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Epoxy based photoresist/carbon nanoparticle composites

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1 Introduction

Micrometer sized cantilevers can be used for label-free biochemical detection[1]. Surface stress changes on one side of the cantilever due to the adsorption of molecules result in a bending of the cantilever. Detection of for example DNA [2], proteins [3], pesticides [4] and TNT explosives [5] has been demonstrated with cantilever-based sensors.

Cantilever bending is normally detected by an optical leverage technique (as known from atomic force microscopy) or by integrating a piezoresistor in the cantilever. Cantilever based sensors with integrated piezoresistive readout have traditionally been realized in silicon based materials [6,7]. Replacing the silicon based cantilever material with a soft polymer can potentially increase the surface stress sensitivity significantly. Moreover polymer processing is faster and cheaper than silicon processing. The challenge is here to find a soft polymer based piezoresistive material.

For a piezoresistive cantilever consisting of one material with Young's modulus, E , and thickness h , with an infinitely thin piezoresistor placed at the top, the surface stress sensitivity is given by [7]:

$$\frac{\Delta R}{R} = -K \left(\frac{4}{Eh} \right) \sigma_s, \quad (1)$$

where K is the gauge factor of the piezoresistor and σ_s is the surface stress induced at the top surface of the cantilever. For a fixed geometry and disregarding the noise, the surface stress sensitivity is proportional to the relationship, $\Delta R/R \propto K/E$. To maximize the signal a soft material with a high gauge factor is needed. For single crystal silicon, $K_{Si}/E_{Si} \approx 150/150 \text{ GPa} = 1 \text{ GPa}^{-1}$. Our aim is to fabricate an all polymer cantilever using SU-8 (a negative tone epoxy based photoresist) as the cantilever material. We have chosen to realize

the cantilevers in SU-8, which is straightforward to structure with standard UV lithography. SU-8 has a Young's modulus of $E \approx 4.4$ GPa, so only a gauge factor of $K > 4.4$ is needed for the piezoresistor in order to compete in sensitivity with silicon cantilevers.

We have previously fabricated SU-8 cantilevers with integrated gold strain gauges [8–10]. The gauge factor of gold is approximately $K \sim 3.5$ and we thus look for new soft materials with a higher gauge factor. We therefore started to investigate SU-8/carbon NP strain gauges. In our initial work we reported on the realization of an all polymer cantilever with integrated SU-8/carbon NP piezoresistive readout [11]. In this work only one type of carbon particle was tested and the focus was on the possibility of fabricating a complete micro-mechanical device with an SU-8 based strain gauge.

In the present work we concentrate on the characterization of different SU-8/carbon NP strain gauges with respect to gauge factor and stability.

2 Experimental

2.1 Polymer/carbon NP composites

When adding conductive particles to an insulating polymer matrix the composite undergoes a transition from insulator to conductor. By adding more and more conductive filler particles the average interparticle distance is decreased. At a certain critical filler concentration (the percolation threshold) an infinitely connected network is formed and the conductivity increases with a power law dependence (see ref. [12] for a detailed review). When a polymer

composite is stretched the interparticle distance increases, some of the conductive paths are broken and the resistance goes up. This is the basic idea behind a polymer composite piezoresistor.

Polymer composites are made of SU-8 2002 (the "8" refers to the 8 epoxy groups in each SU-8 monomer) from micro resist technology and carbon black NPs. SU-8 is a negative toned epoxy based photoresist, which consists of SU-8 monomers, organic solvent and a photo acid generator (PAG). The PAG is sensitive to ultra-violet (UV) light (350-400 nm), hence upon UV-exposure the PAG generates an acid, the epoxy rings are opened and the crosslinking starts.

The composites are ultrasonically mixed at 20 kHz for ~ 15 minutes using a BioLogics Model 150 V/T ultrasonic homogenizer. During mixing the composite is immersed in ice water for cooling. Three different carbon black NPs are used: Printex XE2 (Degussa), CD7051U and CD975U (Columbian Chemicals Company) with a mean size of 30 nm, 56 nm and 21 nm, respectively.

