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Direct Graphene Growth on Co₃O₄(111) by Molecular Beam Epitaxy: Graphene Growth on an Oxide Substrate

By Mi Zhou, Frank L. Pasquale, Jeffry A. Kelber , Peter A. Dowben, Alex Boosalis, and Mathias Schubert, Vanya Darakchieva, Rositza Yakimova*

[*] Prof. J. Kelber, Corresponding-Author, Mi Zhou, Frank Pasquale
Department of Chemistry, University of North Texas
1155 Union Circle, #305070, Denton, TX USA 76203-5017
E-mail: ((kelber@unt.edu))

Prof. P. A. Dowben
Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience
Theodore Jorgensen Hall, 855 North 16th Street, University of Nebraska-Lincoln, P.O. Box
880299, Lincoln, Nebraska 68588-0299

Alex Booslais, Prof. Mathias Schubert
Dept. Electrical Engineering, 209N Walter Scott Engineering Center, University of Nebraska
– Lincoln, Lincoln, NE 68588-0511

Prof. Vanya Darakchieva, Rositza Yakimova
Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83
Linköping, Sweden

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Graphene displays electronic properties, including high room temperature carrier mobilities, long carrier mean free paths,^[1-3] polarizability in proximity to a magnetic substrate^[4] and long spin diffusion lengths^[5] with exciting potential for charge or spin-based device applications. A critical step in practical device development, however, is the direct, controlled growth, by industrially feasible and scalable methods, of high quality single or few layer graphene films on dielectric substrates. Methods such as chemical or physical vapor deposition or molecular beam epitaxy (MBE) are of interest, but must occur at growth temperatures allowing integration with Si CMOS or other device materials. Most reports, however, have involved graphene/substrate interfaces formed by one of two approaches: (a) physical transfer of graphene sheets—grown by chemical vapor deposition on metal substrates^[6, 7] or taken from HOPG;^[1, 2] or (b) the growth of graphene layers by high temperature evaporation of Si from SiC(0001).^[8-10] The former method presents significant problems for practical device production, including formation of nanoscale interfacial

electronic inhomogeneities.^[11] The second method appears limited to SiC(0001) substrates. Recent reports of MBE graphene growth on SiC(0001)^[12, 13] are also limited to SiC substrates. The ability to grow single or few layer graphene on oxides or other dielectric substrates of choice would not only enhance graphene integration with Si CMOS, but also facilitate the development of novel multifunctional non-volatile devices^[14, 15] that exploit substrate functionality and graphene/substrate interactions.

Direct graphene growth by chemical or physical vapor deposition has been reported on monolayer h-BN(0001)/Ru(0001)^[16] and bulk MgO(111) single crystals^[17] at or below 1000 K. In both cases, however, strong substrate/graphene interactions, consistent with commensurate graphene/substrate interfaces,^[16, 18] result in pronounced substrate-induced modification of the graphene electronic structure.^[17, 19] Recently, the growth of continuous graphene layers by chemical vapor deposition on Al₂O₃(0001) has been reported,^[20] but the temperatures involved (> 1800 K for few-defect films) suggest limited applicability to device fabrication involving materials other than alumina. The growth temperature reported here, 1000 K, is fully compatible with Si CMOS front end processing, and is significantly lower than that previously reported (~ 1300 K)^[12, 13] for MBE growth on SiC(0001).

Growth studies were carried out in a chamber equipped for Auger electron spectroscopy, and reverse-view low energy electron diffraction (LEED) I(V) measurements, as described previously,^[16] but with the addition of a commercial multi-target electron beam evaporator for MBE. Co and graphite rod sources were used, and chamber pressure during deposition was < 1 x 10⁻⁸ Torr. The intensities of LEED diffraction spots were determined using commercial imaging software, as described previously.^[17] X-ray photoemission (XPS) spectra were acquired in a separate system^[21] with a hemispherical analyzer in constant pass energy mode (23.5 eV), using an unmonochromatized Al K α X-ray source operated at 15 kV, 300 W. Spectroscopic ellipsometry data were acquired and analyzed by methods described previously.^[24, 25]

Co films were deposited onto commercially available 1 cm^2 $\text{Al}_2\text{O}_3(0001)$ substrates at 750 K, with estimated Co thicknesses $> 40\text{ \AA}$, as determined by Auger spectroscopy. These films yielded well-defined LEED images characteristic of $\text{Co}(111)$.^[26] Subsequent annealing resulted in the surface segregation of dissolved oxygen and the evolution of a ~ 3 monolayer (ML) Co oxide film with LEED pattern identical to that of few-layer $\text{Co}_3\text{O}_4(111)$.^[27] Graphene films were subsequently grown at 1000 K by carbon MBE, and the presence of a graphene overlayer was confirmed by Raman spectroscopy.

