

Understanding the Growth Kinetics of Graphene on Cu and Fe₂O₃ Using Inductively-Coupled Plasma Chemical Vapor Deposition

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High-quality graphene was synthesized on Cu foil and Fe₂O₃ film using CH₄ gas via inductively-coupled plasma chemical vapor deposition (ICPCVD). The graphene film was formed on Fe₂O₃ at a temperature as low as 700°C. Few-layer graphene was formed within a few seconds and 1 min on Cu and Fe₂O₃, respectively. With increasing growth time and plasma power, the graphene thickness was controllably reduced and ultimately self-limited to a single layer. Moreover, the crystal quality of graphene was constantly enhanced. Understanding the ICPCVD growth kinetics that are critically affected by ICP is useful for the controllable synthesis of high-quality graphene on metals and oxides for various electronic applications.

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INTRODUCTION

Graphene, a two-dimensional sp²-bonded carbon system, has been extensively studied during the last several years to understand the synthesis, physics, and potential device applications (Geim & Novoselov, 2007). Various synthesis methods have been developed, including mechanical exfoliation of highly ordered pyrolytic graphite (Geim & Novoselov, 2007), chemical reduction of exfoliated graphene oxide (Becerril et al., 2008), thermal decomposition of SiC (de Heer et al., 2007), and chemical vapor deposition (CVD) growth (Bae et al., 2010; Li et al., 2009a; Nang & Kim, 2012; Reina et al., 2009). Of the many synthesis methods available, CVD is potentially the most attractive technique for direct synthesis of graphene on various large-area substrates for the practical transparent electrodes and electronic device applications (Bae et al., 2010). In particular, plasma-enhanced CVD (PECVD) is a useful approach for controllable high-quality graphene synthesis. Compared with thermal CVD, PECVD possesses the unique advantage of additional high-

density reactive gas atoms and radicals, which facilitate low-temperature, rapid, and controllable synthesis of carbon nanostructures (Gopichand et al., 2010; Küttel et al., 1998; Li et al., 2004; Wang et al., 2004; Zhu et al., 2007). Recently, there have been considerable research reports on graphene synthesis on metal and oxide substrates using PECVD (Dato et al., 2008; Kim et al., 2011a, 2011b; Lee et al., 2011; Nandamuri et al., 2010; Nang & Kim, 2012, 2013). However, direct CVD synthesis of high-quality graphene on insulators or oxides at a moderate growth temperature remains a challenge. Moreover, little information is available on the fundamental aspects of PECVD, i.e., the effect of plasma on graphene synthesis which results in a synthesis behavior that is different from that of thermal CVD. In this study, we study the unique CVD growth kinetics of graphene on metal (Cu) and oxide (Fe₂O₃) substrates under inductively-coupled plasma (ICP). ICPCVD has several advantages for high-quality film growth because it provides a high-density plasma via a simple and low-cost plasma-generating setup.

MATERIALS AND METHODS

The Cu foil (Alfa Aesar, USA) was pre-treated with an acetic acid solution at 60°C for 10 min, followed by washing with de-ionized water. The foil was heated to 950°C and annealed for 10 min using a gas flow (100 SCCM; standard cubic centimeter per minute) to remove native oxides from the Cu foil and to enlarge its grains. The Fe₂O₃/Si substrate was prepared via sputter deposition of a 250-nm-thick Fe film on the Si wafer, followed by annealing under an O₂ environment at 800°C for 2 h. The oxidation process formed a polycrystalline α -Fe₂O₃ film with ~0.2 to 0.3- μ m-sized grains. For graphene growth, CH₄ gas at 1 SCCM and a mixed gas including 10% H₂ and 90% Ar at 100 SCCM were introduced in a hot-wall tubular reaction chamber (Fig. 1), and the reactor pressure was maintained at 1 torr. The growth temperature and ICP power varied from 700°C to 1,000°C and from 0 to 600 W, respectively. The growth time also varied from 5 s to 60 min. The synthesized graphene on Cu was transferred to SiO₂/Si or a Cu grid for various characterizations. Details of the transfer process have been

