## Graphene-based piezoresistive strain sensors obtained via spray deposition technique

A. Rinaldi, A. Tamburrano, G. De Bellis, F. Marra, M.S. Sarto

# CNIS - Sapienza University of Rome, via Eudossiana 18, Rome, Italy andrea.rinaldi@uniroma1.it

### Abstract

The piezoresistive effect is often used in sensing applications, requiring the measurement of strain. Since the development of piezoresistive materials for strain measurement by Mason et al.[1], several efforts have been concentrated on fabricating piezoresistive strain sensors with high gauge factor and high cut-off frequency. During the last decade a new kind of strain sensors made of nanocomposites has been developed [2][3]. Very recently, innovative graphene-based nanocomposite strain sensors have been fabricated for structural health monitoring applications [4]. These sensors are characterized by a high gauge factor up to 2% strain, cut off frequency up to 50-100 kHz depending on their size, but limited sensitivity for small strain due to the polymeric matrix [4]. To overcome such limitation, sensing coating made via spray casting technique can be developed [5].

The work presented here is part of a larger study whose goal is to realize a sensing coating for structural health monitoring. The proposed sensor consists of a graphene-based film, obtained through the deposition of a colloidal suspension of Graphene Nanoplatelets (GNPs) over the substrate to be monitored. GNPs are produced by liquid exfoliation of thermally expanded Graphite Intercalation Compound (GIC) (commercially available Grafquard 160-50N), as reported in [6]. After thermal expansion of GIC at 1150°C for 5 s, the resulting Wormlike Expanded Graphite (WEG) is dispersed in 1-propanol, and the resulting mixture is tip sonicated using an ultrasonic processor, thus obtaining GNPs (Fig. 1). The sonication process is carried out with a pulsed cycle under thermally controlled conditions. The selection of 1-propanol as WEG solvent was inspired by the consideration that 1-proponol is a volatile alcohol with a low boiling point (97 °C) and more environmentally friendly than the usual WEG solvent, such as N,N-Dimethylformamide (DMF) and N-Methyl-2-pyrrolidone (NMP), used in [6]. According to Hansen theory, each materials or solvents is characterized by three Hansen Solubility Parameters (HSPs), representative respectively of the dispersive ( $\delta_d$ ), polar ( $\delta_r$ ) and hydrogen ( $\delta_H$ ) bondings. The sum of the square of the previous terms give the square of the Hildebrand solubility parameter ( $\delta_t$ ). In [7], it is reported that good solvents for graphene are characterized by a  $\delta_t$  close to the Hildebrand solubility parameter of graphene ( $\cong$  23 MPa<sup>1/2</sup>) and by HSPs  $\delta_d \cong$  18 MPa<sup>1/2</sup>,  $\delta_p \cong$  9.3 MPa<sup>1/2</sup>,  $\delta_H \cong$  7.7 MPa<sup>1/2</sup>. 1-propanol is characterized by  $\delta_t \cong$  24.6 MPa<sup>1/2</sup>,  $\delta_d \cong$  16 MPa<sup>1/2</sup>,  $\delta_p \cong$  6.8 MPa<sup>1/2</sup>,  $\delta_H \cong$  $\simeq$  17.4 MPa<sup>1/2</sup>. The  $\delta_t$  is coherent with Coleman observation in [8]. Moreover the sum between  $\delta_p$  and  $\delta_H$  is within the magic range individuated in [9] for the choice of good solvents for highly reduced graphene oxide.

Spray deposition allows a very easy, fast and uniform deposition over a large area. In case of strain sensors having dimensions of 1 cm<sup>2</sup>, in order to minimize suspension dispersion and to increase the spraying efficiency, GNP concentration should be optimized. Therefore, we investigated the stability of several suspension having different concentrations in the range from 0.05 mg/ml to 0.5 mg/ml. The highest concentration that after three weeks does not show a visible sedimentation with no visible agglomerates is the suspension with a MLG concentration of 0.1 mg/ml. Temperature control of the substrate is a key parameter in order to avoid droplets coalescence before drying; for this reason the deposition process is performed in a chamber with controlled temperature.

The selected suspension is then deposited over a polycarbonate beam having silver contact pads and a detachable mask in order to allows GNPs deposition only over the selected area.

The piezoresistive effect results from three contributions: the change of the tunneling resistance, the contact resistance between adjacent GNPs, the modification of the number of percolation conduits [10].

The produced GNP films have an average thickness of 10-30 µm. Electromechanical tests, carried out according to ASTM D70-03 and ASTM E251-92 standards, show a quasi-linear increase of the sensor electrical resistance with strain (Fig.2(a)) and a hysteretic behavior (Fig.2(b)) that disappears after 18 mechanical cycles. The reason behind such behavior is investigated through electron microscopy performed at CNIS, using a Zeiss Auriga FESEM. It is observed that before mechanical testing the film surface is rough (Fig.3(a), due to the random distribution of the GNPs resulting from the spray deposition. After a certain number of mechanical stabilization cycles, the film surface becomes smoother due to an alignment of the GNPs along the substrate surface (Fig.3(b)). GNPs reorganization is a direct consequence of the mechanical stabilization.

As shown in Fig.(4), the measured gauge factor of the new sensor ranges from 14 to 80 for strains below 0.2%. Moreover, their cut off-frequency is limited only by the substrate characteristics. These sensors show

their best performances for very small strain, typically from 1 to 2000 microstrain (as depicted in the inset of Fig.4), because for larger strain the GNPs film begins to deteriorate.

#### References

- [1] W.P. Mason, R.N. Thurston, Journal of the Acoustical Society of America. 29 (1957) 1096–1101
- [2] C. Xing; Z. Xiaohu, K. Ji-Kwan, L Xinxin, D. Lee, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures 6 (2011)
- [3] G. Yin, N. Hu, Y. Karube, Y. Li, H. Fukunaga, Journal of composite materials 45(12) 1315-1323
- [4] A. Tamburrano, F. Sarasini, G. De Bellis, A. D'Aloia, M. S. Sarto, Nanotechnology. 24(2013), 465702.
- [5] J.F.Capsal, C. David, E. Dantras, C. Lacabanne, Smart Materials and Structures, 21 (2012) 1-7
- [6] G De Bellis, A Tamburrano, A Dinescu, ML Santarelli, and MS Sarto. Carbon 49 (2011):4291-4300
- [7] E.Y. Choi, W.S. Choi, Y.B. Lee, Y. Y.N, Nanotechnology 22 (2011)
- [8] Y. Hernandez, M. Lotya, D. Rickard, S.D. Bergin, J.Coleman, Langumir 26 (2010) 3208-3213
- [9] S. Park, J.An, I.Jung, R.D.Piner, S.J.An, X.Li, A.Velamakani, R.S. Ruoff, Nanoletters 9 (2009), 1593-1597
- [10] G. D'Aloia, A. Tamburrano, G. De Bellis, M.S. Sarto, IEEE NANO 2011, Aug. 15-19 2011, Portland, (OR).

### Figures



Fig.1 SEM of a GNP flake.



Fig. 2 Sensor resistance versus strain measured at the first mechanical cycle (a) and sensor resistance variation during mechanical stabilization tests (b).



Fig.3 SEM images of the GNP film as deposited (a) and after mechanical stabilization (25 cycles) (b).

Fig.4 Gauge factor versus strain after mechanical stabilization (25 cycles).