Graphene substrate selection for the optimization of biosensor performance

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Abstract

The use of graphene in healthcare biosensing applications will be a disruptive technology in the near future [1]. Graphene sensors greatly outperform existing diagnostic analytical techniques - such as enzyme-linked immunobsorbant assays (ELISAs) in terms of sensitivity and sample throughput time. Advances such as these are crucial in the early detection of disease biomarkers, which greatly enhances the like of successful treatment and patient life expectancy [2].

Different methods of producing graphene are currently being investigated, such as chemical vapor deposition (CVD) methods on transition metal substrates [3][4], epitaxial growth on silicon carbide (SiC) by annealing at high temperature [5], and chemical exfoliation techniques [6], to name a few. These production routes all offer both advantages and disadvantages when compared to one another.

In this work, we fabricate sensor devices from graphene produced by mechanical exfoliation, CVD on Cu, epitaxial growth on 4H-SiC(0001), 4H-SiC(000-1), and chemical exfoliation. We compare the morphology, defect density, and chemical purity of these graphene devices using scanning electron microscopy, Raman spectroscopy, and x-ray photoelectron spectroscopy, respectively.

The surface modification is performed by firstly terminating the graphene with -OH groups using a Fenton reaction [7], then reacted with 3-Aminopropyl-triethoxysilane (APTES) in order to obtain an amine-terminated surface [8]. The surface amine groups are then used to link the graphene to a monoclonal antibody.

In order to be able to react with the surface amine groups, the carboxylic acids on the antibody are activated. However, in order to prevent the antibody from cross-linking, the majority of amine groups on the antibody are blocked using Di-tert-butyl dicarbonate. The antibody can now be reacted with the amine on the surface. The groups blocking the amines on the antibody are subsequently removed by mild acidic treatment.

Raman spectroscopy, Fourier-transform IR spectroscopy, and fluorescence microscopy are used to monitor the chemical modification and attachment of the monoclonal antibody to the graphene device.

Electron-beam induced defects are used to control the defect density of graphene, which are monitored using Raman spectroscopy. Defects cause a significant change in the chemical behavior of the graphene surface, creating local energy minima and maxima on the surface [9], which leads to the inhomogenous attachment of the covalently attached species.

In this work, we demonstrate the sensitivity of graphene biosensor devices fabricated on a number of substrates, with the aim of producing a generic, adaptable biosensor platform that can be used with any monoclonal antibodies. We also consider other practical issues such as cost and processability of the biosensor devices.

References

[1] M. Pumera, A. Ambrosi, A. Bonanni, E. L. K. Chng, and H. L. Poh, "Graphene for electrochemical sensing and biosensing," *Trac-Trends In Analytical Chemistry*, vol. 29, pp. 954–965, Oct. 2010.

[2] M. Pepe, R. Etzioni, Z. Feng, J. Potter, M. Thompson, M. Thornquist, M. Winget, and Y. Yasui, "Phases of biomarker development for early detection of cancer," *Journal of the National Cancer Institute*, vol. 93, no. 14, pp. 1054–1061, 2001.

[3] L. De Arco, Y. Zhang, A. Kumar, and C. Zhou, "Synthesis, transfer, and devices of single-and few-layer graphene by chemical vapor deposition," *Nanotechnology, IEEE Transactions on*, vol. 8, no. 2, pp. 135–138, 2009.

[4] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. Dresselhaus, and J. Kong, "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition," *Nano Letters*, vol. 9, no. 1, pp. 30–35, 2008.

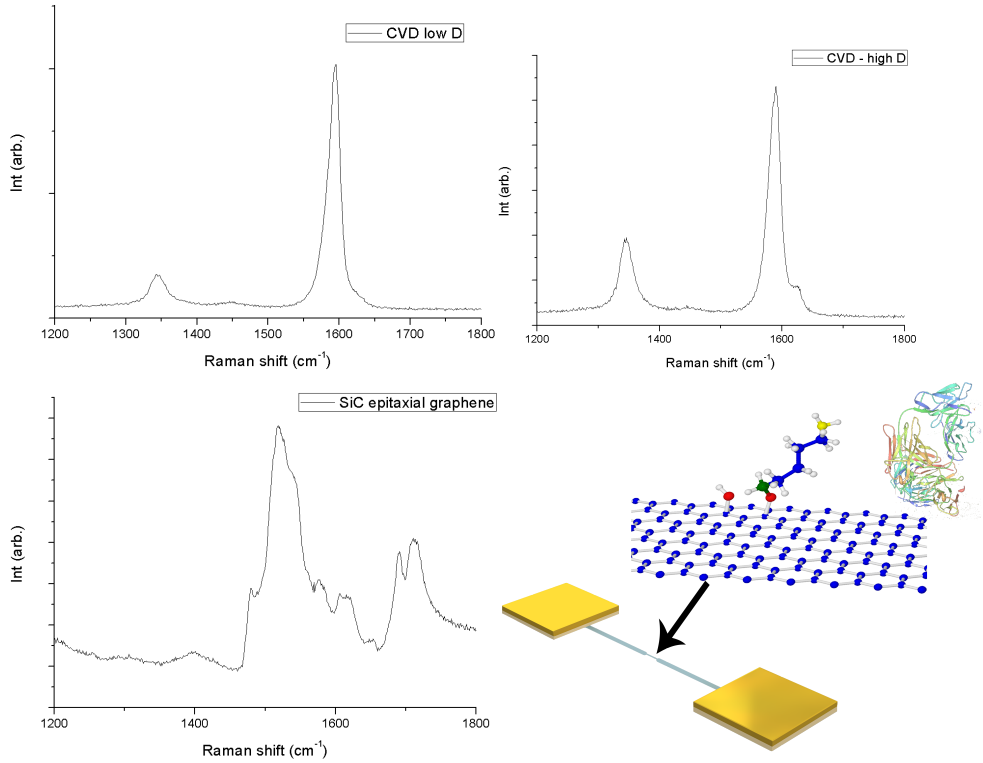

Figure 1: Raman spectra of CVD grown graphene with low (Top, LHS) and high (Top, RHS) defect densities, SiC epitaxial graphene (Bottom, LHS), Schematic of chemical attachment (Bottom, RHS)

[5] P. Sutter, "Epitaxial graphene how silicon leaves the scene," *Nature Materials*, vol. 8, pp. 171–172, Mar. 2009.

[6] S. Park and R. Ruoff, "Chemical methods for the production of graphenes," *Nature nanotechnology*, vol. 4, no. 4, pp. 217–224, 2009.

[7] R. Bradley, K. Cassity, R. Andrews, M. Meier, S. Osbeck, A. Andreu, C. Johnston, and A. Crossley, "Surface studies of hydroxylated multi-wall carbon nanotubes," *Applied Surface Science*, 2012.

[8] J. Kathi and K. Rhee, "Surface modification of multi-walled carbon nanotubes using 3-aminopropyltriethoxysilane," *Journal of Materials Science*, vol. 43, no. 1, pp. 33–37, 2008.

[9] D. Boukhvalov and M. Katsnelson, "Chemical functionalization of graphene with defects," *Nano letters*, vol. 8, no. 12, pp. 4373–4379, 2008.