SU8-graphene: a new photo-patternable conductive polymer composite

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ABSTRACT

Graphene-based SU8 nanocomposite is developed as a novel conductive polymer, which benefits from remarkable electrical conductivity of graphene, along with photo-patternability and transparency of SU8. Well defined structures with minimal resolution of 10 μm have been successfully patterned using photolithography technique. The electrical conductivity of the composite is significant even at low filler loadings compared to other graphene-based polymer composites Thanks to the effective dispersion of the graphene nanofillers in the SU8 matrix. The composites demonstrate superior mechanical properties compare to pure SU8, which we believe is due to the covalent bonding between SU8 and the functional groups on the surface of graphene flake. To confirm that, Raman spectroscopy was employed to study the chemical structure of the composite.

Keywords: SU8, nano-composite, Graphene, Electrical properties, Mechanical properties

1 INTRODUCTION

SU8 is a negative tone photoresist with wide use in MEMS application, due to its outstanding properties like chemical and mechanical robustness combined with high sensitivity to UV [1]. Having eight reactive epoxy sites in each monomer molecule, a high degree of cross-linking is attainable for SU8 after photo-activation. This makes SU8 the most favorable material for photo-patterning of low-cost, high aspect ratio structures [2]. However, besides the attractive features, drawbacks like being electrically and thermally insulator Have been driving force for studying SU8 based composites [3]. One major advantage of adding nanofillers in a polymer matrix is the possibility of tailoring the functionalities of both components to improve mechanical, thermal, and electrical properties of the composite, while preserving the favaroble properties of the host material.

Graphene is an attractive material for nanoelectronic and optoelectronic devices considering advantageous electrical and mechanical properties [4]. Considering the possibility of large scale and low cost production of reduced graphene oxides (RGO) using chemical exfoliation methode [5], RGO is a promising filler for making nanocomposite polymers. Presence of functional groups (such as hydroxyls, carbonyls, carboxyls …) on the surface of RGO flakes, can enhance the dispersion of the flakes in polymer matrices, and facilitate interfacial bonding and load transfer between the host polymer and the RGO flakes [6]. In this respect, Raman spectroscopy can be used as an informative technique to assess the interactions between RGO fillers and polymer matrix.

Herein, we present SU8-graphene-based nano-composite containing RGO flakes as a patternable conductive polymer with electrical properties superior to other graphene-based polymer composites and well-enhanced mechanical properties. We claim that this material has the potential to be used in direct fabrication of electrically conductive micro-components in MEMS industry.

2 MATERIALS AND METHODS

SU8-graphene composites were fabricated using RGO flakes from ACS Materials as nanofillers, with concentrations ranging from x=0.04 wt% to x=3 wt% with respect to the weight of SU8. The specification of the RGO flakes is presented in table 1. The SU8 polymer matrix used in this work was provided by Gersteltec (grade GM 1060). This material contains SU8 resin, 40% of Gamma butyrolacton as solvent, and a triarylsulfonium hexafluoroantimonate salts as photoinitiator for activation of the crosslinking of the polymer when exposed to UV irradiation.

BET surface area (m^2/g)	650-750
Conductivity (S/m)	500-700
Layers	1-5 atomic layer graphene
Lateral size (μm)	0.5-5
Oxygen (atm%)	7-7.5

Table 1: Characteristics of the RGO flakes.

Sample preparation: A combination of stirring and sonication was used as a simple and effective procedure to attain uniform and stable dispersion of flakes in the composite matrix. To obtain even better dispersions, in another set of composites (denoted hereafter as SU8-SRGO) a derivative of phosphoric acid ester salt, was employed as surfactant for composite fabrication.

In order to prepare samples for characterization, the ink was spread on a clean glass slide using doctor blade. For soft-bake step, samples were heated to 95˚C with ramp of 3 °C/min. We observed that at 95˚C samples weight loss has already reached a plateau and no more solvent evaporation took place. Finally. the matrix was thermally cross-linked by baking at 150 °C in a furnace.