Fig. 1 displays the Auger electron spectra (Fig. 1a) acquired after depositions corresponding to 0.4 ML (first deposition) and 3.0 ML (last deposition). The C(KVV) spectral region of the Auger electron spectra (Fig. 1a, inset) shows lineshapes characteristic of sp^2 carbon.^[28] The “growth curve” abstracted from the evolution of the Auger electron spectra determined average thickness of the carbon overlayer with MBE deposition time, as plotted in Fig. 1b. The data may be fit by a series of straight lines, with breaks in the curve corresponding to completion of one monolayer and beginning of another. Such behavior is strongly suggestive of layer-by-layer growth.^[29] Thus, the Auger data demonstrate growth of multilayer sp^2 carbon films by MBE on $\text{Co}_3\text{O}_4(111)$.

Fig. 2 shows LEED images and corresponding line scans for films of 0.4 ML (Fig. 2a,b) and 3 ML (Fig. 2c,d) average thickness. Both LEED images (Fig. 2a,c) consist of an outer six-fold array of bifurcated spots, and an inner array of spots (3 strong, 3 weak, marked by arrows, Fig. 2a) rotated 30° from the outer ring of spots. The outer spots in the bifurcated six-fold array (e.g., G1, G2—Fig. 2b,d) increase in relative intensity with increasing carbon deposition while the other spots in the bifurcated outer ring (e.g., O1, O2—Fig. 2b,d) as well as the inner ring of spots (arrows, Fig. 2a,b) decrease in intensity during this process. This identifies the outer spots in the bifurcated array as related to a six-fold sp^2 $\text{C}(111)$ overlayer—graphene. The other spots are characteristic of the $\text{Co}_3\text{O}_4(111)$ substrate, and an estimate of the O-O surface nearest neighbor distance can be obtained from the line scans, with the

reciprocal length from G1 to G2 (Fig. 2b,d) corresponding to $2.5(\pm 0.1)$ Å. The O-O nearest neighbor distance is thus estimated at $2.8(\pm 0.1)$ Å, in excellent agreement with that obtained for adsorbate-free $\text{Co}_3\text{O}_4(111)$ films.^[30] These data also show that the graphene/oxide interface is incommensurate or encompasses a very large unit cell. The LEED data thus indicate that graphene grows on the $\text{Co}_3\text{O}_4(111)$ substrate without significant reconstruction of the oxide surface.

Following the acquisition of Auger electron spectra and LEED data, the sample was exposed to ambient, and then re-inserted into UHV. Subsequently acquired Auger electron spectra and LEED data showed no change from those in Fig. 1a (solid line) and Fig. 2c, respectively, indicating that the sample was inert to ambient exposure. This effect has been observed for other reactive surfaces covered with graphene layers^[16, 19, 26, 31] and indicates that the graphene multilayers form a macroscopically continuous film shielding the 3 ML $\text{Co}_3\text{O}_4(111)/\text{Co}(0001)$ film from reaction with ambient. The XPS spectra of the 3 ML graphene film on $\text{Co}_3\text{O}_4(111)/\text{Co}(0001)$ substrate are shown in **Fig. 3**. The C(1s) spectrum (Fig. 3a) shows an asymmetric main feature characteristic of graphene.^[13] Referencing the spectrometer energy scale to the Al(2p) binding energy of 74.4 eV, characteristic of bulk sapphire,^[23] yields a Co(2p) peak maximum binding energy of $778.3(\pm 0.1)$ eV (Fig. 3b), in excellent agreement with literature values for both bulk and thin film Co.^[23, 32] A shoulder at higher binding energies (Fig. 3b) is also consistent with the formation of Co_3O_4 ,^[33] and the intensity ratio of the Co(2p) oxide and metal features indicates an oxide thickness of 3 ML. The O(1s) peak maximum is at $530.9(\pm 0.1)$ eV, consistent with O(1s) spectra from both bulk sapphire^[32] and $\text{Co}_3\text{O}_4(111)$ thin films,^[33] with a small shoulder at higher binding energy indicating some hydroxylation. The C(1s) main peak binding energy (Fig. 3a) is at $284.9(\pm 0.1)$ eV, substantially higher than the 284.5 eV binding energy commonly reported for bulk graphite, but similar to the 284.7 eV binding energy reported for few layer graphene

