Negative Differential Resistance in a Flexible Graphite Silicone Composite.

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ABSTRACT

The need for flexible electronic devices that are compatible with biology is driving the search for novel materials. Here we report a composite of graphite nanoparticles incorporated into a silicone rubber matrix that exhibits a robust negative differential resistance (NDR) region. Through consideration of the lamellar structure of the nanoparticles and the formation of electric field domains within the sample, we show that the NDR originates from a semimetal to insulator transition of an embedded bilayer within the graphite nanoparticle. We employ the rubber's intrinsic flexibility to demonstrate how strain induced in the composite, through an axial deformation, modifies the NDR region. A strain of $\varepsilon = 17.5\%$ shifts the onset of the NDR by 30%.

Keywords: graphite, silicone, composite, flexible, strain

1 Introduction

There is an increasing need for soft flexible materials, that generate a voltage gain, to obtain flexible integrated circuits for bioelectronic applications [1]. Currently these materials are based around passive piezoresistive devices, which means that they remain hybrid hard/soft circuits that require silicon logic chips to interpret the signal [2]. Self contained flexible integrated circuits are required to lead the way for fully flexible solutions. These devices require non-linearities in their current - voltage ($I-V$) characteristics. Thus a flexible material that exhibits a robust negative differential resistance (NDR) region would be one such solution and allow for logic gates, oscillators and amplifiers to be realized [3].

There has recently been a great deal of excitement regarding graphene and its superior electrical conductivity [4]. Much attention has also been given to bilayer graphene which has been shown, through applying a potential across the layers, to have an electrically tunable band-gap [5]. Here we show a NDR region in a composite of highly orientated pyrolytic graphite (HOPG) nanoparticles and silicone rubber that is explained through a semimetal to insulator transition of a bilayer embedded within a nanoparticle [6]. The transition takes place due to the formation of a potential across two graphite planes. This occurs when the current through the nanoparticle makes an acute angle to the electric field and thus conduction jumps, from in the plane to perpendicular to the plane, at a critical value of the electric field. The potential causes a partial breaking of the conduction band across the layers.

The composite is a biocompatible material retaining the flexible and elastic nature of rubber, whilst having a high conductivity due to a high filling fraction of HOPG nanoparticles. The NDR region is shown to be robust and well suited for making oscillators and amplifiers. Furthermore, we demonstrate that the electrical properties of these composites can be tuned through applying strain. Bending the sample leads to a shift in the NDR region that could be used to gradually tune the frequency of spontaneous oscillations, possibly yielding electromechanical sensors.

2 Experimental

2.1 Fabrication

The composites were fabricated through incorporating 450 nm HOPG nanoparticles into silicone rubber. Particles are gradually added and mixed into the rubber, ensuring the particles are homogeneously incorporated before adding more. The composites become highly viscous at high volume fractions where $p > 32\%$. The addition of the liquid catalyst restores miscibility and allows the mixture to be compressed and moulded into ribbon templates 100 μm high, 1 mm wide and 8 mm long. The templates are placed onto a cellulose acetate mount, which the composite readily adheres to as it is cured over a 48 hour period. Gold contact areas, that provide ohmic contacts, are thermally evaporated onto the composite and mount.

2.2 Measurement

Measurement of the $I-V$ characteristics were made through sweeping the voltage whilst measuring the current. A four terminal measurement of the voltage drop through the composite was made. The voltage was ramped at a rate of 0.5 V/s.

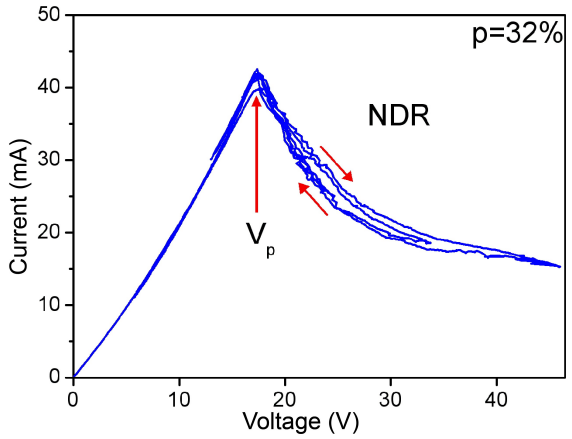

Figure 1: Before the peak the sample behaves ohmically. At V_P a transition occurs and the current decreases with increasing bias. This creates a wide NDR region that is robust and has little hysteresis.