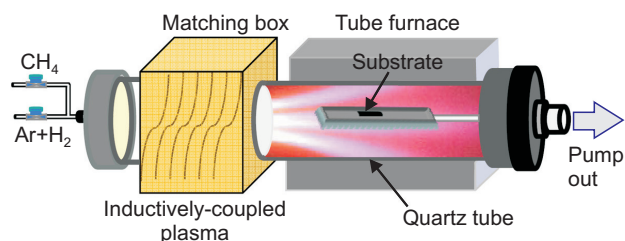


Fig. 1. Schematic of the inductively-coupled plasma chemical vapor deposition used to synthesize graphene (Nang & Kim, 2012). Reproduced with permission from *J. Electrochem. Soc.* **159**, K93-K96 (2012). Copyright 2012, The Electrochemical Society.

described elsewhere (Nang & Kim, 2012). Graphene was characterized using Raman spectroscopy (514.5-nm line of an Ar⁺ laser, JY LabRam HR with CCD, USA) and transmission electron microscopy (TEM; operated at 200 kV, JEOL 2100F; JEOL, Japan).

RESULTS AND DISCUSSION

Fig. 2A shows the Raman spectra of the graphene synthesized on Cu at a fixed rf plasma power of 200 W as a function of various growth times (5 s and 1, 5, 10, and 60 min). The D band peak at 1,346 cm⁻¹, which is attributed to disordered structures, has the highest intensity for the 5 s growth period. Moreover, the D' peak at 1,616 cm⁻¹, which is also characteristic of the structural disorder, was observed. As shown in Fig. 2B, the D-to-G peak intensity ratio (I_D/I_G) significantly decreased for the 1-min growth period, indicating a significantly improved graphene structural quality. The I_D/I_G decreased further for the 5-min growth period and became saturated with increased growth time. However, the 2D-to-G peak intensity ratio ($I_{2D}/I_G=1.05$) of the graphene growth for 5 s corresponds to the few-layer graphene (Graf et al., 2007). With increasing growth time, the I_{2D}/I_G gradually increased, suggesting that the thickness of the graphene film continued to decrease (Fig. 2B). The high-resolution TEM images in Fig. 3 reveal that the graphene film that was synthesized on Cu for 5 min comprises mainly monolayer and bilayer graphene, and it agrees well with the Raman results. The effect of growth time on graphene thickness is significantly different from the growth behavior that was induced by thermal CVD. The graphene growth mechanism via thermal CVD has been previously explained by the formation of a single-layer graphene domain, followed by its expansion onto the Cu substrate (Li et al., 2009a, 2009b). In our results, the graphene

