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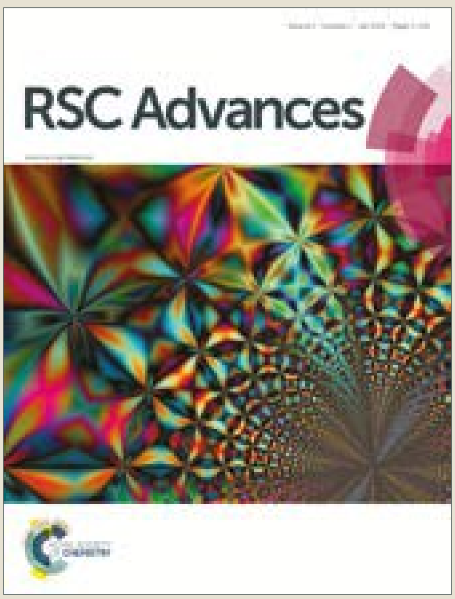

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ARTICLE

High performance tunable piezoresistive pressure sensor based on direct contact between printed Graphene Nanoplatelet composite layers

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This article details the developement of a thin film piezoresistive screen printed pressure sensor on flexible substrate using a composite ink based on functionalised graphene nanoplatelets (GNPs). The sensor operates through direct interfacial contact between two distinct films of the composite ink deposited over conductive substrates, without requiring any intermediate gap through spacers. The sensors showed consistent results and sensitivity forces ranging between 10 N to 2000 N. The piezoresistive range of the sensor can be tuned with the number of layers deposited per side.

Introduction

Printed electronics is an important area of academic and industrial research. Established applications include photovoltaics, biosensors and organic Light Emitting Diodes. Printed pressure sensors are an area with a large market potential.[1] Possible applications include monitoring load distribution on hospital beds and wheelchairs, the assessment of the physical condition of elite athletes and patients using force platform and seat occupancy in cars.[2-4] The need for electronic skin which will enables robots to sense their surroundings is another application of flexible pressure sensors. [5, 6]

A range of mechanisms exist to sense pressure, key types include capacitive, piezoelectric and piezoresistive. Here we focus on piezoresistive sensors, i.e. devices which change electrical resistance in response to applied pressure. Much research is focused on the development of novel composite materials or structures with enhanced piezoresistive performances.[7-10] The piezoresistitive range significantly depends on the properties of both the conductive filler and the binder. The percentage of the filler can be detrimental for the mechanical properties of the resin. For this reason, nano materials are favoured as they have a low percolation concentration.

Webb *et al.* presented a printed piezoresistive touch sensor; a titanium dioxide nanoparticles based ink was sandwiched between two electrodes. [11] The sensor exhibited switch like properties and reached saturation at 3 N.

Nanocarbons, including graphene, carbon nanotubes, graphene nanoplatelets, have been at the forefront of research in nanomaterials, showing incredible potentials.[12] Janczak et al. developed screen-printed resistive pressure sensors using PMMA or PVDF as resin and graphene nanoplateles (GNP) or carbon nanotubes as conductive filler.[13] The sensors showed good piezoresistivity, however the presence of a physical gap induced by the dielectric separator meant that the working mechanism of the sensor could be potentially reliant on the relative bending of substrates, leading to an macroscale increase area of contact with pressure. Better reproducibility was obtained with GNP compared to CNT base sensors due the deformation of the CNTs which created additional contacts.

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Most piezoresistive pressure sensors feature elastomeric binders.[14] These materials deform upon compression and the resistivity typically drops as the conductive material get closer.

Here we present a fully screen printed single sensor based on plasma functionalised GNPs dispersed in a non elastomeric resin. Functionalisation of GNPs is known to improve their dispersion in polymer and solvents.[15] The use of a non elastomeric binder leads to a sensor which responds due to interfacial interactions and does not require an air gap created by a spacer frequently featured in other designs. We test the piezoresistivity of single sensors and investigate the effect of the thickness of the printed layer on the performance.

Experimental set up

Functional materials: Plasma oxygen functionalised GNP supplied by Haydale Ltd (HDPlas® GNP) were used as the functional material. The supplied GNPs have a typical planar size ranging from 0.3 µm to 5 µm and thickness of 50 nm. For this work the GNP were printed as an ink dispersion with vinyl chloride based polymers as insulating binder[16].

