IMPROVING THE SHEET RESISTANCE OF CVD-GRAPHENE FILMS VIA DOPING

Gülsüm ERSÜ [1], Fethullah GÜNEŞ [2, *], Ahmet AYKAÇ [3], Mustafa CAN [4]

[1, 2] Department of Material Science and Engineering, Faculty of Engineering and Architecture, İzmir Katip Çelebi University, İzmir, Turkey

[3, 4] Department of Engineering Sciences, Faculty of Engineering and Architecture, İzmir Katip Çelebi University, İzmir, Turkey

ABSTRACT

We report on the synthesize high quality and large area graphene and modifying their electrical properties by non-covalent doping methods. Large area graphene film was synthesized by chemical vapor deposition method on pre-treatment Cu foil and demonstrated to be greatly efficient to the quality of graphene. The films are mostly monolayer with the transmittance of about 98%. Graphene film was transferred onto Si/SiO$_2$ substrate followed by various Self-Assembled Monolayers (SAMs) solution dropping. After doping, the number of charge carrier changes due to the nature of SAMs. Electrical measurement shows that doping method can effectively manipulate the electrical properties of graphene and also doped graphene sheets can use in optoelectronics, solar cells, and thermoelectric solar cells etc.

Keywords: Graphene, CVD, Transparent conducting films, Doping, Electrical properties

1. INTRODUCTION

Graphene, two-dimensional form of crystallized carbon, has attracted great interest since 2004 due to its outstanding electrical, mechanical, chemical and optical properties [1, 2]. Experimentally isolated single-layer graphene attracted a large amount of attention in physics and material science. Graphene with extraordinary electronic properties due to its unique band structure opens a way for using in the electronic application such as field-effect transistors (FETs), supercapacitors and transparent conducting films [3, 4]. The development of graphene-based electronics depends on our ability to modulation of its electronic properties and band structure. Graphene energy band structure is suitable for p-type or n-type chemical doping, for instance after doping with B or N atoms, graphene become p-type or n-type, respectively [5-7]. The chemical doping, using heteroatoms or covalent bonds with specific functional groups or even other molecules, provides charge transfer or opening a band gap around the Fermi level and also modification of the carbon sp^2 lattice [8]. Theoretical and experimental studies have shown that chemical doping alter the Dirac point of graphene above the Fermi level and can reduced sheet resistance of graphene films [9-12]. Therefore, graphene can be utilized as transparent and flexible conducting film for variety of applications. In addition, the synthesis of low-defect graphene is crucial to develop large-area graphene-based applications. On the other hand, the synthesis of low-defect graphene is crucial to develop large-area graphene-based applications. Chemical vapor deposition (CVD) synthesis is a reliable and scalable method for producing large area graphene [13-15].

Self-assembled monolayers (SAMs) are a one molecule thick, well-oriented molecular structures that are formed onto a surface by the adsorption of an active surfactant. SAMs are used as interlayers and electrically active layers to obtain charge carrier injection and also SAMs are a good candidate for using in organic electronics owing to flexibility, inexpensively, versatility and changeable physical properties [16-18]. SAM modification of graphene electronically inactivates graphene edges and defects and also manipulate the number of charge carriers in graphene so that the graphene's conductivity could be enhanced ensures graphene to be utilized as transparent and flexible conducting film for the variety of applications.

In this work, development of electrically conductive graphene structures are targeted. Graphene was synthesized on pre-treatment Cu foil by CVD method and transferred onto another substrate followed by 10^{-4} M SAM molecules doping. Structure and distribution of the fabricated graphene were studied by Raman Spectroscopy, SEM characterization techniques and Atomic Force Microscopy (AFM). The influence of doping on the electrical properties of graphene were measured by Hall-effect measurement device.