Photolithography: The composites were patterned on 4 inches Pyrex wafers after optimizing the standard process of photolithography for pure SU8. SU8-RGO nanocomposites were first spin-coated at 200 rpm onto the Pyrex substrates. The low spinning speed is to avoid the segregation between the matrix and the fillers, and to preserve the uniformity of the composite. This followed by a soft-bake at 130 °C for 10 minutes, with temperature ramps of 5 °C/min. UV irradiation was performed using Süss MJB4 single side mask aligner, at exposure dose of 15 mW cm^{-2}, to activate the photoinitiator. Increase in UV exposure time compared to standard procedure for pure SU8 helped us to enhance the lateral resolution and enabled the patterning of more delicate structures. The polymerization was completed during post-exposure baking at 100 °C for 30 min. Finally, the patterned structures were developed in propylene glycol monomethyl ether acetate and rinsed by isopropanol.

Sample characterization: Transmission Electron Microscope (TEM) Philips/FEI CM12 was employed for TEM analysis of 80nm slices of SU8-RGO composite prepared by ultramicrotomy. The accelerating voltage for TEM imaging was 100 kV.

For electrical characterization, electrical resistance was measured with Keithley 2400 and Keithley 6517 source meters using two- and four-point-probe methods, depending on the RGO concentration.

Mechanical properties of the composites were measured by nanoindentation using XP (NanoInstrument Inc.) A Berkovich-type three-sided diamond pyramidal tip was used with a maximal displacement of 2000 nm. The mechanical uniformity of the samples was tested by 9 indents for each composite.

Raman spectra of Pure SU8 epoxy and SU8-RGO nanocomposites were obtained under laser excitation wavelength of 1064nm using a Bruker FT Raman spectrophotometer RFS 100.

Transmission of UV light in the photopatterned SU8-RGO nanocomposites was measured by Cary 500 (Varian) UV-Vis-NIR spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Photopatterned structure

Continuous films of SU8-RGO composites, with various concentrations have been patterned by UV-lithography process. As illustrated in Figure 1, a minimal resolution of 10 μm was obtained for SU8-0.3 wt% RGO, which is as good as the values reported for SU8-CNT composites [6]. This implies that our composite materials are entirely compatible with current MEMS fabrication processes.The transparency of these composites can be tuned by variation the content of RGO nanofillers, as illustrated in Figure 1(a-d) Optical transmission of the composites for 700nm wavelenght light as a function of the graphene loading is demonstrated in Figure 2.

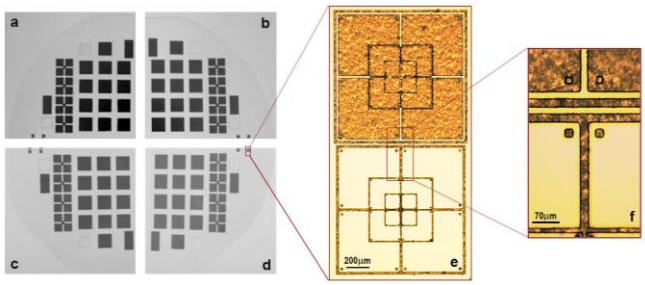

Figure 1: Well defined SU8-RGO nanocomposites, patterned by UV-lithography process containing: a) 1.2 wt.%, b) 0.9 wt.%, c) 0.6 wt.% and d) 0.3wt% RGO filler. Higher magnifications of patterned structures are illustrated e,f) SU8-0.3wt.% RGO.

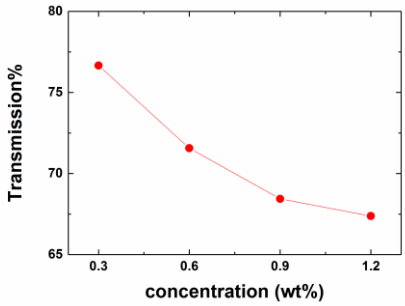

Figure 2: Optical transmission versus RGO loading at λ=700nm.