Sensor design and manufacture: the sensor was produced by printing on an Indium Tin Oxide substrate (Multek Flexible Circuit Inc, USA). The ITO substrate had a sheet resistance of 60 Ω/sq and an average roughness of 11 ± 3 nm. The low average roughness of the ITO substrate ensures that the piezoresistivity of the sensor does not rely on the roughness of the substrate. A 100 mm X 100 mm square of GNP ink was printed on ITO using DEK 248 flatbed. This screen printer allows easy registration between the successive prints. Each layer was dried at 100 °C for 5 minutes. A sensor was made by cutting two strips of 110 mm long and 20 mm wide. The strips where stacked perpendicularly to each other (see Figure 1).

Testing layout: The piezoresistivity of single sensors were tested using a Hounsfield compression tester. The sensing area was delimited with a stainless steel disk with an area of 1.5cm^2. The sensor was subjected to compression forces ranging from 10 N to 2000 N. The resistance of the sensor was monitored using Keysight technologies U1231A digital Multimeter. Each sample was tested over seven compression and relaxation cycles.

Complementary electrical tests were performed over screen printed GNP ink films on a non-conducting substrate (Polythylene terephathalate), which showed the absence of any lateral conductance (tested with a RS-Pro DT-5500 insulation tester, >200MOhm).

Characterisation: The thickness, average roughness and the peak to peak height of the GNP layers were measured using white light interferometry. The roughness and the peak to peak height of the compressed area were re-measured after 56 compression cycles with forces from 10 N to 2000 N. The surface topography of the prints was characterised using an Infinite Focus microscope (Alicona, Austria), a 3D optical surface topographic measurement device, and a Hitachi S4800 Scanning Electron Microscope

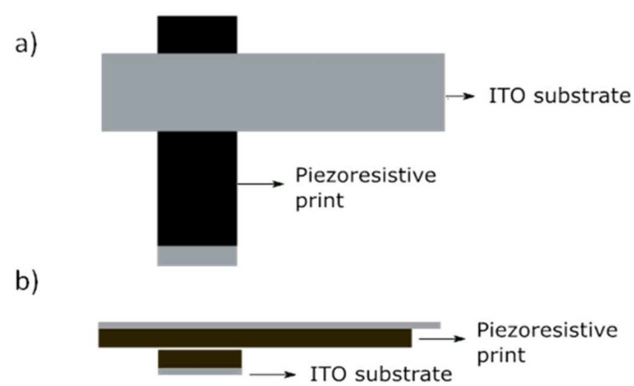

Figure 1: a) top view of the single sensor design b) side view of the sensors.

Results

As a preliminary control test, the contact resistance between two ITO substrates (without any GNP layer) was measured at varying force. In the specific case, the resistance varied from 141 Ω at 10N to 137 Ω at 2000 N, showing therefore no significant piezoresistive effect, as expected. The influence of the number of printed layers of GNP ink on the piezoresistive range was studied by characterizing sensors with different layers. Three combinations were studied: a pressure sensor with one printed layer ink on the top and bottom substrates (ITO:1GI/1GI:ITO). A sensor with two layers on the bottom substrate and one layer of GNP ink on the top substrate (ITO:2GI/1GI:ITO). To finish, a sensor with two printed GNP layers on the top and bottom substrates (ITO:2GI/2GI:ITO). For each combination three samples were tested. A summary of results is reported on Figure 2 in log-log scale. Hysteresis was observed in the first three compression/relaxation cycles. The sensors response stabilised after the fourth run. On Figure 2 each data point is the average over the last four runs. Figure 2a shows the response of sensors with one printed layer on the top and bottom substrates. The resistance dropped from 7 KΩ at 10 N to 0.5 kΩ at 2000 N i.e the sensor has a piezoresistive range of 6.5 kΩ over 1990 N. Beyond 500 N the resistance of the sensor is constant; it is said to be saturated. The sensor with two printed layers on the bottom substrate and one print on the top has a range of 9 kΩ over 1990 N (see figure 2b). This sensor does not reach saturation in the range of forces studied and the resistance is a power of the force applied. The sensor with two prints of GNP ink on the bottom substrate and on top substrate has a range of 45 kΩ and saturates at 1000 N (see Figure 2c).

