A Study of Graphene Obtained by PECVD Technique Depending on RF Power

O. Özakın, C. Aykaç, M. Odabas, A. Taşer, B. Güzeldir and M. Saglam

Abstract— The advantage of plasma enhanced chemical vapor deposition (PECVD) exhibits to grow graphene films at relatively low growth temperature, which is nearly 350 °C lower than that for graphene synthesis using thermal CVD. In this work, we have successfully synthesis graphene on FTO substrate at relatively low temperature and try to optimize the synthesis conditions by adjusting the RF power. Low temperature growth of graphene was optimized at 500°C and by varying plasma powers in the range of 60 - 80 W. The graphene samples were characterized by Raman Spectroscopic Mapping, Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy.

Index Terms— PECVD, Graphene, SEM, EDAX, XPS, Plassma Power, FTO

1 INTRODUCTION

Graphene is two-dimensional structure of sp2 -hybridized carbon. It is known as basic of all graphitic forms because its extended honeycomb network is the block form of other important allotropes; it can be stacked to form 3D graphite, rolled to form 1D nanotubes (CNT), and wrapped to form 0D fullerenes [1]. Graphene exhibits unique properties which have amazing the scientific community and has made it the major research topics in the last decade. Historically, graphite studies to achieve several layers have led to a sensation in 2004, when Geim and friends at Manchester University first isolated single layer samples from graphite using micro-mechanical cleavage method. There are three different types of graphenes: mono-layer graphene (MG), bilayer graphene (BG), and few-layer graphene (FG) [3]. Mono-layer graphenes has only one layer of two-dimensional carbon sheets. Bilayer and few-layer graphenes have from 2 to 10 layers of two-dimensional carbon sheets. Thick graphene layers which have more than 10 layers are of less scientific interest[4]. There are different ways for C atoms to be stacked in bi- and few-layer graphene, generating hexagonal or AA stacking, Bernal or AB stacking and rhombohedral or ABC stacking. Within a plane each carbon shows three in-plane σ bonds and one π orbital perpendicular to the plane. While the strong σ bonds work as the rigid backbone of the hexagonal structure, the out of plane π bonds control interaction between different graphene layers [5]. The most important properties of graphene are a quantum Hall effect at room temperature [6], tunable band gap, high elasticity [3], and an am bipolar electric field effect along with ballistic conduction of charge carriers [2]. The anisotropy of graphene properties fascinate both scientists and technologists. The origin of this property is the obvious difference between in plane and out of plane bonds nature, which leads to an out of plane electrical and thermal conductivities 103 times lower than those of their in-plane analogues [1].

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a CVD method used to growth thin film. Chemical Vapor Deposition (CVD) is a chemical reaction process in which thin films are formed from gas precursors at high temperatures[5]. PECVD is a CVD method aimed at obtaining free electrons by forming plasma instead of high temperature. In plasma, when electrons collide with gas molecules, the gases decompose into reactive ions, neutral atoms, molecules and other energetic species. The film begins to grow as radicals and energetic species interact with the substrate. These species reaching the surface locate into the adsorption regions in the substrate. Since the chemical reactions are initiated by the plasma, the system does not require high temperature. For this reason, the film is enlarged by PECVD at a lower thermal energy than conventional CVD and allows to use inexpensive and not resistant to heat materials such as plastic and glass. In the PECVD technique, plasma can be generated by radio frequency (RF) or direct current(DC). In this work, the samples were prepared using RF PECVD. One example of PECVD chamber is shown in Figure 1.

