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SU8 nanocomposite photoresist with enhanced thermal conductivity

V Velmurugan*, J P Raina

Center for Nanotechnology Research, VIT University, Vellore-632014, India.

***Corres.author: vvelmurugan@vit.ac.in, venuvel@yahoo.co.in**
Phone: 91-4162202412

Abstract: Composites with nanoparticles and polymers can improve the functionalities and existing formulations. In this work we synthesized Graphene Oxide and is incorporated into an epoxy based negative tone photoresist in different weight percentages. Thermal conductivity studies were carried out on those composites and it was found that 13 % by weight is the optimized loading to have an enhanced thermal conductivity.
Keywords: SU8, Graphene Oxide, Thermal conductivity, Epoxy composites.

1. Introduction

1.1 SU-8 and its composites

SU8 is a well known epoxy based negative tone photoresist designed for fabrication of MEMS, high aspect ratio structures, material for support, packaging etc,. It is said to have multifunctional glycidyl ether derivatives of biphenol-A, triarylsulfonium, hexafluoroantimonate salt, photoacid generator and a thinning solvent [1]. Even though it posses good chemical resistance, low optical absorption, high sensitivity, high resolution and high thermal stability there are many researches(Table 1) demonstrating the potentials of employing nanomaterials to improve its property depending on the application(s).

Table 1. SU8 composites and property enhancement

Composites	Enhanced property(s) / Application(s)	Reference
SU8 + Silica nanoparticles	Lower the internal stress and decrease the wear rate and frictional coefficient of the SU8 epoxy. gear wheels, multilayer capping on moving micro-parts	[2]
SU8 + CNT /Diamondoids /Gold	Reduced residual stress and potentially tunable stiffness properties, decreasing viscosity and decreased elastic modulus	[3]
SU8 + Nanosilica particles	More sensitive, low internal stress, lower coefficient of thermal expansion.	[4]
SU8 + Silver nanoparticles	Electrical conductivity and better adhesion	[5]
SU8 + Multi walled carbon nanotube	Enhanced electrical conductivity	[6]
SU8 + Nickel nanospheres	Magnetically active photoresist. Magnetically-actuated micromirrors,	[7]

	cantilever of ferromagnetic photoresist	
SU8 + perfluoropolyether /graphite/SiO_2/CNT	Reduction in the initial coefficient of friction, increased wear life. Self-lubricating structural material for MEMS	[8]
SU8 + MWCNT	Increase in Young's modulus, Poisson's ratio	[9]
SU8+ TiO_2 nanoparticle	Specific mechanical impedance and attenuation. Lab in chip high frequency acoustic microscope	[10]

To the best of our knowledge the thermal analysis of the SU8 and its composites is not reported so far. In this work we tried to investigate the thermal property of SU8 composite. The motivation of this study is to enhance the thermal conductivity of the resist. The need of the modification is to enhance thermal conductivity can be viewed from different angles. Thermally stable resists are needed to fabricate structures by interference lithography that demands very narrow line widths [11]. In case of thermal resists, high thermal conductivity is a desired property[12]. ITRS[13] also introduces nanotubes and other low dimensional materials as potential thermal management candidates for future package applications and thermal interface materials. Similarly stable photo resist at high temperature that can prevent airborne contamination prior and after exposure[14] and thermal treatment of chemically amplified resists (CARs) helps in the reduction of the bonding and increased mobility[15].

1.2. Graphene Oxide

Graphene is composed of sp2-bonded carbon atoms arranged in a two-dimensional honeycomb lattice. It has gained more importance due to its unusual properties[[16] Graphene components have drawn large attention due to its potential large scale applications through mass production[17]. Even though oxidation of Graphene (G) to form Graphene Oxide (GO) had detoriated the property, still GO has excellent thermal conductivity (~5000W/mK)[18]. High thermal conductivity is achieved [19] due to the formation of three acoustic and three optical modes with the dispersions. The unique 2D nature of Graphene allows out-of-plane atomic displacements, also known as flexural (Z) phonons. These flexural phonons give many unusual thermal properties for graphene. In this work we synthesized Graphene oxide by wet chemical method and made the composites with SU8 in different weight percents. The thermal conductivity of those composites are measured by hot wire technique and the results were analyzed.