Figure 2 shows that the piezoresistive range and the rate at which the resistance decreases are dependent on the number of printed layers of GNP inks. Figure 3a shows a 3D view of one printed layer. The colour scale show that the GNPs correspond with the peaks of the surface. This is to be expected; the GNPs have a typical planar size of 0.3 µm to 5 µm and the thickness of one layer is on average 1.90 ± 0.4 µm. GNPs with planar size bigger than the thickness of the print will stand out at the interface. In addition regardless of their planar size GNPs located in the vicinity of the surface will stand out of the coating. Figure 3c is an SEM image of a one printed layer of GNP ink at an angle of 5°; here it can be seen particles are well dispersed laterally with very few/no

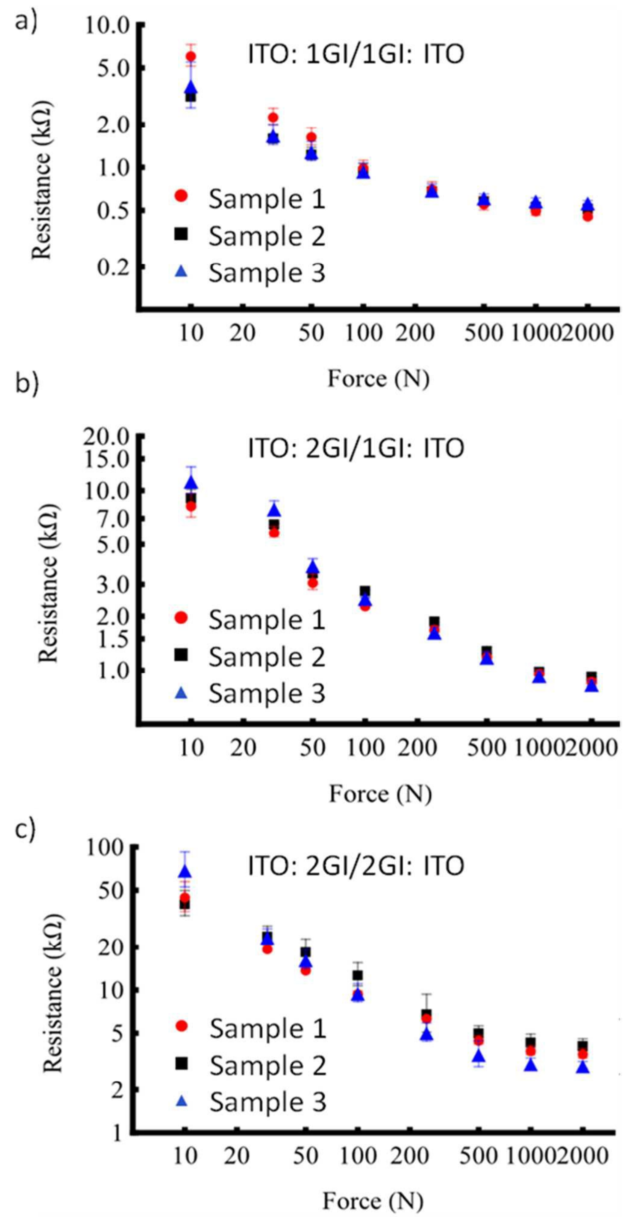

Figure 2: These Figures show the resistance as a function of the compression force for the three combinations studied. a) shows piezoresistive response of the sensor with one printed layer of GNP ink at the top and the bottom substrates. b) shows the response of a sensor with two printed layers on the bottom substrate and one layer on the top substrate. c) shows the piezoresistive response of a the sensor with two layers of ink on the top and bottom substrate. For each combination three samples were tested, the square, circle and triangle correspond to the first, second and third samples, respectively.

