Screen printed resistive pressure sensors fabricated from polymer composites with graphene nanoplatelets.

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Abstract

The paper presents the results of the investigation into flexible layers based on graphene nanoplatelets used as measuring layer in force sensors. Two types of sensors were designed and prepared by using screen printing methods. Compositions of graphene nanoplatelets and multiwall carbon nanotubes (for comparison) in PMMA polymer resin were prepared by modified mixing process used in thick film material preparation. Results of mechanical fatigue tests show that graphene nanoplatelets layers are as good as carbon nanotubes.

Different types of carbon-composites measuring layers were compared in the experiment. Results of bending tests conducted on graphene nanoplatelets layers showed that composition with polymer resin had good adhesion to polymer surface. Due to these properties they can by used for active measuring area in thin flexible sensors.

Resistance between sensor electrodes changes under different pressure for both types of investigated sensors. Results of the observation show that dependence between sensor resistance and force tension is linear in logarithmic scale and similar for different samples. Measurements layers based on graphene nanoplatelets in comparison with corresponding layers based on carbon nanoplatelets show relatively bigger changes for force tension changes in range 10N to 20kN. Better results were observed for sensors with comb electrodes and low content of graphene nanoplatelets in polymer resin. For example, resistance for samples with 2 wt% GNP's fillers changed during the measuring time from 370 Ω to 115 Ω, samples with 2 wt% MWCNT's changed from 110 Ω to 29Ω, while both sensors were prepared in the same way. A small hysteresis was observed in all types of sensors.

1. INTRODUCTION

Nowadays materials in nano scale attract a lot of attention. They are used in many different compositions with variant polymers. Especially interesting and popular in presents times are allotrope forms of carbon. Thanks to their extraordinary properties like extremely good mechanical properties and high electrical conductivity [1] graphene nanoplatelets (GNP's) are used for reinforcing and as a conductive additive in composite materials. Graphene layers are described in various applications like supercapacitors [2-4], FET transistors [5], photovoltaics [6], transparent electrodes [7], chemical and biochemical sensors [8-13].

Several graphene sheets create graphene nanoplatelets which are used in preparing printing pastes and inks. To deposit these inks and pastes ink jet printing as well as screen printing methods are used. Different approaches were done to investigate screen printed graphene layers [14-17]. Recent investigations on screen printed force sensors fabricated from polymer composites with carbon nanotubes were done in ITME.

2. EXPERIMENT DETAILS

2.1 Materials and Preparation of polymer thick film composites

In the present study authors used graphene nanoplatelets as a filler in composite with polymethylmethacrylate (PMMA) as a carrier with butyl carbitol acetate solvent. GNP's supplied by Cheap Tubes Inc. were obtained by chemical method. Scanning electron microscope (SEM) AURIGA CrossBeam Workstation was used to observe dimensions of graphene nanoplatelets and multiwall carbon nanotubes (MWCNT) used in experiments as a comparative materials. GNP's have average thickness of 10nm and 100m2/g of surface area and average particle diameters of 15 μm. Average diameter of the nanotubes in material used is 10-160 nm , and the length is 0,5-5 μm. Carbon nanotubes obtained by a gas phase nucleation process were produced and provided also by Cheap Tubes Inc. Images of nanomaterials were made in Warsaw Institute of Electronic Materials Technology (ITME).

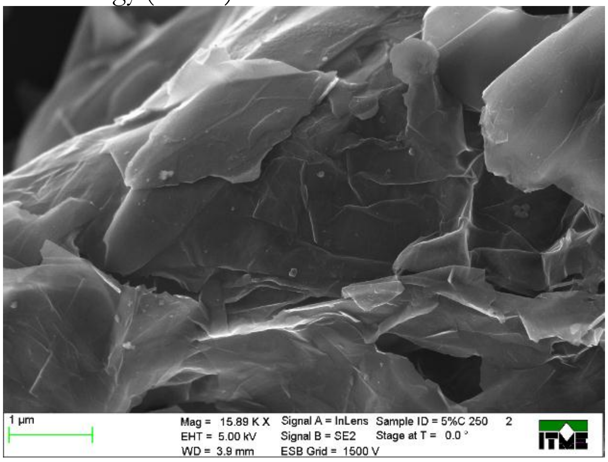

Fig.1. SEM image of used Graphene Nanoplatelets (GNP's) material.

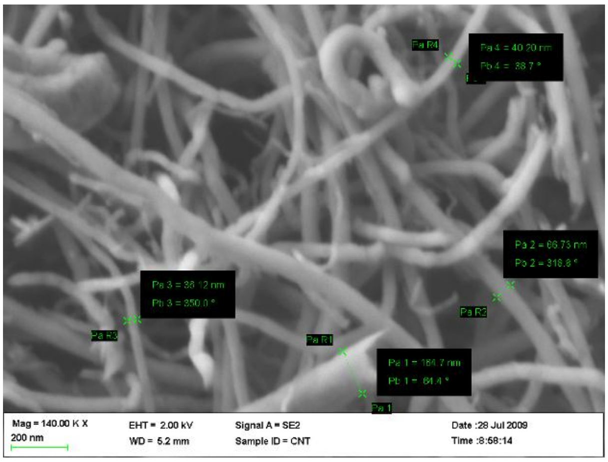

Fig.2. SEM image of used Carbon Nanotubes (MWCNT) material.

