Synthesis of Graphene on Ultra-Smooth Copper Foils for Large Area Flexible Electronics

Emre O. Polat[1], Osman Balci[2], Nurbek Kakenov[2], Coskun Kocabas[2†], Ravinder Dahiya[1†], *Senior Member IEEE*

[1]Electronics and Nanoscale Engineering, University of Glasgow, Glasgow, G12 8QQ, UK

[2]Department of Physics, Bilkent University, Ankara, Turkey

† Corresponding authors

***Abstract* —This work demonstrates the synthesis of high quality, single layer graphene on commercially available ultra-smooth copper foils. The presented method will result in improved scalability of graphene based electronic and optical devices. Our approach is compatible with roll-to-roll printing as well as transfer printing of graphene layers on to a broad range of substrates including flexible and ultra-thin polymers. We propose that using commercially available ultra-smooth coppers provides scalable approach with the reduced variation of transport properties sourced from local graphene quality.**

Keywords—Graphene, chemical vapor deposition, smooth copper foil, scalability.

I. Introduction

There is a growing interest in realizing the electronics over flexible and non-conventional substrates such as soft plastics and even paper [1, 2]. New functionalities and applications such as cell phones with roll-up displays, e-paper, radio-frequency identification (RFID) tags, medical patches that can be attached to the skin to deliver drugs or monitor vital signs, and tactile or electronic skin for robotics and prosthetics etc. are some of the many concepts that will be enabled by the electronic systems on large area flexible substrates [1-4]. So far the flexible electronics landscape has been occupied by the low-mobility organic semiconductors [2, 5]. But, recently major advances have also been reported through silicon [6, 7], metal oxides devices [8], and graphene based flexible optoelectronics [9] and sensing [10].

Carbon based materials have provided a new perspective in electronics owing to their very high carrier mobility and nanoscale dimensions. In particular, the carbon nanotubes [11] and graphene [12] have been shown to have promising performances suitable for high frequency electronics needed for futuristic fields such as internet of things, mobile health and smart cities. For high-performance and scaling up of electronics on large areas it is essential to have high quality samples of these materials. For example, the surface quality of the copper foils and the transfer printing process determine the performance and reliability of the transistors based on graphene. In this regard, the wafer scale synthesis of aligned arrays of single-walled carbon nanotubes on quartz [13] and sapphire crystals [14] is worth noting. In the case of graphene, the interesting scalable route, which is also low-cost method, is the chemical vapor deposition synthesis on copper foils [15]. In this paper, we demonstrate that the commercially available ultra-smooth copper foils can open new avenues for high quality graphene synthesis by chemical vapor deposition (CVD).

II. Importance of Surface Morphology of Graphene and the State of The Art

The large area growth of graphene by using CVD has been investigated since 2009 [16, 17] and many breakthrough improvements on the quality of graphene films have been reported since then [15, 18, 19]. Because of the low solubility limit of carbon in copper, the graphene growth procedure is self-limited on copper substrates [15]. This property of copper provides a straightforward method to synthesize single layer graphene. Further advantaged of this approach are that the copper foils are low-cost and scalable substrates. As said earlier, the surface quality of the copper foils and the transfer printing process greatly influence the performance and reliability of the graphene transistors.

Previous works have showed that the morphology of the copper surface is one of the key parameters to have better quality graphene films [20]. To achieve the continuous and high quality graphene film over large area; impurities, defects, grain boundaries and other surface features that can serve as a nucleation seed should be carefully engineered [20]. Recent progress of large scale production of smooth copper foils can also provide opportunities to improve performance of graphene transistors. To that end, varieties of techniques to smoothen the copper surfaces have been reported. For example, Luo et al. [21] used standard electro-polishing technique to smoothen the copper surfaces. Their Raman investigation implied better quality graphene with higher surface coverage compared to the unpolished copper samples [21]. Similar electrochemical polishing technique was used in the work by Yan. et al [22]. Together with the high pressure annealing, they produced hexagonal single crystal graphene domains nearly 2 mm in size [22]. Alternatively, melted copper surfaces were also used to form similar kind of single crystal hexagonal graphene flakes in previous works [23, 24]. Apart from these techniques, Vlassiouk et al. [25] reported the role of hydrogen gas as a surface activator and etchant. The shape and size of the single crystal graphene domains can be

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controlled precisely just by adjusting the partial pressure of hydrogen gas [25]. In addition, Robertson et al. [26] has showed the formation of few layer, single crystal, graphene flakes by changing the growth conditions.