2. Experimental

2.1. Materials.

Graphite nanopowder, Sodium Nitrate, Potassium Permanganate, 30% Hydrogen Peroxide, Hydro chloric acid, Sulphuric acid, Ethanol, SU8.

2.2 Synthesis

Graphene oxide is synthesized from natural graphite powder by Hummer's method [20]. 2g of Graphite is added to 100ml of concentrated Sulphuric acid in addition with 4g of Sodium Nitrate. The mixture is kept in an ice bath and stirred vigorously by magnetic stirrer and the temperature is maintained below 10^oC. 10g of Potassium Permanganate is added to the resultant mixture. Mixture is stirred at 35^oC for 2 hours and thereby, diluted with 100ml deionized water. Finally to stop the reaction 20 ml of 30% Hydrogen Peroxide is added to it and the whole mixture stirred for 30 min that changed the color to brilliant yellow. GO formed was centrifuged and made impurity free by washing with 800ml of Hydrochloric acid and 1000ml De-ionized water, followed by drying at 60^oC for 24h.

2.3 GO/ SU8 composite preparation.

The SU-8 resin being high viscous cannot form composites easily. For making homogeneous mixing of SU-8 epoxy resin and graphene oxide, a suitable solvent is added [3]. Acetone is added to SU8 and it gets evaporated at later stages and needs no further processing. Composites are made by sonicating 0.5ml of SU-8 and GO separately. Different weight percents (5%, 10%, 15%, 20% and 25%) of Graphene Oxide is taken for the study.

3. Characterization

The formed nano composites were spin coated over glass slides, with a spinning speed of 3000RPM for 90Sec and dried at room temperature. Choice of spin speed and time was made with respect to SU8 speed thickness characteristics. UV spectroscopy is obtained from studied with SPECORD supplied by analytikjena and the transmission is measured.

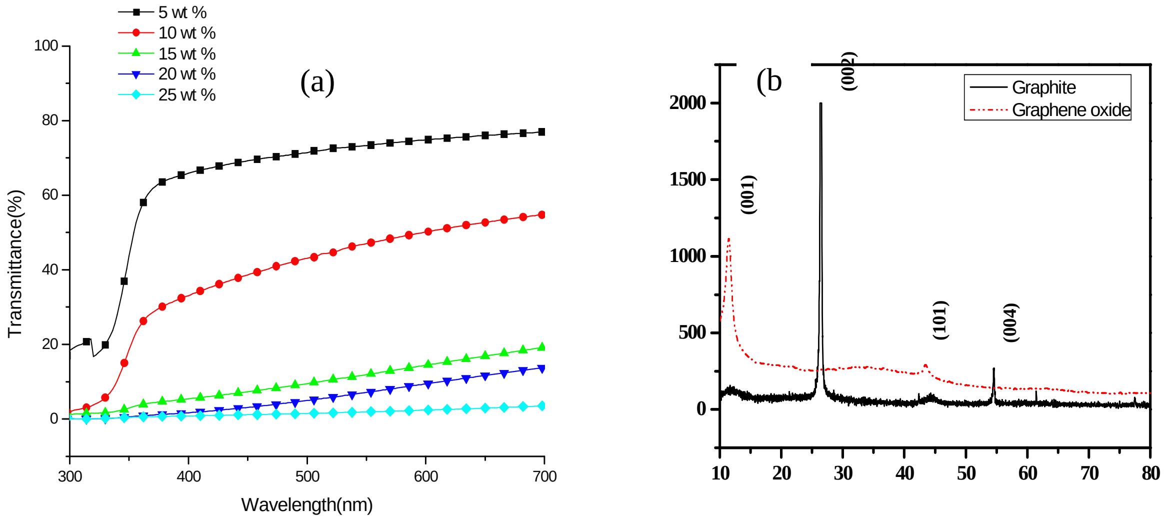

Fig 1(a) UV Spectrogram of SU8 composites with different Weight percent of Graphene oxide.
(b) XRD image of the Graphite powder and Graphene Oxide