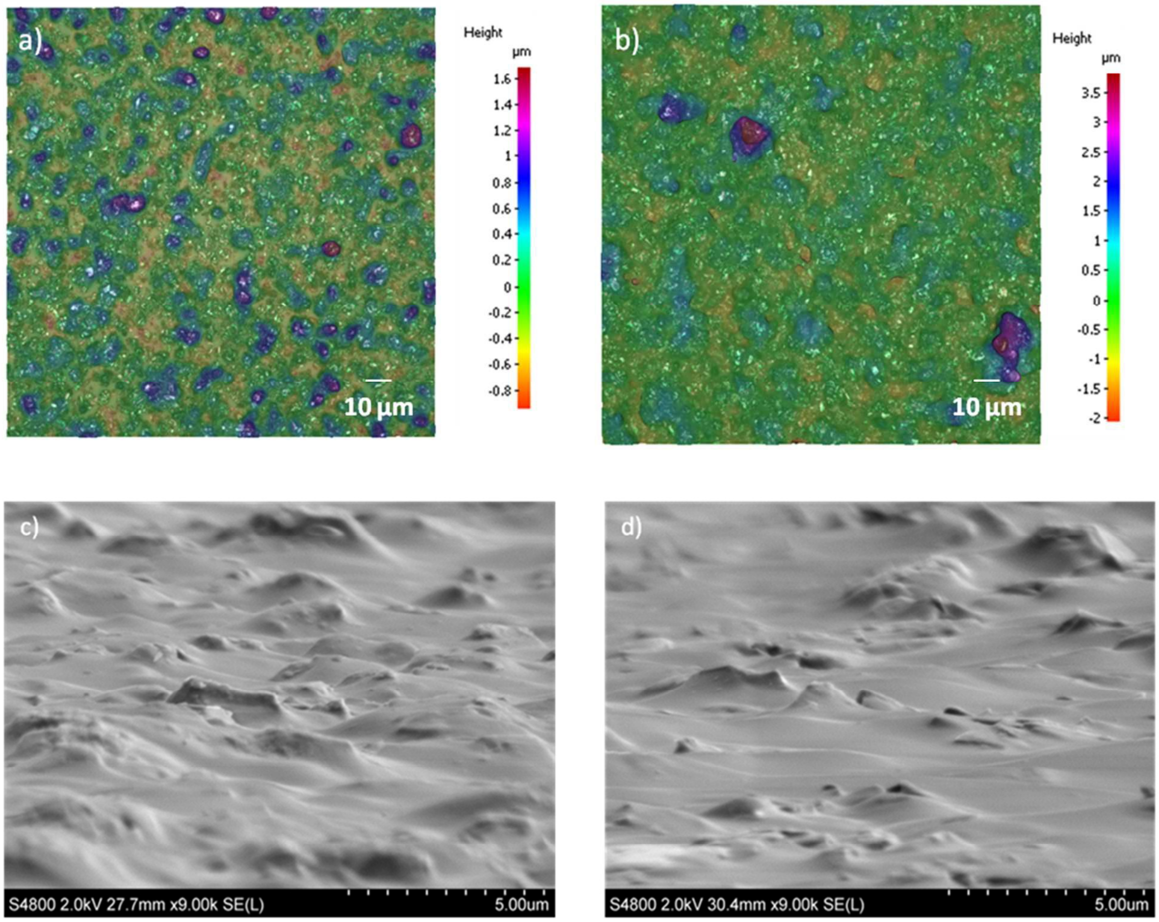

Figure 3: a) 2D image of a print with one printed layer of the GNP ink and b) 2D image of a print and two layers. On these figures individual GNP are distinguishable and the colours scale show their relative height over the surface. Figure c) and d) show the SEM images of the surface of one print of graphene ink and a print with two coating of graphene ink, respectively, at an angle of 5°. GNPs create volcano like structures on the surface.

conduction paths in the direction adjacent to the film. As the two substrates are compressed, conduction takes place via direct GNP to GNP contact at the interface, and electron tunnelling between the vertically stacked GNP in the piezoresistive coating. This vertical electron conduction differs from previously reported printed sensor where conduction takes place between two interdigitated electrodes via a nano carbon based layer.[13, 14] When a second layer is printed, GNP from the second print are stacked on the top of the GNP from the first print creating additional vertical conducting paths The thickness of a coating with two printed layers is on average 5.3 ± 0.1 µm. The resistance range of the sensor increases with the number of layers deposited, with increase in thickness and of the contact resistance. A comparison between Figure 3c) and 3d) shows that there are less GNP at the interface as the thickness of the coating increases and approaches that of the GNP planar size. Table 1) reports the average roughness (Ra) and the peak to valley height (Rz) of the coatings prior and after the compression tests. The coatings with two layers are rougher than the prints with one layer. Rough surfaces have higher contact resistance. This also contributes to widen the piezoresistive range of the sensor when the number of layer printed increases. Finally thicker layers increase the distance that electrons have to travel which increases the internal resistance of the coating.