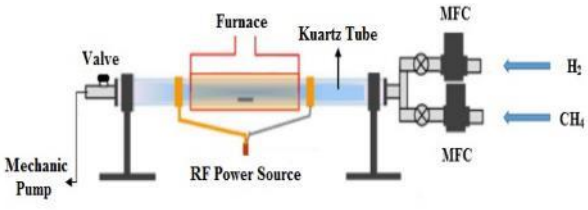
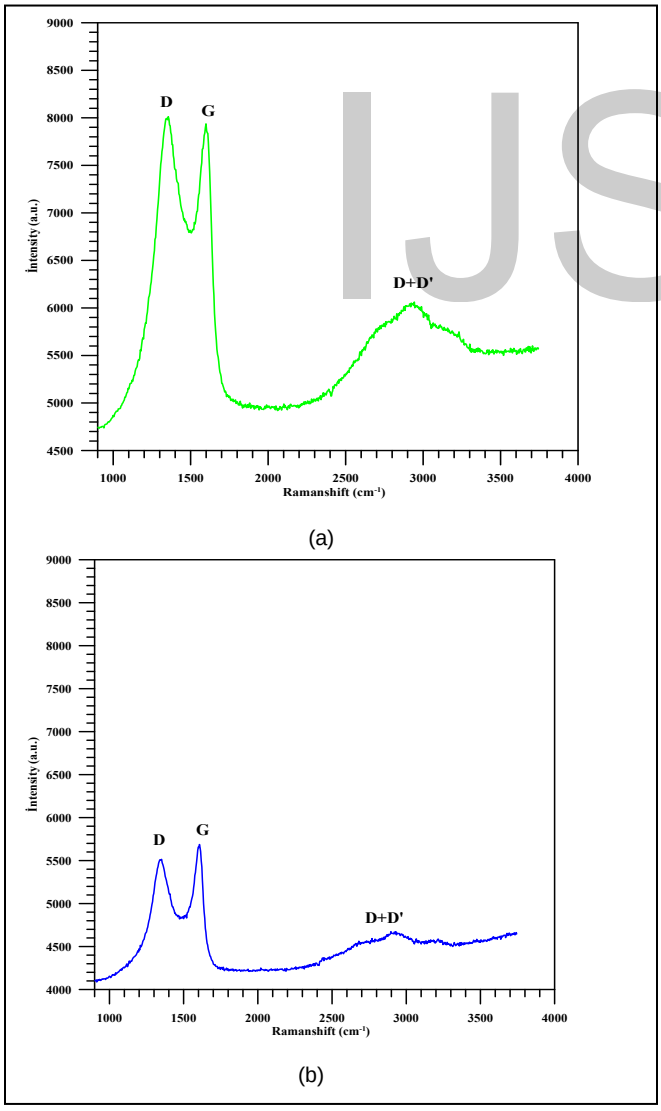


Fig. 1 Schematic presentation of our PECVD system

2 EXPERIMENTAL

In this study we used FTO (Fluorine doped Thin Oxide) as base material. The pre-cleaned substrates were lastly cleaned with IPA (Isopropyl alcohol) before the chamber was placed. Then substrates were placed Nanovak PECVD tube furnace system, which consists of 300W RF plasma source. Gas flow of 80 sccm Ar / H2 for 3 minutes was allowed that to exclude the gaseous residues in the vacuum chamber before the enlargement process was started. Firstly temperature was set at 300 ° C at a heating rate of 3 ° C / min. At 300 ° C plasma cleaning was started 30 sccm (Ar/H_2) flow and 40 W for 3 minutes. Then temperature was set at 600 ° C for growth process. After that the growth was carried out at 20/5/10 sccm Ar / CH_4 / H_2 gas flow and 60 W for 5 minutes. Immediately after the growth, the system was tried to cool and the Ar/H2 was began to add for 10 min to assist fast cooling reaction. The same procedures were performed to observe plasma effect by different plasma powers (60, 70 and 80 W).

