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Rapid ultraviolet-curing of epoxy siloxane films

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ABSTRACT

The ultraviolet (UV) curable epoxy siloxane polymer is shown to cross-link at low UV dosages of 130 mJ/cm^2, making it desirable for use in nanoimprinting and the rapid fabrication of micro/nano-scaled patterns. In this paper, the dielectric and mechanical properties of this UV-cured epoxy siloxane polymer are investigated. The results of these tests show that the rapid UV-cured polymer films have a dielectric constant of 2.7 ± 0.13, leakage current density on the order of 10^{-9} A/cm^2 under 1 MV/cm, dielectric strength of greater than 5 MV/cm, and a reduced modulus of elasticity of 6.2 GPa characterized using nanoindentation. These properties indicate that the epoxy siloxane can be used to fabricate layers for functional device applications.

1. Introduction

The science and technology of nanostructured fabrication is one of the most visible and growing areas of research today. Originating from microelectronics, nanostructured fabrication has been gradually extended to cover a broad and multidisciplinary field of research and emerging applications. In recent years, nanopatterning technology has been an area of intense research and development; further advancement in this area is of primary importance to continue the evolution of nanometer-scale science and technology [1–3].

For the past decades, the typical fabrication method for patterning structures has been optical lithography followed by Reactive Ion Etching (RIE). This technique has been particularly popular in Integrated Circuits (IC) manufacturing. However, the high cost, complex manufacturing equipment, and optical limitations for sub-100 nm critical dimensions have restricted the development and fabrication of nanometer-scaled patterns. To resolve these restrictions, imprint lithography has been explored in recent years [4–7]. Its relatively low setup cost and extended critical dimension range capability (from sub-100 nm to microns) are notable and distinct advantages. Furthermore, the main advantage of imprint lithography is that the micro and nano scale patterns can be replicated from a single template and that the pattern resolution is not governed by the optical diffraction limit. These advantages lead to potential for applications in optical devices, biotech devices, MicroElectroMechanical Systems (MEMS) and the possibility of future on-chip Nanoimprinting Lithography (NIL) technology [8–10].

The optimal imprint process relies on the perfection of the imprint tool, the template, the processing, and particularly the imprint resist. The imprint formulations have to be photo-curable and would be more desirable if they could crosslink/harden swiftly when subjected to the light source. Furthermore, it would be more attractive if the imprinted materials could be functional device layers rather than sacrificial resists. To fulfill all of these demands, the imprint materials require not only an ideal manufacturability for nanometer- and micrometer-sized structures with great efficiency, but also the stringent properties for the device layers.

Polyset epoxy siloxane polymer is a low dielectric constant material ($k = 2.8$) which has shown desirable dielectric properties and stability after being thermally cured at a low temperature of 165 °C [11]. A recent study has further illustrated the appealing photodefinition characteristics of epoxy siloxane by demonstrating that the patterned polymer can be cured upon a low Ultraviolet (UV) dose of only 130 mJ/cm^2 without the need for additional baking steps [12]. These results demonstrate the potential of using the imprinting process to fabricate UV curable epoxy siloxane as the dielectric layers for microelectronics applications. An important question can be raised: Are the properties of the rapidly UV cured polymer the same as that of its thermally cured counterpart? To this end, we have investigated the dielectric and mechanical properties of the epoxy siloxane films directly cured by UV using electrical measurements of the Metal-Insulator-Metal (MIM) capacitors and nanoidentation method, respectively.