2.2 Fabrication

For measuring the resistance of the polymer composite a characterization chip has been designed and fabricated using standard microfabrication techniques. The white square in figure 2 is the polymer composite, which has the dimensions $L \times 3000 \mu\text{m} \times 2.0 \mu\text{m}$ (length $\times$ width $\times$ height). The spacing between the 10 electrodes is designed such that the length of the polymer composite can be varied with the values, $L = 5, 10, 15, 20, 25, 50, 100, 200$ and $500 \mu\text{m}$ (see figure 2). On each chip we can thus do measurements with nine different electrode configurations.

The chips are fabricated through the following steps: (a) a 150 nm electri-

cally insulating SiO_2 layer is thermally grown on top of a 4" Si wafer, (b) 50/3000 Å Ti/Au is e-beam evaporated on top of a patterned layer of AZ 5214E photoresist and electrodes are defined by a lift-off process, (c) the polymer piezoresistor is defined by spin coating 1.5-2.0 μm thick SU-8/carbon NP composite and structuring it by UV-lithography and finally, (d) the chips are cut out from the wafer. Even though the SU-8 composite is completely black it is still possible to UV-structure. As line width wasn't crucial in our design, we used an exposure dose of 1.53 J/cm² to be sure to crosslink the SU-8 composite.

2.3 Setup

The fabricated chips are placed in a four-point bending fixture specially designed for the chips. By applying a force to the two upper blades, the inserted chip is pressed down on two bottom blades and subjected to a pure bending moment, which results in a uniform stress stress along the length axis of the chip between the two upper blades (figure 3 - top) The force is applied by loading a weight on top of the clamped bricks (figure 3 - bottom).

The chip is electrically connected to a Keithley 2700 Multimeter through a Flat Flexible Cable. Using the set-up a well defined stress is applied to the fabricated SU-8/carbon NP composites and simultaneously we measure the two-point resistance. For a detailed description of the experimental setup we refer to ref. [13].

Four-point measurements are the standard method for measuring resistivity; however, measuring the resistivity is not the main goal of this work. We are interested in measuring the piezoresistive effect and if we assume that the contact resistance is constant during strain, two-point measurements can be

used. Furthermore, with our chip design we can measure the resistance for nine different lengths of the resistor, hence if we plot R vs. length we can find the contact resistance as the crossing of the R -axis.

3 Results

3.1 Resistivity

Figure 4 shows a plot of the resistivity, ρ , of the polymer composites as a function of the carbon NP content, when no stress is applied. As the carbon NP amount is increased, the resistivity drops several orders of magnitude and a transition from insulator to conductor is observed. The highest doped composites have resistivities of $\rho \sim 1.0 \times 10^{-2} \Omega\text{m}$, which is in the semiconductor region.

To determine the percolation threshold one would in principle need to scan the whole NP concentration range from insulator to conductor. For XE2 we estimated the percolation threshold to $P_c = 1-2\%$. This value is quite low; however, XE2 is a 'high' structure carbon black with a OAN value (oil absorption value [14]) value of 380 ml/100 g. High structure carbon blacks form elongated aggregates and are known to give lower percolation thresholds[15,16]. For Conductex 975U and Conductex 7051U the resistivities for the lower NP concentrations were too high to be measured with the present setup, hence we cannot positively say that the percolation threshold was reached. However; figure 4 suggests that Conductex 975U and Conductex 7051U should have higher percolation thresholds than XE2, because a higher concentration of NPs is needed to reach a resistivity equivalent to XE2. This is also what

one could expect since Conductex 975U and Conductex 7051U have 'lower' structure than XE2, with OAN values of 169 ml/100 g and 121 ml/100 g, respectively [14]. Lower structure carbon blacks do not form highly aggregated structures, hence a larger amount of NPs needs to be added to make a conductive composite.

