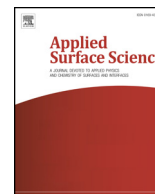




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Silicon- and oxygen-codoped graphene from polycarbosilane and its application in graphene/*n*-type silicon photodetectors



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ABSTRACT

Properties of graphene can be modified by doping heteroatoms. Here we report the synthesis of a monolayer of silicon- and oxygen-codoped graphene (SiOG) using polycarbosilane as both the C and Si sources in a thermal chemical vapor deposition process and compare the SiOG with primitive graphene (PG). Composition and structure of the PG and SiOG are analyzed by X-ray photoelectron spectroscopy and Raman spectroscopy. The SiOG produced from polycarbosilane has a ratio of [Si] to [Si] + [C] of 8.9%. Meanwhile, doping Si forms Si–C and C–Si–O bonds in graphene. Doping Si in graphene also introduces a defective structure in the graphene lattice. Graphene/Si Schottky diodes are prepared for performance comparison. Doping Si increases the barrier height of the graphene/Si Schottky diodes from 0.76 eV to 0.78 eV and changes the ideal factor from 3.8 to 2.8. The graphene/Si photodetectors are self-powered under UV irradiation. The ON/OFF ratios in 0.3 mW cm⁻² of 365 nm light at a zero bias voltage are respectively 3500 and 7600, and the rise times/fall times are respectively 11.6 ms/53.6 ms and 4.8 ms/14.3 ms for the PG/Si and SiOG/Si photodetectors. The relatively better performance of the SiOG/Si over PG/Si in UV sensing is possibly due to the lowering of the Fermi level of graphene by incorporation of Si and O.

1. Introduction

Graphene has attracted considerable research interest due to its unique two-dimensional structure and properties [1]. Primitive graphene (PG) is a semimetal with a negligible band gap with the Fermi level at the charge-neutral Dirac point [2,3]. Surface transfer doping and substitutional doping of graphene change the band structure and properties of graphene [4]. Doping boron and nitrogen in graphene respectively induce *p*-type and *n*-type conducting behaviors that are useful for various applications [5]. Modification of graphene by doping foreign elements including P, S, Se, O, and F also changes the properties of graphene [5–9]. Silicon-doped graphene (SiG) has been theoretically predicted to have a small band gap [10], high capability of H₂ storage [11,12], and high oxygen reduction reactivity [13], along with high sensitivity to the adsorption of small gas molecules [14] and to the interaction of nucleobases [15]. Recently, SiG films have been synthesized and their structures and properties have been characterized [16–19]. Wang et al. [16] prepared monolayer SiG on the surface of Cu foils by chemical vapor deposition (CVD) using triphenylsilane

(C₁₈H₁₅Si) as the C and Si sources, and the SiG demonstrated a *p*-type conduction with a carrier mobility of 660 cm² V⁻¹ s⁻¹. Zhang et al. [17] used CH₄ and SiH₄ to grow SiG, producing a band gap opening of 0.28 eV. Thus prepared SiG/GaAs solar cells exhibited 33.7% higher power conversion efficiency than PG/GaAs solar cells due to increased barrier height [17]. Lv et al. [18] used methoxytrimethylsilane (C₄H₁₂OSi) and hexane as silicon and carbon sources to grow SiG. When compared to PG, the SiG showed higher enhancement of Raman scattering of organic molecules through increased interaction between molecules and Si-doped sites. Wang et al. [19] annealed a mixture of triphenylsilane and graphene oxide (GO) to prepare Si-doped reduced graphene oxide (Si-rGO). As compared to the performance of rGO, the Si-rGO demonstrated a 29.6% increase in energy conversion efficiency when used as a metal-free electrocatalyst in dye-sensitized solar cells, and a 48.5% increase in specific capacity when used as an active electrode for supercapacitors [19].