3 RESULTS AND DISCUSSION



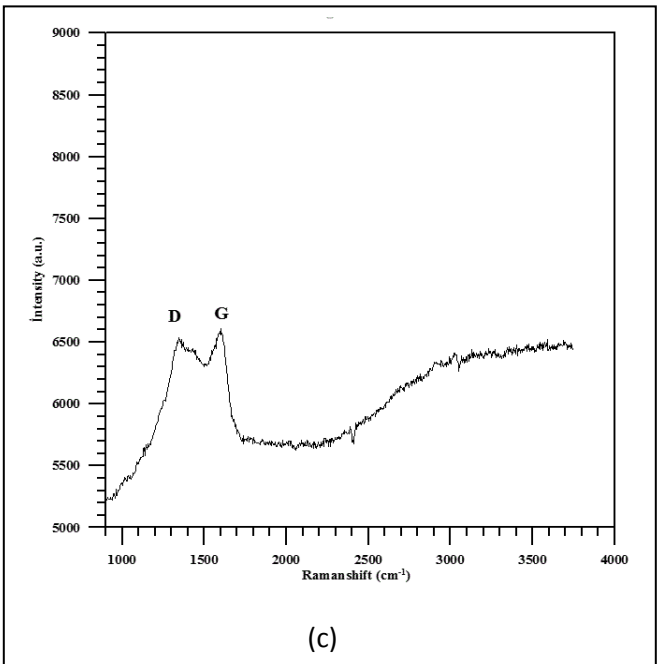
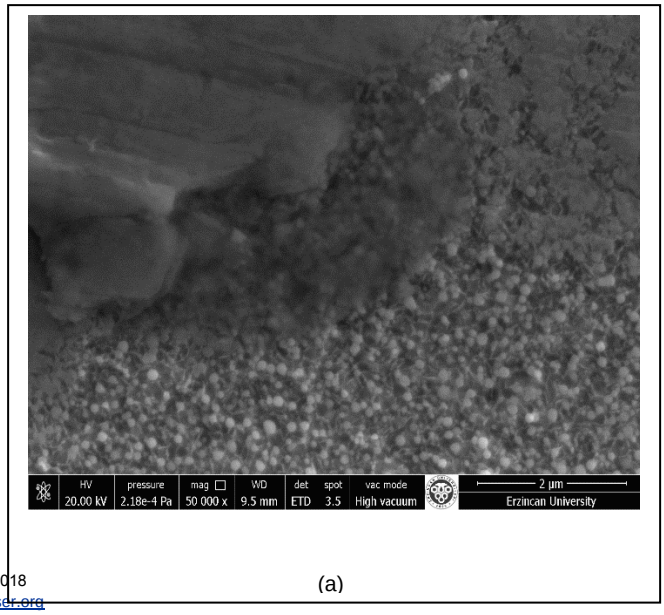
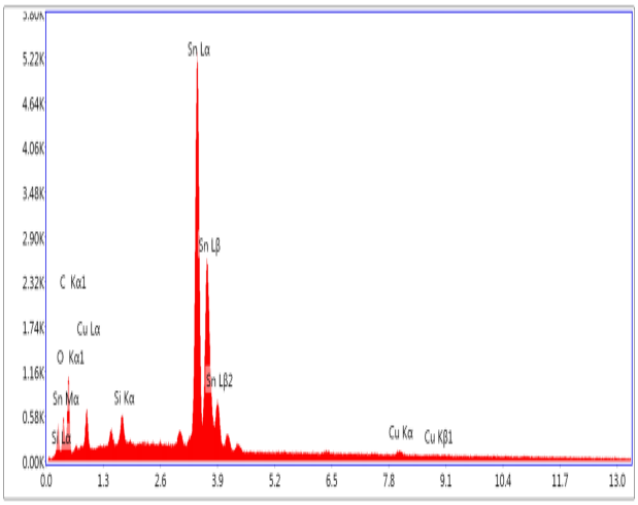


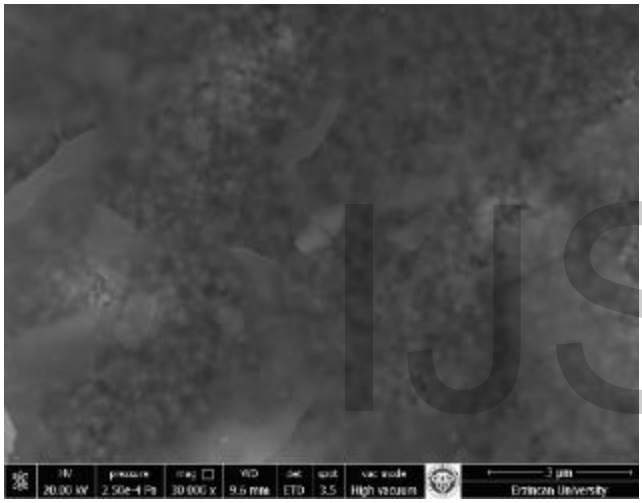
Fig. 2 Raman spectra of graphene (a) for 60W, (b) for 70W and (c) for 80W.