3.2 Structural charcterization

Composite properties (Mechanical, electrical, thermal,…), are directly influenced by the quality of dispersion of the nanofillers in the epoxy matrix. The state of dispersion of the RGO flakes in the polymer matrix, is shown in Transmission Electron Microscopy (TEM) images of Figure 3. Microtome slices of SU8 composites with (a) 0.2 wt% and (b) 0.9 wt% of RGO, and (c) 0.2 wt% and (d) 0.9 wt% of SRGO are presented in the images, where RGO

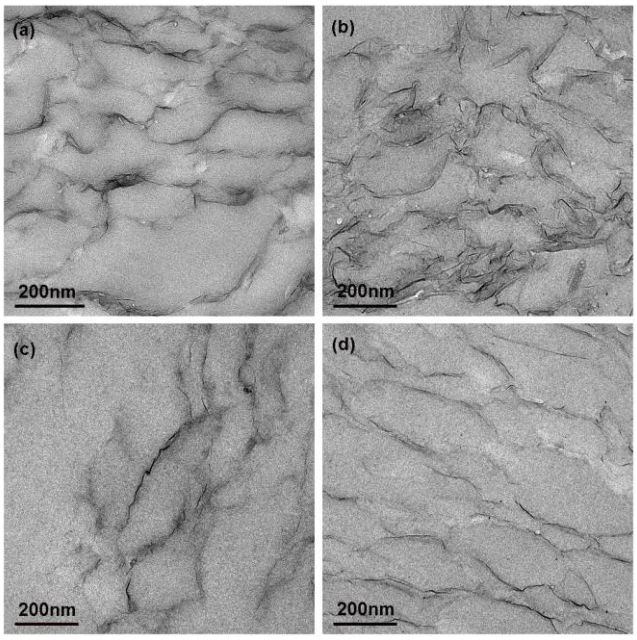

Figure 3: Transmission Electron Microscopy image of microtome slice of SU8 nanocomposites with (a) 0.2 wt% and (b) 0.9 wt% RGO, and (c) 0.2 wt% and (d) 0.9 wt% SRGO.

flakes can be recognized by the dark curvy lines, indicating that the flakes are very well dispersed in the composite. Fig. 3 also illustrates the network formed by RGO flakes inside the SU8 matrix; this network is constituted by conductive and well-dispersed RGO fillers, which are separated by regions of cross-linked SU8. It is through these regions that electrons can tunnel between neighboring fillers, establishing thus electrical connectivity, which allows current to flow throughout the composites.

3.3 Electrical properties

Electrical conductivity data of both SU8-RGO and SU8-SRGO series are shown in Figure 4 as a function of volume fraction of the conducting fillers. Compared to the RGO samples, the SRGO series display somewhat lower values of the conductivity, possibly due to a larger mean inter-filler separation distance as a result of the addition of surfactant. This hypothesis is partially supported by comparison with the TEM images of Figure 3(b) and 3(d), where the composites with added surfactant [Figure 3(d)] appears to have more homogenously distanced RGO flakes compared to the composite without surfactant [Figure 3(b)]. This effect is less visible for lower RGO concentrations [Figure 3(a) and 3(c)].

Besides this difference, both SU8-RGO and SU8-SRGO show exceptional electrical properties when compared to other graphene-based systems, as illustrated in Figure 4, where we show the conductivity data of SU8-RGO and SU8-SRGO (filled symbols) together with those of other polymer-graphene composites (open symbols) taken from recent literature [7]. As is immediately apparent from this figure, the drop of σ as ϕ goes to zero is remarkably smooth: even at loadings as small as 0.038% for RGO and 0.054% for SRGO, the measured value $\sigma \cong 10^{-8}$ S m^{-1} for the composite conductivity is still far larger than that of pure SU8 (about 10^{-14} S m^{-1}). SU8 composites of reduced graphene oxide show thus electrical transport properties that are even comparable to those reported for several polymer-CNT materials. The electrical conduction of SU8-RGO composites are studied and explained with more details in ref [7].