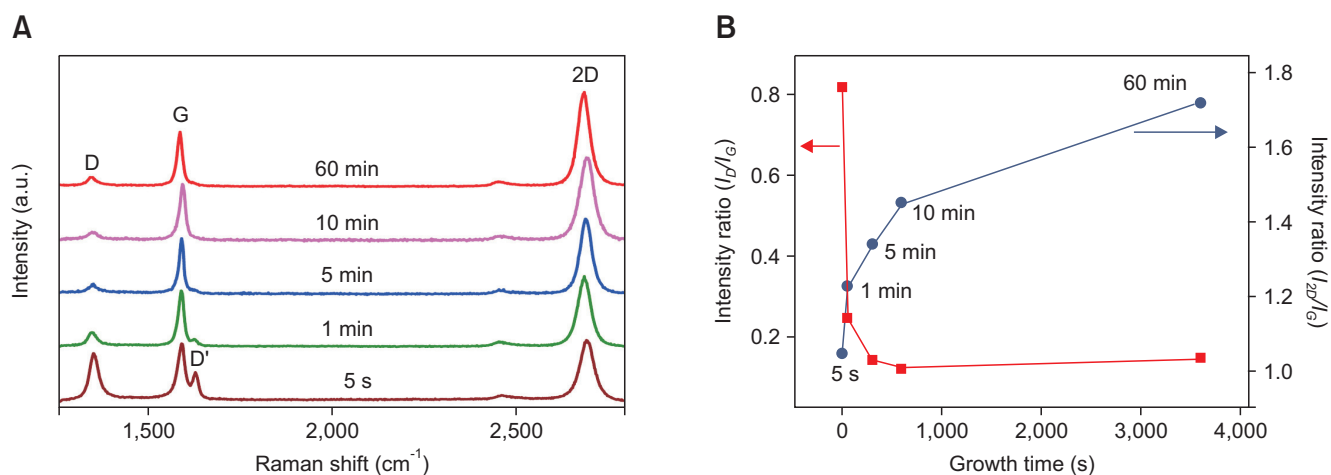


Fig. 2. (A) Raman spectra of graphene films synthesized on Cu at various growth times. (B) The I_D/I_G ratio and the I_{2D}/I_G ratio as a function of growth time (Nang & Kim, 2012). Reproduced with permission from *J. Electrochem. Soc.* **159**, K93-K96 (2012). Copyright 2012, The Electrochemical Society.

thickness did not significantly change with growth time after the first layer of carbon was deposited.

Fig. 4 shows the Raman spectra of graphene synthesized on Cu for 5 min using various plasma powers of 50, 200, 400, and 600 W. Graphene was not formed without ICP. The graphene synthesized at 50 W had the highest and lowest values of I_D/I_G (0.98) and I_{2D}/I_G (1.16), indicating that the graphene film is most defective and thickest when presented as a few-layered one. With increasing plasma power, the structural quality of the graphene films was significantly improved, and the thickness gradually decreased. For a plasma power of 600

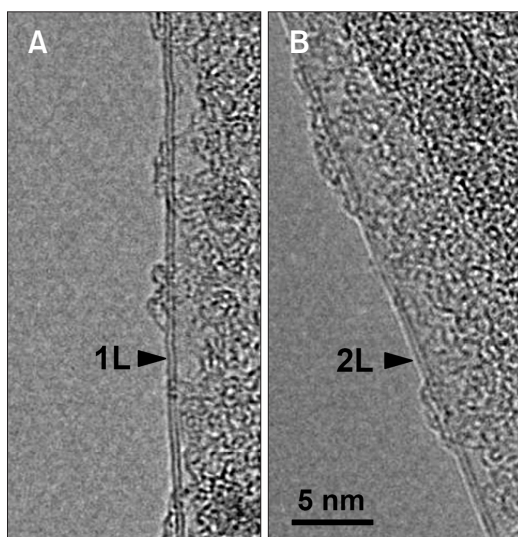


Fig. 3. High-resolution transmission electron microscopy images of (A) single-layer and (B) bilayer graphenes synthesized on Cu at 200 W for 5 min (Nang & Kim, 2012). Reproduced with permission from *J. Electrochem. Soc.* **159**, K93-K96 (2012). Copyright 2012, The Electrochemical Society.