3 Results

3.1 Robust Negative Differential Resistance

In measuring the $I-V$ characteristics of the composite at 77 K an unexpected phenomenon was observed. Initially at low voltages the current increases ohmically. At a threshold voltage, V_P, the current abruptly starts to decrease. The current continues to decrease further as the applied voltage increases, leading to a wide NDR region. This type of NDR is usual seen only in devices with specially engineered band structures, such as resonant tunneling diodes or superlattices. NDR has not previously been observed in graphite composites.

The voltage was swept back and forth through V_P multiple times and the NDR was found to be robust, with little hysteresis between sweeps (see Fig.1). This reveals that the NDR must be due to a reversible transition in the conduction and not a dielectric breakdown within the composite.

3.2 Electric Field Domains

Voltage probes were used to measure the voltage drop across the sample, for different probe separation distances 0.4, 0.7, 1.0, 2.0, 3.0 and 5 mm. At low voltage, $V < V_P$, all probes measure the composite having the same resistivity with the resistance increasing linearly with the length of composite, showing the composite is homegeneous. At $V > V_P$ for large probe separations NDR is observed (see Fig.2). However for small probe separations, 0.4 mm, NDR is not observed. Instead the voltage drop across the probes decreases as the external voltage continues to be increased. This is due to the sample no longer having a homogeneous electric field and the formation of electric field domains. The

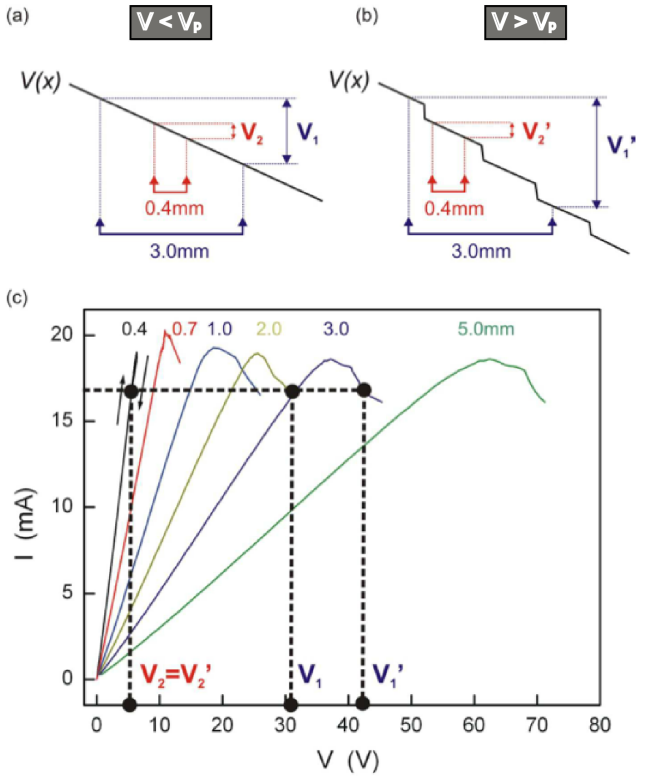

Figure 2: (a) For $V < V_P$ the sample has a uniform electric field along its length. (b) When $V > V_P$ the samples breaks up into domains.

3.3 Semimetal - Insulator Transition

The presence of a NDR region in HOPG composites is due to the switch from in plane to perpendicular conduction in graphite [6]. By considering the percolation path in Fig.3a we demonstrate that, for the majority of HOPG nanoparticles, the current flows inside just one graphene plane. In the remaining nanoparticles, the current jumps one interlayer spacing and rarely more. Whether a nanoparticle conducts through a graphene monolayer, bilayer or trilayer depends upon the angle θ between its planes and the electric field $\vec{E}$. Using Ohm's law, $\vec{J} = \sigma\vec{E}$, the number of graphite interlayers N, between the current entry point A and exit point B of the nanoparticle can be found in terms of: the ratio of the in-plane to perpendicular conductivity of graphite, $\sigma_{\parallel}/\sigma_{\perp} = 3000$ [7]; the distance between graphite planes, c = 0.335 nm; and the average length of a HOPG nanoparticle, $l = 450$ nm. Using the construction in Fig.3b, we obtain

$$N = \frac{l}{c}\frac{\sigma_{\perp}}{\sigma_{\parallel}}\tan\theta \simeq 0.441\tan\theta, \qquad (1)$$

effective voltage dropped within an electrical domain decreases and this decrease is compensated by a local increase in bias voltage across a domain boundary.