Screen printing method was used by authors to prepared samples. Several types of pasts with different concentrations of graphene or nanotubes were done. Nano carbon fillers in toluene solution were sonicated for 60 min at room temperature. After evaporation of toluene graphene nanoplatelets and carbon nanotubes with PMMA matrix were rolled twice on three roll mills with silicon carbide (SiC) roller. Composite materials were fabricated with different amount of GNP's: 3wt%, 2 wt%, 1,5 wt% and 1,25 wt%. For comparison, pastes with 0,25 wt%, 0,5wt% and 2wt% MWCNT's concentrations were used. Samples prepared on screen printer AMI Presco typ 242 were cared at 120°C for one hour.

2. 2 Screen printed resistive pressure sensors

Two types of sensors were designed for experiment. Sensor structure was fabricated by printing polymer-nanoplatelets or polymer-nanotube areas with polymer-silver paths as connection electrodes on substrate foil.. Second type of sensors was prepared with two comb electrodes and single carbon measuring layer. Both types of sensors showed on figure **Fig.3** and **Fig.4** were screen printed on 125μm polymer substrates and on 80 μm kapton, a polyimide film developed by DuPont.

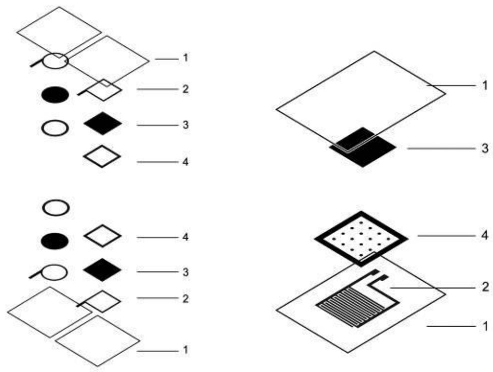

Fig.3., Fig.4. Two types of screen printed resistive pressure sensors:
1 - polymer substrate, 2 - silver electrode with path, 3 - carbon nanotube layers, 4 - distance,

First type of sensors (fig.3) with the same two parts facing each other were prepared for three resistive pasts with 3 wt% GNP's, 2 wt% GNP's and 2 wt% MWCNT's addition. To print the second type sensors pressure-sensitive layers pasts with 1,25 wt% GNP's, 1,5% GNP's and 0,25 wt% MWCNT's, 0,5 wt% MWCNT's concentrations were used. Silver paint L-121 produced by ITME were used to screen print electrodes and conductive paths on substrates foil. Substrate was warmed at 150 degrees for one hour to prevent changes in the dimensions of the substrate during the curing of the printed layers. Combo electrode paths thickness of 0.35 mm spaced 0.3 mm were cured at 130 degrees for half an hour, similarly for the other silver paths. Barium titanate ($BaTiO_3$) was used to screen print nonconductive distance layer in sensor, cured at 120 degrees for 0,5 hour.

2.3 Experiment

Screen printed samples (fig.5.) from polymer-resistive past with silver contact were prepared for banding tests and resistance per square measurements. Electrical and mechanical properties of screen printed layers were examined.
Ten paths on test samples had different length. Paths resistance was measured and results were divided by

the multiple widths to determined resistance per square of screen printed layers. Samples adhesion to polymer and polyimide substrate were checked during the mechanical fatigue test. Durability of printed layers was tested by bending repetitively, while resistance was being measured.

Fig.5. Screen printed sample for electrical and mechanical tests.

Contact Profilometer Dektak 150f-my Vecco was used to measure thickness of printed layers.

Sensors prepared for the experiments were placed in hydraulic press, and pressure was applied to pressure-sensitive resistive area. Results of the measurement were recorded with a frequency of 20 per second on a computer. Resistance changes at the electrodes were confronted with changes in the forces.

3. RESULTS AND DISCUSSION

3.1 Properties of elastic graphene films

Samples prepared for fatigue tests were previously measured, and average resistance per square was designated. Results are summarized in table 1.(**Tab.1.**) Sample based on graphene nanoplatelets and multiwall carbon nanotubes were prepared in the same way. Screen printed layers based on carbon fillers were cured at 120 degrees for half an hour. The average thickness of the layers was 10 um, and it was constant for all samples.

Tab.1.

Results of resistance per square measurement.

Sample	Resistance [kΩ/□]
1,25 wt% GNP's	617,3
1,5 wt% GNP's	23,4
2 wt% GNP's	8,4
3 wt% GNP's	0,734
0,25 wt% MWCNT's	41,7
0,5 wt% MWCNT's	11,4
2 wt% MWCNT's	2,1

As amount of the nanoplatelets or nanotubes filler in pastes decreased, resistance of printed layer increased. Paths length of 20 mm, from 1 to 20 squares were bended by radius of 4 mm. During the fatigue test paths resistance were measured repeatedly. The effect of bending of the GNP's and MWCNT's samples during 60 000 cycles changed the resistance insignificantly (2-3%).