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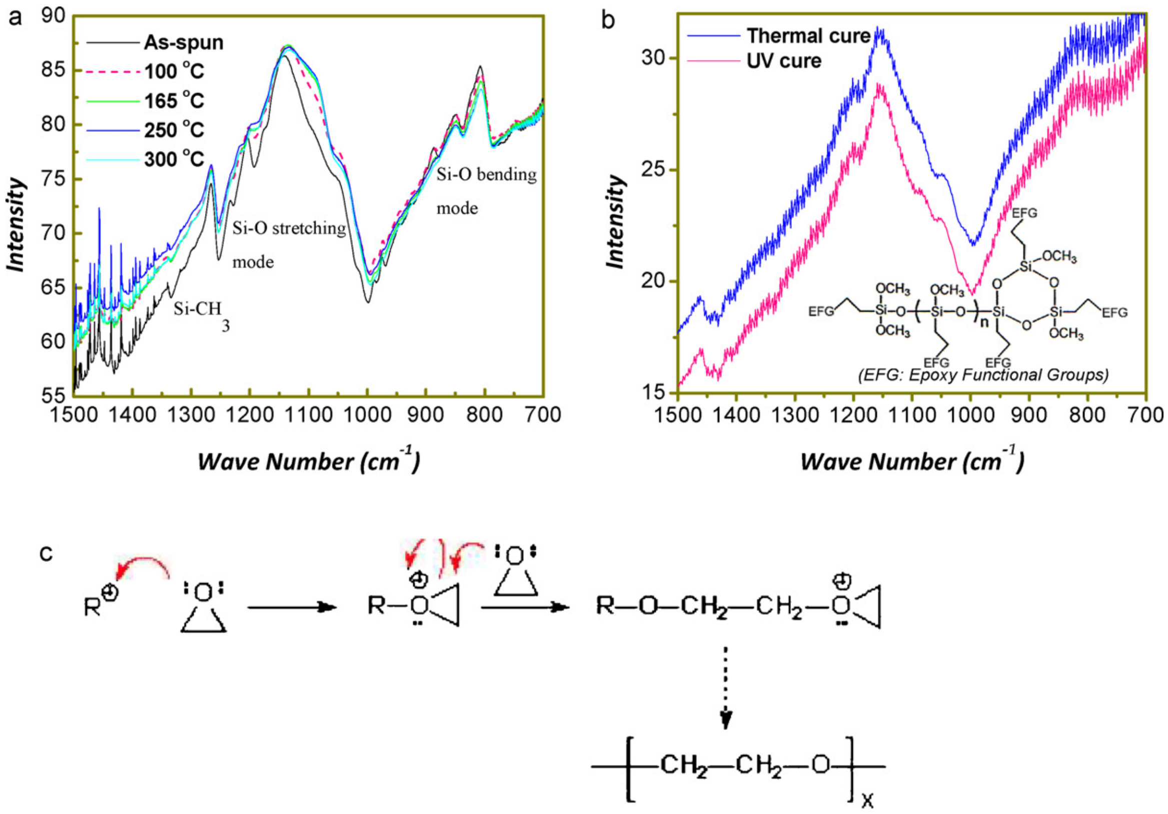

Fig. 1. FTIR spectra of (a) the thermally cured epoxy siloxane films, and (b) the comparison of thermally and UV cured films. The inset is the chemical structure of epoxy siloxane. (c) Generalized reaction mechanism for ring opening of epoxides.

2. Experimental

Epoxy siloxane polymers (obtained from Polyset Co. Inc.) were spin-coated onto n-type wafers with a low resistivity of $\leq 0.02\,\Omega$ cm for Metal-Insulator-Metal (MIM) structures. The epoxy siloxane films were subsequently cured either by UV or annealing. The UV curing process was carried out at room temperature in air ambient using karl Suss contact mask aligner under a broadband UV exposure at 13 mW/cm^2 for 10 s. The thermal curing process was carried out in a quartz tubing furnace with Ar–3% H_2 gas flow at temperatures ranging from 100 °C to 300 °C for 1 h. Fabrication of the capacitor structure was completed by depositing the top gate metal through a shadow mask with holes of different sizes (0.5, 1, and 1.5 mm in diameter). Metallization of Al was performed by e-beam evaporation in a high-vacuum system pumped down to a base pressure of 2×10^{-7} Torr. Capacitance measurements were carried out using an HP4192A impendence analyzer. These values were used, along with the film thicknesses (measured using a variable-angle spectroscopic ellipsometer manufactured by J.A. Wollam Co. Inc.), to extract the dielectric constant. Current–voltage (I–V) measurements were performed on the MIM samples at room temperature using a HP4140B pA meter/voltage source.