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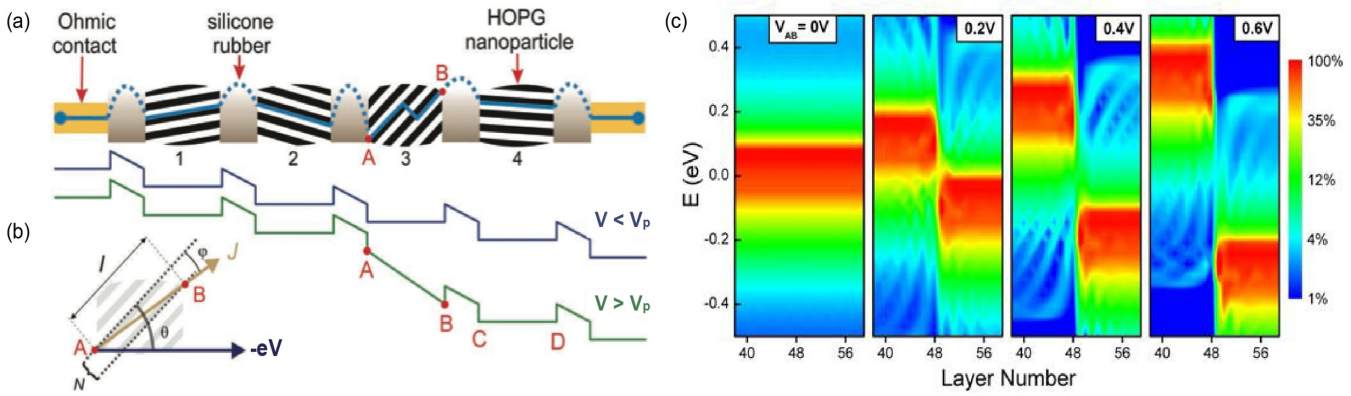

Figure 3: (a) Schematic diagram for a conduction path across the composite. (b) The graphite planes are at an angle θ to the electric field. (c) Opening of a partial energy gap when an electric field is applied across an embedded bilayer

where θ is the angle of the graphite planes to the electric field. Therefore, when θ is between 0 and 66°, HOPG nanoparticles conduct through a single graphite monolayer ($N < 1$). Between 66°and 78°, conduction is through a graphite bilayer ($N < 2$), between 78° and 82°, a graphite tri-layer ($2 < N < 3$) , and so forth.

Since HOPG particles assume random orientations in the matrix, 93.5% of them remain semimetallic at any value of the electric field. In the remaining 6.5%, the current flows into the nanoparticle through one graphite layer (point A), then crosses one interlayer before exiting through the adjacent graphite layer (point B). The (mostly) transverse bias V_{AB} opens a partial energy gap at the Fermi level in graphite. This gap is shown in the local density of states plots (see Fig.3c). Unlike the gap of the freestanding graphene bilayer, the gap of the embedded bilayer opens above a threshold, $V_{AB} > 2\gamma_2$ corresponding to the energy overlap of the π-band ($2\gamma_2$ = 40 meV) [5]. The gap is partial. Nevertheless, it is sufficiently well defined to induce a semimetal-insulator transition, since the density of states at the Fermi level drops from 100% at 0 V to just 3% at 0.6 V. Thus nanoparticles tilted at an angle between 66° and 78° develop a high resistance that breaks the composite into domains of constant electric field.

3.4 Effect of strain within the composite

Strain was induced within the composite through a lateral deformation. The composite mount was pinned between two supports that allow it to rotate freely whilst restricting the horizontal and vertical movement. The supports are horizontally displaced through a lead screw actuator (see Fig.4a). This causes the sample to bend vertically, with a characteristic deformation of Euler buckling with pinned end restraints (see Fig.4b) [8].

Depending on the vertical direction of buckling this leads to a compressive or tensile strain, ε, within the composite. The system was then cooled to 77 K and the $I-V$ characteristics recorded. In order to change the bend radius, the sample was thermally cycled to room temperature.

