Large-area uniform graphene-like thin films grown by chemical vapor deposition directly on silicon nitride

Jie Sun (孙捷),[a), b)] Niclas Lindvall,[b)] Matthew T. Cole,[c)] Kenneth B. K. Teo (张谋瑾),[d)] and August Yurgens[b)]

[b)]*Quantum Device Physics Laboratory, Department of Microtechnology and Nanoscience, Chalmers University of Technology, S-41296 Gothenburg, Sweden*

[c)]*Electrical Engineering Division, Engineering Department, University of Cambridge, 9 JJ Thomson Avenue, CB3 0FA, Cambridge, United Kingdom*

[d)]*AIXTRON Nanoinstruments Ltd., Swavesey, Cambridge, CB24 4FQ, United Kingdom*

Abstract

Large-area uniform carbon films with graphene-like properties are synthesized by chemical vapor deposition directly on Si_3N_4/Si at 1000 °C without metal catalysts. The as-deposited films are atomically thin and wrinkle- and pinhole-free. The film thickness can be controlled by modifying the growth conditions. Raman spectroscopy confirms the sp^2 graphitic structures. The films show ohmic behavior with a sheet resistance of ~2.3-10.5 kΩ/□ at room temperature. An electric field effect of ~2-10% (V_G=-20 V) is observed. The growth is explained by the self-assembly of carbon clusters from hydrocarbon pyrolysis. The scalable and transfer-free technique favors the application of graphene as transparent electrodes.

[a)] Author to whom correspondence should be addressed. Electronic mail: albertjefferson@sohu.com, jiesu@chalmers.se.

Graphene is a monolayer of sp^2 hybridized carbon atoms forming a two-dimensional hexagonal crystal lattice. Graphene has received much attention since 2004.[1] Due to its extraordinary properties, graphene is considered to be one of the candidate materials for post-silicon nanoelectronics.[2] For instance, by virtue of its high optical transparency and high carrier mobility, graphene can be used in transparent electrodes and ultrafast transistors.[3,4] However, while mechanical exfoliation is still widely used to fabricate graphene, the flakes are far too small and irregular for practical applications. Today, there are two common alternative techniques for large-area graphene synthesis. One is the high-temperature annealing of SiC which results in the desorption of Si from the surface leaving excess carbon behind.[5] This method, however, suffers from the lack of availability of large, inexpensive SiC substrates. Another more promising technique in terms of scalability is chemical vapor deposition (CVD) on metals from hydrocarbon precursors. It is fully compatible with the existing semiconductor processes, and has shown significant potential as a cost effective route toward producing high-quality graphene. Commonly, graphene is grown on Ni[6,7] or Cu[8-11] catalysts. For most electronic applications, however, the as-synthesized graphene must be transferred to various dielectric substrates, inevitably resulting in wrinkles, holes and metal etching residues. Thus, there is a substantial need to develop a scalable method for reliable production of large-area graphene directly on insulating substrates.

Previously, we have demonstrated that graphene-like thin films can be synthesized by CVD directly on silicon dioxide (300 nm thermal SiO_2 on Si)[12] or hafnium dioxide (320 nm atomic layer deposited HfO_2 on Si),[13-15] which is promising in applications such as transparent electrodes. Graphene-like thin films can also be realized on nitrides such as GaN[16] and BN.[17] However, the electrical properties of these films on nitrides are unknown. This letter reports the synthesis and

electronic characterization of large-area uniform graphene-like thin films by CVD directly on a silicon nitride substrate. Although Si_3N_4 has a larger number of bulk traps compared with SiO_2, it has higher resistivity (10^{16} Ω·cm) and dielectric strength (10 MV/cm) than most insulators commonly available in microelectronics.[18] The thickness of the as-deposited films on Si_3N_4, which can be reduced to be atomically thin, is controlled by tuning the deposition time and/or the carbon precursor partial pressure. The films are termed "graphene-like" because of the optical and electrical similarity to metal-catalyzed graphene. However, the quality of the thin films requires continued optimization in terms of crystallinity and carrier mobility. The sp^2-C structure was confirmed by Raman spectroscopy. At room temperature, the thin films showed ohmic behavior and electric field effect. This transfer-free process results in highly reproducible fabrication and favors the industrialization of graphene-based technology.