grown by graphitization of SiC(0001)^[34], and indicating charge transfer from graphene to the oxide substrate.

Fig. 4 displays the experimental imaginary part of the dielectric response function for the 3 ML graphene/Co₃O₄(111)/Co(0001) sample. The feature with a maximum near 5.5 eV (Fig. 4, Co₃O₄) attributed to both a π to π^* transition and π plasmon excitation,^[35] is comparable to but blue-shifted with respect to features in the dielectric function reported for graphene physically transferred to SiO₂^[36-38] and for graphene grown on SiC substrates.^[35, 37] These energies have been shown to be somewhat dependent on both the graphene substrate^[37] and number of graphene layers.^[35] We suggest, however, that the substantial observed blue shift (Fig. 4) is consistent with the significant graphene-to-oxide charge transfer deduced from the XPS C(1s) binding energy (Fig. 3). The spectroscopic ellipsometry data confirm that the dielectric response of the graphene film and Co₃O₄ system are similar to few-layer graphene films grown on SiC(0001) or transferred to SiO₂.

In conclusion, Auger, LEED, XPS and spectroscopic ellipsometry data demonstrate the layer-by-layer growth of graphene films, up to at least 3 ML thickness, on Co₃O₄(111)/Co(0001) at 1000 K by MBE. The substantially lower growth temperature for graphene MBE on Co₃O₄(111), compared to graphene MBE on SiC(0001), indicate that C/oxide interactions play an important role in the initial graphene nucleation and growth, since only amorphous C is obtained by MBE on SiC below 1273 K^[12, 13]. LEED data indicate that the graphene/oxide substrate is incommensurate, without significant reconstruction of the Co₃O₄(111) surface. XPS C(1s) data reveal the expected $\pi \rightarrow \pi^*$ shakeup feature, and the 284.9(±1) binding energy for the peak maximum indicates graphene-to-oxide charge transfer. The spectroscopic ellipsometry data are similar to those of graphene on SiO₂ or SiC.

Bulk- or OH-terminated MgO(111) has a similar O-O nearest neighbor distance to Co₃O₄(111)^[39] Therefore, the difference between the incommensurate graphene/Co₃O₄(111)

interface and the apparently commensurate^[17, 18] graphene/MgO(111) interface is striking, and may reflect the tendency of highly polar (111) oxides with the rocksalt structure to reconstruct,^[39-41] especially upon reaction with metal overlayers.^[42] In contrast, relaxations at the Co₃O₄(111) surface greatly reduce the surface polarity, and therefore the driving force for reconstruction.^[30] This in turn suggests that numerous metal oxides with similar O-O surface nearest neighbor distances and non-polar surface layers may serve as templates for graphene growth, with possibilities for numerous multifunctional charge- or spin-based devices. Additionally, highly (111)-oriented Co₃O₄ films have been grown on Si(100) by plasma-enhanced atomic layer deposition,^[25] suggesting a new pathway towards graphene integration with Si CMOS.

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References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jian, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **2005**, 438, 197.
- [3] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, 81, 109.
- [4] H. Haugen, D. Huertas-Hernando, A. Brataas, *Phys. Rev. B* **2008**, 77, 115406.
- [5] N. Tombros, C. Jozsa, M. Popinciuc, H. T. Jonkman, B. J. van Wees, *Nature* **2007**, 571.
- [6] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* **2009**, 324, 1312.

