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Negative Differential Resistance in Graphite-Silicone Polymer Composites

Samuel Littlejohn, Alain Nogaret

Department of Physics, University of Bath, Bath BA2 7AY, UK

Abstract. We report a robust negative differential resistance in silicone rubber filled with graphite nanoparticles. The sharp increase in resistance at high electric field is interpreted as the opening of energy gaps at the K points of graphite.

INTRODUCTION

Bilayer graphene is now known to be a tuneable band gap semiconductor. The theoretical reason[1-3] resides in the differences in strength of the π bonds attached to the A and B atoms of the hexagonal unit cell. Atoms A of one graphene layer stand directly on top of another atom in the next graphene layer whereas atoms B sit at the centre of the hexagons. Applying a transverse electric field breaks the hexagonal symmetry in the plane and lifts the degeneracy of the conduction and valence band at the K points of the Brillouin zone. The asymmetry induces an energy gap that increases with transverse bias as:

$$\Delta = \frac{eVt_\perp}{\sqrt{t_\perp^{2} + e^{2}V^{2}}}, \qquad (1)$$

where $t_\perp = 0.22V$ is the coupling energy between the graphene planes[2]. The opening of the gap in graphene bilayers has now been confirmed by angular resolved photoemission spectroscopy[4-5], by an extra plateau in the quantum Hall effect[1] and by thermally activated transport[6]. Here we show that the gap opening also manifests as a negative differential resistance region in the I-V curves of graphite nanoparticles embedded in an insulating silicone matrix[7].

EXPERIMENTAL

We have prepared samples by mixing carbon nanoparticles in a low viscosity liquid silicone rubber that vulcanizes at room temperature. Three composites were prepared A, B and C based on the carbon nanoparticles listed in Table 1.

TABLE 1.	Filler nanoparticles	
Sample	**Material**	**Particle radius**
A	Graphite	225nm
B	Amorphous carbon	25nm
C	Pyrolithic graphite	25nm

Pyrolithic graphite (sample C), was obtained by annealing the amorphous carbon nanoparticles (sample B) at 1050°C. The X-ray diffraction spectra of samples A and C display the signature peaks of sp2 bonding which indicate the formation of graphene planes. The presence of additional (101) Bragg peaks in graphite indicates that graphene planes are stacked in the three sequences AAA, ABA and ABC. In sample C, the graphene planes have no periodicity along the c-axis. Amorphous carbon nanoparticles, sample B, show no diffraction peaks as expected. We have moulded the conductive elastomer to form Hall bars 1mm wide, 10mm long with a distance of 1.25mm between voltage probes. Current-voltage characteristics were measured in the 4-terminal geometry at temperatures below the glass transition temperature of silicone rubber (T<174K). This is to avoid spurious effects associated with the thermal expansion of the elastomer under Joule heating. The I-V characteristics measured at different temperatures are plotted in Fig.1.

The I-V curves of composites A and C have a peak current followed by a negative differential resistance region. The peak-to-valley current ratio is >2. This peak is very robust. It is observed over a range of carbon filling fractions using different distances

between voltage probes. By contrast composite C has a conductivity 3 orders of magnitude smaller and no current peak. Fig.1 shows the current peak in sample A and its temperature dependence. The peak position shifts to higher voltage with decreasing temperature saturating at a field F_p =12kV/m at 77K.
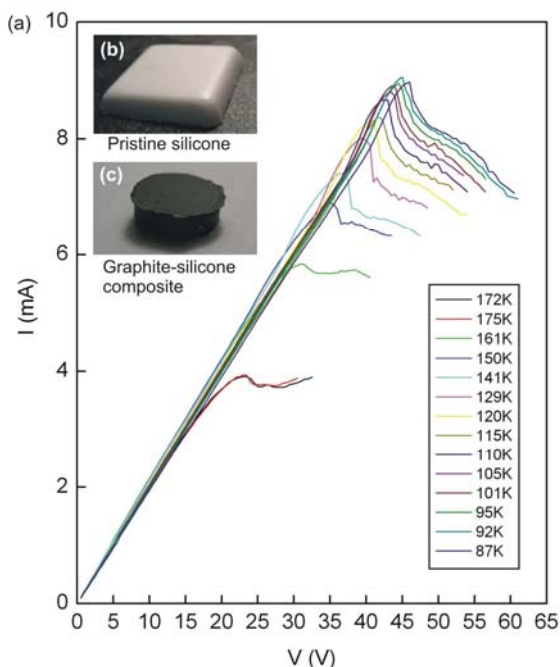

FIGURE 1. (a) Current voltage characteristics of silicone filled with 28% graphite nanoparticles in volume (sample A). Temperature dependence of the I-V curves below the glass transition temperature of silicone (Tg=174K); (b) Pristine silicone and (c) graphite silicone composite.

INTERPRETATION

The low field conductivity follows a power law dependence on the carbon filling fraction. This demonstrates that conductivity paths percolate through the sample as schematically shown in Fig.2(a). At low temperature, electrons hop between nanoparticles by tunnelling[7] through silicone rubber barriers. At low (average) electric field, $F<F_p$, the resistance of graphite is negligible compared to that of silicone. The applied bias is supported by the silicone barriers, the local electric field in graphite being zero. At the peak, $F=F_p$, the resistance of the tunnelling barrier decreases enough to become comparable to that of a nanoparticle. A finite electric field appears inside graphite. Its vector component perpendicular to the graphene planes opens a gap[1-3] at the K points of the band structure. Since graphite is undoped, the Fermi energy crosses the K-points – see Fig.2(b,c). Since electrons tunnel in the K-point energy gap of the second particle, the tunnelling current decreases. The semi-metal-to-insulator transition of graphite explains the NDR of the composite. At higher temperature, the thermoactivated current reduces the resistance of the barrier. This implies that less bias is required to match the resistance of the barrier to that of graphite. The peak then moves to lower bias as observed.
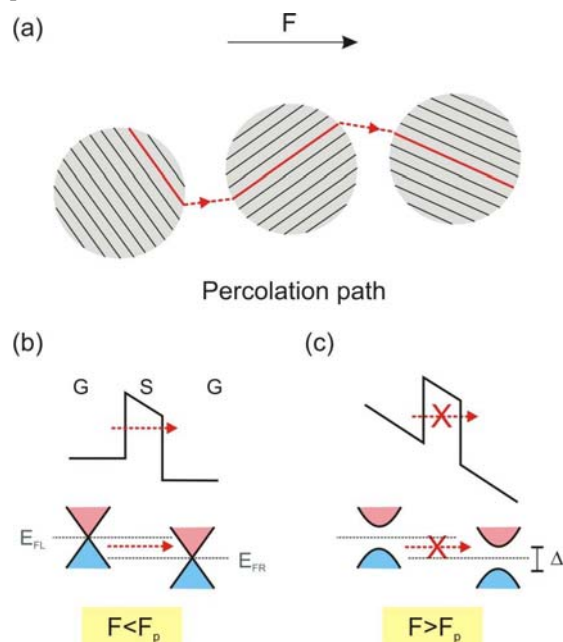

FIGURE 2. (a) Percolation path through the silicone graphite composite assisted by tunnelling between graphite nanoparticles. (b,c) Tunnelling process in real space and momentum space shown at low electric field ($F<F_P$) and above the peak ($F>F_p$). The electric field induced gap Δ (Eq.1) quenches tunnelling giving the NDR.

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