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Abstract Book

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Contents

Elatomer - nanographite composites for large scale pressure and impact sensing J. Zavickis¹, M. Knite¹, A. Linarts¹, L.Matzui², R. Orlovs¹

J. Zavickis, M. Knite, A. Linarts, L.Matzui, R. Oriovs

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Electro-conductive polymer nanocomposites have been intensively used as a new structural and functional materials over last decades. They possess all benefits of light, easy to produce and cheap polymer materials, combined with advanced electrical and structural properties. Electrical percolation in carbon particle filled rubbers is well known phenomena, but only recently it has been shown, that at certain concentrations of conductive filler, these composites exhibit remarkable mechano-electrical effects (piezo- and tenzo-resistivity). In our work we have used polyisoprene – nanographite composites (PNGC) as a hyperelastic piezoresistive material for elaboration of soft pressure sensors. As excellent conductive filler different nanographite powders have been proved for sensitive composite material. They were: graphitized high structured carbon black, carbon nanotubes and thermo-exfoliated graphite flakes as well. Such sensors can be made in different sizes and shapes so they can be easily tailored to meet specific requirements. They are proved to be functional for uniaxial operational pressures up to 1 MPa and can be successfully used in different industrial and engineering applications, like civil security, industrial monitoring, robotics, traffic surveillance and many more. In this work we reveal the basic concepts, necessary to successfully obtain piezoresistive PNGC, as well as to investigate their mechano-electrical properties. We propose the concept of entirely hyper-elastic piezoresistive pressure sensor element, which can be made from rubbery structural parts only, thus providing outstanding mechanical integrity and resistance to mechanical impacts.

Exceptional enhancement of photoluminescence lifetime of ZnO nanorods making use of thiourea

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Zinc oxide (ZnO) is a wide band gap ($E_g \approx 3.37$ eV at 300 K) semiconductor with good carrier mobility and can be doped n-type or p-type. It has many applications in much important area such as ultraviolet light emitting diodes and nanolaser. ZnO shows pronounced excitonic effects at high temperatures (> 300 K) due to its large exciton binding energy (60 meV). The material quality and optical properties of the nanostructures such as ZnO are commonly followed by using the photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements. TRPL provides significant information in relation to the exciton lifetime which is an important indicator for the material quality and efficiency of the radiative recombination. The lifetime is related to the radiative decay of the exciton polariton and various non-radiative processes, such as leak by deeplevel traps, low-lying surface states, and multiphonon scattering. The exciton polariton photoluminescence is, however, quite sensitive to the amount of defects and structural factors of the nanostructures. Different deposition methods as well as growth conditions play a key role for ZnO nanostructures. The important one is chemical spray pyrolysis system which is elegant method to the preparation of good-quality ZnO nanostructures. This method has some advantage over the other methods as short time, cost-effective, catalyst, template-free. In present study, in order to obtain smaller ZnO nanorods, which is highly desirable in nanotechnology applications, we doped a little amount of thiourea (tu:CH4N2S) into zinc chloride (ZnCl2) solution. ZnO nanorods and ZnO nanorods containing thiourea have been made on a cheaper ordinary glass by the chemical spray pyrolysis method at different substrate temperatures. Their optical and structural properties have been analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and time-resolved photoluminescence (TRPL) techniques. The diameters of the ZnO nanorods decreased and, their height increased with containing thiourea additive. Besides, the photoluminescence lifetime of ZnO nanorods and ZnO nanorods containing thiourea were determined as $\tau = 1.56 \pm 0.05$ ns ($\chi = 0.9$) and $\tau = 2.12 \pm 0.03$ ns ($\chi = 1.0$), respectively. It was reported that the lifetime of ZnO nanorods was increased by thiourea addition because of the change of the dimension of ZnO nanorods containing thiourea compared to ZnO nanorods without thiourea.



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Elastomer - nanographite composites for large scale pressure and impact sensing

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Abstract: Electro-conductive polymer nanocomposites have been intensively used as a new structural and functional materials over last decades. They possess all benefits of light, easy to produce and cheap polymer materials, combined with advanced electrical and structural properties. Electrical percolation in carbon particle filled rubbers is well known phenomena, but only recently it has been shown, that at certain concentrations of conductive filler, these composites exhibit remarkable mechano-electrical effects (piezo- and tenzo-resistivity). In our work we have used polyisoprene nanographite composites (PNGC) as a hyperelastic piezoresistive material for elaboration of soft pressure sensors. As excellent conductive filler different nanographite powders have been proved for sensitive composite material. They were: graphitized high structured carbon black, carbon nanotubes and thermo-exfoliated graphite flakes as well. Such sensors can be made in different sizes and shapes so they can be easily tailored to meet specific requirements. They are proved to be functional for uniaxial operational pressures up to 1 MPa and can be successfully used in different industrial and engineering applications, like civil security, industrial monitoring, robotics, traffic surveillance and many more.