Nanoindentation data was acquired via a Hysitron Triboindenter. For each sample 100 indents were taken at different positions on the sample using a Berkovich diamond tip with a 50 nm radius of curvature. Indents were taken to a depth of 100 nm for all samples. Previous data at depths between 10 nm and 200 nm show no substrate effects for the 2 μm thick films at 100 nm. Furthermore, tip area calculations were found to be accurate at depths greater than 30 nm. Upon completion of the 100 indents, the data was analyzed to gain the necessary values for calculating the reduced modulus (E_r) via Eq. (1) [13,14]. In Eq. (1), β represents the tip correction factor ($\approx$1), dP/dh represents the slope of the fitted section, and $A(h_c)$ represents the tip area at a depth of h_c. Curve fitting was executed for the first 20% of tip unloading for each sample and each indent.

$$E_r = \frac{1}{2\beta}\frac{dP}{dh}\frac{\sqrt{\pi}}{\sqrt{A(h_c)}} \qquad (1)$$

With the reduced modulus calculated for each indentation a plot of the resulting values was generated to verify the consistency of data for each sample. Measurement error was inspected using the standard deviation of the 100 data points per sample. Finally the mean results were tabulated for each sample along with the deviation values.

3. Results and discussion

Polyset epoxy siloxane is UV curable with photoinitiator chemistry based on cationic polymerization. Cationic photoinitiators, Diaryliodonium Hexafluoroantimonate (Ar_2ISbF_6) (PC-2506 from Polyset Company), form a super acid, Fluoroantimonic acid ($HSbF_6$), when exposed to UV light and consequently start the ring opening of the epoxide. Cationic curing is not affected by the presence of oxygen and therefore eliminates the need for an inert curing zone [15]. In addition, cationic reactions continue after the UV light source has been removed. This phenomenon is due to the long-lived initiating species or living cationic species. This effect has been shown to improve the material properties [16] and is particularly beneficial to the rapid fabrication utilizing the Polyset epoxy siloxane polymer.

Previously we have shown the feasibility of utilizing a multi-tier template and epoxy siloxane resist for the fabrication of the dual-damascene structures using a UV imprinting technique [12]. The template was made of Polyvinyl alcohol (PVA) that possesses a high modulus of 1.9 GPa [17] compared to a modulus of 2 MPa for a commonly used Polydimethylsiloxane (PDMS) imprint template. Therefore, the common distortion issue for the soft template can be minimized, enabling the faithful replication of nanometer-scale features across the 200 mm Si wafer. In particular, it demonstrates that UV-imprinting lithography is a promising technology for the fabrication of multilayer interconnect structures in microelectronics manufacturing, in fewer steps than required for conventional lithography. This result is of particular interest because it exhibits the potential of epoxy siloxane to be used in microchip applications. Furthermore, the epoxy siloxane holds advantages in the rapid fabrication due to the low UV dosage required for hardening the polymer films.