- [7] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2009**, 9, 30.
- [8] C. Berger, Z. Song, T. Li, Z. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer, *Journal of Physical Chemistry B* **2004**, 108, 19912.
- [9] C. Berger, Z. Spon, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov., E. H. Conrad, P. N. First, W. A. de Heer, *Science* **2006**, 312, 1191.
- [10] I. Forbeaux, J.-M. Themlin, J.-M. Debever, *Phys. Rev. B* **1998**, 58, 16396.
- [11] Y. Zhang, V. W. Brar, C. Girit, A. Zettl, M. F. Crommie, *Nature Physics* **2009**, 5, 722.
- [12] J. Park, W. C. Mitchel, L. Grazulis, H. E. Smith, K. G. Eyink, J. J. Boeckl, D. H. Tomich, S. D. Pacley, J. E. Hoelscher, *Adv. Mat.* **2010**, 22, 4140.
- [13] E. Moreau, F. J. Ferrer, D. Vignaud, S. Godey, X. Wallart, *Phys. Stat. Sol. A* **2010**, 207, 300.
- [14] Y. Zheng, G. Ni, C. Toh, M. Zeng, S. Chen, K. Yao, B. Özyilmaz, *Appl. Phys. Lett.* **2009**, 94, 163505.
- [15] P. Michetti, P. Recher, G. Iannaccone, *Nano Lett.* **2010**, 10, 4463.
- [16] C. Bjelkevig, M. Zhou, J. Xiao, P. A. Dowben, L. Wang, W. Mei, J. A. Kelber, *J. Phys.: Cond. Matt.* **2010**, 22, 302002.
- [17] S. Gaddam, C. Bjelkevig, S. Ge, K. Fukutani, P. A. Dowben, J. A. Kelber, *J. Phys.: Cond. Matt.* **2011**, 23, 072204.
- [18] J. A. Kelber, S. Gaddam, C. Vamala, S. Eswaran, P. A. Dowben, *Proc. SPIE (in press)*.
- [19] L. Kong, C. Bjelkevig, S. Gaddam, M. Zhou, Y. H. Lee, G. H. Han, H. K. Jeong, N. Wu, Z. Zhang, J. Xiao, P. A. Dowben, J. A. Kelber, *J. Phys. Chem. C* **2010**, 114, 21618.
- [20] M. A. Fanton, J. A. Robinson, B. E. Weiland, M. LaBella, K. Trumbell, R. Kasarda, C. Howsare, M. Hollander, D. W. Snyder, Abstract, Graphene 2011 Conference (June 23, 2011) Bilbao, Spain (available at www.programmaster.org)
- [21] C. Bjelkevig, J. Kelber, *Electrochim. Acta* **2009**, 54, 3892.
- [22] D. Briggs, M. P. Seah, Eds, *Practical Surface Analysis, Second Edition, Volume 1--Auger and X-ray Photoelectron Spectroscopy*, Vol. 1, 2nd edn., John Wiley and Sons, New York, NY **1990**.
- [23] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, Eden Prairie, Minnesota **1995**.
- [24] T. Hofmann, A. Boosalis, P. Kuhne, C. M. Herzinger, J. A. Woollam, D. K. Gaskill, J. L. Tedesco, M. Schubert, *Appl. Phys. Lett.* **2011**, 98, 041906.