Si_3N_4 thin films (100 nm) grown at 770 °C from $SiCl_2H_2$ and NH_3 precursors by low-pressure CVD (Centrotherm) on Si were used as the substrates. The graphene-like thin films were produced in a home-built hot-wall CVD system under atmospheric pressure. The Si_3N_4/Si substrates were heated to 1000 °C in a flow of 50 sccm hydrogen and 1000 sccm argon. The samples were kept at 1000 °C for 3 min. Then, 300 sccm methane was introduced into the chamber to initiate the deposition. The growth time was 30 min for sample A and 45 min for sample B. Sample C was grown at CH_4:H_2=1000:50 sccm (no Ar) at 1000 °C for 30 min. After growth, the CH_4 flow was terminated, and the system was held at high temperature for a further 3 min before ambient cooling to room temperature in the same H_2+Ar atmosphere. The temperature profile for the deposition of sample A is depicted in Fig. 1. To test the reproducibility, the growth of graphene-like thin films on Si_3N_4/Si was repeated in a cold-wall low-pressure CVD system (Black

Magic, AIXTRON). The deposition temperature was 1000 ^{o}C with C_2H_2 as the precursor. A 30 min deposition at 20 sccm C_2H_2, 20 sccm H_2 and 1000 sccm Ar produced graphene-like thin films similar to sample A in terms of optical and electrical properties.

The Raman spectra of the thin films grown directly on Si_3N_4/Si are summarized in Fig. 2. The G band centered at ~1604 cm^{-1} and the 2D band at ~2704 cm^{-1} are clearly resolved for all samples. The G- and 2D bands are Raman signatures of sp^2 graphitic materials.[19] The well-defined peaks differentiate the thin films from amorphous carbon (*a*-C).[19] The D band at ~1349 cm^{-1} and the G+D band (higher order Raman signals) at ~2953 cm^{-1} are also noted. The large D band indicates the high defect densities within the as-synthesized thin films. The graphene-like films on samples A and B are much thinner than sample C because of the lower CH_4 concentration. As a result, spectral features associated with the substrate were detected at approximately 1000 cm^{-1}.

An overview of the samples is shown in Fig. 3(a). The bare Si_3N_4/Si, samples A_1 and B are in the upper row; sample C and sample A_2 (after device processing) are in the lower row. After the growth, there was no apparent change in color except for sample C. Fig. 3(b) shows an optical image of a device made on sample A by traditional photolithography using a Shipley S1813 resist. A rather weak contrast between the graphene-like thin film and Si_3N_4/Si can be seen at this scale. Atomic force microscopy line-scans across the steps in the fabricated devices indicate that the thickness of the thin films was ~2, 4 and 70 nm for samples A, B and C, respectively. It is known that exfoliated monolayer graphene typically has a height of 0.6-0.8 nm[20] which often increases to ~2 nm after lithographic processing.[21,22] Samples A and B have depths that are largely consistent with these values, which may correspond to monolayer and few-layer graphene-like thin films, respectively. Sample C is a shiny-gray graphite-like film. Clearly, the number of graphene layers

in the thin films increases as the deposition time and/or C precursor partial pressure increases, permitting accurate control over the film thickness. Neither wrinkles nor pinholes are observed in the deposited thin films in Fig. 3, implying a high degree of macroscopic uniformity.