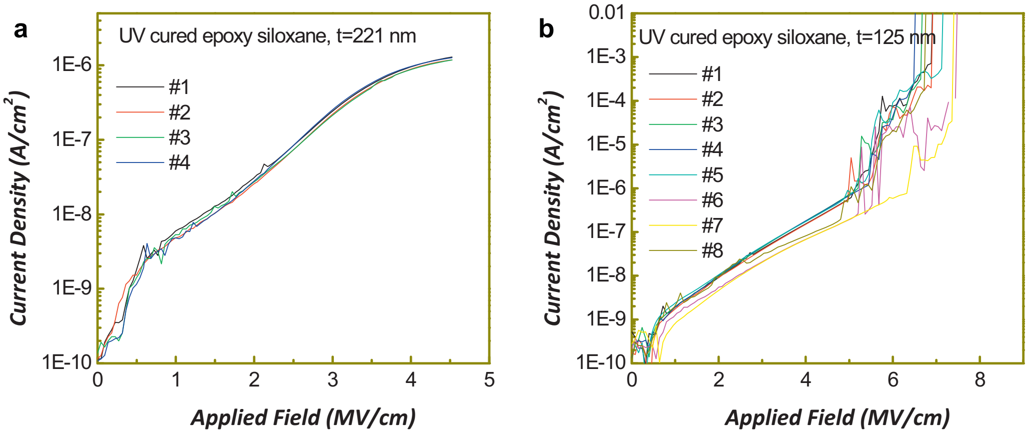

Fig. 2. *I*–*V* curves of the UV cured epoxy siloxane films.

In order to validate the completion of polymer curing in the epoxy siloxane films, two sets of thermally cured and UV cured samples (as showed in Fig. 1a and b, respectively) were prepared and characterized using ex situ Fourier Transform Infrared Spectroscopy (FTIR). Each sample set was characterized sequentially at the same period of time to eliminate ambient environment variance induced data perturbation. Fig. 1a shows the FTIR spectra of the spin-coated polymer films thermally treated at various conditions: as-spun, thermally cured at 100 °C, 165 °C, 250 °C, and 300 °C, respectively. It is observed that the low-frequency component of IR band associated with the Si–O–Si chain-stretching structure evolved with the increasing curing temperature. This evolution is associated with the ring opening of the epoxides (as shown in Fig. 1c), which is responsible for the formation of the crosslink at the pendant epoxy groups. Note that the intensity increase of the 1100 cm^{-1} peak position reaches equilibrium at a curing temperature of 165 °C. No additional intensity increase of the 1100 cm^{-1} peak is observed as the films were subjected to higher curing temperatures. Because the low-frequency component is associated with long chains and the high-frequency component is associated with short chains, this result suggests the cross-linking process has occurred at 100 °C and reaches the maximum cross-linking density at165 °C. Fig. 1b shows the FTIR spectra of another set of samples, the first was thermally cured at165 °C and the second UV cured with a low dosage of 130 $\mathrm{mJ/cm^2}$. There is no observable difference between the spectrum of the UV cured film and that of the thermally cured film, suggesting the UV cured film has achieved the same cross-linking density as its counterpart.

Fig. 2a and b show *I*–*V* plots measured at different positions on the Al/UV cured epoxy siloxane/conductive Si MIM capacitors, in which the polymer films were 221 nm and 125 nm in thickness, respectively. All of the *I*–*V* curves exhibit similar behaviors with the intrinsic leakage current densities on the order of 10^{-9} $\mathrm{A/cm^2}$ under an applied field of 1 MV/cm. Moreover, the leakage current densities do not exceed 10^{-6} $\mathrm{A/cm^2}$ as the applied field approaches 5 MV/cm. Due to instrument limitation, the leakage current characteristics beyond the applied field of 5 MV/cm can only be measured for the capacitors using a thinner polymer film (as shown in Fig. 2b). It is seen that the capacitors do not catastrophically fail until the applied field approached 7 MV/cm.

The dielectric constant of the UV cured epoxy siloxane was determined from the capacitance data obtained from the aforementioned MIM capacitors using the equation $k = Ct/(\varepsilon_0 A)$, where ε_0 is the permittivity of vacuum (8.85×10^{-12} $\mathrm{C^2/Nm^2}$), C is the capacitance, t is the thickness of the dielectric film, and A is the area of the metal electrode. Here, Al electrodes of three different dot sizes (with diameters of 0.5, 1, and 1.5 mm) were used to validate the measurements. A dielectric constant of 2.7 ± 0.13 was extracted from the measured capacitance as a function of the electrode area, as shown in Fig. 3. It appears that the dielectric characteristics of the direct UV cured polymer (with no baking steps involved) are the same as those of the thermally cured polymer films [11]. Fig. 4 shows the XPS spectrum of epoxy siloxane film, from which the atomic percentages of the elements C, O, and Si are obtained to be

