 3 micron wet oxide grown on p-type (100) Si wafers. In order to promote adhesion, either hexamethyl di-silazane (HMDS) or A-3000 is first spun onto the substrate and baked at 100°C (10 min). The polymer solution is dispensed at a spin speed of 2000-6000 rpm, resulting in a film thickness of 1-5 microns. In order to evaluate curing cycles, we performed TGA and DSC measurements on as-spun and cured films.

An example TGA scan is shown in Fig. 1. The TGA atmosphere is N_2. The large weight loss below ~150°C is due to evaporation of the solvent. Between 200 and 400°C, the weight is stable. Above ~410°C, the weight again begins to decrease, due to decomposition of the polymer. The curing cycle for high quality optical films consists of a 100°C bake in vacuum to remove most of the solvent, followed by a 2 hour bake in air at 165°C to cross-link the polymer and remove the remainder of the solvent. Efficient cross-linking is achieved by the addition of an acid generating catalyst

[1]. The acid catalyst is necessary for UV curing. We have found that the best optical quality films result when the catalyst is minimized (<0.1% by weight) and a thermal cure is used.

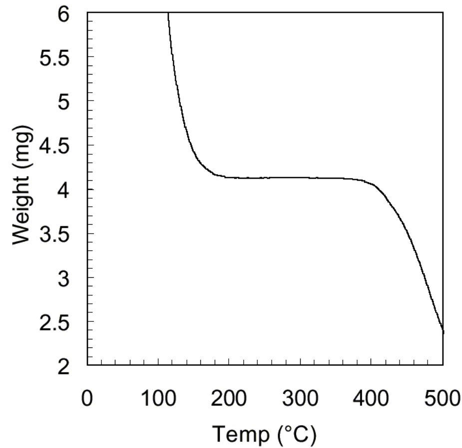

Fig. 1 - Thermogravimetric analysis of uncured polymer with PMA/MEK solvent. The drop below 150°C is due to solvent evaporation. The drop above 400°C is due to decomposition.

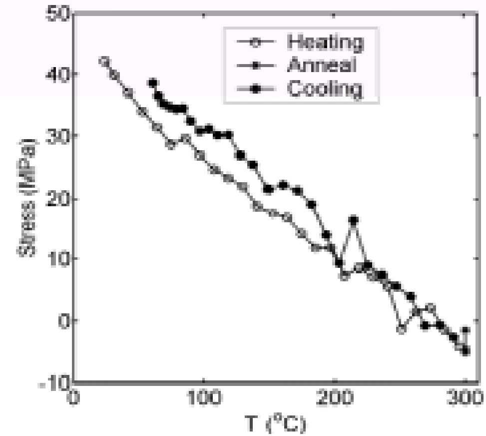

Fig. 2 - Stress plotted as a function of temperature in a 1 micron thick cured film on Si.

In Fig. 2 we show the temperature dependence of the stress in a 1 micron thick cured film. Cured films are slightly tensile at room temperature and compressive at high temperature. The data in Fig. 2 was taken using the following cycle: i) a ramp from 20 to 300°C at 5°/min., ii) hold at 300°C for 20 min., iii) cool at 5°C/min. The change in stress is reversible for temperatures up to 400°C. We propose that the temperature dependence of the stress is entirely due to differential thermal expansion. The thermal expansion between 20 and 300°C is linear, with a coefficient of linear expansion of $-5.5\times10^{-5}/^{o}C$.

OPTICAL PROPERTIES OF FILMS AND SLAB WAVEGUIDES

The index of refraction of cured films was measured by spectroscopic ellipsometry. PC 2003 has an index of 1.51 at 635 nm with a dispersion in the 400-800 nm range described by $1.502+6650/\lambda^2$ (with λ in nm). A sample containing partially fluorinated pendant groups had n=1.46 at 635 nm ($1.46+4310/\lambda^2$).

