Chemical Physics Letters 665 (2016) 121–126

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Sulfur and few-layer graphene interaction under thermal treatments

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ARTICLE INFO

Article history:
Received 29 July 2016
In final form 19 October 2016
Available online 26 October 2016

Keywords:
Graphene
Sulfur
Doping
Raman spectroscopy

ABSTRACT

Confined sulfur between two multilayer graphene films under thermal treatments by means of electrical and Raman spectroscopy characterization was studied. Similarities between the electrical behavior and calorimetry of sulfur immersed into nanoporous alumina during sulfur phase transitions suggest that sulfur has a different thermal behavior when it is in confinement conditions compared to the free state. Additionally, reaction of sulfur with multilayer graphene at 500 °C produced covalent bonds and a p-type doping of about 2×10^{13} cm^{-2} in charge concentration.

1. Introduction

Graphene is a very promising material for electronic applications because of its low sheet resistance, high optical transparency and mechanical properties. But the absence of a gap energy and a zero carrier density at Dirac points are in conflict with real applications [1]. Therefore, a lot of effort has been focused to dope this material in order to improve its electronic properties. Heteroatom doping using nitrogen and boron has served to obtain n-type and p-type graphene respectively [2]. In this work we are mainly interested in graphene-sulfur system because of its amazing properties and potential applications in supercapacitors, Li-S batteries, catalyst supports, solid acids and many other areas [3].

Previously it has been found that sulfur modifies electrical properties of carbon-based materials, such as carbon nanotubes [4,5] and graphite [6]. For graphene, it has been reported experimental and theoretically [7–9] that this material can act as a gas sensor [10], but S-doped graphene is much more reactive and can serve as a better sensor for polluting gases such as NO and NO_2 [7,11] than pristine graphene. Also it was predicted that sulfur doping could open an energy band gap in graphene [8,9]. On the other hand, Zhu and coworkers [12] found that sulfur dopants quench magnetic ordering in graphene and in general sulfur changed the magnetic behavior of their samples. Other experimental studies in graphite-sulfur composites have found superconducting behavior below 35 K [13]. But this superconducting behavior is lost in monolayer graphene because layer-layer interactions in graphite play a key role [7,14]. Also, confinement of sulfur in a nanoporous anodic alumina template [15,16] have shown that the behavior of sulfur under this condition was different to that in bulk. These two last results suggest that sulfur confined between graphene layers can exhibit interesting properties. That is why the main purpose of our work is to confine sulfur (S) between two films of multilayer graphene (MG) and also we propose a simple and effective method to induce sulfur doping in graphene using thermal treatments.

2. Experimental

Multilayer graphene was synthesized by chemical vapor deposition technique (CVD) using 3 cm × 1 cm copper foils. The Cu foils were put into a quartz tube of a horizontal furnace which was heated from room temperature to 1000 °C with a hydrogen flow of 146 sccm. The system was maintained at these conditions during 90 min for annealing copper foils. Then, 40 sccm of methane passed through the quartz tube during 30 min at the same temperature. Finally methane flow was cut off and the furnace was cooled down to room temperature. In order to create a cross junction we cut 2 mm × 10 mm ribbons of MG on copper foils. Then ferric nitrate solution was used to etch copper during 12 h. MG ribbons were washed in de-ionized water to eliminate ferric nitrate solution residuals. One ribbon was translated to a glass substrate, when the sample was dried we deposited a sulfur film in the middle of the ribbon by spin coating using a sulfur and CS_2 solution (1 g of

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http://dx.doi.org/10.1016/j.cplett.2016.10.056
0009-2614/

sulfur powder with 5 ml of CS_2, J.T. Baker 99.999% and Tecsiquim 99.9% respectively). In order to cover with sulfur just an area of 2 mm × 2 mm on the MG ribbon we used a wet paper mask. Finally another MG ribbon was put on top on S/MG making a cross junction as is shown in the inset of Fig. 1(a), we called MG/S/MG to the final sample. Our MG films are a mixture of crystals with a different number of graphene layers, from one to about 5 layers.

For electrical measurements MG/S/MG samples were mounted on a sample holder which is introduced into a sealed chamber. Silver paste was used to make electrical connections, in a pair of MG ends an electrical current was passed and the voltage drop was measured in the opposite arms in the cross junction configuration, such as is illustrated in the inset of Fig. 1(a). In an argon atmosphere, voltage drop as a function of temperature was monitored during two cycles, from room temperature to 200 °C and back to room temperature.