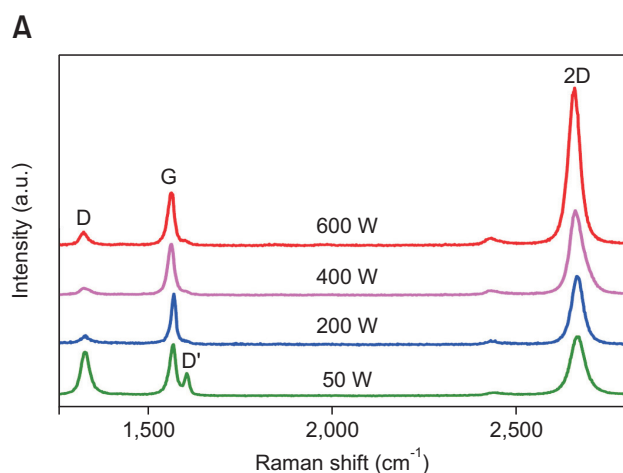
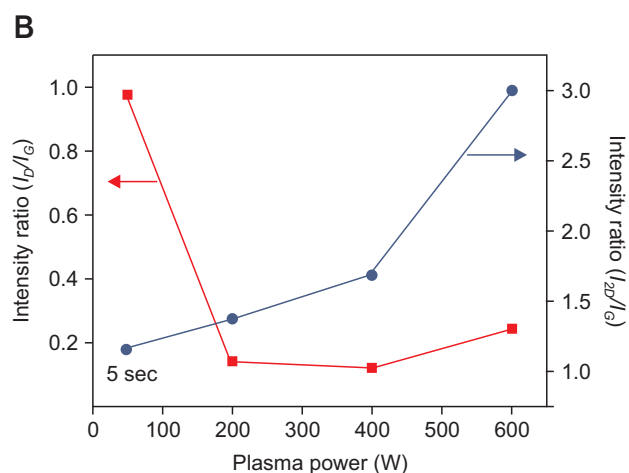


Fig. 4. (A) Raman spectra of graphene films synthesized on Cu at various plasma powers (50, 200, 400, and 600 W). (B) The I_D/I_G ratio and the I_{2D}/I_G ratio as a function of plasma power (Nang & Kim, 2012). Reproduced with permission from *J. Electrochem. Soc.* **159**, K93-K96 (2012). Copyright 2012, The Electrochemical Society.

W, the I_{2D}/I_G reached approximately 3, corresponding to a single layer of graphene (Ferrari et al., 2006; Li et al., 2009b). However, the I_D/I_G (0.24) was slightly larger than that (0.14) of the graphene grown at 200 W, likely because of the defects resulting from plasma damage.

Fig. 5 shows the Raman spectra of the matrix of graphene synthesized on Fe₂O₃ at a fixed plasma power of 200 W for 1 min at various growth temperatures (700°C, 800°C, 900°C, and 1,000°C). The very low intensity of the D band peak at 1,346 cm⁻¹ confirmed that high-quality graphene was formed even at a temperature as low as 800°C. The I_D/I_G ratio increased to 0.47 when the growth temperature was reduced to 700°C. Nevertheless, the I_D/I_G ratio was significantly lower than ratios previously reported for graphene on oxides (Bi et al., 2012; Chen et al., 2011; Fanton et al., 2011; Song et al., 2012). The I_{2D}/I_G ratio of ~1 of graphene grown at 900°C and 1,000°C suggests the formation of few-layer graphene (Nang & Kim, 2012; Reina et al., 2009).

ICP was a key factor in the graphene formation on Fe₂O₃. The graphene film formed over the entire Fe₂O₃ surface within 1 min of growth with the plasma, whereas graphene did not form even with 60 min of growth without plasma (Fig. 6). The I_D/I_G and I_{2D}/I_G ratios of graphene on Fe₂O₃ as a function of the plasma power exhibit a similar trend as graphene on Cu. At a low plasma power of 100 W, the Raman spectra showed a relatively high value (0.33). The I_D/I_G ratio was significantly reduced at a plasma power of 200 W, and it finally reached almost zero above 400 W. Similarly, the I_{2D}/I_G ratio gradually increased with increasing plasma power (Fig. 6B). In addition, the full width at half maximum (FWHM) of the 2D band peak continuously decreased. These results clearly suggest that the thickness of the graphene film continues to decrease and can be controllably manipulated with the appropriate plasma



power. The graphene synthesized at 600 W resulted in a I_{2D}/I_G of 1.62 and of a FWHM of $\sim 29 \text{ cm}^{-1}$ for the single Lorentzian 2D band peak at $2,700 \text{ cm}^{-1}$, which corresponds to a single layer of graphene (Nang & Kim, 2012; Reina et al, 2009).