2. EXPERIMENTAL

2.1. Synthesis of Graphene Film and Transfer Process

Firstly, commercially available Cu foils were pre-annealed and chemically-mechanically polished (CMP) for reducing the impurity or defect density on copper foils. To investigate the effect of the roughness, graphene was grown on unpolished and polished Cu foil using atmospheric pressure CVD. The foil was placed in a CVD quartz tube with a flow of hydrogen (H_2, 80 sccm) and argon (Ar, 1000 sccm). The temperature was increased from room temperature to 1079 °C and annealed 30 min. with the same gas atmosphere. Graphene was synthesized at 1079 °C by a carbon source methane gas flow for 1 min. and then chamber cooled to room temperature in the Ar/H_2 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 etched away, the graphene films with PMMA rinsed with deionized (DI) water several times and then, PMMA-coated graphene sheets were transferred onto a Si/SiO_2 substrate. The sample was finally dipping into hot acetone to remove the PMMA layer and dried using a nitrogen gun.

2.2. Preparation of Doped Graphene Film

4-Fluorophenyl boronic acid (F1-PBA), 3,4,5 Trimethoxyphenyl boronic acid (M3-PBA), 4,4''-bis(diphenylamino)-1,1':3',1''-terphenyl-5'-carboxylic acid (TPA) and 4,4''-di-9H-carbazol-9-yl-1,1':3',1''-terphenyl-5'-carboxylic acid (CAR) aromatic molecules were dissolved in Dimethyl sulfoxide (DMSO) for preparing 10^{-4} M solution. Transferred graphene onto Si/SiO_2 were kept in prepared SAMs solution for 24 hours to be coated with SAMs. Finally, the substrates were rinsed with DMSO to remove some SAMs residues and dried using a nitrogen gun.

2.3. Characterizations

Sheet resistance measurements were performed by a Hall-effect measurement system (ECOPIA, HMS 3000) at room temperature. Optical properties of graphene were characterized using UV-vis spectroscopy (Thermo Scientific, Evolution Array) and Raman spectroscopy (Renishaw, 532 nm). Structure of graphene were studied SEM (Zeiss Sigma 300VP) and AFM (Nanosurf, easyscan 2) characterization techniques.

3. RESULTS AND DISCUSSION
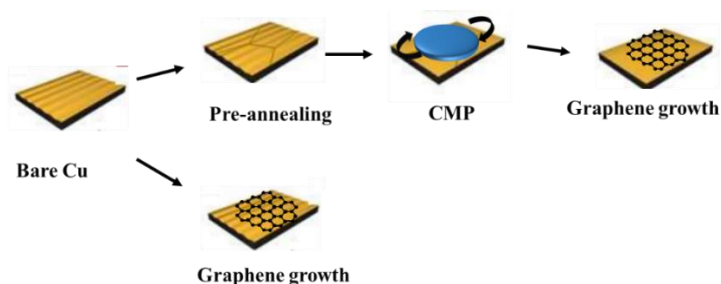
**Figure 1.** Schematic representation for the graphene synthesis

Figure 1 shows a schematic of synthesis strategy. Optical microscopy and AFM analysis were used to understand effect of pretreatment on Cu. Optical images shows that the surface morphology of bare Cu