It has been known that the quality of the copper surface directly effects the transport properties of the resulting graphene layer [27]. Orofeo et al. [27] demonstrated the hole mobility of the graphene grown on the Cu film is nearly 10 times greater than that of the graphene grown on the Cu foil by chemical vapor deposition. In addition to the surface morphology, crystallography of copper substrate also plays a crucial role in the formation of the graphene film [28]. Wood et al. [28] reported that, higher carbon diffusion rates at (111) direction, causes effective formation of single layer graphene on (111) direction compared to other crystal directions.

III. Graphene Synthesis and Flake Formation on Ultra-Smooth Copper Foils

Advancing the research on graphene synthesis, in this work we demonstrate the synthesis of high quality single layer graphene on commercially available ultra-smooth copper foils. As against previous reported works, our method does not require chemical treatment of copper foils before graphene growth and also the overall cost is low – both of which underline the novelty of our work. To compare the surface quality we used relatively rough *Alfa Aesar* foil (*item #13382*) which is commonly used for CVD graphene growth (Fig. 1 (a-c)) and commercially available ultra-smooth surface copper foils (*Mitsui mining and smelting co., LTD, B1-SBS*) (Fig. 1 (d-f)). To investigate the effect of the surface roughness to the quality of the graphene layer, both the ultra-smooth copper and the rough copper foils were placed in the same growth chamber to be exposed to same growth conditions.

We investigated the surface topography of the ultra-smooth copper foils with scanning electron microscopy (SEM) and atomic force microscopy (AFM). By sending the methane gas into the chamber with different intervals, we obtain both the graphene flakes (Fig. 2(a), 2(b)) and full coverage graphene film (Fig. 2(c)) on the ultra-smooth copper foils. Fig. 2(a) shows the SEM images of copper surface partially covered by graphene flakes. The rms surface roughness of the ultra-smooth copper is around 100 nm before annealing which is two times greater than the value reported for the copper foils commonly used in graphene growth [29]. According to our observations, the formation of continuous graphene layer initiates with the single crystal graphene flakes. Increasing the growth time, under the same methane flow rate and partial pressure, results in the formation of continuous graphene layer. Also we observed that the flake size and shape is directly related with the ratio of flow rate and partial pressure of hydrogen to methane gases as reported in previous work [25]. Moreover, the graphene flakes and continuous graphene layers that we synthesized includes ripples (Fig. 2(c)) because of the physical instability of perfectly flat graphene layer [30-33].

After transfer printing of the graphene layer to the dielectric surfaces, we performed Raman spectroscopy to

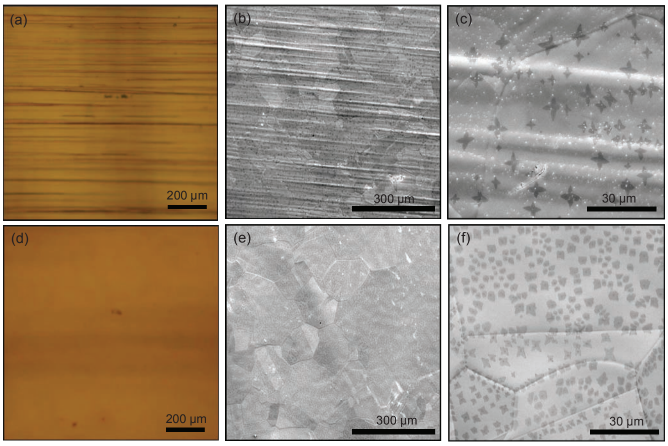

Fig. 1. Effects of copper surface morphology on graphene growth: (a) The optical microscope image of rough copper foil (Alfa Aesar foil (item #13382)). Deep scratches on the rough copper foil due to the rolling process are clearly visible (b) Scanning electron microscopy (SEM) image of the rough copper surface. (c) The magnified SEM image of the rough copper foil surface. The growth was terminated after 10 sec. to obtain dispersed graphene flakes. (d) Optical microscope image of ultra-smooth copper foil (Mitsui mining and smelting co. LTD., B1-SBS) and (e) SEM image of ultra-smooth copper surface after the graphene growth. (f) Ultra smooth copper surfaces with graphene flakes. The density and shape of the graphene flakes are different on the rough and smooth foils. The averaged grain size of the smooth copper foil after the growth is around 200 μm.