In this work we reveal the basic concepts, necessary to successfully obtain piezoresistive PNGC, as well as to investigate their mechano-electrical properties. We propose the concept of entirely hyperelastic piezoresistive pressure sensor element, which can be made from rubbery structural parts only, thus providing outstanding mechanical integrity and resistance to mechanical impacts







Fig.3 TEM picture of high aspect ratio carbon nanotubes. Scale mark 200 nm

Fig.4 TEM picture of thin gold coated thermally exfoliated graphite flake. Scale mark 100 microns

Experiments and results: It has been proven previously, that in the middle of electrical percolation transition, similar conductive rubber composites exhibit large and reversible tenzo- and piezo-resistive effect [1]. The optimal concentrations of each filler were found out to obtain the rubber composite with best possible piezoresistive properties: 8 m.p. for CB, 9 m.p. for SCNT, 5 m.p. for LCNT and 15 m.p. for TEG filled composites. Such compositions were used to elaborate the single completely hyperelastic sensing element (CHSE). CHSE were made using double stage vulcanization technique, where elementary parts of sensor element (sensitive element 2, rubber electrodes 3&4 and isolative shell 1) were made of the same kind of PI rubber, only with different concentrations of electro conductive carbon. They were pre-vulcanized on the first stage, then they were assembled as shown in Fig.5 (left) and then suspected to final vulcanization, thus cured together into monolithic peace of rubber. Only small wires were added to the structure of the sample to help to make electrical connection for measurements. Electrodes were always wires were added to the structure of the sample to help to make electrical connection for measurements. Electrodes were always made from CB filled rubber, with CB concentration high enough to maintain good and unchanging electrical conductivity (usually around 8 to 12 m.p.). The relative comparison of piezoresistivity for such elements is shown on Fig.8. As it can be seen, TEG filled rubber composite showed best piezoresistivity for forward cycle, in the same time suffering from comparably highest hysteresis on unloading cycle. Both CNT filled CHSE showed comparably lower piezoresitivity, but still retaining serious hysteresis. CB filled CHSE revealed the absolutely lowest piezoresistivity, but scored highest with practically no hysteresis. By using the same concept of two stage vulcanization and CB filled sensitive elements, two types of CHSE mat were designed and successfully elaborated, connecting piezoresistivity elements in parallel and in series. They were tested for piezoresistivity and showed replicable results for mapped elements (Fig.9) and good overall piezoresistivity for series elements (Fig.10). However there were a downedrit tendency of the overall electrical electrical resistive tendency on the same time suffering which can be attributed to the there were a down-drift tendency of the overall electrical resistivity for series connection, which can be attributed to the differences of piezoresistive behavior of individual elements.



NR/R。(%) 0,6 P (kPa) Fig.10 The overall piezoresistivity of with 6 CB filled sensing elements co series (Fig.7 right) overall piezoresistivity of CHSE mat

1.2

0,9

Conclusions

- It has been proven, that piezoresistive elastomer nanographite composites can be made from all specific conductive 1) nanographite fillers provided: Graphitized carbon black, short and long aspect ratio conductive carbon nanotubes and thermally exfoliated graphite as well.
- Despite thermally expanded graphite filled sensor shows the best piezoresistivity in forward cycle, it suffers from 2) remarkable hysteresis when relaxed. It can be explained by large surface area of separate entangled graphite flakes, making them difficult to rearrange after the removal of load.
- Short aspect ratio carbon nanotube filled sensor revealed good piezoresistivity, in the same time still retaining 3) somehysteresis, thanks to their aspect ratio and reduced mobility in the composite structure. Piezoresistivity of carbon black filled sensor can be accounted as completely reversible, thanks to the small size and
- 4) good mobility of carbon particles.
- Completely hyperelastic pressure sensing mat can be made, using double stage vulcanization technique, by assembling pre-vulcanized structural elements with different concentrations of electroconductive filler. The sensitive 5) elements can be arranged in series or parallel connection all and encoded and proposed usage criteria. They are mechanically integrate, soft but strong substitute for conventional large area pressure sensors. Similar CHSE can be used in various industrial and civil branches for relative detection and mapping of pressure.
- 6)

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Materials and methods: Natural polyisoprene (PI) rubber (grade SWR-3L) was used as a matrix for all compositions. The classical vulcanization system was mixed used as a finality to all compositions. The classical volcanization system was fined into to raw caoutchouc on cold rolls, including sulphur, ZnO, Stearic acid and Cyclohexilbenzothiazole sulfenamide. Four types of nanostructured carbon fillers: extra conductive highly structured carbon black (CB, Degussa Printex XE2), short and long aspect ratio carbon nanotubes (SCNT and LCNT, producer -SigmaAldrich) and thermally extoliated graphite (TEG) were used as various conductive fillers. To achieve uniform dispersion, they were introduced into matrix using solvent mixing technique in chloroform. The TEG was kindly supported by L.Matzui from Kyiv National Taras Shevchenko University, Department of Physics, Ukraine. The concentration of fillers were expressed as relative mass parts, added to 100 mass parts of raw PI caoutchouc. The materials were tested on piezoresistivity using Zwick/Roell Z2.5 universal materials testing machine, coupled with advanced electrical measurement system, consisting of Agilent A34970 digital multimeter and Keithley 6487 picoammeter.



Fig.5 CHSE with single sensor configuration (on the right). Diameter of the whole element – 18 mm. Elemental parts in the left picture: 1) Isolative and protective 2) Piezoresistive rubber ele 4) Electrically conductive rubb 5) Small wires



Fig.6 Unassembled elementary layers of completely hyperelastic piezoresistive sensing mat. From left to right: cover layer, electrode layer, layer with piezoresistive elements, electrode layer and cover layer.



Fig.7 Two types of CHSE matswith 6 piezoresistive elements: Left side – sensitive elements connected in parallel. Such design is applicable for determination of relative pressure distribution. Right side – sensitive elements connected in series, giving integral response to relative pressure over all area of the mat. Elemental parts in the upper drawings: 1) Isolative and protective shell; 2) Piezoresistive rubber element; 344) Electrically conductive rubber electrodes; 5) Small wires.

Proposed branches of application includes, but are not limited to:

- Medicine and orthopedics
- Sensitive bushings and dampers
- Smart vibration detection and management
- Control of traffic and pedestrians



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 Security systems Tactile sensors of robotics