Surface & Coatings Technology 299 (2016) 22–28

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Foldable and electrically stable graphene film resistors prepared by vacuum filtration for flexible electronics

Xin Jiang [a,b], Rujing Zhang [b], Tingting Yang [a,b], Shuyuan Lin [a,b], Qiao Chen [a,b], Zhen Zhen [a,b], Dan Xie [c], Hongwei Zhu [a,b,*]

[a] State Key Laboratory of New Ceramics and Fine Processing, and MOE Key Laboratory for Advanced Materials, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China
[c] Tsinghua National Laboratory for Information Science and Technology (TNList), Institute of Microelectronics, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 23 February 2016
Revised 26 April 2016
Accepted in revised form 28 April 2016
Available online 29 April 2016

Keywords:
Graphene
Resistor
Flexible
Electronics

ABSTRACT

Flexible electronics have shown great application potential in mobile telemedicine, man-machine interaction system, and smart robotics. As a key electronic element, resistor's electrical properties should remain stable over their bending range of operation. Here, a shortcut fabrication strategy, vacuum filtration and cutting, to construct foldable and electrically stable graphene-based film resistors are demonstrated. Through investigation of resistor behavior under different stress conditions, it is found that micro-cracks appeared on the surface are correlated to curvature and percolation theories. The effects of ionic cellulose ethers on the contact state of graphene layers under tension and bending are investigated, which efficiently prevent surface crack from happening. This rapid fabrication method to carry out individual customization may further realize other environmental friendly, portable and multifunctional devices.

1. Introduction

Development of rapid prototyping for flexible electronic circuit is critically significant for flexible electronic devices such as mobile telemedicine electronic skins [1–2], flexible displays [3], flexible energy device [4–5], human-machine interaction system [6–7] and so on. Graphene, a two-dimensional carbon nano-material, is comprised of a single sheet of sp^2-bonded carbon atoms, exhibits extraordinary properties which gains intensive attention since its first isolation by Geim and Novoselov in 2004 [8]. Graphene shows great potential in the application of flexible electronic devices with current densities [9] up to 4×10^7 A/cm^2, and outstanding mechanical [10] and optical properties [11]. It has been applied in many different types of flexible devices, including flexible electronic circuits, flexible energy conversion/storage devices [12–13], strain/chemical sensors [14–15] and so on. Meanwhile, several methods have been demonstrated for preparation of graphene films optimizing various characteristics, such as uniformity, cost, reproducibility and practicability. Chemical vapor deposition (CVD) and mechanical exfoliation have been applied efficiently in preparation of high-quality graphene [16], while it is relatively more complicated for mass and rapid production. Graphene nano-platelets prepared by liquid phase method could be easily achieved in high-quality batch-production. Therefore, it is very meaningful for flexible device to achieve rapid fabrication based on liquid-phase-processable graphene, like printing technology [17], direct pen-writing [18–19], self-assembled film [20–21] and so on. The vacuum filtration method is a rapid manufacturing process to assemble different kinds of materials like nano-platelets and nanoparticles into macroscopic film for various applications [22]. This process provides an easy method for achieving low-cost, rapid and functional material integration, which makes it a promising method for various functional films. Graphene nano-sheets could also be quickly deposited and assembled to macroscopic film by vacuum filtration, which contain layer-by-layer structure. However, it is quite common for layer-by-layer structure to lose its electrical stability due to the cracks existed in the overlapped sheets structure under bending state. To date, many groups have measured the performance stability of flexible devices after cycles [23–25], and the mechanical stability is quite important for developing suitable applications. Understanding the mechanism of surface cracks happened under folded state has great significance for achieving high electrical stability. Therefore, the modification of conductive ink for vacuum filtration is a key parameter. Ionic cellulose ethers, which act as the surfactant assistant due to its functional group, has positive effect on the contact state of graphene layers, and further influence the film morphology under tension and bending. However, achieving better performance stability during the bending state is still challenging.

The electronic circuits are composed of basic components, namely resistors, inducers and capacitors. Conventionally, the electronic

* Corresponding author at: Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China.
E-mail address: hongweizhu@tsinghua.edu.cn (H. Zhu).

http://dx.doi.org/10.1016/j.surfcoat.2016.04.066
0257-8972/

components are fabricated by complex procedure with high environmental requirement and expensive facilities. Several studies about graphene resistors based on graphene films grown by chemical vapor deposition has been carried out [26–27]. However, there were few works focusing on the foldable resistor fabrication based on graphene made by liquid phase method, which will enable rapid, low cost and convenient fabrication. Here we introduce a rapid prototyping process of foldable and electrical stable graphene film resistor by vacuum filtration. We measured the graphene resistor's electrical behavior and surface morphology with different stress and applied the device to the foldable circuits with a LED chip, which showed stable performance under different kinds of deformation conditions. It is found that ionic cellulose ethers have positive influence on the contact state of graphene layers under tension and bending, preventing micro-cracks on the surface.