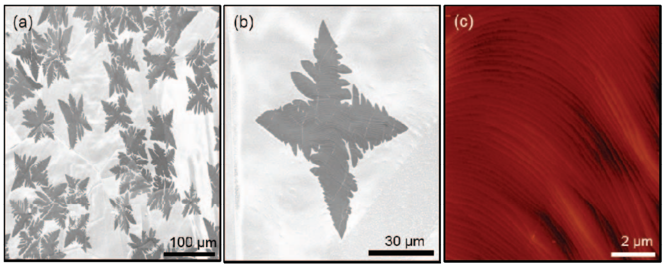

Fig. 2. Graphene flake formation at early stages of growth: (a, b) SEM images of the surface of the ultra-smooth copper partially covered by graphene flakes. To achieve ~60μm flakes, methane gas was flushed into chamber for 5 seconds then left to cooling to room temperature. Smoothness of the surface and size of the grain boundaries of the copper are clearly visible. (c) AFM image showing the surface topography of full graphene layer on the ultra-smooth copper foil. Graphene ripples, which are formed from the graphene flakes, are clearly seen.

check the graphene quality. Fig. 3(a) shows the Raman spectrum of the graphene on quartz substrate. The Raman fingerprints of the single layer graphene, namely the peaks of G band and 2D band are clearly seen in the spectrum. The laser excitation wavelength is 532 nm and the G band peak is

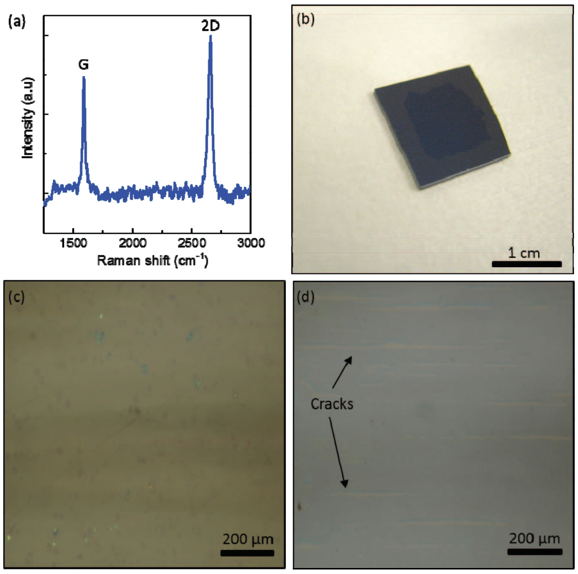

Fig. 3. Graphene on dielectric surfaces: (a) Raman spectrum of graphene on quartz substrate. Shape and place of the G and 2D peaks indicates single layer graphene. (b) Photograph of ~ 1cm^2 graphene on 100nm SiO_2 coated Si. The optical microscope images of graphene on SiO_2/Si synthesized by (c) using ultra-smooth copper foil, and (d) rough copper foil. Formation of the cracks on the graphene layer is a due to the deep trenches of rough-surface copper foil. However graphene synthesized by ultra-smooth copper does not have any crack. Instead, partial early-stage bilayer formation can be seen on the surface.

at 1587 cm^{-1}. The FWHM (full width at half maximum) of 2D peak at 2658 cm^{-1} is 36.79 and G/2D ratio ~1.5 which is likely due to the partial bilayer formation on single layer graphene. We did not observe any defect mode peak (D peak) in Raman spectrum which yields the high quality of the graphene.

Fig 3(b) shows the photograph of transfer printed graphene on 100 nm SiO_2 coated Si wafers. Due to dielectric thickness and viewpoint, single layer graphene is clearly visible. Fig 3(c) and 3(d) shows the optical microscope images of large area graphene on SiO_2/Si which were synthesized by using ultra-smooth and rough copper foils respectively. The rough copper graphene includes longitudinal cracks along the graphene layer. These cracks are the graphene-free areas and correspond to the deep trenches of the rough copper surface. Graphene synthesized on these trenches are not compatible to transfer printing techniques since they exist in the lower level to surface and when transfer printed to solid substrates these areas remain without graphene. The negative impact of trenches is that the transfer printing of graphene on flexible and large areas will also lead to graphene-free spots and this is detrimental to attaining devices and circuits as per the designs and layouts. The graphene-free spots can also cause variations in charge carrier transport and optical properties. This means the sensors in an array (e.g. active matrix display) or electronic devices in a circuit are likely to have non-uniform response. Therefore usage of commercially available ultra-smooth copper foils in CVD synthesis of graphene and resulting reduced variation in its transport and optical properties can open new avenues for its use in large area electronics and sensing applications.