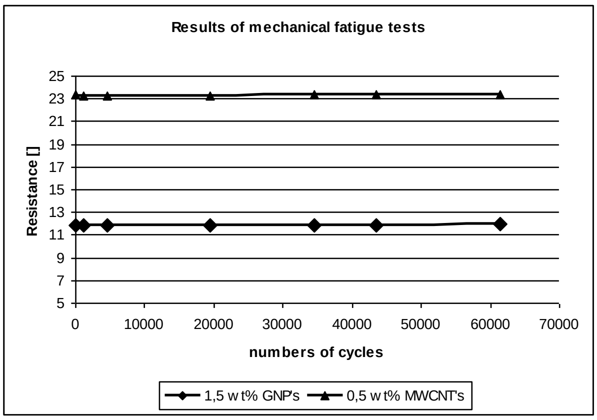

Fig.6. Results of the mechanical fatigue tests.

Fatigue tests conducted on graphene nanoplatelets layers showed that composition with polymer resin has good adhesion to polymer surface. Due to this properties they can by used for active measuring area in thin flexible sensors.

3.2 Characteristics of screen printed sensors

In figure 7 results from measurements of resistance changes for sensors with two resistive layers are presented. All the characteristics are similar to the linear. Resistance changes for sensors based on past with GNP's fillers were much larger than similar with MWCNT's. A wider range of resistance in the same measurement area for GNP's based composites makes them more appropriate fillers to produced accurate sensors.

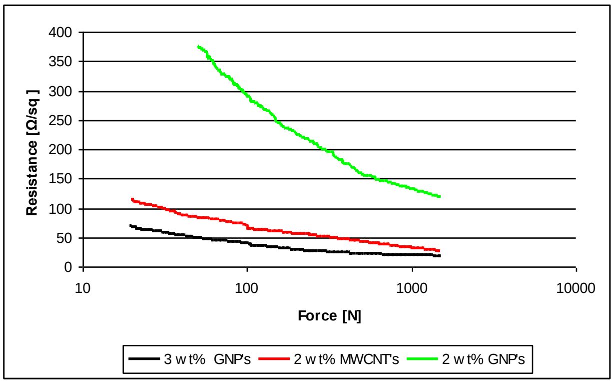

Fig.7. Resistance changes under pressure on a logarithmic scale for the sensors 2 wt%, 3 wt% GNP's and 2 wt% MWCNT 's shown on fig. 3.

Sensors based on paste with 2 wt% GNP's content between 50 and 1500 [N] show resistance changes from 370 to 120, while sensors based on CNT reacted from smaller loads (20 N), but resistance changed from 110 to 27.

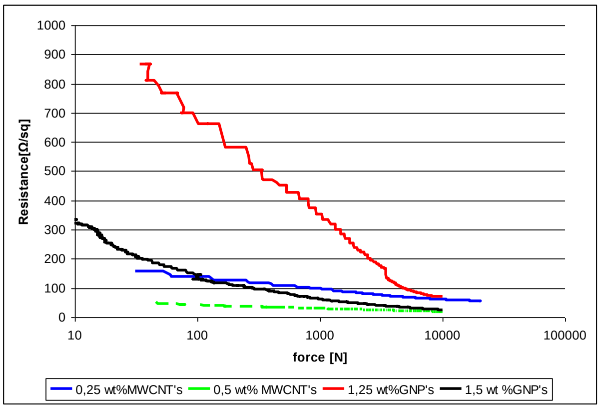

Fig.7. Resistance changes under pressure on a logarithmic scale for the sensors1,25 wt%, 1,5 wt% GNP's and 0,25 wt%, 0,5 wt% MWCNT 's shown on fig.4.

Sensors with comb electrodes were tested for resistive layers printed from pasts with the content of filler in the percolation threshold near. As in previous type of sensors, sensors based on GNP's are characterized by larger resistance changes. Resistance for samples from pasts near threshold were higher for both types of fillers.

A small hysteresis was observed in all types of sensors. Measurement errors were + / - 5%.

4. Conclusion

Resistance between sensor electrodes changes under different pressure for both types of investigated sensors. Results of the observations show that dependence between sensor resistance and force tension is linear in logarithmic scale and similar for different samples. Measurements layers based on graphene nanoplatelets in comparison with corresponding layers based on carbon nanoplatelets show relatively bigger changes for force tension changes in range 10N to 20kN.

Sensor designed with comb electrode can be used in subsequent studies to prepare sensor matrix. Preparing and checking pasts with GNP's content between 1,5 wt % and 2 wt % is necessary. Electronic measuring system with microcontroller and network of comb electrodes will be used to compile 3D maps of pressure. This can be used for early detection of flat feet in children of school age.

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