	1 piezoresistive layer		2 piezoresistive layer	
	Ra (nm)	Rz (µm)	Ra (nm)	Rz (µm)
Non tested	414 ± 87	7.9 ± 1.1	646 ± 64	10.4 ± 1.4
After testing	381 ± 66	6.8 ± 2.7	808 ± 156	9.4 ± 0.9

Table 1: Roughness of the prints with one layer and two layer of GNP ink before and after compression testing up to 2000N.

The sensor with the architecture ITO:2GI/2GI:ITO has a piezoresistive range of 45 KΩ between pressure ranges of 66 KPa to 13 MPa. This is a significantly higher working range than reported for elastomeric binders, as reviewed by Stassi et Al.[14], or in the work by Webb *et al.* with nanoparticles[11]. Janzack[13] reported a sensor based on GNP and PVDF as non elastomeric binder. In this work, the sensor had a working range from 50 KPa to 150 MPa; however the electrode and the piezoresistive layer were separated by a dielectric separator and it was based on an interdigited structure, where the GNP layer bridged laterally the contacts, whereas the GNP layer reported here showed the absence of any lateral conductance .

The temporal response of the sensor with one layer at the bottom substrate and two layers on the top substrate is shown in Figure 4. The sensor was compressed from forces ranging from 10N to 2000N and the response was recorded over a minute. This showed a good stability of result over time, especially at increase forces. This temporal stability is enabled by the non elastomeric properties of the resin as there is no relaxation taking place in the coating.

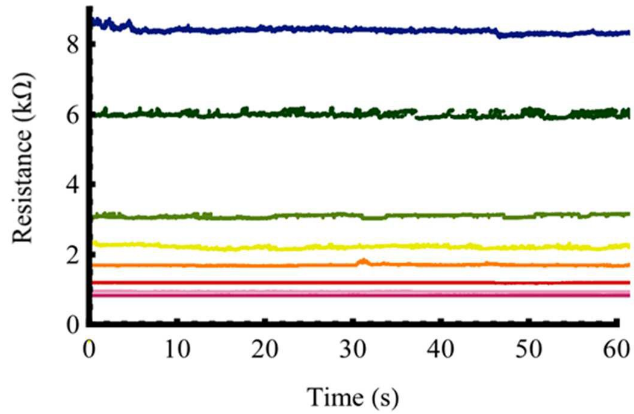

Figure 4: The temporal stability of the pressure sensor with one layer of graphene ink on the bottom substrate and two layers of GNP ink on the top substrate. The lines from top to bottom (colours blue, green, light green, yellow, orange, pink and dark pink) correspond the forces of 10 N, 30 N, 50 N, 100 N, 250 N, 500 N, 1000 N and 2000 N, respectively.

The resilience of the coating was tested. The samples were compressed 7 times for each force from 10 N up to 2000 N (for a total of 56 tests). The average roughness(Ra) and the peak to valley roughness (Rz) were measured before and after compression. The results are reported in Table 1. The roughness of a print with one layer showed good resilience with very little change it roughness. Despite the wider variance obtained the average roughness of the print with two layers of ink is in agreement with the roughness on the non compressed two layer print within the specified error.

Conclusions

A nanocomposite ink with anisotropic electrical conductivity was developed. This ink enables the production of single sensors without the need of a gap or an insulating layer. The piezoresistive range of the sensor and the rate at which the resistance decreases can be tuned by altering the contact resistance (interfacial topology) or the internal resistance (thickness).

Acknowledgements

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Screen printed pressure sensors based on direct contact of Graphene Nanoplatlets composite layers, with no intermediate physical gap, showed an effective piezoresistive response over a large force range