3.4 Mechanical properties

Regarding broad range of potential applications of SU8 composites in MEMS area, characterization of mechanical properties such as hardness (H) and Young's modulus (E) through nano-indentation is crucial. As demonstrated in Figure 5, the load-displacement curves of the 9 indentation tests were overlapping for SU8-0.6wt% RGO composite (as well as all other tested samples). This indicates the mechanical homogeneity of the composites. The evolution of E and H as a function of RGO wt% show a percolation like behavior (with the threshold between 1.5 and 2.5wt%). This needs to be confirmed with composites prepared with higher RGO content.

The efficient load transfer of RGO-SU8 might be due to the covalent bonding formed between SU8 matrix and the functional groups present on the surface of the graphene flakes.

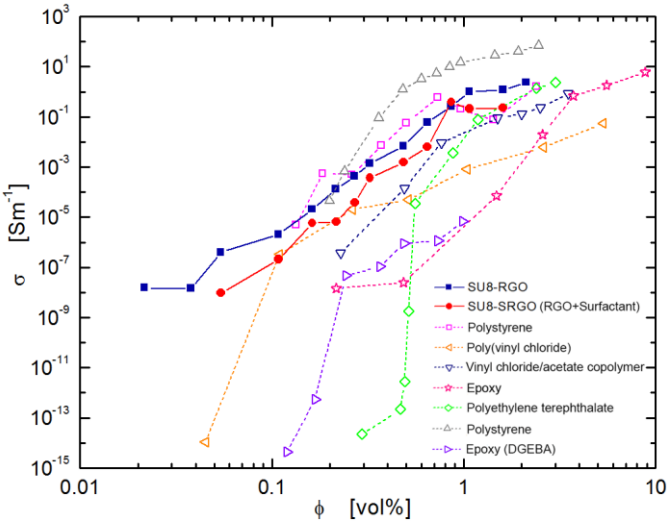

Figure 4: Conductivity of SU8-RGO and SU8-SRGO composites (filled symbols) as a function of the volume fraction of reduced graphene oxide. Open symbols are the measured conductivity values of different polymer-graphene composites [7].

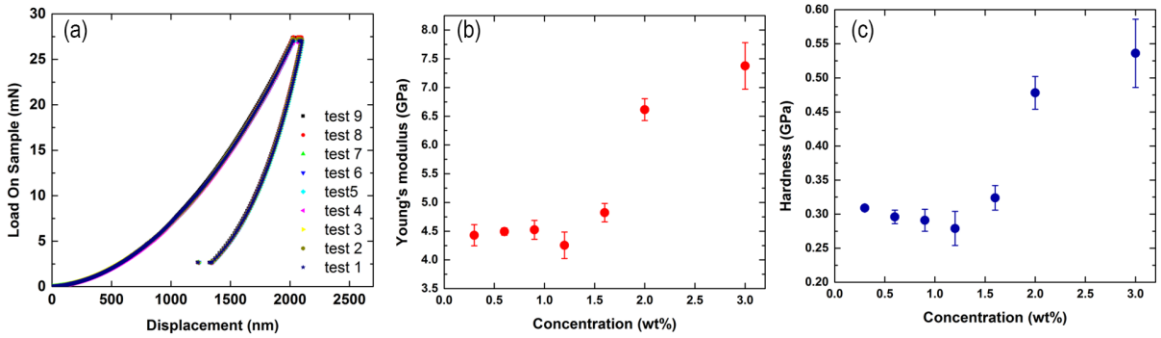

Figure 5: (a) Load displacement curve for composite SU8-0.6%wt RGO. (b) Young modulus and (c) Hardness of SU8-RGO composites with as a function of the concentration. For pure SU8, E= 4 GPa and H=0.12 GPa [1].