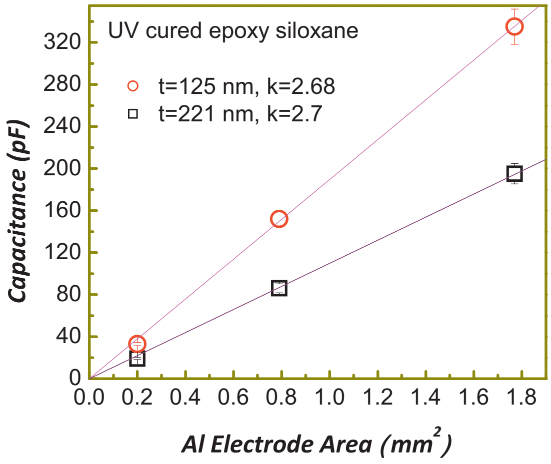

Fig. 3. Capacitance of Al/epoxy siloxane/conductive Si MIM structures is plotted as a function of Al electrode area for dielectric constant measurements. The polymer films were UV cured prior to metallization.

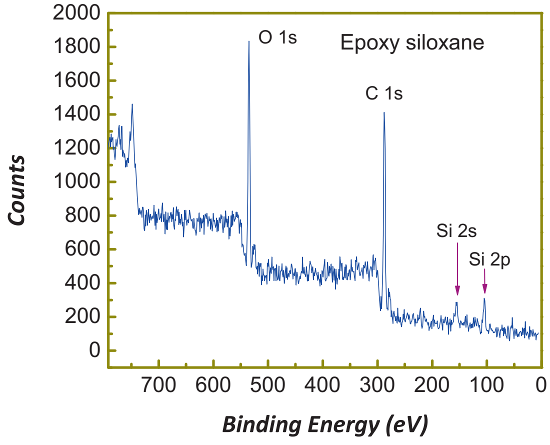

Fig. 4. XPS spectrum of epoxy siloxane film.

Table 1
Summary of the mechanical property of epoxy siloxane measured using nanoindentation.

Cure	Film thickness	Reduced modulus (E_r)	Hardness (H)	Depth (h_c)
165 °C	1717.8 nm (±6.3)	5.5 GPa (±0.18)	839.8 MPa (±25.0)	63.7 nm (±1.1)
250 °C	1678.5 nm (±6.7)	5.8 GPa (±0.18)	917.6 MPa (±55.7)	62.8 nm (±1.1)
UV	1661.2 nm (±4.7)	6.2 GPa (±0.13)	585.3 MPa (±12.8)	74.6 nm (±0.6)

68%, 21%, and 11%, respectively. The repeating units of the polymer thus have low polarizability and a high molar volume [18], which allows the dielectric constant of the epoxy siloxane to be significantly lower than those of existing siloxanes [19].

The mechanical properties of the cured epoxy siloxane films were characterized using nanoindentation. Table 1 summarizes the results of the nanoindentation tests on the UV cured and thermally cured polymer films. The data is calculated from the indentation force-depth curves using a Berkovish tip area function. The representative indentation force vs. indentation displacement curves are shown in Fig. 5. The UV cured film has a modulus of 6.2 GPa while the films thermally cured at 165 °C and 250 °C exhibit comparable modulus of 5.5 and 5.8 GPa, respectively. It is observed that the UV cured film exhibits a lower hardness (585.3 MPa) than its thermally cured counterparts (839.8 and 917.6 MPa for samples annealed at 165 °C and 250 °C, respectively).