Room temperature electrical measurements were performed on samples A, B and C. In Fig. 3(b), electrodes (5 nm Cr/45 nm Au) in the Hall-bar structures were used for current biasing (left and right) and voltage probing (upper and lower). The device active area was 4×4 μm^2. Figs. 4(a) and (b) show the measured properties of samples A and B, respectively. Linear *I-V* curves (at zero gate voltage) were obtained for all three samples, indicating an ohmic behavior of the thin films and their contacts with metals. Four-terminal resistance measurement gave the sheet resistance R_s of ~10.5, 2.3 and 0.15 kΩ/□ for samples A, B and C, respectively. The R_s values of samples A and B are comparable to that of Cu-catalyzed graphene.[8-11] Fig. 4 also shows R_s versus the back-gate voltage V_G (-20 V to 38 V) applied to the doped Si substrate. The dielectric properties of the Si_3N_4 films were changed by the lengthy high temperature CVD, and therefore higher V_G may lead to the breakdown of Si_3N_4. Electric field effects of 10.38% and 2.48% were observed at V_G=-20 V in samples A and B, respectively, whereas no field effect was seen in sample C. Here, the field effect is quantified by $\Delta\Sigma_s/\Sigma_s(0)=[\Sigma_s(V_G)-\Sigma_s(0)]/\Sigma_s(0)$, where $\Sigma_s=1/R_s$.[1,23] The Dirac point was not seen over this V_G range, possibly related to the charge doping effect associated with photoresist residues.[24] Nevertheless, a down-bending trend in the curves was observed, implying the possible ambipolar behavior of the materials. By virtue of a thinner dielectric with higher *k* value, the field effect observed here was more pronounced compared to the graphene-like thin films deposited directly on SiO_2.[12]

To date, graphitization on insulators has rarely been studied and the mechanism associated with

it is not well understood. Some authors suggest that the substrates play a catalytic role.[25] However, in this letter, a different explanation is proposed, because there is no direct evidence of the catalytic chemical reaction. In this case, the CVD of graphene-like thin films is much more likely a self-assembly process of C clusters, resulting from the pyrolysis of the hydrocarbon precursor. At 1000 ^{o}C, most CH_4 molecules thermally decompose, liberating the C atoms, which arrange themselves, through thermal activation, into hexagonal structures forming sp^2 hybridized graphene flakes (~10-100 nm). Usually, these flakes chaotically aggregate into large porous lumps, as is widely used in industry for the large-scale production of carbon black.[26] Nevertheless, under our conditions, hot flat substrates allow the graphene flakes to self-organize into continuous textured thin films. This process, however, is a slow procedure, requiring longer deposition time and higher CH_4 concentration compared with the catalytic CVD of graphene, on Cu for example. The crystallinity of the as-synthesized graphene-like thin films is relatively poor compared to Cu-catalyzed graphene, but is still significantly superior to atomically thin *a*-C.[27] The graphene-like thin films produced here are electrically conducting and optically transparent, and hence are promising in applications involving transparent electrodes. They can be grown on virtually any substrate that can withstand the high temperature processing at ~1000 ^{o}C. Indeed, it was found that large-area uniform graphene-like thin films with controlled thickness can be deposited on sapphire, quartz, mica, etc.

In conclusion, uniform large-area carbon thin films with graphene-like properties were synthesized directly on silicon nitride by CVD using CH_4 or C_2H_2 as precursors. The thin films show a high degree of topographic uniformity, with no observable wrinkles or pinholes. The sp^2-C network was confirmed by Raman spectroscopy. At room temperature, the thin films were ohmic

and showed a modest field effect. This work demonstrates the feasibility of directly forming graphene-like thin films on Si_3N_4 and other dielectric substrates by CVD and favors the industrialization of graphene-based materials in applications such as transparent electrodes.

The authors thank Prof. J. Liu and T. Wang at Chalmers and Dr. J. Svensson at Lund for their help with CVD systems. Financial support from the Swedish Research Council and the Swedish Foundation for Strategic Research is greatly appreciated. M. T. Cole wishes to thank the Schiff studentship and St. John's College Cambridge for generous financial support. The CVD growth and other clean-room processing were performed on the equipments funded by the Knut and Alice Wallenberg Foundation.

1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).

2 F. Schwierz, Nature Nanotechnol. **5**, 487 (2010).

3 S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, and S. Iijima, Nature Nanotechnol. **5**, 574 (2010).

4 Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and Ph. Avouris, Science **327**, 662 (2010).

5 J. Hass, W. A. de Heer, and E. H. Conrad, J. Phys.: Condens. Matter **20**, 323202 (2008).

6 A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, Nano Lett. **9**, 30 (2009).

7 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Hong, Nature **457**, 706 (2009).