To calculate the differential strain, the interface between the composite and the acetate mount was considered. The bend radius was found as a function of the horizontal deformation, $\eta = \frac{l_0 - l}{l_0}$; where l_0 is the length of the mount when flat and l is the chord of the arc when bent (see Fig.4c). Then the relationship between the strain and horizontal deformation can be derived [9]:

$$\varepsilon(\eta) = \frac{h}{l_0}\left(14 + \frac{E_1}{E_2} + \frac{E_2}{E_1}\right)\sqrt{\frac{\eta}{24}}, \qquad (2)$$

where $E_1 \approx 4$ MPa and $E_2 \approx 400$ MPa are the Young moduli of the composite and acetate respectively; and $h = 200$ μm is the combined thickness of the composite and acetate.

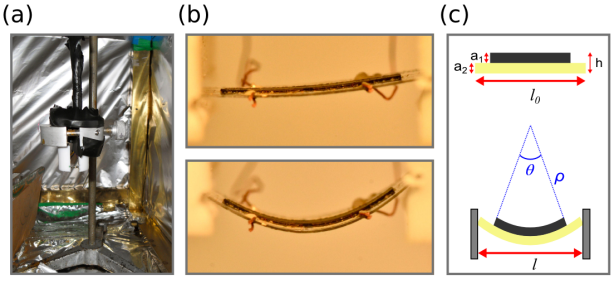

Figure 4: Strain is induced in the composite through an axial load (a) Low temperature probe for the actuator (b) Sample deformed from flat to being in compressive strain. (c) Schematic of sample under strain.

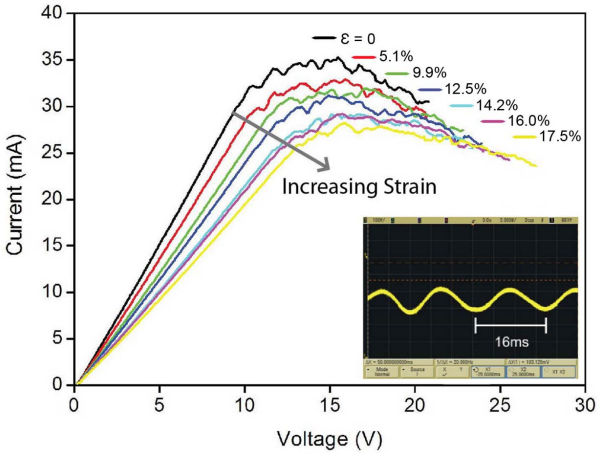

Figure 5: Induced compressive strain causes a significant change in the $I-V$ characteristics. The low field resistance increases by 78% and V_P is shifted by over 30% for $\varepsilon = 17.5\%$. (*inset*) The NDR region is able to support spontaneous oscillations.

The effect of increasing strain on the $I-V$ characteristics of the composite is two-fold (see Fig.5). Firstly the low field, $V < V_P$, resistance can be seen to increase. This increase is from 313 Ω to 556 Ω, when the strain is increased by 17.5%. This allows the longitududianal piezoeresistive constant to be calculated from:

$$\frac{\Delta R}{R} = E_1 \varepsilon \pi_L, \tag{3}$$

to a first approximation of $\pi_L = 1.1 \times 10^{-6}$ Pa^{-1}. This is two orders of magnitude greater than the longitudinal piezoresistance reported for silicon nanowires [10].

The second effect is that the voltage threshold for the onset of NDR increases substantially. A 17.5% increase in strain leads to a 30% increase in V_P. The shift in V_P showed little hysteresis over numerous strain and thermal cycles. Only when the bend radius was taken to extremely tight radii did the sample not come back to the initial V_P for zero strain. This is due to the rubber being deformed beyond its elastic limit.

To demonstrate that the NDR is capable of sustaining spontaneous oscillations, the sample was included as the active element of a resonant circuit; with an inductance of 1 H and a capacitance of 5.7 μF. Stable oscillations with a frequency of 62.5 Hz and an amplitude of 110 mV were observed, (see Fig.5 *inset*). The oscillations were only present when the sample was biased into the NDR region.

The shift in position of the NDR region with strain allows for precise control of the oscillations. It is envisaged that this would enable sensitive electromechanical sensors.

4 Conclusion

We have shown a robust negative differential resistance region in a graphite silicone composite. The NDR originates from a semimetal-insulator transition of an embedded bilayer within a graphite nanoparticle and causes the formation of electric field domains across the composite.

Through applying an axial load in the sample, a compressive strain is induced within the composite. This causes a significant change in the $I-V$ characteristics. The low field resistance increases by 78% and the onset of the NDR region is shifted by 30% for a 17.5% increase in strain.

This can be utilized for the control of a new generation of flexible active devices such as flexible oscillators of amplifiers.

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