3.2 Piezoresistivity

To investigate the basic mechanism of the polymer composite piezoresistor a measurement series was made, where tensile and compressive stress was applied alternately. Figure 5 shows the resistance, R , of an SU-8/carbon NP composite as a function of time. From the figure it is clear that the behavior is as expected: (a) Onset of tensile (compressive) stress, (b) conductive paths are broken (established) and R increases (decreases), (c) tensile (compressive) stress is released and (d) conductive paths are re-established (broken) and R returns to its initial value.

As can be seen from figure 5 the baseline, R_0 , drifts, but the *height* of the peaks is stable, which means that the piezoresistive effect is reversible. Such a reversible piezoresistive effect has previously been reported by Knite et al. for macro-size structures[17]. We thus verify that a similar behavior is found for microstructures.

3.3 Gauge factors

We have measured gauge factors for the three different types of carbon NPs at different concentrations. The gauge factors were measured in two different

ways:

(1) A tensile stress of 160 MPa was applied in a cyclic manner, hence 2 minutes stress off, 2 minutes stress on, 2 minutes stress off and so on. Three complete cycles were made for a total of 14 minutes. Figure 6 (left) shows the measured resistance, R , as a function of time for a 6.5% XE2 composite. As $\Delta R/R = K\varepsilon$, where K is the gauge factor and ε is the strain, we can calculate the gauge factor from the values of the graph: ΔR is the height of the peaks, R_0 is the baseline and the strain is related to the stress through Hooke's law, $\sigma = \varepsilon E$, where E is Young's modulus for silicon. [18]. For the three peaks we find a gauge factor of $K=11$. The spike observed at the start of each stress cycle is due to the fact, that a weight load is manually placed on top of the four point bending probe. Even though the weight is loaded very gently, the stress goes momentarily up; however, the resistance rapidly stabilizes.

(2) A tensile stress is stepped from zero to 200 MPa in five equidistant steps over a period of 10 minutes. Again we have $\Delta R/R = K\varepsilon$, so if we plot $\Delta R/R$ as a function of the strain, ε , we can find the gauge factor, K , as the slope of the graph. Figure 6 (right) shows a plot for a 6.5% XE2 composite. We do not observe a linear behavior in the whole strain range. A similar behavior has previously been measured and theoretically explained by Zhang et al. [19].

To estimate the gauge factor, we decided to make a linear fit (the dotted line) in the interval $\varepsilon \geq 0.37 \cdot 10^{-3}$, since the strain applied in method (1) lies in this interval. We find a gauge factor of $K=11$. There is good agreement between the gauge factors measured with method (1) and (2).

In figure 7 we have plotted the measured gauge factors as a function of the NP content for the three different carbon NPs used. As we go towards lower concentrations the gauge factors increase; however, the spread in the measured values increase for lower concentrations (indicated by the error bars). As an

example, for the 10% 975U composite we measured gauge factors in the range $K=22-54$ on a single chip using different electrode configurations.

For higher NP concentrations we observe lower, but more reliable gauge factors. To illustrate this trend we have plotted the resistance, R , as a function of time for a 3.8% and an 8.6% XE2 composite in figure 8. The measurements shown are similar to the one in figure 6 (left). From the figure we find gauge factors of $K=14-19$ for the 3.8% composite and $K=5-6$ for the 8.6% composite; however, the measurements for the 3.8% composite have fluctuations of $\simeq 1\%$, whereas it is less than 0.1% for the 8.6% composite. This trend can be illustrated if we plot the standard deviation of the resistivity, $\sigma(\rho)$, as a function of the resistivity, ρ , for different XE2/SU-8 composites. The graph in figure 9 yields a straight line in a log-log plot, hence as the resistivity increases, the fluctuations increase with a power law dependence.

The noise of the equipment was estimated by measuring the resistance once every minute for 3 hours for (a) an ordinary resistor and (b) a 6.5% XE2 composite resistor, both with a resistance of $650\text{ k}\Omega$. We found that the fluctuations in the composite was around a factor of 100 times larger than in the ordinary resistor. Thus it can be concluded that the observed fluctuations are not instrumental.

4 Conclusion

Composites of SU-8 and three different types of carbon NPs have been fabricated. The resistivity has been measured and we have observed an insulator to conductor transition, when increasing the NP content of the composites. The percolation threshold seems to be correlated with the OAN number, such that high OAN number gives a low percolation threshold.