3.5 Raman spectroscopy

The characterization of the chemical structure of the SU8-RGO composites has been performed by Fourier transform Raman spectroscopy (FTRaman), in order to gain insights into the possible covalent bonding between the polymer matrix with the functional groups attached to the RGO flakes, but also the influence of the RGO on the polymerization kinetic and mechanism of SU8. The opening of the epoxy rings during the polymerization is clearly evident in FTraman spectra by looking at the intensity of the peaks located at 1259 cm^{-1} (C-O stretch in epoxide) before and after polymerization (inset of Figure6). The influence of the presence of RGO inside the polymer matrix is illustrated in Figure 6 by significant shifts in peak position as well as changes in peak ratio as a function of RGO loading. The most significant effect of RGO content is visible with the peak located at 1296, 1302 and 1303 cm^{-1} for respectively 0.001, 0.005 and 0.01wt%. The intensity of this peak, is attributed to the D band increases the RGO content. D band is seen because of sp3 carbon where functional groups are attached to the graphene. The peak shift could indicate a chemical bonding between the RGO and SU8 via these functional groups.

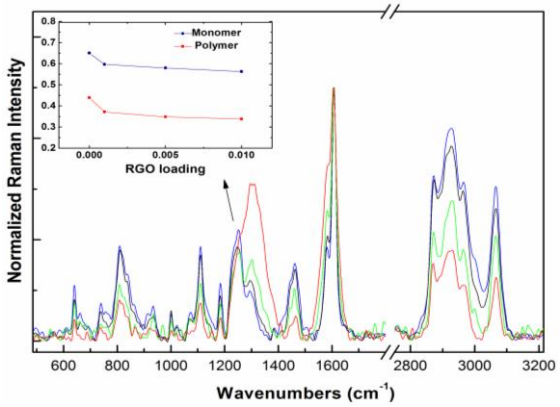

Figure 6: FTraman spectra of SU8 epoxy (blue) and SU8 containing, 0.001wt% (black), 0.005wt% (green) and 0.01wt% (red) of RGO. Inset: Normalized intensity of the peak at 1259 cm^{-1} for SU8-RGO composites versus RGO content before and after polymerization.

4 CONCLUSION

In this paper, we have presented novel conductive, photopatternable, polymer composites made of reduced graphene oxide nano-flakes dispersed in SU8 epoxy resin, which has strong potential in MEMS applications. Our SU8–graphene nanocomposites exhibit good lateral resolution, comparable to that reported for photo-patterned CNT-SU8 composites. We observe significant enhance in electrical conduction and mechanical properties of the polymer. This remarkable behavior of transport results from the combination of effective dispersions of the graphene flakes in the SU8 matrix and strong covalent bonding between the fillers and the matrix.

REFERENCES

[1] A. Delcampo and C.Greiner, "SU-8: a photoresist for high aspect ratio and 3D submicron lithography, J. Micromech. Microeng. 17, R81-R95, 2007.

[2] A. Bertsch and P. Renaud, "Special Issue: 15 Years of SU8 as MEMS Material Microelectronic" Micromach., 6, 790-792, 2015.

[3] H.C. Chiamori, "Suspension of nanoparticles in SU-8: processing and characterization of nano-composite polymers" Microelec. J., 39, 228-36, 2008.

[4] Y.Zhu, "Graphene and graphene oxide, Synthesis, properties and application", Adv. Mat., 22, 3906-3924, 2010.

[5] S.Lee, " Large-scale production of high-quality reduced graphene oxide" Chem. Eng. J., 233, 297-304, 2013.

[6] H. Cong, "CNT-based photopatternable nano-composites with high electrical conductivity" J. Micromech. Microeng., 20, 025002, 2010

[7] M. Majidian, "Electrical conduction of photo-patternable SU8–graphene composites", Carbon, 80, 364-372, 2014.