These results can be attributed to the competition between the graphene formation via C atoms and the C etching via H atoms. ICP, a high-density plasma, is effective in decomposing CH_4 and H_2 gases. Carbon atoms and methyl radicals created by plasma assistance are adsorbed on the Cu, rapidly forming the few-layer graphene within a few seconds. However, this fast graphene synthesis results in defective graphene layers and even in amorphous and nanographitic layers (triangle marker in Fig. 7A) because the C atoms may not find an appropriate site within 5 s. Once the Cu surface is covered by the graphene layer, the rates of C adsorption and graphene

formation on the graphene layer can significantly decrease because of a very weak van der Waals interaction between the C layer and C atoms (Reina et al., 2009). Thus, C etching by H atoms appears to be a more dominant factor. Atomic H in the plasma acts as an etchant for the C layer (Zhu et al., 2007). The loosely-bonded amorphous and nanographitic layers are first etched off. The top layers on the first graphene layer are also etched off. As shown in Fig. 7B and C, the amorphous and nanographitic layers were significantly reduced at an increased growth time of 1 min and were finally removed at 5 min of growth. The graphene thickness continuously decreased with increasing growth time (Fig. 2). The effect of C etching by H atoms is more pronounced for a higher plasma power, which induces more atomic H (Fig. 4). The graphene thickness gradually decreased with increasing plasma power, and finally reached a single layer at 5 min of growth at 600 W. The first graphene layer on Cu can also be etched off, but it can be recovered by the rapid C adsorption and reaction on the catalytic surface. Consequently, the thickness of high-quality graphene was self-limited to a single layer. This process enhances the graphene quality by refreshing the initially-formed defective graphene layer with a highly-ordered structure.

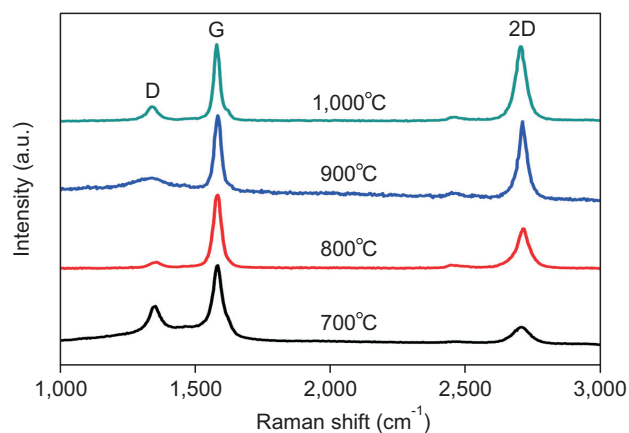


Fig. 5. Raman spectra of graphene films synthesized on Fe_2O_3 at various growth temperatures (700, 800, 900, and $1,000^\circ\text{C}$). Reproduced with permission from *Mater. Lett.* **92**, 437-439 (2013). Copyright 2012, Elsevier.

CONCLUSIONS

In conclusion, high-quality graphene was synthesized on Cu foil and Fe_2O_3 film using ICPCVD. The growth kinetics on Cu and Fe_2O_3 were governed by the competition between the graphene formation via C atoms and the C etching via H atoms, which were critically affected by the ICP. Few-layer graphene was rapidly synthesized within a few seconds and in 1 min on Cu and Fe_2O_3 , respectively, whereas, graphene was