foil is dominated by striation lines (Figure 2a). After CMP, the morphologies were mostly reformed and grain boundaries became more pronounced while the structural defect lines are reduced (Figure 2b). 3D AFM images of unpolished and polished Cu show that polished Cu surface more flatten than unpolished Cu (Figure 2 c and d). Root mean square (RMS) roughness parameter was used to measure the roughness degree of Cu surface. The RMS values of unpolished and polished Cu were calculated 138 nm and 7 nm, respectively. It is clear that unpolished Cu has relatively rough surface than polished Cu. These results are consistent with earlier reports indicating that annealing and polishing of Cu reduces surface contamination and obtain a flat surface [19, 20]. However, CMP method for the preparing metal substrate before graphene growth is rarely reported. Our procedure is a simple method to polish the Cu foils, which here surface roughness was decreased to 7nm.
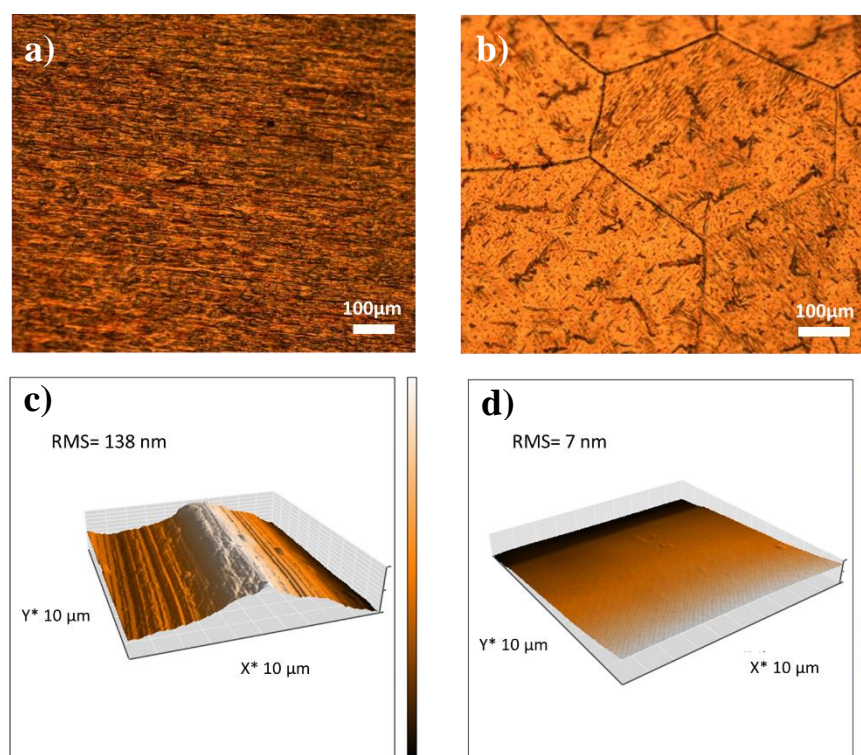

Figure 2. Surface morphology characteristics (a), (b) Optic microscopy, (c), (d) 3D AFM image of as-received Cu foil (a, c) and polished Cu (b, d), roughness mean square is abbreviated as RMS.

To demonstrate the effect of Cu foil on graphene quality, graphene film was synthesized on both unpolished and CMP Cu foils and transferred onto Si/SiO$_2$ substrate. Figure 3a and 3b are the transferred graphene on Si/SiO$_2$ substrate from unpolished and CMP Cu foil, respectively. Impurities on the unpolished Cu act as nucleation centers and graphene prefer growth around this centers. The graphene which was grown on unpolished Cu was nucleated randomly and contained incomplete areas due to the existence of impurity particles (Figure 3a). With CMP process, impurities of Cu were decreased effectively and thus the number of graphene domains was decreased (Figure 3b).
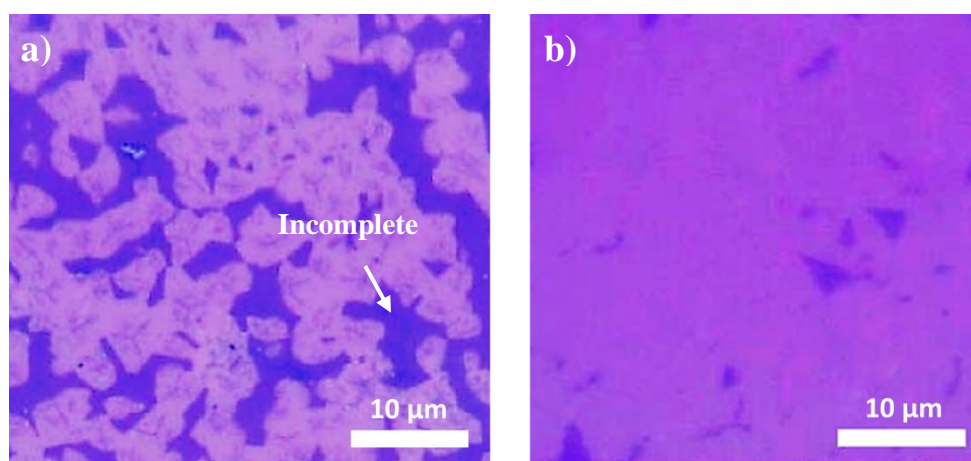
Figure 3. Optical microscopy image of graphene grown on (a) unpolished and (b) polished Cu.