We characterized the graphene by using raman spectroscopy (WITec alpha 300 R Series High-Resolution Optical and Scanning Probe Microscopy Systems), scanning electron microscopy (Zeiss Sigma 300) and x-ray photoelectron spectroscopy (XPS). From Raman analysis, shows in Figure 2, the appearance of graphene are observed by the rises of D, G and D+D′ peak at ~1380 cm^{-1} ~ 1600 cm^{-1} and ~ 2946 cm^{-1} respectively[6]. The D, G and D+D′ peaks in the Raman spectra indicate defects in the graphene structure. Raman spectrum of graphene depend on plasma power presented in figure 2. It illustrated that the D, G and D+D′ peaks can be clearly observed at 60,70 W. However, when the plasma power increased, there was no evident D+D′ peak observed for 80 W.

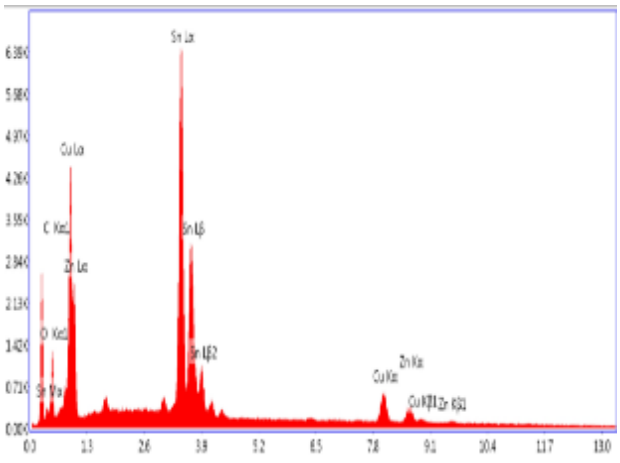




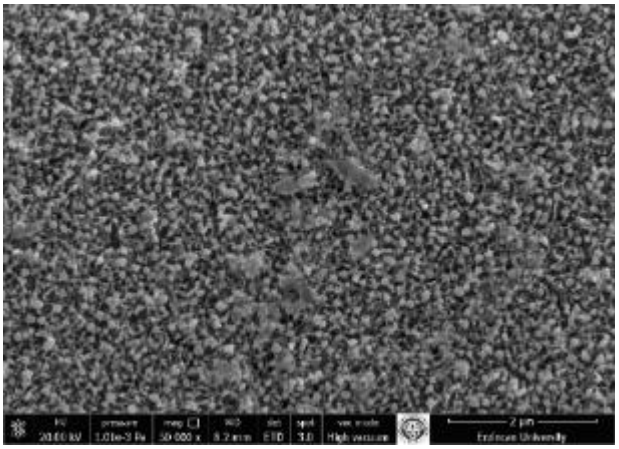
(b)



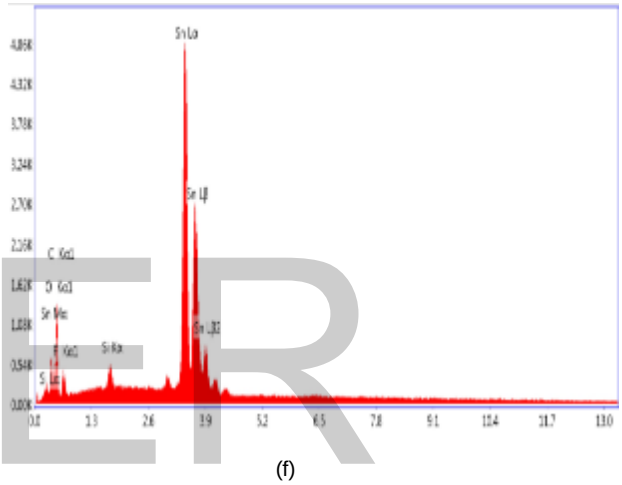
(c)



(d)



(e)



(f)