IV. Conclusion

As a conclusion we have demonstrated synthesis of high quality single layer graphene on commercially available ultra-smooth copper foils and compared the quality of resulting graphene with the one from commonly used copper foils. The smooth copper foils are commonly used as negative electrodes for lithium-ion batteries. Recent industrial progress of large scale production of smooth copper foils can also provide opportunities to improve the quality of graphene grown by chemical vapor deposition. Our approach is compatible with various printing and transfer techniques such as roll to roll processes to extend the sample dimensions or wet and dry transfer printing techniques.

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References

[1] A. Nathan, A. Ahnood, M. T. Cole, L. Sungsik, Y. Suzuki, P. Hiralal, *et al.*, "Flexible Electronics: The Next Ubiquitous Platform," *Proceedings of the IEEE,* vol. 100, pp. 1486-1517, 2012.

[2] S. Khan, L. Lorenzelli, and R. Dahiya, "Technologies for Printing Sensors and Electronics over Large Flexible Substrates: A Review," *IEEE Sensors Journal,* vol. XX, pp. 1-22, 2014.

[3] D.-H. Kim, N. Lu, R. Ma, Y.-S. Kim, R.-H. Kim, S. Wang, *et al.*, "Epidermal Electronics," *Science,* vol. 333, pp. 838-843, 2011.

[4] R. S. Dahiya, P. Mittendorfer, M. Valle, G. Cheng, and V. Lumelsky, "Directions Towards Effective Utilization of Tactile Skin -- A Review," *IEEE Sensors Journal,* vol. 13, pp. 4121 - 4138, 2013.

[5] H. Sirringhaus, "25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon," *Advanced Materials,* pp. n/a-n/a, 2014.

[6] R. S. Dahiya and S. Gennaro, "Bendable Ultra-Thin Chips on Flexible Foils," *IEEE Sensors Journal,* vol. 13, pp. 4030-4037, Oct 2013.

[7] R. S. Dahiya, A. Adami, C. Collini, and L. Lorenzelli, "Fabrication of Single Crystal Silicon Mirco-/Nanostructures and Transferring them to Flexible Substrates," *Microelectr. Engg,* vol. 98, pp. 502-507, 2012.

[8] Y. H. Kim, J. S. Heo, T. H. Kim, S. Park, M. H. Yoon, J. Kim, *et al.*, "Flexible metal-oxide devices made by room-temperature photochemical activation of sol-gel films," *Nature,* vol. 489, pp. 128-U191, Sep 6 2012.

[9] E. O. Polat, O. Balci, and C. Kocabas, "Graphene based flexible electrochromic devices," *Scientific Reports,* vol. 4, Oct 1 2014.

[10] Y. Wang, R. Yang, Z. W. Shi, L. C. Zhang, D. X. Shi, E. Wang, *et al.*, "Super-Elastic Graphene Ripples for Flexible Strain Sensors," *Acs Nano,* vol. 5, pp. 3645-3650, 2011.

[11] C. Kocabas, H. S. Kim, T. Banks, J. A. Rogers, A. A. Pesetski, J. E. Baumgardner, *et al.*, "Radio frequency analog electronics based on carbon nanotube transistors," *Proc. Natl. Acad.Sc,.* vol. 105, pp. 1405-1409, 2008.

[12] Y. M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H. Y. Chiu, A. Grill, *et al.*, "100-GHz Transistors from Wafer-Scale Epitaxial Graphene," *Science,* vol. 327, pp. 662-662, Feb 5 2010.

[13] C. Kocabas, M. Shim, and J. A. Rogers, "Spatially selective guided growth of high-coverage arrays and random networks of single-walled carbon nanotubes and their integration into electronic devices," *J. American Chemical Society,* vol. 128, pp. 4540-4541, 2006.

[14] N. Ishigami, H. Ago, K. Imamoto, M. Tsuji, K. Iakoubovskii, and N. Minami, "Crystal plane dependent growth of aligned single-walled carbon nanotubes on sapphire," *J. Am. Chem. Soc.,* vol. 130, pp. 9918-9924, 2008.

