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Improvement of mechanical properties of graphene/substrate interface via regulation of initial strain through cyclic loading

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ABSTRACT

To analyze the effect of initial strain of graphene, a systematic experimental investigation of the mechanical properties of graphene/polyethylene terephthalate (PET) interface was performed. Several graphene/PET specimens were designed by applying various cyclic loading treatments. The Raman mapping method was used to compare the strain field information before and after these cyclic-loading treatments. The analysis suggests that the initial strain of graphene can be effectively reduced by repeated interfacial shear deformation and load transfer, which improves the resulting interfacial bonding degree. After the cyclic loading treatments, the graphene samples were stretched using a micro-tensile device, and the strain distributions of graphene were measured using Raman spectroscopy. The debonding evolution was monitored, and the interfacial parameters of graphene for the different treatments were quantitatively compared. The experimental results indicated that the graphene/PET interfacial properties can be effectively improved using cyclic loading treatment. Finally, the internal mechanism for improvement of the tangential interfacial properties was analyzed from micro-nano and atomic viewpoints. This work provides a reference for engineering application of graphene interface improved via strain regulation.

1. Introduction

Graphene has important application prospects in nanoelectronics, wearable sensing devices, and supercapacitors because of its unique thermal, electrical, optical, and mechanical properties [1,2]. The deformation of graphene has significant effects on the electron mobility, carrier density, and energy band gap of microelectronic devices [3]. Therefore, the development of a method to characterize and improve graphene/substrate interfacial properties is a significant scientific need for the advancement of new technologies in microelectronics.

Recently, strain engineering has been recognized as an effective approach to tailor the properties of graphene. For example, based on theoretical calculations, Choi et al. [4] proposed that uniaxial strain affects the Dirac conical displacement of graphene and thus affects the electronic structure of graphene. Cocco et al. [5] reported that the graphene gap energy value can be modulated from 0 to 0.9 eV by combining shear deformation and uniaxial strain. In addition, Ni et al. [6] proposed that the uniaxial tensile strain of graphene can open a band gap, which provides an alternative method to experimentally tune the band gap of graphene. Furthermore, in optics, strain-induced anisotropy absorption and other effects open up the prospect of the application of graphene in atomic optical components. Ni et al. [7] observed that prestrained graphene transferred onto polyethylene terephthalate (PET) exhibited polarization-dependent transparency. Because graphene has only atomic thickness, generally, it must be attached to a substrate material to realize its functions. Much research progress has been made in the theory and simulation of the interface between graphene and a substrate. Yue et al. [8] studied the van der Waal's interaction between graphene bubbles and a substrate using membrane and nonlinear plate theories and deduced that the adhesion energy of the graphene/silicon interface was 97∼–430 mJ/m^2. In addition, Guo et al. [9] analyzed the interfacial load transfer between graphene and a substrate using cohesive shear lag theory and 3D finite element simulation; they observed that the interfacial shear stress (ISS) between graphene and a PET plastic substrate was 0.5 MPa. There have also been some experimental works on the strain/stress transfer at the interface between graphene and a substrate. Jiang et al. [10] measured the buckle delamination blisters using atomic force microscopy and found that the interfacial adhesion energy between graphene and PET was ∼0.54 mJ/m^2. In addition, Koenig et al. [11] observed that the interfacial adhesion energy between single-layer graphene and a silicon oxide substrate was 450 ± 20 mJ/m^2 using a pressurized blister test. Because of the large variation in the experimental results of similar graphene/substrate interface in previous research, Xu et al. [12–14] experimentally investigated the size effect and deformation transfer of the interface between graphene and a polymer substrate. They designed and measured eight different sized composite specimens and found that the maximum interfacial shear stress varied from 0.004 to 0.314 MPa, indicating that the interfacial strength increases sharply with decreasing graphene length. Therefore, it was concluded that the

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mechanical parameters of graphene/substrate interface have an obvious size effect.

Currently, a prominent problem in research on the interfacial properties of nanomaterials such as graphene is the large discrepancy between the predicted data given by theory and simulation and the experimentally measured results, with the difference reaching 1–3 orders of magnitude. It is known that the theory and numerical simulation are usually based on ideal materials and an ideal interface between graphene and the substrate, whereas experimental results are affected by many factors, including the quality of the nanomaterial and its geometry such as the appearance of any intrinsic ripples, the properties and surface roughness of the substrate, and any wrinkles or residual strain produced in the transfer preparation process. Recognition and analysis of these influencing factors has posed new challenges to the quantitative characterization of nanomaterials such as graphene. There have been some studies on these factors. Xu et al. [15] studied a new class of corrugations that is ubiquitous in exfoliated graphene using scanning tunneling microscopy. Kusminskiy et al. [16] studied the pinning of a two-dimensional membrane to a patterned substrate using elastic theory and observed that both the in-plane strain and bending rigidity can lead to depinning. In addition, theoretical simulation results obtained by Zhang et al. [17] indicated that topological defects such as disclinations and dislocations can induce graphene wrinkling. Robinson et al. [18] reported that the strain distribution of epitaxial graphene grown on SiC is inhomogeneous, which is correlated to the physical topography of the substrate. Lanza et al. [19] observed that graphene grown on a copper substrate using chemical vapor deposition has wrinkles and that the subsequent transfer process also produces new wrinkles. The work of Raju et al. [20] showed that cyclic loading can improve the inhomogeneous strain distribution of graphene. We speculate that these main influencing factors are often intertwined with each other. In addition, the comprehensive effect of these factors cause the formation of initial strain in graphene. Currently, there remains a lack of comprehensive and systematic research on these factors. In addition, problems with experimental measurements and effective characterization of graphene interfacial properties have also been encountered.