The uniformity of the thin graphene layers was investigated by the Raman spectroscopy and SEM. For this purpose graphene film was synthesized on polished Cu and transferred on Si/SiO$_2$ substrate. Raman spectrum indicates typical appearance of transferred graphene on Si/SiO$_2$ including G (1586 cm^{-1}) and 2D band (2700 cm^{-1}) respectively (Figure 4a). The G band is the first Raman peak is related to C-C stretching of sp^2 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 2.74 verifying the presence of monolayer graphene. As seen from Figure 4b, some wrinkles were observed due to the difference their thermal expansion coefficients between graphene and metal throughout cooling [21, 22].
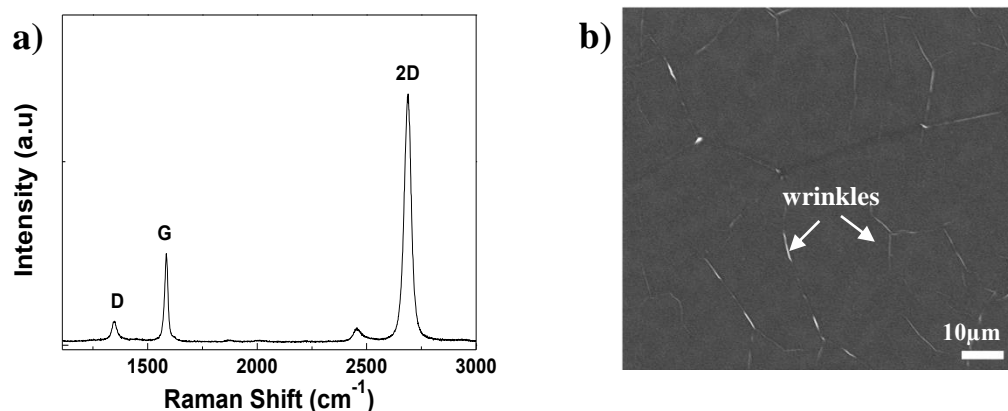
Figure 4. a) Raman spectroscopy b) SEM image of transferred graphene film on Si/SiO$_2$ substrate.

As a next step, graphene films were doped using various SAM molecules in order to examine the modification of its electrical properties. The SAMs form densely packed monolayer on graphene and interact with graphene by van der Waals interaction without damage to its chemical structure. Raman analysis and Hall-effect measurement were performed to understand the doping effect. The doping effect was visible in the G- and 2D-band shift. In the p-type of doping, the G band position upshifts due to the phonon stiffening effect by charge extraction. In the n-type doping, the G band position downshifts [23-25]. Doped graphene film G band has shifted about 3 cm^{-1} from 1586 cm^{-1} to 1583 cm^{-1} as shown in Figure 5b. These result demonstrated that the graphene was effectively doped by SAMs.
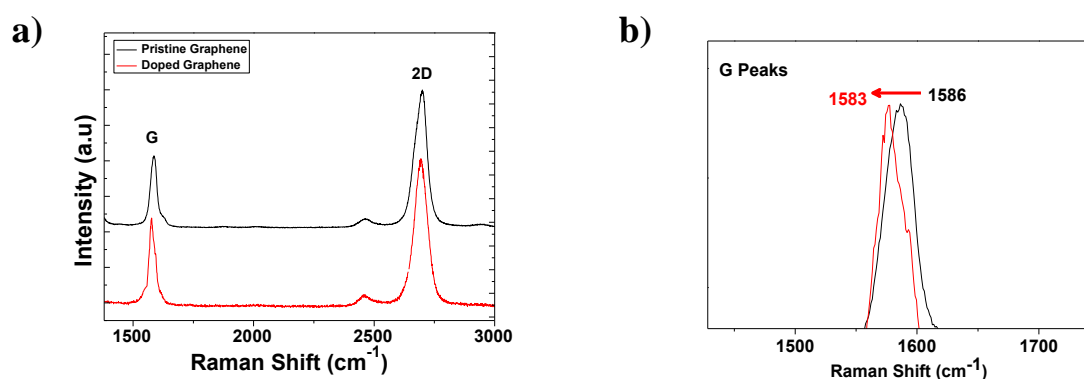
Figure 5. Raman spectra of (a) pristine (top) and doped (bottom) graphene film. (b) The shifted G band peak of graphene