Polycarbosilane (PCS) is a silicon-containing polymer which releases CH and SiH species and converts to SiC through pyrolysis in an inert environment or in a vacuum [20,21]. In a previous study we grew

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carbon nanotubes via a catalytic pyrolysis process using PCS as the C source and Fe nanoparticles as the catalyst [22]. In this study, we grow graphene by CVD using PCS as the carbon and silicon sources and obtain silicon- and oxygen-codoped graphene (SiOG). We also synthesize PG using CH₄ as the carbon source for comparison [23]. We further transfer SiOG and PG films on *n*-type Si to make Schottky diodes and compare their performance in sensing 365 nm UV light.

2. Experimental

SiOG films were deposited on copper substrates by CVD in a quartz tube furnace. Polycarbosilane (PCS; Nippon Carbon, Inc., 1290 g mol⁻¹), a silicon-containing polymer with a formula of $-(\text{HSiCH}_3-\text{CH}_2)_n-$, was used as the carbon and silicon sources for growing SiOG films. To grow PG films for comparison, CH₄ (99.999%) was used as the carbon source. Ar (99.9995%) and H₂ (99.999%) were used as the working gases for growing both the SiOG and PG films. Copper foils measuring 25 μm thick (Alfa Aesar, 99.8%) and Si(1 0 0) wafers measuring 500 μm thick with 300 nm of thermally grown SiO₂ film were cut into 1.5 × 1.5 cm² substrates, and quartz and sapphire plates measuring 1 mm thick were cut into 1 × 1 cm² substrates. Details of the substrate cleaning and the PG deposition processes are described elsewhere [23,24]. To grow SiOG, one piece of Cu substrate was placed at the center of the quartz tube furnace and 0.12 mg of PCS was filled in the upstream side of a quartz crucible beside the Cu substrate, as shown in Fig. 1. The quartz tube furnace was heated in a 50 cm³ min⁻¹ flowing mixture of 10% H₂ and 90% Ar to 1050 °C in 2 min and maintained at a pressure of 5.33 kPa for 30 min to grow SiOG film on Cu substrate. After growing SiOG film, the tube furnace was cooled down with the same flowing mixtures. The SiOG film was then transferred to Si(1 0 0), sapphire and the quartz substrates through the PMMA-assisted transfer technique [25,26] for structural and optical characterizations. A PG film was also grown and transferred to the Si and quartz substrates to compare the effect of doping Si and O to the structure and optical absorption of graphene.

Structure of the graphene films on SiO₂-covered Si substrates was characterized by a micro-Raman spectroscopy (Horiba iHR550) using a 532 nm laser source with a power of 8 mW through a 50 × objective lens. Surface morphology and apparent thickness of the SiOG film on sapphire substrate was inspected by an atomic force microscope (AFM, Bruker Dimension ICON). The composition of the graphene films on the Cu substrates was analyzed by an X-ray photoelectron spectroscopy (XPS, Ulvac-Phi Quantera) using Al K α radiation (1486.6 eV). Transmission spectra of graphene films on quartz substrates were measured using a UV-Vis-IR spectrophotometer (Jasco V-670).

Graphene films were transferred to a pre-patterned *n*-type Si (*n*-Si) surface to fabricate Schottky diodes. For this purpose, *n*-type Si(1 0 0) wafers (1–10 Ω cm) with 300-nm-thick thermal oxide (SiO₂) were cut into 15 × 15 mm² substrates and then sequentially cleaned with acetone, deionized water, isopropanol, and deionized water. To make the Schottky diodes, a 100-nm-thick Ag top electrode with a 5 × 5 mm² open window was deposited on the oxide-covered Si substrate by sputter deposition through a shadow mask. The SiO₂ films on the back side and on the window area of the top surface of the SiO₂/Si substrate were then etched away by 3% diluted HF. A Ti film of 10 nm thick and an Ag film of 100 nm thick were then sequentially deposited on the back side of the substrate as a contact electrode by sputter deposition. The Si substrate with the top and bottom Ag electrodes was dipped into

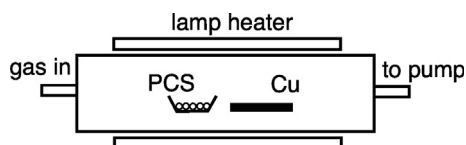


Fig. 1. Schematic of the furnace for growing SiOG films.

dilute HF for 10 s to remove the native oxide on the window area prior to the graphene transfer. Finally, PG and SiOG were transferred onto the top window area of the Si substrates to fabricate PG/Si and SiOG/Si Schottky diodes. The current-voltage (*I*-*V*) characteristics of the Schottky diode were measured using a Keithley 2410 SourceMeter in dark and under light irradiation. An LED with a 365 nm wavelength was used as the light source. For photoresponse measurements, the LED was powered by a function generator and the responses for the PG/Si and SiOG/Si photodetectors were recorded by an oscilloscope.