The UV-VIS-IR absorption spectrum measured by normal transmission through a 5 micron thick film is shown in Fig. 1. The polymer exhibits a sharp UV absorption edge at about 300 nm with a weak tail extending up to 350 nm. Absorption is unmeasurably small (<5 cm^{-1}) between 400 nm and 1100 nm. At longer wavelengths we observe overtones of C-H, C-C, and O-H IR vibrational modes with weak peaks at 1210 nm and 1410 nm, and successively stronger peaks at ~1750 and ~2300 nm. A strong set of C-H fundamentals is observed above 3000 nm.

In transmission measurements, uncertainty in the subtraction of the baseline gives rise to uncertainties in loss of order 5 dB/cm for a 5 micron thick film. In order to quantify smaller losses, we used two methods. First, we fabricated slab waveguides on quartz and prism coupled to the lowest order mode using semiconductor lasers at 635 and 840 nm. A small amount of light in this mode is scattered out of the film surface by surface and interface roughness. This scattered light was imaged using a CCD. The rate at which the intensity falls off is due to the sum of scattering and absorption losses and therefore represents an upper limit on fundamental absorption. Due to sensitivity limitations of Si-based CCD

detectors, we were unable to image the scattered light from a 1550 nm laser. We therefore used photothermal deflection spectroscopy[5] to measure the change in temperature of the film due to absorbance of the laser beam. The upper limits for absorption losses in fully cured PC2003 are thus: 0.2 ± 0.1 dB/cm at 635 and 830 nm, and 0.5 ± 0.5 dB/cm at 1550 nm.

We have also fabricated slab waveguides on xerogel cladding films in order to increase the index difference between cladding and epoxy polymer core[3,6]. A thin (51 nm) plasma deposited oxide is first deposited on the xerogel substrate in order to prevent penetration of the xerogel by polymer solvent[3]. The low index xerogel cladding results in increased confinement of the optical modes and the consequent ability to design smaller bend radius features. Losses as low as 1 ± 1 dB/cm (noise limited) have been achieved[6].

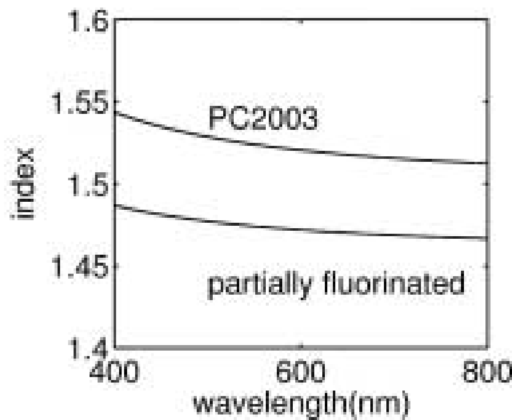

Fig. 3 - Spectral dependence of the index of refraction for typical high and low index siloxane films.

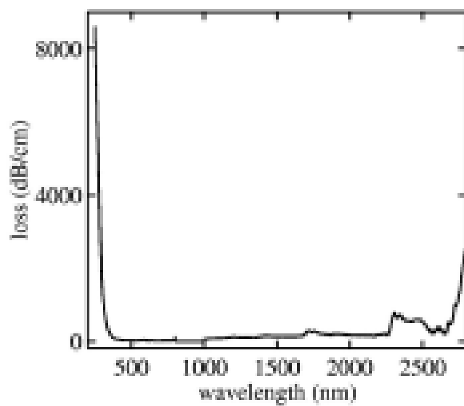

Fig. 4 - Spectral dependence of the absorption loss in PC2003. Measured by transmission through a cured 5 micron film on quartz.

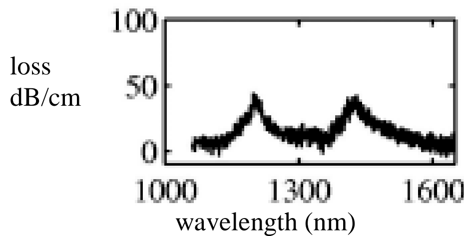

Fig. 4a - Expanded view of the spectral dependence of the absorption loss in PC2003. Measured by transmission through a cured 5 micron film on quartz.