[15] X. S. Li, W. W. Cai, J. H. An, S. Kim, J. Nah, D. X. Yang, *et al.*, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science,* vol. 324, pp. 1312-1314, 2009.

[16] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, *et al.*, "Large-scale pattern growth of graphene films for stretchable transparent electrodes," *Nature,* vol. 457, pp. 706-710, 2009.

[17] A. Reina, X. T. Jia, J. Ho, D. Nezich, H. B. Son, V. Bulovic, *et al.*, "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition," *Nano Letters,* vol. 9, pp. 30-35, 2009.

[18] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, *et al.*, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," *Nature Nanotechnology,* vol. 5, pp. 574-578, Aug 2010.

[19] X. S. Li, C. W. Magnuson, A. Venugopal, J. H. An, J. W. Suk, B. Y. Han, *et al.*, "Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process," *Nano Letters,* vol. 10, pp. 4328-4334, Nov 2010.

[20] G. H. Han, F. Gunes, J. J. Bae, E. S. Kim, S. J. Chae, H. J. Shin, *et al.*, "Influence of Copper Morphology in Forming Nucleation Seeds for Graphene Growth," *Nano Letters,* vol. 11, pp. 4144-4148, Oct 2011.

[21] Z. T. Luo, Y. Lu, D. W. Singer, M. E. Berck, L. A. Somers, B. R. Goldsmith, *et al.*, "Effect of Substrate Roughness and Feedstock Concentration on Growth of Wafer-Scale Graphene at Atmospheric Pressure," *Chemistry of Materials,* vol. 23, pp. 1441-1447, Mar 22 2011.

[22] Z. Yan, J. Lin, Z. Peng, Z. Sun, Y. Zhu, L. Li, *et al.*, "Towards the Synthesis of Wafer-Scale Single-Crystal Graphene on Copper Foils," *Acs Nano,* 2012.

[23] D. C. Geng, B. Wu, Y. L. Guo, L. P. Huang, Y. Z. Xue, J. Y. Chen, *et al.*, "Uniform hexagonal graphene flakes and films grown on liquid copper surface," *Proc. Natl. Acad.Sc.,* vol. 109, pp. 7992-7996, 2012.

[24] Y. M. A. Wu, Y. Fan, S. Speller, G. L. Creeth, J. T. Sadowski, K. He, *et al.*, "Large Single Crystals of Graphene on Melted Copper Using Chemical Vapor Deposition," *Acs Nano,* vol. 6, pp. 5010-5017, 2012.

[25] I. Vlassiouk, M. Regmi, P. F. Fulvio, S. Dai, P. Datskos, G. Eres, *et al.*, "Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene," *Acs Nano,* vol. 5, pp. 6069-6076, Jul 2011.

[26] A. W. Robertson and J. H. Warner, "Hexagonal Single Crystal Domains of Few-Layer Graphene on Copper Foils," *Nano Letters,* vol. 11, pp. 1182-1189, 2011.

[27] C. M. Orofeo, H. Hibino, K. Kawahara, Y. Ogawa, M. Tsuji, K. Ikeda, *et al.*, "Influence of Cu metal on the domain structure and carrier mobility in single-layer graphene," *Carbon,* vol. 50, pp. 2189-2196, 2012.

[28] J. D. Wood, S. W. Schmucker, A. S. Lyons, E. Pop, and J. W. Lyding, "Effects of Polycrystalline Cu Substrate on Graphene Growth by Chemical Vapor Deposition," *Nano Lett.,* vol. 11, pp. 4547-4554, 2011.

[29] B. Zhang, W. H. Lee, R. Piner, I. Kholmanov, Y. P. Wu, H. F. Li, *et al.*, "Low-Temperature Chemical Vapor Deposition Growth of Graphene from Toluene on Electropolished Copper Foils," *Acs Nano,* vol. 6, pp. 2471-2476, 2012.

[30] A. Fasolino, J. H. Los, and M. I. Katsnelson, "Intrinsic ripples in graphene," *Nature Materials,* vol. 6, pp. 858-861, 2007.

[31] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, "The structure of suspended graphene sheets," *Nature,* vol. 446, pp. 60-63, 2007.

[32] R. C. Thompson-Flagg, M. J. B. Moura, and M. Marder, "Rippling of graphene," *Epl,* vol. 85, 2009.

[33] Z. Wang and M. Devel, "Periodic ripples in suspended graphene," *Physical Review B,* vol. 83, 2011.