- [25] Donders. M. E., H. C. M. Knoops, van de Sanden, M. C. M., W. M. M. Kessels, P. H. L. Notten, *J. Electrochem. Soc.* **2011**, *158*, G92.
- [26] H. Ago, Y. Ito, N. Mizuta, K. Yoshida, B. Hu, C. M. Orofeo, M. Tsuji, K. Ikeda, S. Mizuno, *ACS Nano* **2010**, *4*, 7407.
- [27] C. A. F. Vaz, D. Prabhkaran, E. I. Altman, V. E. Henrich, *Phys. Rev. B.* **2009**, *80*, 155457.
- [28] P. E. Viljoen, W. D. Roos, H. C. Swart, P. H. Holloway, *Appl. Surf. Sci.* **1996**, *100/101*, 612.
- [29] C. Argile, G. E. Rhead, *Surf. Sci. Rep.* **1989**, *10*, 277.
- [30] W. Meyer, K. Biedermann, M. Gubo, L. Hammer, K. Heinz, *J. Phys. : Cond. Matt.* **2008**, *20*, 265011.
- [31] Y. S. Dedkov, M. Fonin, U. Rudiger, C. Laubschat, *Phys. Rev. Lett.* **2008**, *100*, 107602.
- [32] S. A. Chambers, T. Droubay, D. R. Jennison, T. R. Mattson, *Science* **2002**, *297*, 837.
- [33] S. C. Petit, M. A. Langell, *J. Vac. Sci. and Technol. A.* **2004**, *22*, 1690.
- [34] K. V. Emtsev, F. Speck, T. Seyller, L. Ley, *Phys. Rev. B.* **2008**, *77*, 155303.
- [35] I. Santoso, P. K. Gogoi, H. B. Su, H. Huang, Y. Lu, D. Qi, W. Chen, M. A. Majidi, Y. P. Feng, A. T. S. Wee, K. P. Loh, T. Venkatesan, R. P. Saichu, A. Goos, A. Kotlov, M. Rubhausen, A. Rusydi, *Phys. Rev. B.* **2011**, *84*, 081403
- [36] V. G. Kravets, A. N. Grigorenko, R. R. Nair, P. Blake, S. Anissimova, K. S. Novoselov, A. K. Geim, *Phys. Rev. B* **2010**, *81*, 155413.
- [37] A. Boosalis, T. Hofmann, S. Schoche, P. Dowben, S. Gaddam, C. Vamala, J. Kelber, V. Darakchieva, R. Yakimova, L. O. Nyakiti, V. D. Wheeler, R. L. Myers-Ward, C. R. Eddy Jr., D. K. Gaskil, M. Schubert, *Conference Abstract, Nano DDS Aug. 29, 2011. (Brooklyn, N.Y.)*
- [38] F. J. Nelson, V. K. Kamineni, T. Zhang, E. S. Comfort, J. U. Lee, and A. C. Diebold, *Appl Phys. Lett.* **2010**, *97*, 253110
- [39] V. K. Lazarov, R. Plass, H. -. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, M. Gajdardziska-Josifovska, *Phys. Rev. B* **2005**, *71*, 115434.
- [40] F. Rohr, K. Wirth, J. Libuda, D. Cappus, M. Baumer, H.-J. Freund, *Surf. Sci.* **1994**, *315*, L977.
- [41] D. Cappus, C. Xu, D. Ehrlich, B. Dillmann, C. A. Ventrice Jr., K. Al Shamery, H. Kühlenbeck, H.-J. Freund, *Chem. Phys.* **1993**, *177*, 533.
- [42] J. Goniakowski, C. Noguera, *Physical Review B* **2002**, *66*, 085417.

Figure 1. (a) Auger spectra acquired after deposition of 0.4 ML graphene (solid line) and 3.0 ML graphene (dashed line), inset—detail of C(KVV) spectral region showing characteristic sp² lineshape; (b) Growth curve showing evolution of Auger-derived average carbon overlayer thickness (number above each data point) as a function of deposition time at 1000 K. Lines are guides to the eye.

Figure 2. LEED and corresponding line scan data for (a,b) 0.4 ML graphene on Co₃O₄(111), and (c,d) 3 ML graphene on Co₃O₄(111). Arrows (a,b) mark diffraction spots associated with

$\text{Co}_3\text{O}_4(111)$, as do inner spots in the outer ring of bifurcated features (e.g., O1,O2—b,d).
Outer spots in the outer ring of bifurcated features (e.g., G1, G2—b,d) are graphene-related.
LEED beam energy is 65 eV.

Figure 3. (a) $\text{C}(1s)$, (b) $\text{Co}(2p)$ and (c) $\text{O}(1s)$ XPS spectra for a 3 ML graphene film on $\text{Co}_3\text{O}_4(111)$. The magnified portion of the $\text{C}(1s)$ spectrum (a, inset) near 291 eV binding energy indicates the presence of a $\pi \rightarrow \pi^*$ shakeup feature.

Figure 4. The imaginary part of the dielectric optical response function for the 3 ML graphene/Co₃O₄(111)/Co(0001) system as interpreted directly from data (a). This is compared to the pure dielectric response of graphene sublimated from 4H-silicon carbide, on the carbon face (b), and on the silicon face (d); and graphene transferred to SiO₂ (c), adapted from ref. 38. Negative numbers for (b-c) are the vertical offsets of the data.