The influence of SAM doping on the electrical properties of graphene were measured by Hall-effect measurement and summarized in Table1. The sheet resistance of undoped graphene was found about 770 ohm/sq at a transmittance 98%. The mobility of pristine graphene was measured about 1000 cm^2/V.s. This values are consistent for CVD grown graphene as reported in the literature [26-29]. With SAMs doping, the sheet resistance was improved compared to that of the pristine graphene. The reducing in mobility after doping indicates that the graphene becomes n-type. Due to electron-donor nature of SAMs, electron transfer is occurred from SAM molecules to graphene due to π-π interaction. As a result sheet resistance of graphene increased and mobility decreased so that graphene became n-type. With this method, sheet resistance and mobility of graphene were modified with little sacrifice in transmittance.

Table 1. Sheet resistance (R$_s$) mobility and transmittance (T %) of pristine and doped graphene.

Dopant	R$_s$ (ohm/sq)	Mobility (cm^2/V.s)	T %
pristine graphene	770	1000	98
F1-PBA	1355	464	95.2
M3-PBA	1110	858	96
TPA	2011	584	97.5
CAR	1848	268	97.9

4. CONCLUSION

In this study, it was presented a pre-annealing and chemical-mechanical polishing (CMP) method to reduce defect density on Cu foil and to enhance the quality of graphene. Using this method, large area, high-quality graphene film was synthesized on CMP Cu foil. The presence of the high-quality monolayer graphene was confirmed by Raman spectroscopy and Hall-effect measurements. In order to modify electrical properties, graphene films were doped with various SAM molecules. It is founded that the mobility and the sheet resistance of graphene can be controlled by SAM modification with little sacrifice in transmittance, which makes graphene n-type. The doping approach described here offers that electronic properties of graphene can be modified with SAM by simple dipping in a solution without using a plasma or high-temperature annealing. We believed that this study could open up a wide range of possibilities for electronic and optoelectronic applications

REFERENCES

[1] Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, and Geim AK, The electronic properties of graphene. Rev mod phys 2009; 81(1): 109-162.

[2] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, and Firsov AA, Electric Field Effect in Atomically Thin Carbon Films. Science 2004; 306(5696): 666-669.

[3] Geim AK and Novoselov KS, The rise of graphene. Nat Mater 2007; 6(3): 183-191.

[4] Nguyen BH and Nguyen VH, Promising applications of graphene and graphene-based nanostructures. Adv nat sci-nanosci 2016; 7(2): 023002.

[5] Panchakarla L, Subrahmanyam K, Saha S, Govindaraj A, Krishnamurthy H, Waghmare U, and Rao C, Synthesis, Structure, and Properties of Boron-and Nitrogen-Doped Graphene. Adv mater 2009; 21(46): 4726-4730.

[6] Wang L, Zhang X, Yan F, Chan HLW, and Ding F, Mechanism of boron and nitrogen in situ doping during graphene chemical vapor deposition growth. Carbon 2016; 98: 633-637.

[7] Lu H, Guo Y, and Robertson J, Charge transfer doping of graphene without degrading carrier mobility. J appl phys 2017; 121(22): 224304.

[8] Giovannetti G, Khomyakov P, Brocks G, Karpan Vv, Van den Brink J, and Kelly PJ, Doping graphene with metal contacts. Phys rev lett 2008; 101(2): 026803.

[9] Gebhardt J, Koch R, Zhao W, Höfert O, Gotterbarm K, Mammadov S, Papp C, Görling A, Steinrück H-P, and Seyller T, Growth and electronic structure of boron-doped graphene. Phys rev B 2013; 87(15): 155437.

[10] Wu T, Shen H, Sun L, Cheng B, Liu B, and Shen J, Nitrogen and boron doped monolayer graphene by chemical vapor deposition using polystyrene, urea and boric acid. New j chem 2012; 36(6): 1385-1391.

