

Doping of Graphene Film for Transparent Conducting Film

¹Gülsüm Ersü and ^{*2}Fethullah Güneş

^{1,*2} Izmir Katip Celebi University, Material Science and Engineering Department, 35620, Cigli Main Campus, Izmir, Turkey

Abstract

We propose a method of doping graphene films in order to use in transparent conducting films. Graphene film was synthesis on copper film by chemical vapor deposition method (CVD) and transferred onto polyethylene terephthalate substrate. Phenylboronic acid acceptor and donors were used to promote graphene's electrical properties. The doping mechanism based on the modify valence band structure of graphene. The existence of the boron was verified based on Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) images. The influence of doping on the electrical properties of graphene were measured by Four-probe measurement and sheet resistance was decreased up to 55%.

Key words: graphene; CVD, chemical doping; transparent conducting film, sheet resistance

1. Introduction

Graphene is a two-dimensional form of carbon allotropes. It is also the building block of other carbon allotropes such as three-dimensional graphite, one-dimensional carbon-nanotube and zero-dimensional fullerene. Graphene is the strongest materials due to its strong carbon bonds even though being the thinnest material known [1]. In addition to, its electrical, optical and thermal conductivity are very high [2]. Graphene is a material that can be utilized as a metallic, semi-conductor or insulator with its own unique and manipulable electrical band structure. Graphene with extraordinary carrier mobility and electron conductivity opens a way for using in electronic application [3]. At present, the material with the highest market share in touch screen and electrode is indium tin oxides (ITO). This material is advantageous compared to graphene because of its easy processability, low surface resistance, and high conductivity values. However ITO economic reserves are expected to be depleted in 2025 and their costs are increasing each year. In addition, the modern society demands the multifunctional portable and even wearable electronic devices. Therefore, graphene with extraordinary properties, makes it an alternative materials to ITO [4, 5]. Compared to that of ITO the higher sheet resistance of the graphene prevents the use of it as transparent electrode; thus, modulation of its electrical properties and band structure is of particular interest [4, 6-8].

The chemical doping method that use reduce to sheet resistance of graphene film is an effective approach [9]. Graphene energy band structure is suitable for p-type or n-type chemical doping. The sheet resistance of graphene films can be reduced by manipulated the number of hole carriers by chemical doping so that graphene can be utilized as transparent and flexible conducting film for variety of applications. The purpose of this study is to determine a chemical approach to improve the electronic structure of transparent graphene film. Graphene was synthesized on

*Corresponding author: Address: Izmir Katip Celebi University, Material Science and Engineering Department, 35620, Cigli Main Campus, Izmir, Turkey. E-mail address: fethullah.gunes@ikc.edu.tr, Phone: +902323293535

copper foil by chemical vapor deposition (CVD) method and doped using commercially available phenylboronic acid. Our results demonstrate that sheet resistance was decreased up to 55%.

2. Materials and Method

2.1. Graphene Film Preparation

Graphene was synthesized on 60 μm thick copper foil by CVD method. The substrate was placed in a CVD quartz tube with a flow of hydrogen (80 sccm) and argon (1000 sccm). The temperature was increased from room temperature to 1084 $^{\circ}\text{C}$ and annealed 30 minute with same gas atmosphere. Graphene was synthesized at 1084 $^{\circ}\text{C}$ by a carbon source CH_4 gas flow for 2 min. and then chamber cooled to room temperature in the same atmosphere. After synthesis, poly (methyl methacrylate) (PMMA) was spin-coated onto the graphene films and immersed into Cu etchant (FeCl_3) solution. After Cu was completely etch away, the graphene film with PMMA rinsed with deionized (DI) water several times and then, PMMA-coated graphene sheets were transferred onto a Si/SiO₂ substrate. The sample was finally dipping into acetone to remove the PMMA layer.

2.2. Doping with Phenylboronic acid

Trifluorophenyl Boronic acid powder was purchased from Sigma Aldrich. 10^{-4} M solution was prepared by dissolving powder in dimethylformamide. The 10^{-4} M solution was then dropped on the graphene film by a micropipette.

2.3. Characterizations

Sheet resistance measurements were performed by a four-point method (Keithley 2400 multimeter) at room temperature. Structure and distribution of the fabricated graphene were studied by Raman Spectroscopy (Renishaw, 532nm Ar⁺ion laser) and SEM (Zeiss Sigma 300VP) characterization techniques.