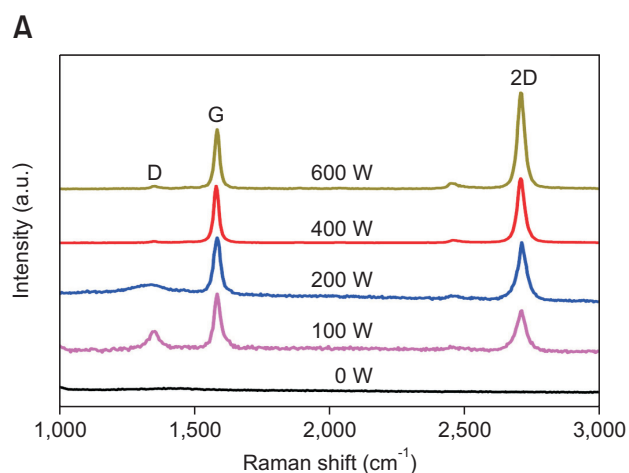
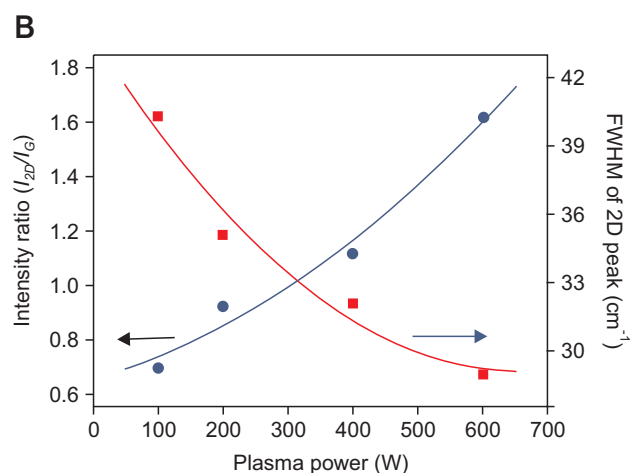


Fig. 6. (A) Raman spectra of graphene films synthesized on Fe_2O_3 at various plasma powers (0, 100, 200, 400, and 600 W). (B) The I_{2D}/I_G ratio and the full width at half maximum (FWHM) of the 2D band peak as a function of inductively-coupled plasma power (Nang & Kim, 2013). Reproduced with permission from *Mater. Lett.* **92**, 437-439 (2013). Copyright 2012, Elsevier.