[11] Marconcini P, Cresti A, Triozon F, Fiori G, Biel B, Niquet Y-M, Macucci M, and Roche S, Atomistic Boron-Doped Graphene Field-Effect Transistors: A Route toward Unipolar Characteristics. ACS Nano 2012; 6(9): 7942-7947.

[12] Yao W, Yao K, Gao G, Fu H, and Zhu S, Boron-doping controlled peculiar transport properties of graphene nanoribbon p–n junctions. Solid State Commun 2013; 153(1): 46-52.

[13] Li XS, Cai WW, An JH, Kim S, Nah J, Yang DX, Piner R, Velamakanni A, Jung I, Tutuc E, et al., Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. Science 2009; 324(5932): 1312-1314.

[14] Rao C, Gopalakrishnan K, and Govindaraj A, Synthesis, properties and applications of graphene doped with boron, nitrogen and other elements. Nano Today 2014; 9(3): 324-343.

[15] Kumar P, Singh AK, Hussain S, Hui KN, San Hui K, Eom J, Jung J, and Singh J, Graphene: synthesis, properties and application in transparent electronic devices. Reviews in Advanced Sciences and Engineering 2013; 2(4): 238-258.

[16] Chaki NK and Vijayamohanan K, Self-assembled monolayers as a tunable platform for biosensor applications. Biosens and Bioelectron 2002; 17(1): 1-12.

[17] Ulman A, Formation and Structure of Self-Assembled Monolayers. Chemical Reviews 1996; 96(4): 1533-1554.

[18] Love JC, Estroff LA, Kriebel JK, Nuzzo RG, and Whitesides GM, Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. Chem Rev 2005; 105(4): 1103-1170.

[19] Han GH, Güneş F, Bae JJ, Kim ES, Chae SJ, Shin H-J, Choi J-Y, Pribat D, and Lee YH, Influence of Copper Morphology in Forming Nucleation Seeds for Graphene Growth. Nano Lett 2011; 11(10): 4144-4148.

[20] Soo Min K, Allen H, Yi-Hsien L, Mildred D, Tomás P, Ki Kang K, and Jing K, The effect of copper pre-cleaning on graphene synthesis. Nanotechnology 2013; 24(36): 365602.

[21] Mattevi C, Kim H, and Chhowalla M, A review of chemical vapour deposition of graphene on copper. J mater chem 2011; 21(10): 3324-3334.

[22] Li Z, Kinloch IA, Young RJ, Novoselov KS, Anagnostopoulos G, Parthenios J, Galiotis C, Papagelis K, Lu C-Y, and Britnell L, Deformation of Wrinkled Graphene. ACS Nano 2015; 9(4): 3917-3925.

[23] Ryan B, Luiz Gustavo C, and Lukas N, Raman characterization of defects and dopants in graphene. J phys-condens mat 2015; 27(8): 083002.

[24] Li Y, Intrinsic Doping Dependence of Raman 2D Mode in Graphene: Signatures of Electron– Electron Interaction, in Probing the Response of Two-Dimensional Crystals by Optical Spectroscopy. 2016, Springer International Publishing: Cham. p. 9-18.

[25] Kim KK, Bae JJ, Kim SM, Park HK, An KH, and Lee YH, Control of p-doping on single-walled carbon nanotubes with nitronium hexafluoroantimonate in liquid phase. phys status solidi B 2009; 246(11-12): 2419-2422.

[26] Gunho J, Minhyeok C, Sangchul L, Woojin P, Yung Ho K, and Takhee L, The application of graphene as electrodes in electrical and optical devices. Nanotechnology 2012; 23(11): 112001.

[27] Pang S, Hernandez Y, Feng X, and Müllen K, Graphene as Transparent Electrode Material for Organic Electronics. Adv mater 2011; 23(25): 2779-2795.

[28] Song HS, Li SL, Miyazaki H, Sato S, Hayashi K, Yamada A, Yokoyama N, and Tsukagoshi K, Origin of the relatively low transport mobility of graphene grown through chemical vapor deposition. Sci Rep-UK 2012; 2: 337.

[29] Chen J-H, Jang C, Xiao S, Ishigami M, and Fuhrer MS, Intrinsic and extrinsic performance limits of graphene devices on SiO2. Nat Nanotechnol 2008; 3: 206.