The similarity between the mechanical properties of the two thermally cured samples agrees with the FTIR characterization. This similarity suggests that the samples thermally cured at 165 °C and 250 °C exhibit the same degree of curing. The lower hardness obtained from the UV cured sample may be attributed to its inferior crosslink uniformity with respect to the thermally annealed samples. Cationic cure rates are proportional to acid concentration and the diffusivity of the cation through the matrix. Acid concentration is controlled by initial cationic photoinitiator concentration and the amount of energy absorbed by the photoinitiator. The diffusion of the cation through the epoxy siloxane matrix is governed by Fick's first law $J = -D(\partial\phi/\partial x)$.

D, the diffusion coefficient, is proportional to the squared velocity of the diffusing particles, which depends on the temperature, viscosity of the fluid, and the size of the particles according to the Stokes–Einstein relation. In a UV cured system, the temperature of the epoxy siloxane will be lower than a thermally cured system, which results in its viscosity being higher than its thermally cured counterpart. This, in turn, leads to a lower diffusion rate of the cations, and therefore a possible lower crosslink density.

Note that the dielectric property of the UV cured films discussed above does not exhibit any difference from that of the thermally cured films. Also, by using FTIR, there is no detectable discrepancy existing between samples cured by two different means, suggesting that the degree of deficient cross-linking density in the UV cured sample is very limited. Therefore it does not significantly impact its comparable mechanical property with that of the thermally cured counterpart, apart from the lower hardness.

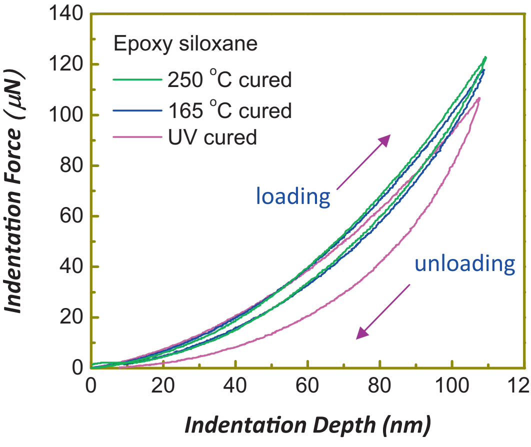

Fig. 5. Typical indentation force (μN) vs. indentation depth (nm) curves from nanoindentation measurement for thermally cured and UV cured epoxy siloxane films.

In the current imprint technology, there are two types of imprint materials are used: a sacrificial imprint resist or a functional material that the imprinted material directly becomes part of the device. The imprint process using a sacrificial resist requires dry etching steps to transfer the patterns into the substrates, whereas the imprint using functional materials holds the advantages in saving time and the cost of ownership for device fabrication. However, it is more challenging to formulate the imprint resist with functionalities due to the facts that they have to satisfy both the requirements for achieving nanometer patterns with high fidelity and properties of device. Our study in this paper shows the UV curable epoxy siloxane can fulfill these requirements and be a functional material for imprint process.

4. Conclusions

The photo-curable epoxy siloxane polymers were directly cured using a low UV dosage of 130 mJ/cm^2. FTIR spectra showed that the UV cured polymer reached the same state of cure as its thermally cured counterpart. The dielectric and mechanical properties of the direct UV cured polymers were validated. The results show that the rapid UV cured polymer films achieve a dielectric constant of 2.7, leakage current density of approximately 10^{-9} A/cm^2 under 1 MV/cm, a dielectric strength of greater than 5 MV/cm, and a reduced modulus of 6.2 GPa. The observed lower hardness of the UV cured film with respect to that of the thermally cured sample may be attributed to the inferiorly uniform crosslinked state due to the lack of cation diffusion at lower temperatures. However, this behavior appears to be very limited due to the fact that is not detectable by FTIR and there is no indication it affects the dielectric property. Overall, these results show that Polyset epoxy siloxane cured directly using UV can achieve the properties required for functional dielectrics used in devices. It further illustrates the potential advantages in using Polyset epoxy siloxane in fast fabrication of functional device layers using imprinting technique.

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