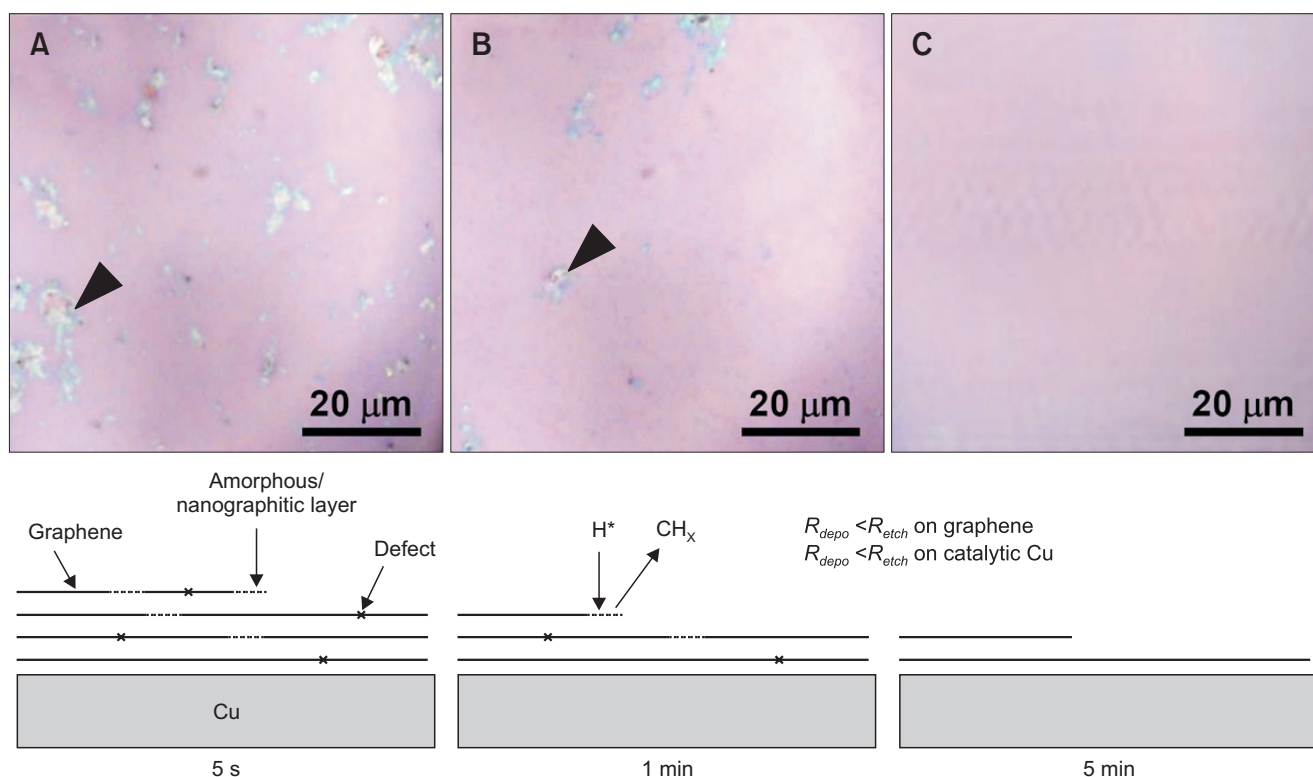


Fig. 7. Optical microscope images and corresponding schematics of graphene films synthesized on Cu at a plasma power of 200 W for (A) 5 s, (B) 1 min, and (C) 5 min. The triangle marker indicates amorphous and nanographitic layers (Nang & Kim, 2012). Reproduced with permission from *J. Electrochem. Soc.* **159**, K93-K96 (2012). Copyright 2012, The Electrochemical Society.

not formed at all without plasma. With an increasing growth time and ICP power, the graphene thickness continued to decrease because of the etching by atomic H and was finally self-limited to a single layer. The graphene structural quality was also enhanced via the preferential etching of structurally-disordered C structures, followed by the newly synthesized graphene layer. The understanding of ICPCVD growth kinetics can be exploited to control the growth of high-quality graphene on various substrates, including metals and oxides, for transparent electrodes and electronic device applications.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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REFERENCES

- Bae S, Kim H K, Lee Y B, Xu X F, Park J S, Zheng Y, Balakrishnan J, Lei T, Kim H R, Song Y, Kim J Y, Kim K S, Özyilmaz B, Ahn J H, Hong B H, and Iijima S (2010) Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.* **5**, 574-578.
- Becerril H A, Mao J, Liu Z, Stoltenberg R M, Bao Z, and Chen Y (2008) Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* **2**, 463-470.
- Bi H, Sun S, Huang F, Xie X, and Jiang M (2012) Direct growth of few-layer graphene films on SiO₂ substrates and their photovoltaic applications. *J. Mater. Chem.* **22**, 411-416.
- Chen J, Wen Y, Guo Y, Wu B, Huang L, Xue Y, Geng D, Wang D, Yu G, and Liu Y (2011) Oxygen-aided synthesis of polycrystalline graphene on silicon dioxide substrates. *J. Am. Chem. Soc.* **133**, 17548-175451.
- Dato A, Radmilovic V, Lee Z, Phillips J, and Freklach M (2008) Substrate-free gas-phase synthesis of graphene sheets. *Nano Lett.* **8**, 2012-2016.
- de Heer W A, Berger C, Wu X, First P N, Conrad E H, Li X, Li T, Sprinkle M, Hass J, Sadowski M L, Potemski M, and Martinez G (2007) Epitaxial graphene. *Solid State Commun.* **143**, 92-100.
- Fanton M A, Robinson J A, Puls C, Liu Y, Hollander M J, Weiland B E, Labella M, Trumbull K, Kasarda R, Howsare C, Stitt J, and Snyder D W (2011) Characterization of graphene films and transistors grown