We have shown that the composites are piezoresistive and measured stable and reversible gauge factors of $K=5-9$, but gauge factors of up to $K=40-50$ have also been measured. A gauge factor of $K\sim 5$ is sufficient for an all polymer based cantilever to compete in sensitivity with a silicon based cantilever.

We have shown that for a specific NP, composites with a lower NP content gives larger, but less stable gauge factors compared to composites with a higher NP content.

Future work involves integration of the polymer piezoresistor in an all polymer based cantilever sensor system. The noise level of the composites needs to be investigated thoroughly.

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Fig. 1. An SEM image of a 10% CD975U/SU-8 polymer composite. The aggregated NP structures are seen as the bright points.

Fig. 2. A picture of the fabricated chip. The white square in the middle of the chip is the structured SU-8/carbon black NP composite. The gold electrodes are also visible.

Fig. 3. Top: A schematics of the four-point bending principle. The two upper blades are pressing the chip down on the two lower blades, the chip is subjected to a pure bending moment and a uniform stress is applied along the length axis of the chip in the region "b". Bottom: A picture of the four-point bending fixture with a chip inserted. The two bricks are clamped together and a force is applied to the upper brick, by loading a weight on it.

Fig. 4. The resistivity, ρ , as a function of the carbon NP particle content for three different types of particles. A clear insulator to conductor phase transition is observed. The resistance was measured with a Keithley 2700 Multimeter in two-point resistance mode passing a $0.7 \mu\text{A}$ current through the resistor and measuring the voltage drop across. The graph suggests that a lower OAN value gives lower percolation threshold.

Fig. 5. An 8.65% XE2/SU-8 composite, where tensile and compressive stress is applied alternately. (a) Tensile stress applied, (b) conductive paths are broken and R increases, (c) tensile stress released and (d) conductive paths are re-established and R returns to initial value. The peaks correspond to time intervals of nonzero tensile stress and the valleys to periods of nonzero compressive stress.

Fig. 6. LEFT: The resistance, R , as a function of time for a 6.5% XE2 composite, where a tensile stress of 160 MPa corresponding to a strain of $\varepsilon = 1.1 \cdot 10^{-3}$, is applied in a cyclic manner. From the baseline, R_0 , and the height of the peaks, ΔR , we can calculate the gauge factor, K . For the three peaks in the figure we find a gauge factor of $K=11$. RIGHT: The relative change in resistance, $\Delta R/R$, as a function of the strain, ε . The overall behavior is not linear. We have decided to make a linear fit (the dotted line) in the interval $\varepsilon \geq 0.37 \cdot 10^{-3}$ and from the slope we find $K=11$ for the gauge factor.

Fig. 7. The measured gauge factors as a function of the NP content for the three different carbon NPs used. The gauge factors increase for lower concentrations; however it can be seen that the spread in the measured values increase (indicated by the error bars). For 7051U only two data points were obtained as we could not measure gauge factors for concentrations lower than 20%. The data presented represents measurements for several chips and at different electrode spacings.

Fig. 8. The resistance, R , as a function of time for 3 tensile stress cycles of 180 MPa. The measured values are for a 3.8% (right R-axis) and 8.6% (left R-axis) XE2 composite with a resistivity of $\rho=1860 \text{ } \Omega\text{m}$ and $1.5 \text{ } \Omega\text{m}$, respectively. The resistance was measured using the same method as in figure 6 - left. For the 8.6% XE2 composite peak 1-3 give gauge factors of 5.4, 6.1 and 6.5, respectively. For the 3.8% XE2 composite we get 14.6, 16.7 and 18.9, respectively. However, the resistance of the 3.8% composite fluctuates up to $\sim 1\%$ ($1 \text{ M}\Omega$).

Fig. 9. The standard deviation of the resistivity, $\sigma(\rho)$ as a function of the resistivity for the XE2 composites. The graph shows a straight line in a log-log plot indicating a power law dependence.