The optical properties of films with low catalyst content (<0.1% by weight) do not degrade measurably with thermal cycling, even for heat treatment as high as 300°C. Films are stable in air to ~225°C and in vacuum or inert atmosphere to ~400°C. Films with higher catalyst content (to enable UV curing) appear to degrade somewhat. In these high-catalyst films loss increases to ~0.5 dB/cm at 635 and 840 nm after heat treatment at 300°C.

PROCESSING AND WAVEGUIDE COMPONENTS

Because of the presence of both –Si-O-Si- chains and C-H in the network, mixed O_2/CHF_3 or O_2/CF_4 gas is used for plasma etching. Etching was carried out at room temperature in a PlasmaTherm 73 under a total pressure of 40 mTorr, rf power of 150 W, and flow rate of 50 sccm. Etching in pure O_2 produces an Si-O rich protective layer that prevents etching after an initial build-up[2]. This behavior has been previously reported for other siloxane polymers[7]. A maximum etch rate of 400 nm/min was found for O_2/CHF_3 flow ratio of 1:4, with nearly zero etch rate in pure CHF_3.

Plasma etching has also been performed with CF_4/O_2 mixtures[3]. The dependence of etch rate of PC2003 on O_2/CF_4 gas ratio is shown in Fig. 5. Etching under pure O_2 is negligible. Etching under pure CF_4 is also slow. The maximum etch rate is found for $CF_4/(O_2+CF_4)$ flow ratios of 0.3, but the smoothest surface is found for $CF_4/(O_2+CF_4)=0.5$.

Al provides an excellent plasma etch mask, although we have also used plasma deposited silicon nitride and silicon oxide. Conventional photoresist can also be used directly as an etch mask but the low selectivity means that the resist thickness must typically be thicker than the siloxane polymer being etched. The etch rates of SiO_2 and 1813 photoresist are also shown in Fig. 5 to provide estimates of relative selectivity.

In Fig. 6 we show the side view of an example of the transfer of an angle in S1813 resist (top layer) into PC2003 by RIE. A flow ratio of 50:50 has only a small selectivity of 1.2 under our etching conditions, so the angle in the PC2003 (second layer from top) is nearly equal to that of the S1813. Note that the PC2003 surface is smooth and uniform.

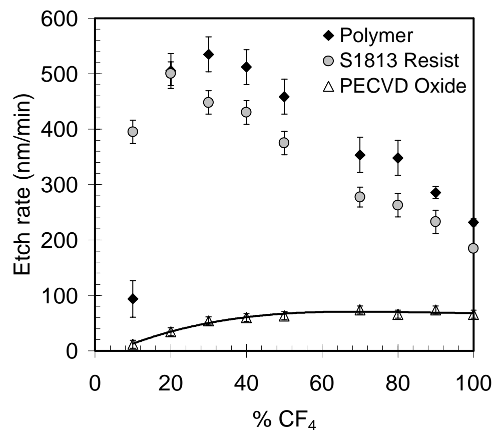

Fig. 5 - Etch rates in Reactive Ion Etching mode at room temperature for PC2003 siloxane epoxy polymer, S1813 resist, and plasma deposited SiO_2.

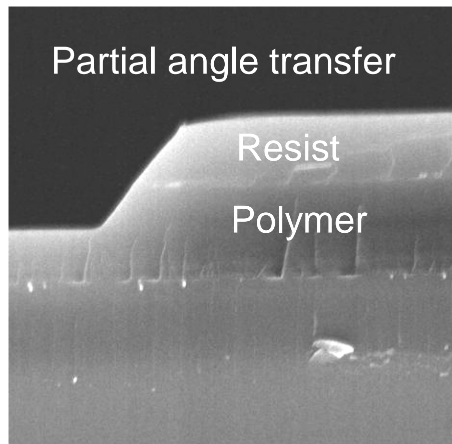

Fig. 6 - An example of use of RIE to transfer an angle from S1813 photoresist to PC2003 polymer. About ½ of the PC2003 film is etched.

ACKNOWLEDGEMENTS

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