Pure SU8 gives a transmittance of 92%(not shown) and is reduced to 70% by embedding GO into it. The graphene composite has higher absorbance in the UV-Vis region and hence can be better candidate for anti-UV applications. The UV-Vis cutoff for SU8 is preserved and only the transmittance decreases with increase in wt% of GO.

The samples were characterized using a Bruker D8 Advance X-Ray Diffractometer, using Cu Kα (1.5406 Å), Ni filtered radiation with 40 kV voltage and 30mA intensity in a 2θ range from 20 to 80^0 at a scan rate 0.02degree/0.3 sec.The FTIR spectrum for GO(fig 2.a) confirms different types of functionalities were confirmed at 3415cm^{-1} (O–H stretching vibrations), at 3122cm^{-1}(=CH stretching vibrations), at 1703cm^{-1} (C=O stretching vibrations), at 1641cm^{-1} (C=C) indicates incomplete oxidation, at 1402cm^{-1}(O –H bending vibrations), at 1220cm^{-1}(C–OH vibrations) and peaks in 1220cm^{-1} to 1060cm^{-1} indicate skeletal vibrations from un-oxidized [21-24].

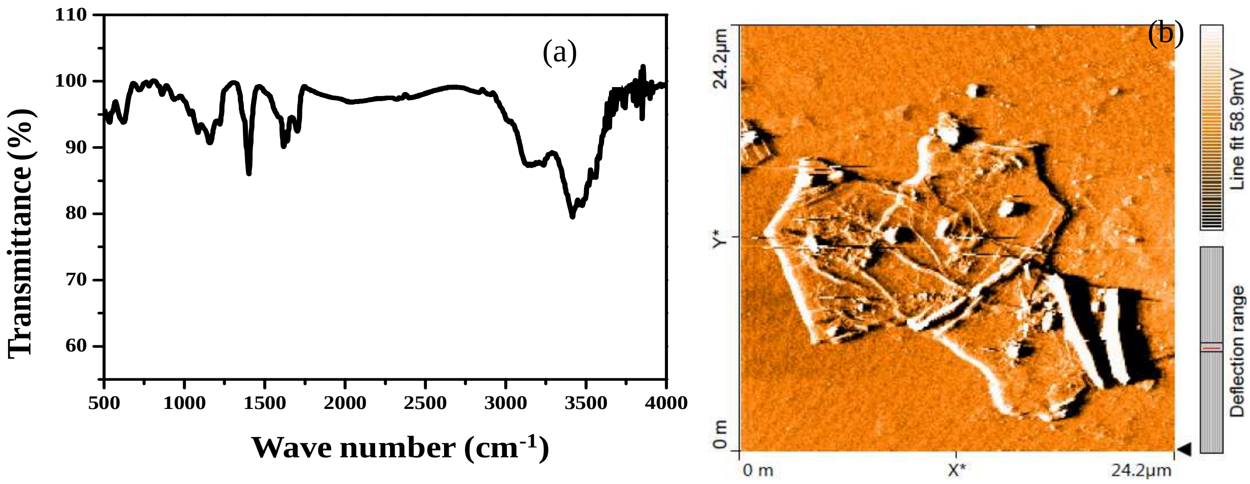

Fig 2(a) FTIR of Graphehe Oxide, **(b)** Atomic force image of the Graphene Oxide flake.

