Contents lists available at ScienceDirect

Materials Letters

Synthesis of transfer-free graphene by solid phase reaction process in presence of a carbon diffusion barrier

Muhammed Emre Ayhan [a], Golap Kalita [a,b,*], Remi Papon [a], Ryo Hirano [a], Masaki Tanemura [a]

[a] Department of Frontier Materials, Nagoya Institute of Technology, Gokiso-cho, Nagoya 466-8555, Japan
[b] Center for Fostering Young and Innovative Researchers, Nagoya Institute of Technology, Gokiso-cho, Nagoya 466-8555, Japan

ARTICLE INFO

ABSTRACT

Synthesis of transfer-free high quality graphene on an arbitrary substrate by metal assisted graphitization with control carbon diffusion process has lot of significance for device applications. Here, we demonstrate the synthesis of monolayer graphene using common triblock co-polymer ($EO_nPO_mEO_n$) as carbon source by solid phase reaction. In the synthesis process, we used Ni and NiO thin film as catalyst and carbon diffusion barrier, respectively on the top of polymer deposited SiO_2/Si substrate. The long carbon chain of triblock co-polymer pluronic F127($EO_{106}PO_{70}EO_{106}$) can be graphitized in presence of Ni layer, where carbon diffusion to the top surface is controlled by NiO thin layer. The effects of carbon diffusion, thickness of polymer layer and annealing process are studied to obtain high quality monolayer graphene. Our findings reveal that the NiO/Ni stacked, thickness of polymer layer and reaction process in H_2 atmosphere strongly influence the quality of synthesized graphene.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Carbon based materials, especially well-tailored fullerene [1], carbon nanotubes (CNTs) [2] and mesoporous carbons (MCs) [3,4] have been significantly developed for various applications. Among these frontier materials, two dimensional (2D) graphene crystal is considered to be the main building block of sp^2 hybridized carbon nanomaterials [5]. Graphene, the zero band gap semiconductor shows exciting properties such as anomalous quantum hall effect [6], high carrier mobility ($> 200,000 \, cm^2 \, V^{-1} \, S^{-1}$) [7], optical transparency independent of wavelength ($\sim 97.7\%$) [8] and mechanical strength ($> 1 \, Tpa$) [9]. Graphene has been derived or synthesized by various approaches, including, micromechanical cleavage of highly ordered pyrolytic graphite (HOPG) [10], epitaxial growth on silicon carbide (SiC) [11], reduction of chemically exfoliated graphene oxide [12] and chemical vapor deposition (CVD) on transition metals [13–17].

Synthesis of graphene in CVD process by hydrocarbon decomposition on transition metal surface, such as copper (Cu), nickel (Ni), and cobalt (Co) has been significantly investigated [13–19]. On the other hand, noble metals such as gold (Au) and silver (Ag) were also demonstrated as possible substrate materials for graphene growth [20,21]. However, in regards to practical device applications, high quality CVD graphene must be transferred to an insulating arbitrary substrates. To overcome the drawback of transfer process, direct synthesis of graphene on required substrate has been explored for practically feasible device applications [22–26]. Previously, Ismach et al. have demonstrated direct growth of few-layer graphene on dielectric surface by a CVD approach owing to evaporation of Cu catalytic layer during the growth process [22]. Similarly, direct graphene growth has been achieved on germanium (Ge) in a CVD process [25]. We have also demonstrated synthesis of bi-layer and few-layer graphene on SiO_2/Si substrate by Co catalytic layer assisted crystallization of a-C thin film [20]. Direct synthesized few-layer graphene has been integrated with n-Si substrate for fabrication of a Schottky junction [26]. However, controlled carbon diffusion and graphitization process at the metal catalytic layer and substrate interface were inhomogeneous to obtain monolayer graphene. Crystallization of the a-C thin film at the substrate interface remains a challenge to obtain high quality monolayer graphene. In this context, we studied a triblock co-polymer with long carbon chains to synthesis graphene directly on insulating substrate in presence of Ni and NiO layers as catalyst and carbon diffusion barrier, respectively.

Here, we used Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) co-polymer as carbon source to synthesize graphene directly on SiO_2/Si substrate. The co-polymer can be easily dissolved in common organic solvents such as acetone, ethanol, methanol or water considering
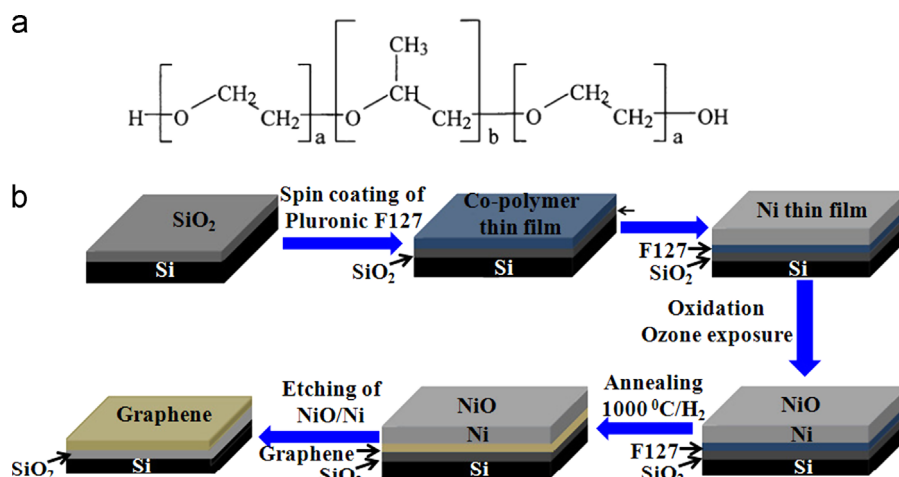
Fig. 1. (a) Chemical formula of triblock co-polymer Pluronic F127 and (b) schematic diagram of the transfer-free graphene synthesis on SiO_2/Si substrate by the solid phase reaction process.