2. Experimental

2.1. Preparation of the graphene conductive ink

The graphene powder (XF001W, XF Nano) was prepared by physical exfoliation of natural graphite. Graphene powder was dispersed in water at a concentration of 0.1 mg/mL. CMC (Shanghai Reagent, 200 cP at 20 g/L) was dispersed in the solution at a concentration of 0.25 mg/mL, with poly(4-styrenesulfonic acid) (PSS, Sigma-Aldrich, molecular weight $\approx$ 75,000) as assistant at a concentration of 0.1 mg/mL. Then a non-contacting sonication system was used to sonicate the dispersion for 4 h at 50 W to disperse graphene power into graphene conductive ink. The detail of graphene conductive ink is discussed in the Supplementary materials.

In Fig. S1, the graphene conductive ink, formed by graphene aqueous solution with ionic cellulose ethers as assistant agent, namely carboxymethyl cellulose (CMC), could be produced in large-scale. The dispersion status of graphene ink modified with CMC is much better, which has significant influence on the preparation of the graphene film as shown in Figs. S2 and S3. The structure of the starting graphene material was evaluated based on the SEM/TEM images in Fig. S2. The Fourier transform infrared (FTIR) spectra in Fig S4 prove that the CMC was successfully introduced to the surface of the graphene.

2.2. Preparation of graphene-based resistors

The Nylon membrane filter (diameter 50 mm, pore size as 0.22 μm, Taoyuan Company) was applied in graphene film assembly, and the graphene film was cut directly by scissors or knife with grid paper assisted. Then two ends of the obtained graphene film were daubed with the rectangular silver (Ag) paste to lead to the conductive line. To test the electrical properties under stress, transparent adhesive tape was pasted on the surface of the graphene-based resistor.

2.3. Characterizations

SEM was recorded with LEO 1530 (5 kV) for graphene film resistors' morphology characterization. TEM was recorded with JEM-2010 (120–200 kV) for the graphene sheets' structure characterization. The current-voltage curve and the resistance were measured by digital universal meter (Keithley 2601). The square resistance was tested by four-point probe measuring instrument produced by 4 PROBES TECH. Raman spectra were collected by LabRAM HR Evolution (He-Ne laser excitation at 532 nm, 5 mW). The FTIR spectrum was performed with a Spectrum GX FTIR system. The step profiler (Bruker Corporation, DektakXT) measurement was employed to measure the thickness of graphene film.

3. Results and discussion

3.1. Fabrication process

The processing method could rapidly fabricate film resistors with different resistances from graphene conductive ink in <10 min, namely individual customization. As shown in Fig. 1, the foldable graphene-based resistor process could be divided into two steps. The first step is to assemble the graphene nano-sheets into graphene film by vacuum filtration and it takes less than 5 min. Under the vacuum induced pressure, the graphene nano-sheets in graphene ink were uniformly deposited on the membrane filter. The membrane filter is made by nylon with pore size of 0.22 μm and filtering diameter of 4 cm in this system. Then, the second step involves the cutting of graphene film on the membrane with scissors, while figure and resistivity could be totally self-defined, and it takes less than 5 min. This method should be commonly used for assembling other kinds of two-dimensional materials into flexible devices. One could customize the resistance of graphene film resistor with graphene conductive ink, and the key preparation parameter of graphene film resistors was demonstrated in Fig. 2.

3.2. Characterization of graphene resistor

The surface morphology was measured by scanning electron microscope (SEM) and optical microscope to demonstrate the percolation theory in graphene film. Some small cracks on the graphene film would weaken the electrical conductivity, while increasing the amount of graphene dispersion could decrease the amount of cracks, as shown in Fig. 2a–b. The assemble of micrometer sized graphene sheets forms percolative network of graphene layers, and the overlap between neighboring flakes occurs [28] when the volume of graphene conductive ink is high enough. Charge transportation in the graphene film occurs via overlapped graphene sheets as indicated by the schematic diagram of percolation theory shown in the Fig. 2c. The electrical property changes according to the percolation theory, and this phenomenon is quite similar with other groups' result [28]. According to the percolation theory, the fact that critical exponents are greater than three is a consequence of strictly geometrical effects and tunnelling effects. At higher graphene dispersion amounts, the graphene sheets set up a stable conductive system which leads to rapid change in resistance as indicated by the curve fit in Fig. 2d. The percolation threshold was found experimentally to occur at graphene dispersion of ~8 μg/cm^2. The percolation threshold could be modified by improving dispersal uniformity, and the effect of CMC on graphene films' surface morphology is shown in Fig. S5. The graphene conductive ink without CMC has higher percolation threshold as 15 μg/cm^2, higher resistance with same amounts of ink and rough surface.

The major parameters of customizing graphene film resistors with certain resistance are shown in Fig. 2e and f. According to the Pouillet's law, the electrical resistance is $R = \rho L/A$, where ρ is the electrical resistivity, L is the length of the resistor, and A is the cross-sectional area of the resistor. The resistance of graphene film resistor is represented as a linear function of resistors' width or length, which matches the Pouillet's law correctly. Through controlling those parameters, the graphene film resistor could be produced with various resistances, especially in the high value range. Therefore, this rapid method could be applied in customize production of graphene resistor.

3.3. Electrical properties

The volt-ampere characteristic of the graphene film resistors shows that they are linear resistors (Fig. 3a and b). In the photographs of graphene film resistors, it shows that resistors with different resistances have various orders of grey color. The resistors with lower resistance look darker, and the ones with higher resistance looks grey. Just as traditional resistors, the graphene film resistors could be connected in