3. Results and discussion

Raman spectroscopy has been used to study the structure of graphene [27–30]. High quality monolayer and few-layer graphene are characterized by a strong G peak at about 1580 cm⁻¹ and a 2D peak at about 2700 cm⁻¹, and the intensity ratio *I*_{2D}/*I*_G decreases as the number of graphene layers increases [27,28]. An additional D peak arises at around 1350 cm⁻¹ in defective graphene which might be associated with edges and sub-domain boundaries [27,28], and a weak D' peak at about 1620 cm⁻¹ is attributed to disorder-induced features [28,29]. Doping foreign elements in graphene concurrently increases the D band intensity and generates an extra D' band [5,16,18,29–31]. Fig. 2 shows the Raman spectra of the PG and SiOG on Si substrates in this study. The Raman spectrum of the PG has a weak D band at 1340 cm⁻¹, a strong G band at 1584 cm⁻¹ and a 2D band at 2689 cm⁻¹, and the integral *I*_{2D}/*I*_G ratio is 3.7. Hence the PG is a high-quality monolayer graphene [27,28]. On the other hand, the Raman spectrum of the SiOG is composed of a strong D band, an overlapping G and D' bands, and a weak 2D band. The presence of the D' band at 1621 cm⁻¹ and a strong D band in the Raman spectrum of the SiOG might be due to the structural disorder by doping Si [16,18] and O [31], similar to that in the N- and B-doped graphene [29,30]. It is likely that the intensity of the 2D band was weakened in the SiOG by the doping processes, as compared to that in the PG [16,18,29–31].

XPS analyses confirmed that Si was doped in graphene using PCS as both the C and Si sources. Fig. 3 shows the Si 2*p* and C 1*s* spectra for the as-grown PG and SiOG on Cu substrates. The Si 2*p* peak is absent in the PG, as shown in the lower spectrum in Fig. 3(a). Contrarily, a small Si 2*p* peak appears in the XPS spectrum of the SiOG specimen, as shown in the upper curve in Fig. 3(a). The atomic percentage of [Si] to [Si] + [C] in the SiOG is about 8.9%, calculated from the ratio of areal intensity of the Si 2*p* and C 1*s* peaks with corresponding sensitivity factors of 0.339 and 0.296 [32]. The Si 2*p* peak for the SiOG is further decomposed into

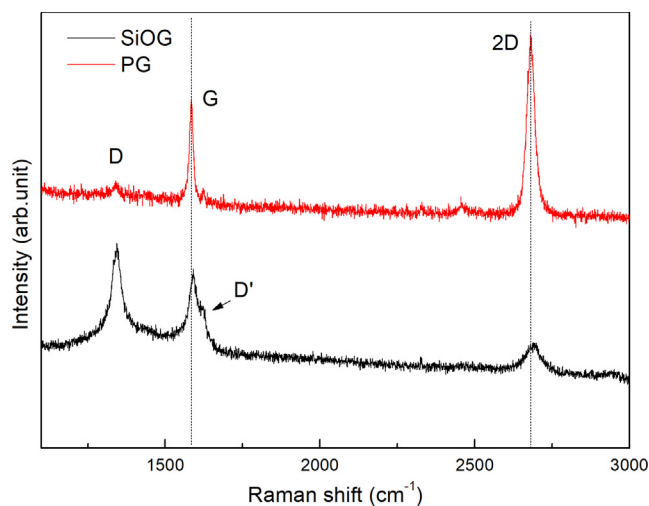


Fig. 2. (Color online) Raman spectra of the PG (lower spectrum) and SiOG (upper spectrum). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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