- on sapphire by metal-free chemical vapor deposition. *ACS Nano* **5**, 8062-8069.
- Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S, and Geim A K (2006) Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **97**, 187401.
- Geim A K and Novoselov K S (2007) The rise of graphene. *Nat. Mater.* **6**, 183-191.
- Gopichand N, Sergej R, and Raj S (2010) Remote plasma assisted growth of graphene films. *Appl. Phys. Lett.* **96**, 154101.
- Graf D, Molitor F, Ensslin K, Stampfer C, Jungen A, Hierold C, and Wirtz L (2007) Spatially resolved Raman spectroscopy of single- and few-layer graphene. *Nano Lett.* **7**, 238-242.
- Kim J, Ishihara M, Koga Y, Tsugawa K, Hasegawa M, and Iijima S (2011a) Low-temperature synthesis of large-area graphene-based transparent conductive films using surface wave plasma chemical vapor deposition. *Appl. Phys. Lett.* **98**, 091502.
- Kim Y, Song W, Lee S Y, Jeon C, Jung W, Kim M, and Park C Y (2011b) Low-temperature synthesis of graphene on nickel foil by microwave plasma chemical vapor deposition. *Appl. Phys. Lett.* **98**, 263106.
- Küttel O M, Groening O, Emmenegger C, and Schlapbach L (1998) Electron field emission from phase pure nanotube films grown in a methane/hydrogen plasma. *Appl. Phys. Lett.* **73**, 2113.
- Lee B J, Lee T W, Park S, Yu H Y, Lee J O, Lim S H, and Jeong G H (2011) Low-temperature synthesis of thin graphite sheets using plasma-assisted thermal chemical vapor deposition system. *Mater. Lett.* **65**, 1127-1130.
- Li X S, Cai W W, An J H, Kim S, Nah J, Yang D X, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee S K, Colombo L, and Ruoff R S (2009a) Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **324**, 1312-1314.
- Li X S, Zhu Y W, Cai W W, Borysiak M, Han B Y, Chen D, Piner R D, Colombo L, and Ruoff R S (2009b) Transfer of large-area graphene films for high-performance transparent conductive electrodes. *Nano Lett.* **9**, 4359-4363.
- Li Y M, Mann D, Rolandi M, Kim W, Ural A, Hung S, Javey A, Cao J, Wang D W, Yenilmez E, Wang Q, Gibbons J F, Nishi Y, and Dai H J (2004) Preferential growth of semiconducting single-walled carbon nanotubes by a plasma enhanced CVD method. *Nano Lett.* **4**, 317-321.
- Nandamuri G, Roumimov S, and Solanki R (2010) Remote plasma assisted growth of graphene films. *Appl. Phys. Lett.* **96**, 154101.
- Nang L V and Kim E T (2012) Controllable synthesis of high-quality graphene using inductively-coupled plasma chemical vapor deposition. *J. Electrochem. Soc.* **159**, K93-K96.
- Nang L V and Kim E T (2013) Low-temperature synthesis of graphene on Fe₂O₃ using inductively coupled plasma chemical vapor deposition. *Mater. Lett.* **92**, 437-439.
- Reina A, Jia X T, Ho J, Nezich D, Son H B, Bulovic V, Dresselhaus M S, and Kong J (2009) Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* **9**, 3087.
- Song H J, Son M, Park C, Lim H, Levendorf M P, Tsen A W, Park J, and Choi H C (2012) Large Scale metal-free synthesis of graphene on sapphire and transfer-free device fabrication. *Nanoscale* **4**, 3050-3054.
- Wang J, Zhu M, Outlaw R A, Zhao X, Manos D M, and Holloway B C (2004) Synthesis of carbon nanosheets by inductively coupled radio-frequency plasma enhanced chemical vapor deposition. *Carbon* **42**, 2867.
- Zhu M, Wang J, Holloway B C, Outlaw R A, Zhao X, Hou K, Shutthanandan V, and Manos D M (2007) A mechanism for carbon nanosheet formation. *Carbon* **45**, 2229-2234.