Fig 3. SEM images of graphenes growth at 60 W (a), 70W (c) and 80W(e) and EDAX spectrum of graphene for 60W (b), 70W (d) and 80W (f)

SEM is similar to optical microscopy but it has an edge over latter one. Geim's group did compare optical and SEM micrographs of graphene deposited over large areas, only to conclude that certain portions of the film were clearly visible in SEM rather than in optical images[6]. SEM was used to observed the surface morphology of graphene grown on FTO substrate in Fig. 3. Fig. 3 (a) and (c) shows that graphene covers the surface of FTO substrate homogeneously but fig. 3(e) shows that the graphene was growing locally on the FTO substrate. Quantitative analysis of the graphene was performed to determine the distribution of the materials in the films, using the EDAX technique. Fig 3 (b), (d) and (f) shows that typical EDAX patterns of graphene and carbon element has been found in this analyzes.

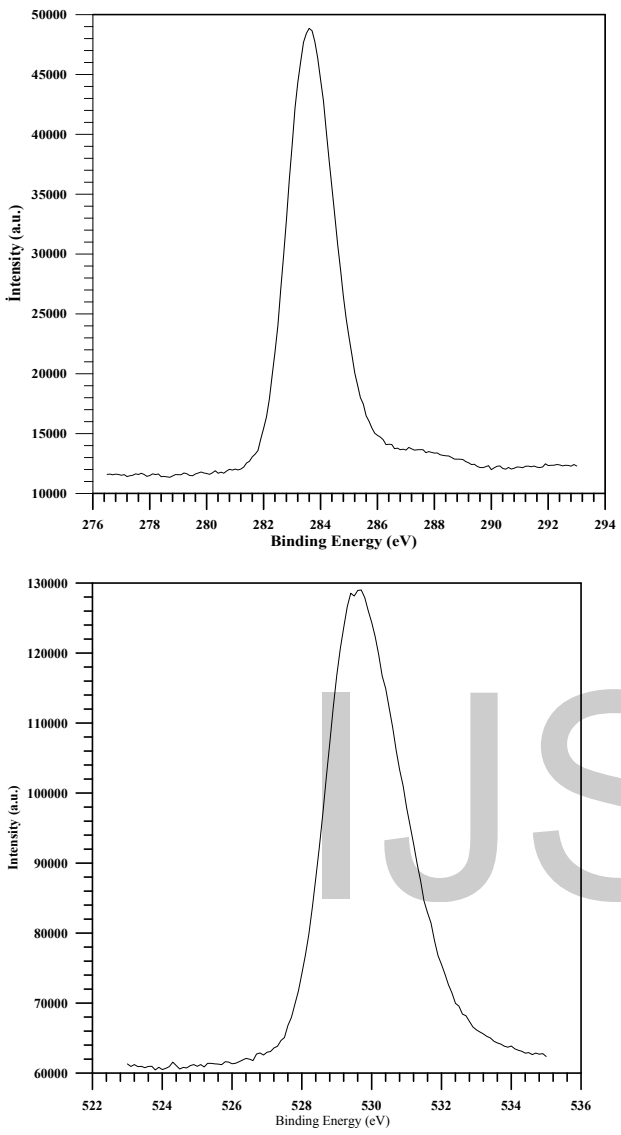


Fig 4. XPS analysis of selected graphene

Analyzing by XPS of the chemical bonding of graphene were illustrated that in Fig. 4. In our studies we observed the best results at 70 W and for this reason the XPS measurements was taken for this sample. Fig. 4 exhibits the XPS spectrum of graphene on FTO. We identified C-C, C=O bonding with XPS spectrum[7]. We think that the carbon-oxygen bonds are welded from substrate or growth proses.

4 CONCLUSION

It is possible to grow the multilayer graphene at 60 W of plasma power and at a low temperature of 600 ° C. In the PECVD technique plasma power supported the reaction energy and formation of graphene. It was seen that the graphene could not be obtained by increasing the plasma power. To increase the quality of the grafen can be done by optimizing the growth time, pressure and tunning the amount of $CH_4/H_2/Ar$ gas flow. Reducing the growth temperature will ensure that graphenes grow on flexible substrates without transfer.

ACKNOWLEDGMENT

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