4. Thermal conductivity studies

Since Graphene oxide has high thermal conductivity (~5000W/mK), it was planned to make the epoxy to have better thermal conductivity with the graphene. We measured the thermal conductivity at ambient atmosphere by a non steady state method- Hot Wire Technique. A single wire is heated for certain time and the temperature of the wire is monitored for equal amount of time that was spent on heating. The temperature during heating, temperature during cooling and the thermal conductivity is computed from equations (1), (2) and (3) respectively.

$$T = m_0 + m_2 t + m_3 \ln(t) \text{-------------} (1)$$

$$T = m_0 + m_2 t + m_3 \ln\left[\frac{t}{(t - t_h)}\right] \text{-----------} (2)$$

$$k = \frac{q}{4\pi m_3} \text{---------------------} (3)$$

m_0 is the ambient temperature during heating , m_2 is the rate of background temperature drift, m_3 is the slope of a line relating temperature rise to logarithm of temperature, q is the heat input.

Kd2 pro supplied by Decogan Inc was used to measure the thermal conductivity. Stainless probe of 60mm long and 1.27mm diameter is used for measurement. The machine follows IEEE 442-1981 and ASTM D 5334-00 standards. The temperature (T) and time (t) data are collected over the complete heating and cooling cycle at an interval of 1second. The computations are done with an inbuilt microcontroller unit and Glycerin is used for calibrating the probe. The error in the measurement of the thermal conductivity is due to the change in the temperature of the sample, mechanical noise, long /short time interaction of the wire with the sample [25].

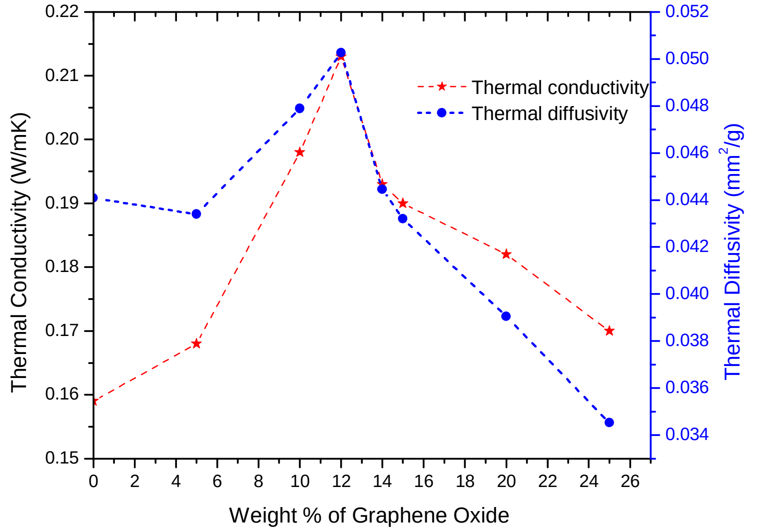

Fig 3. Thermal conductivity of composites as a function of Graphene Oxide loading.

Fig 3 shows the rise and fall of the thermal conductivity with the increase in the weight percent of Graphene Oxide in SU8. The maximum thermal conductivity is obtained for 13 wt% of GO. This is in agreement with the earlier experiments [26] demonstrated. The rise and fall of the thermal conductivity is explained by the filling of the voids that are created along the surface of GO flakes. In case of GO content being less that 13% there are enough SU8 that fills the voids, but beyond 13% there is lack of SU8 to fill the void. Therefore an insufficient interface between GO and SU8 is created and have led to increased interfacial thermal resistance. So we can conclude that the optimal weight percent of GO in SU8 is 13% for effective enhancement in thermal conductivity.

5. Conclusion

In this study we synthesized Graphene Oxide and made composites with an epoxy based photoresist-SU8. The composites were characterized and thermal property enhancement studies were carried out. It was found that 13wt% of Graphene Oxide gave a high thermal conductivity, beyond that due to insufficiency of the epoxy to fill in the voids the thermal conductivity decreased.

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