2. Experimental

PluronicF127 co-polymer was purchased from Wako Chemicals and used as received for thin film deposition by spin coating. Fig. 1a shows the molecular structure of the block co-polymer used for graphene synthesis. The co-polymer was dissolved in water (0.1 wt%) and spin coated onto SiO_2/Si substrate at 5000 rpm for 2 min. The top Ni thin layer was deposited by pulsed laser deposition (PLD) technique using Nd:YAG laser ($\lambda = 355$ nm, energy density of 30 mJ and $f = 10$ Hz). Ni layer (100 nm) with high carbon solubility was used as a catalyst layer. Subsequently, NiO carbon diffusion barrier was created on the top of Ni by ozone ultra–violet (UV) irradiation. In-situ annealing of the NiO/Ni/co-polymer stack layers on SiO_2/Si substrate was performed at 1000 °C in 50 sccm of H_2 atmosphere using infrared heater with rapid cooling process. Finally, NiO and Ni layers were removed by chemical etching with diluted nitric acid solution (30%) and graphene film was obtained directly on SiO_2/Si substrate. Schematic of transfer-free graphene synthesis by the solid phase reaction process is demonstrated in Fig. 1b.

Morphological and structural analysis of the deposited material on SiO_2/Si substrate was carried out with Raman spectroscopy, optical and atomic force microscopy (AFM). Raman studies were performed with NRS 3300 laser Raman spectrometer with laser excitation energy of 532.08 nm. The optical microscopy studies were carried out with VHX-500 digital microscope. AFM study was performed with a JSPM-5200 scanning probe microscope. Scanning electron microscope (SEM) analysis was carried out by ultra-high resolution Elionix ESM-9000 to identify the graphene layer.

3. Results and discussion

Thermally decomposable block co-polymer Pluronic F127 is highly soluble in water due to presence of hydroxyl groups (–OH) in the carbon chain. Deposition of a thin and uniform polymer film was possible due to high solubility in the solvent. Graphene
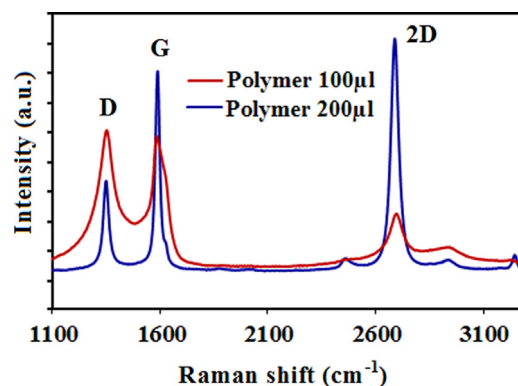

Fig. 2. Raman spectra of synthesized graphene directly on SiO_2/Si substrate using 100 and 200 μl of triblock co-polymer Pluronic F127.

formation and graphitization process using a block co-polymer as carbon source was investigated considering presence of a long carbon chain. Graphene growth was explored with different concentration of the polymer to optimize thickness of the spin-coated film. Fig. 2 shows Raman spectra of graphene directly obtained on SiO_2/Si substrate by the solid phase reaction approach using 100 and 200 μl of Pluronic F127 precursor. The most prominent peaks in the spectra are observed at 1350, 1580 and 2695 cm^{-1}, corresponding to disorder-induced D, graphitic G and second order 2D peak, respectively. The synthesized graphene by using 100 μl polymer shows a strong D peak and a higher I_D/I_G ratio of 1.03. Whereas, synthesized graphene using 200 μl polymer shows much better graphitization with a less intense D peak with I_D/I_G ratio of 0.54. This shows that the amount of carbon source significantly affect graphene growth in the solid phase reaction. Thickness of the triblock co-polymer films is controlled by simply adjusting the amount of Pluronic F127 solution used for spin coating. The study shows that lower quantity of the polymer is not sufficient for good graphitization and graphene growth on the substrate surface. A higher amount of triblock co-polymer effectively decomposes and precipitates on the SiO_2/Si substrate to obtain monolayer and bilayer graphene formation.

Fig. 3 shows Raman studies and corresponding optical microscope images of the synthesized graphene with different annealing durations in the reaction process. Good graphitization and graphene formation were not observed with an annealing time of 10 min. Synthesized carbon material shows a strong D peak and a less intense second order 2D peak, corresponding to disordered