CARBON 86 (2015) 69–77

Available at www.sciencedirect.com

ScienceDirect

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

Biaxial compressive behavior of embedded monolayer graphene inside flexible poly (methyl methacrylate) matrix

Guorui Wang [a,b], Luqi Liu [a,*], Zhaohe Dai [a,c], Qing Liu [a,c], Hong Miao [b], Zhong Zhang [a,*]

[a] National Center for Nanoscience and Technology, Beijing 100190, PR China
[b] Department of Modern Mechanics, University of Science and Technology of China, Hefei 230026, PR China
[c] University of Chinese Academy of Science, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 9 October 2014
Accepted 13 January 2015
Available online 20 January 2015

ABSTRACT

We systematically investigated the in-plane biaxial compression behavior of the monolayer poly (methyl methacrylate) (PMMA)/graphene/PMMA system by in situ Raman spectroscopy. The shifts of Raman G-band peak position exhibited three-stage features with increasing compressive strain, including elastic deformation, local Euler-buckling and continuous compression. Our results demonstrated that the mechanical stability of graphene based flexible electrodes greatly depended on the deformation modes, applied strain level and interfacial adhesion. The embedded graphene sheets performed reversible compressibility at lower strain level over many cycles. With further increasing compressive strain, the strain distribution of the embedded graphene sheet turned non-uniform, and the interfacial debonding occurred. An analytical model based on the mechanical instability theory was proposed to depict the interfacial debonding behavior of individual graphene sheet, which agreed well with the experimental results.

1. Introduction

Stretchable and flexible electronics have drawn great attention over the past decade due to their good flexibility, lightweight, transplantable, and portable capabilities. To meet various desires required by flexible electronics, many alternative transparent electrodes have been developed to replace commercially available indium tin oxide (ITO) electrodes, and materials used include metal grids [1], metallic nanowires [2], conductive polymers [3], and carbon nanotubes (CNTs) [4,5]. Recently, the discovery of graphene brought a new alternative to conventional ITO electrodes due to its unique combination of extraordinary electrical, optical and mechanical properties [6]. Many research groups have demonstrated the resilience of graphene based flexible electrodes as a promising candidate in a wide range of applications, such as field effect transistors (FETs), solar cells, organic light-emitting diodes (OLEDs), touch screens, and electrochemical sensors [7–9]. Apart from the high electrical, optical performance as required by flexible opto-electronic devices, the mechanical stability of electrodes and recoverability under deformation were major factors to determine the device stability and durability. Various mechanical deformations such as tension, bending, and twisting would apply to the device under the various harsh working conditions during the fabrication, assembling, and manipulation processes. The

* *Corresponding authors:* Fax: +86 10 6265 6765 (L. Liu), +86 10 8254 5586 (Z. Zhang).
E-mail addresses: liulq@nanoctr.cn (L. Liu), zhong.zhang@nanoctr.cn (Z. Zhang).
http://dx.doi.org/10.1016/j.carbon.2015.01.022
0008-6223/

occurrence of mechanical failure (e.g. interfacial delamination) could severely deteriorate the performance and reliability of device when the desired properties of the flexible devices are proposed to be tunable through reversible and repeatable mechanical manipulation [10,11]. Therefore, it is crucially important to monitor the mechanical responses of flexible electrodes under various stress states, evaluate the interface stability and recoverability, clarify the possible failure modes as well as the limit of strain-induced irreversible structure deformation.