In this paper, the initial strain of graphene on a PET substrate and its effect on the interfacial properties were studied. The graphene/PET specimens were exposed to different types of cyclic loading treatment. Raman spectroscopy was used to experimentally measure the whole-field deformation of graphene and analyze the effect of different strain amplitudes and loading modes on the strain distribution and initial strain of graphene. Then, uniaxial tensile tests were performed to characterize the interfacial properties of the graphene/PET specimens. The strain distributions of the graphene upon axial stretching were measured, and the interfacial debonding evolution during the loading process was monitored. In addition, the mechanical parameters of the graphene interface were quantitatively characterized. Finally, the effect and mechanism of cyclic loading on the graphene/PET interface was discussed.

2. In situ Raman spectroscopy and specimens

In this study, Raman spectroscopy and a micro tensile device were employed for in situ characterization of the interfacial properties of graphene/PET. A schematic diagram of the experimental setup is presented in Fig. 1. Raman-spectra-based mechanical measurements have the advantages of being nondestructive, noncontact, online, and real-time, and the spatial resolution is related to the laser beam diameter. The measurement principle is that the change of the atomic bond length caused by the strain of the material microstructure causes the vibration frequency of the lattice vibrations (phonons) to change, which results in a corresponding shift of the characteristic peak frequency. Strain information for materials such as porous silicon materials, carbon nanotubes, and graphene has been previously obtained using Raman spectroscopy [21–24]. The peak position shifts of 2D and G of graphene are related to its deformation, and the 2D peak position (hereafter, the 2D peak position will be referred to as “peak position”) is selected as the measuring target because its shift is highly sensitive to the strain of graphene. The peak position values associated with the strain were obtained using the Lorentzian function to fit the Raman spectrum, as shown in Fig. 2(a). The peak position shifts to the left under tensile deformation (the wave number decreases), termed a “red shift”; in the opposite case, the shift is termed a “blue shift”. In this experiment, the measured peak position data were converted into strain information by calibrating the proportionality coefficient between the strain of graphene and the peak position shift, which was determined to be $-8\ \mathrm{cm}^{-1}/\%$ as shown in Fig. 3(b). The well-defined Raman spectra were obtained using a Renishaw InVia system with a 633-nm He−Ne laser as the excitation source. The spot size of the laser was about 1 μm in diameter, after being focused through a 50 × objective lens (numerical aperture = 0.75). A low laser power of 0.85 mW was used to avoid local heating effect or damage of graphene, and real-time contour maps of the peak position were constructed.

The graphene used in the specimens was monolayer polycrystalline graphene synthesized on copper foil using chemical vapor deposition. The substrate was PET, which is a flexible large-deformation material with good light transmission, creep resistance, and fatigue resistance. The monolayer graphene film was transferred to the top surface of the PET substrate using the poly (methyl methacrylate) (PMMA)-assisted wet transfer method. The composite samples haven’t received any chemical modification, physical and glue-bonding treatments. Therefore the graphene film was physically adsorbed on the PET substrate by Van der Waals forces at the interface [10,12–14,28]. Because the surface roughness of substrate affects the interfacial properties, a series of 5 μm × 5 μm surface areas on the PET substrate were measured using a FM-Nanoview 100 atomic force microscope, and then the root mean square (RMS) and roughness average (Ra) values (~10 and 6.5 nm, respectively) and maximum height difference (~49.7 nm) were calculated by mathematical statistics. In the experiment, the substrate was loaded using a micro-loading device, and the stress–strain curve which was measured by a CARE IBTC-100 tensile testing machine is shown in Fig. 2(b). To ensure linear loading and uniform deformation throughout the substrate, the entire loading process was conducted in the elastic region (the gray area in Fig. 2(b) in the strain range from 0% to 2.5%), and the loading step was set to a strain of 0.25%, marked as red dots in Fig. 2(a), to obtain the Raman spectrum. The graphene length of all the specimens was 100 μm, and the experiments were conducted under the same conditions.

3. Results

3.1. Initial strain and cyclic loading

In this study, the initial Raman peak position of graphene on top of PET without any cyclic treatments was analyzed. Fig. 3(a) shows the statistical distribution of the peak positions of 2500 points in the entire 50 μm × 50 μm graphene area. The inset presents a contour map of all the measured peak positions, which shows that the strain of the original graphene was not uniform. The statistical results of the peak position indicate a normal distribution, where the peak positions range from 2633 to 2649 cm^{-1}. The central peak of the normal distribution curve was approximately 2641 cm^{-1}; however, the maximum difference between the peak positions was 14 cm^{-1}. Assuming 2641 cm^{-1} is the approximate zero strain in the initial state of graphene, this finding indicates that the graphene without cyclic treatment has initial strain consisting of tensile strain and compressive strain. Initial strain mainly originates from the preparation and transfer processes, material factors such as the structural stability of the material itself, polycrystallinity, defects, and the substrate surface, which is inevitable. The existence of initial strain has a substantial effect on the strain transfer of the graphene/substrate microstructure. Fig. 3(b) shows the peak position of graphene of the original specimen without any cyclic loading as a function of substrate