For Raman characterization we used a Nicolet Almega XR spectrometer and 532 nm of laser excitation, for these measurements samples were translated on silicon with 306 nm of silicon dioxide substrates. It should be noted that for all Raman characterization presented in this work, only graphene zones were selected on the MG film. A Linkam-THMS600 cell for Raman characterization at different temperatures in an Argon atmosphere was used. We found that when these measurements were made above 100 °C, most of the sulfur evaporates; consequently we used other method to induce doping in graphene with sulfur, which consists on using sulfur in vapor phase. Samples were put into a quartz tube inside a tubular furnace. The system was heated from room temperature to 500 °C in an argon atmosphere, sulfur powder was put into the same tube but in a position where the temperature was around 200 °C. At this temperature sulfur can evaporate and vapor flows along the tube and finally react with MG at 500 °C. We called MG + S to the resulting sample. Then Raman spectroscopy was used again to analyze these samples and compared with the cross junction samples (MG/S/MG). To determine the incorporation of sulfur into MG structure we used a K-Alpha Thermo Fisher Scientific equipment for XPS characterization. Also electrical measurements were performed for these kind of samples using glass as substrate. Silver paste was used as electrodes for two terminal electrical configuration. This electrical characterization was carried out in a chamber equipped with a heater and a cold stage for cooling below room temperature using liquid nitrogen. The measure-

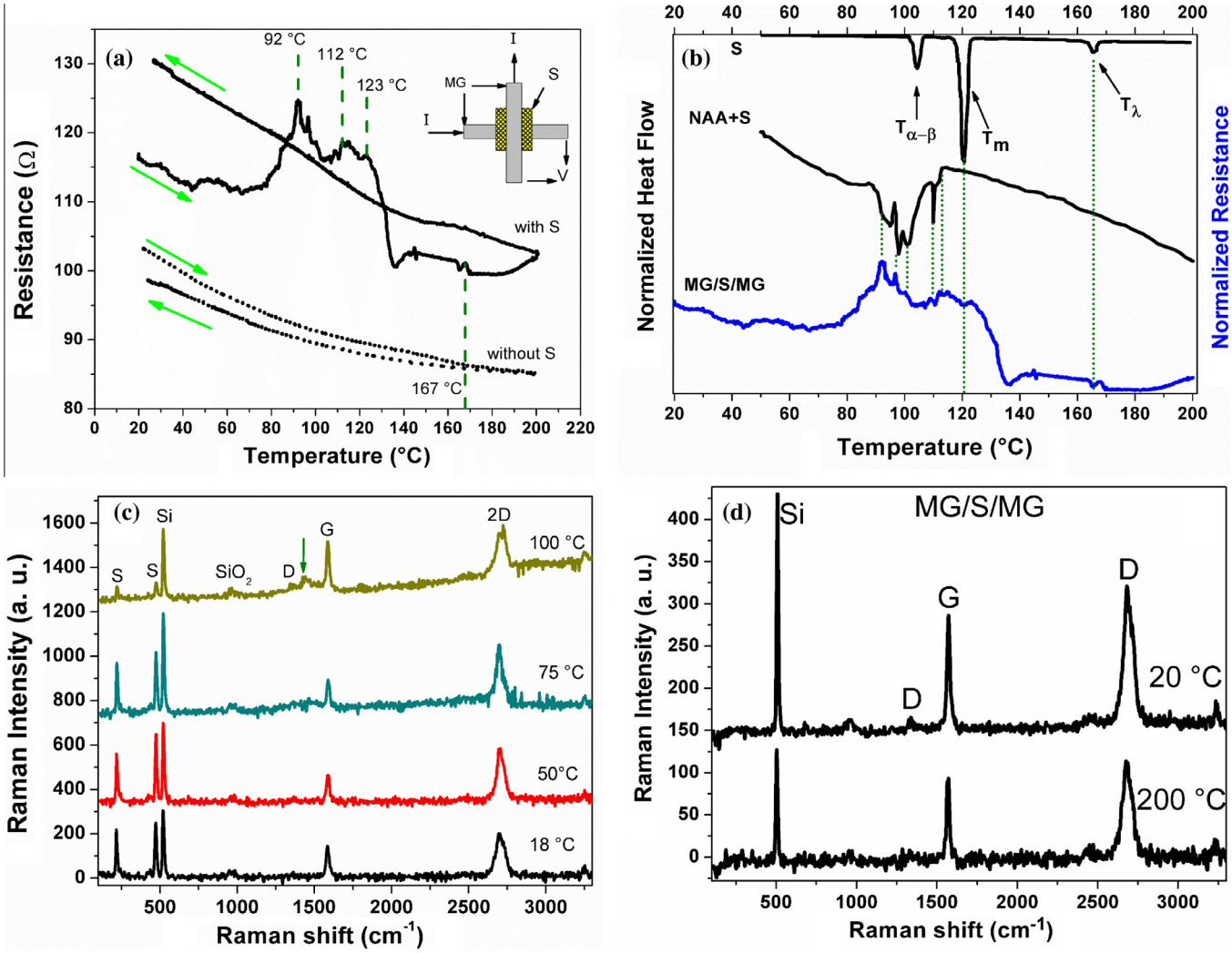

Fig. 1. (a) Resistance as a function of temperature of a cross junction with and without sulfur in the junction. (b) Differential scanning calorimetry of bulk sulfur (S), sulfur immersed in a nanoporous anodic alumina (NAA + S) template (adapted from Ref. [15]) and resistance of MG/S/MG as a function of temperature, the same sample in (a); (c) Raman in situ of a MG/S/MG on a silicon substrate, from room temperature to 100 °C; (d) Raman spectra of MG/S/MG at 200 °C and back to 20 °C, in both sulfur Raman signal does not appear, which means that it has been evaporated.