As determined by the stiffness of substrates, electrodes as well as their microstructure features, the mechanical design is generally required for the flexible electrodes to fulfill the desired properties when subjected to repeatable mechanical manipulation. For example, the wrinkled, rippled and/or crumpled microstructure features were introduced to graphene based rubbery electrodes to endow it with good recoverability under cyclic mechanical stretching [12]. However, from the viewpoint of the mechanical stability of graphene based flexible electrodes, earlier works have concentrated on the loading role of monolayer or few-layer graphene sheets carried, interfacial shear stress, and the possible deformation mode of the graphene sheets under tensile and compressive mode [13–16]. For example, Young et al. monitored the strain distribution of the embedded graphene inside PMMA beam under tensile deformation. The experimental data indicated that strain distribution was relatively uniform at low applied strain levels, but became highly non-uniform above certain strain level due to the crack propagation of the resin layer [17]. Later, Galiotis and coworkers investigated in detail both stress uptake and buckling strain of embedded graphene under compressive deformation. The critical buckling strain was found to be greatly dependent on the length to width ratios (l/w) of individual graphene platelets, and a permanent wrinkle was formed after cyclic deformation [18]. In addition, theoretical simulation based on coarse-grain model has predicted the possible buckling deformation of the embedded graphene under compression, and found that the buckling mode greatly depends on the adhesion strength and effective stiffness of graphene and substrate [19]. It should be noted, however, that the mechanical mode aforementioned is relatively simple, and it is not comparable to the deformation states of flexible electrodes suffered in reality. In general, for thin solid film based flexible electrodes, the stress states of the embedded graphene platelet suffered at least come from biaxial directions.

Raman spectroscopy is an inelastic photo scattering spectrum, which reflects unique information concerning the vibration and electronic properties of materials. It has become a powerful technique to identify the structures of carbon materials such as the diameter and distribution of carbon nanotubes, their metallic or semiconducting nature, the number of graphene layers, and the crystallographic orientation of graphene [20–23]. Furthermore, due to the high sensitivity to shift-induced symmetry, the non-destructive quality, and the ability to be used in micro-analytical studies, Raman spectroscopy has been successfully utilized to unravel microstructure deformation of carbon materials suffered under the external loads [24,25].

To reveal the mechanical response and evaluate mechanical stability of the embedded graphene inside plastic matrix, herein, we systematically investigated the mechanical deformation of the embedded graphene when subjected to in-plane biaxial compression as induced by thermal shrinkage method. The compressive deformation modes of the embedded graphene sheets were monitored by in situ micro-Raman spectroscopy. Interestingly, unusual three stages of mechanical deformation were observed during compression process: namely, elastic deformation, local Euler-type buckling, and continuous compression. On the basis of the shifts of specific Raman band, we calculated the compressive stress acting on the individual graphene sheets, estimated the effective flexural rigidity of the embedded graphene, and demonstrated a permanent and irreversible interfacial debonding behavior occurred in the graphene–PMMA system. Furthermore, a simplified model to predict the critical interface debonding compression strain was proposed and fitted well with the experimental data. Our results will be beneficial to the design of graphene based flexible devices with excellent mechanical stability and durability, and open up the possibility of utilizing strain engineering to improve devices performance.

2. Experimental methods

The graphene samples were prepared by micromechanical cleavage [26] and adhered to Si wafer substrate with a 300 nm SiO_2 capping layer. Optical microscopy was used to locate the graphene sheet and the thickness was further confirmed by Raman spectroscopy. A thin layer of PMMA (2 wt.% in chloroform) was spin-coated on the substrate prior to the transfer [6,27]. Afterwards the detachment of the PMMA–graphene layer from the initial surface was done by partially etching the surface of SiO_2 with a 1 M NaOH aqueous solution. As a result, a PMMA membrane with all of the graphite/graphene sheets attached to it was obtained. Finally, this membrane was laid over the target substrate of PMMA with the localization of graphene sheets as Alfonso Reina explained [22]. The detailed procedures were plotted in Fig. 1 and three prepared samples were shown in Supporting information S1 including their optical images as well as Raman spectra in the full spectral range.

The Raman spectra were obtained with a Renishaw Raman spectroscope, using the 514 nm line of an Ar laser, equipped with a Linkam cooling cell. The temperatures in our experiments ran from 60 down to −150 °C by liquid nitrogen as the cooling agent in the cooling cell, while liquid helium was further employed to introduce larger compressive strains to the embedded graphene that was placed in a liquid helium pot, when the ambient temperature was reduced to −263 °C (10 K). Here the temperature at 60 °C was selected as a reference based on the fact that the thermal stress of embedded graphene maintained during the curing process could be entirely released. Thermal equilibrium in each case was reached by holding the specimen for 3–5 min at constant temperature. The Raman spectrum was taken at a minimum of three points in the central area of graphene flake at a certain temperature. All bands in the Raman spectra of graphene were fitted with Lorentzians. To obtain the Raman images,