8 C.-A. Di, D. Wei, G. Yu, Y. Liu, Y. Guo, and D. Zhu, Adv. Mater. **20**, 3289 (2008).

9 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, and R. S. Ruoff, Science **324**, 1312 (2009).

10 M. P. Levendorf, C. S. Ruiz-Vargas, S. Garg, and J. Park, Nano Lett. **9**, 4479 (2009).

11 H. Cao, Q. Yu, L. A. Jauregui, J. Tian, W. Wu, Z. Liu, R. Jalilian, D. K. Benjamin, Z. Jiang, J. Bao, S. S. Pei, and Y. P. Chen, Appl. Phys. Lett. **96**, 122106 (2010).

12 J. Sun et al., to be published.

13 J. Sun, M. Larsson, I. Maximov, and H. Q. Xu, Appl. Phys. Lett. **96**, 162107 (2010).

14 J. Sun, E. Lind, I. Maximov, and H. Q. Xu, IEEE Electron Device Lett. **32**, 131 (2011).

15 See supplementary material at http://dx.doi.org/ for details about graphene-like thin films on HfO_2.

16 W. Han and A. Zettl, Adv. Mater. **14**, 1560 (2002).

17 X. Ding, G. Ding, X. Xie, F. Huang and M. Jiang, Carbon **49**, 2522 (2011).

18 Y. Nishi and R. Doering, Handbook of Semiconductor Manufacturing Technology, CRC Press, pp. 324-325.

19 M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, and R. Saito, Nano Lett. **10**, 751 (2010).

20 F. Giannazzo, S. Sonde, V. Raineri, G. Patane, G. Compagnini, F. Aliotta, R. Ponterio, and E. Rimini, Phys. Status Solidi C **7** 1251 (2010).

21 Y. Dan, Y. Lu, N. J. Kybert, Z. Luo, and A. T. C. Johnson, Nano Lett. **9**, 1472 (2009).

22 Z. Cheng, Q. Zhou, C. Wang, Q. Li, C. Wang, and Y. Fang, Nano Lett. **11**, 767 (2011).

23 A. V. Butenko, Dm. Shvarts, V. Sandomirsky, Y. Schlesinger, and R. Rosenbaum, J. Appl. Phys. **88,** 2634 (2000).

24 S. Lara-Avila, K. Moth-Poulsen, R. Yakimova, T. Bjornholm, V. Falko, A. Tzalenchuk, and S. Kubatkin, Adv. Mater. **23**, 878 (2011).

25 A. Scott, A. Dianat, F. Borrnert, A, Bachmatiuk, S. Zhang, J. H. Warner, E. Borowiak-Palen, M. Knupfer, B. Buchner, G. Cuniberti, and M. H. Rummeli, Appl. Phys. Lett. **98**, 073110 (2011).

26 J. Biscoe and B. E. Warren, J. Appl. Phys. **13**, 364 (1942).

27 J. Kotakoski, A. V. Krasheninnikov, U. Kaiser, and J. C. Meyer, Phys. Rev. Lett. **106**, 105505 (2011).

Figure captions:

FIG. 1: (Color online) A typical temperature profile for the deposition of graphene-like thin films on Si_3N_4/Si. The shadowed region indicates the growth time.

FIG. 2: (Color online) Raman spectra (514 nm) of samples A, B and C. For all samples, distinct G, 2D, D and G+D peaks are observed.

FIG. 3: (Color online) (a) Optical micrograph of the ~6×6 mm^2 samples. Top row: bare substrate (left), sample A_1 (middle), and sample B (right). Bottom row: sample C (left) and sample A_2 highlighting the fabricated Hall-bar devices (right). (b) Optical micrograph of a typical Hall-bar device fabricated by standard photolithography and O_2 plasma etching on sample A.

FIG. 4: Electric field effect observed in Hall-bar structures fabricated on samples (a) A and (b) B. Sheet resistance R_s is plotted against back-gate voltage V_G. Inset: *I-V* curves of the devices fabricated on samples (a) A and (b) B, showing linear ohmic behavior. R_s values are calculated from four-probe resistance measurements (not shown).