3. Results and Discussion

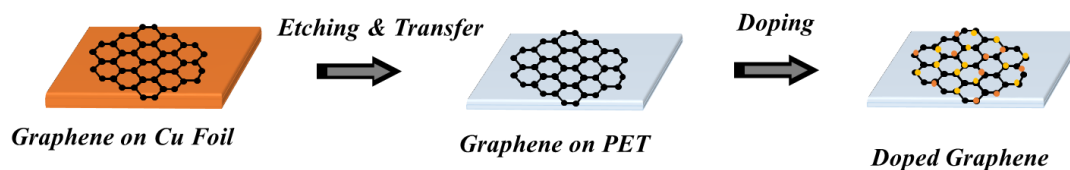


Figure.1: Schematic representation for the synthesis and doping processes.

Figure 1 shows a schematic of synthesis and doping strategy. A graphene layer synthesized on Cu foil is mostly a single layer except for a portion of bilayers and triple layers (Figure 2a). After the

CVD process of the graphene growth, SEM images (Figures 2b) show that the substrate covered with a layer of graphene.

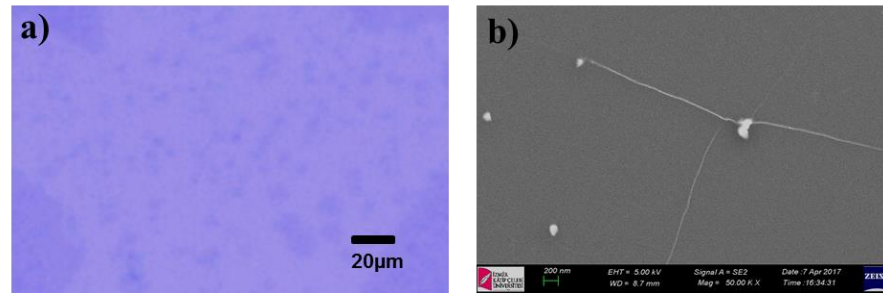


Figure.2. (a) Optical image (b) SEM image of pristine graphene

Raman spectrum indicates typical appearance of transferred graphene on SiO₂/Si including G (1586 cm⁻¹) and 2D band (2700 cm⁻¹) respectively (Figure 3a). The G band is the first Raman peak is related to C-C stretching of sp² carbon, the 2D band is the second order graphene peak. Intensity ratio of 2D/G have been utilized to identify to number of graphene layers and I_{2D}/I_G was calculated about 1.9 verifying the presence of monolayer graphene. The doping effect was also visible in the G- and 2D-band shift. Doped graphene film G band has shifted about 3 cm⁻¹ as shown in figure 3b.

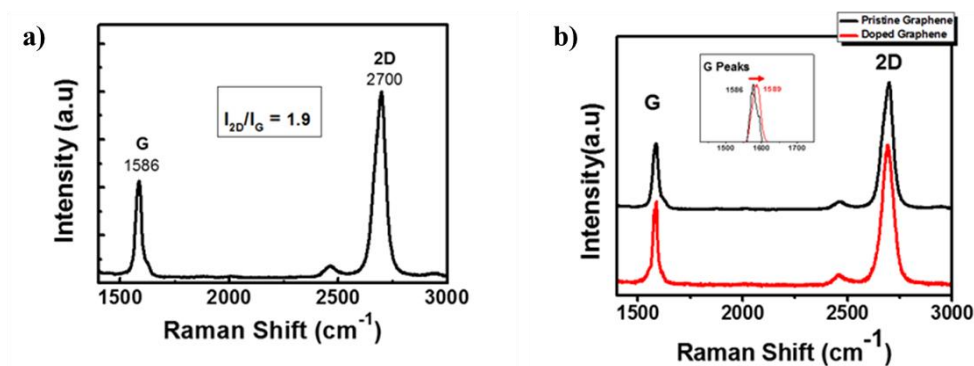


Figure 1562 Raman spectra of (a) pristine graphene film transferred on 300 nm SiO₂/Si wafer (b)pristine (top) and doped (bottom) graphene film. The shifted G peak of graphene is given onto spectra.

Sheet resistance measurement of transferred graphene was performed using four-point method. In this method, the current was measured on two isolated contacts and the voltage is determined on opposing two contacts. The sheet resistance of p-doped graphene decreased to 550 Ω/□, compared to 1000Ω/□ for pristine graphene film.

Conclusions

We have shown that the sheet resistance of graphene grown on Cu substrate decreases substrate decreases up to 55% via chemical doping. The performance of our graphene films can further be

improved by reducing defects and damage formation during synthesis and transfer processes to meet requirements of different applications.

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