Efficient growth of high-quality graphene films on Cu foils by ambient pressure chemical vapor deposition

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We developed an ambient pressure chemical vapor deposition (CVD) for rapid growth of high-quality graphene films on Cu foils. The quality and growth rate of graphene films are dramatically increased with decreasing H_2 concentration. Without the presence of H_2, continuous graphene films are obtained with a mean sheet resistance of $<350\ \Omega/\mathrm{sq}$ and light transmittance of 96.3% at 550 nm. Because of the ambient pressure, rapid growth rate, absence of H_2 and readily available Cu foils, this CVD process enables inexpensive and high-throughput growth of high-quality graphene films. © *2010 American Institute of Physics*. [doi:10.1063/1.3512865]

Graphene, a monolayer of sp^2-bonded carbon atoms, has been attracting great interests because of its fascinating physical properties.[1] The unique two-dimensional structure and large intrinsic electron mobility make graphene a promising material in electronic applications, in which high-quality graphene films are highly desired.[2] Besides the micromechanical cleavage of graphite crystals,[3] chemical vapor deposition (CVD) approach recently has demonstrated to be able to produce high-quality graphene films on Ni (Refs. 4–7) and Cu.[8–13] In particular, Cu is considered to be an excellent substrate for making high-quality graphene films with uniform thickness due to the low solubility of C in Cu.[8] However, different from the growth on Ni, a low pressure CVD process, with a total pressure of 0.5–50 Torr, is usually used for the growth of graphene films on Cu foils.[8–11] Such low pressure condition and specific reaction system limit its wide use, to a certain extent, for large-scale production of graphene films at low cost.

In the present work, graphene films were grown on 25 μm thick Cu foils (Alfa Aesar, item no. 13382) at 1000 °C in a furnace with a 22 mm inner diameter fused silica tube under ambient pressure. The total flow rate of Ar and H_2 was maintained at 300 SCCM (SCCM denotes cubic centimeter per minute at STP), and 1 SCCM of CH_4 was adopted as carbon source in all experiments. The growth time was kept for 10 min. In order to optimize the growth of graphene, we investigated the effect of H_2 concentration on the quality and growth rate. After growth, the graphene films were transferred to different target substrates,[5,11] such as Si/SiO_2 substrate for Raman and optical, glass for transmittance, and scotch tape for electrical measurements (details, see Ref. 14).

Figure 1(a) shows the graphene films transferred to a Si/SiO_2 substrate. We can easily observe the graphene films on the Si/280 nm thick SiO_2 substrate due to the light interference effect,[15] which shows good macroscopic uniformity. The microstructure and quality of the graphene films were determined by Raman spectroscopy (JY HR800, 632.8 nm laser) and optical microscopy (Nikon LV100D). All the Raman spectra in Fig. 1(b) show a feature similar to that of monolayer graphene, 2D to G intensity ratio of >1 and symmetric 2D band centered at 2643–2648 cm^{-1} with a full width at half maximum of 27–31 cm^{-1}, indicating that each sample is monolayer dominant. The D and D′ bands are related to defects in graphene,[16] such as disordered carbon, edges or wrinkles. It is worth noting that the intensity of D and D′ bands increases with increasing the H_2 concentration, indicating the quality degradation of graphene films. Optical observations show that the graphene films prepared with the use of H_2 are not even, with some few-layer graphene islands and wrinkles [Fig. 1(c)]. As a contrast, very uniform graphene films are obtained without the use of H_2 during growth, with most of the sheets being monolayer (light color) and a small amount of bilayer (dark color) [Fig. 1(d)]. All these results suggest that the quality of graphene films can be improved by decreasing H_2 concentration, and the graphene with best quality is obtained without the presence of H_2.

To further evaluate the quality of graphene films, their transmittance and sheet resistance were measured. Five samples were measured for each growth condition, and both the transmittance and sheet resistance show good reproduc-

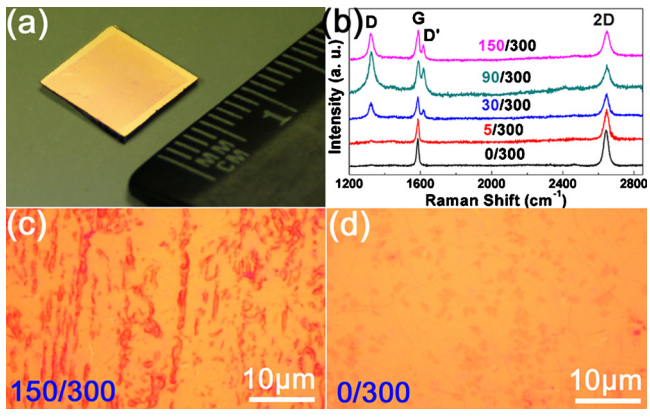


FIG. 1. (Color online) Graphene films transferred on a Si/SiO_2 substrate. (a) Photograph of a graphene film prepared without H_2, with a size of ~10 mm. (b) Raman spectra of graphene films grown by different H_2 flow rates (0, 5, 30, 90, and 150 SCCM) but a constant total flow rate (300 SCCM). Typical optical images of the graphene films grown by a H_2 flow rate of 150 SCCM (c) and 0 SCCM (d).

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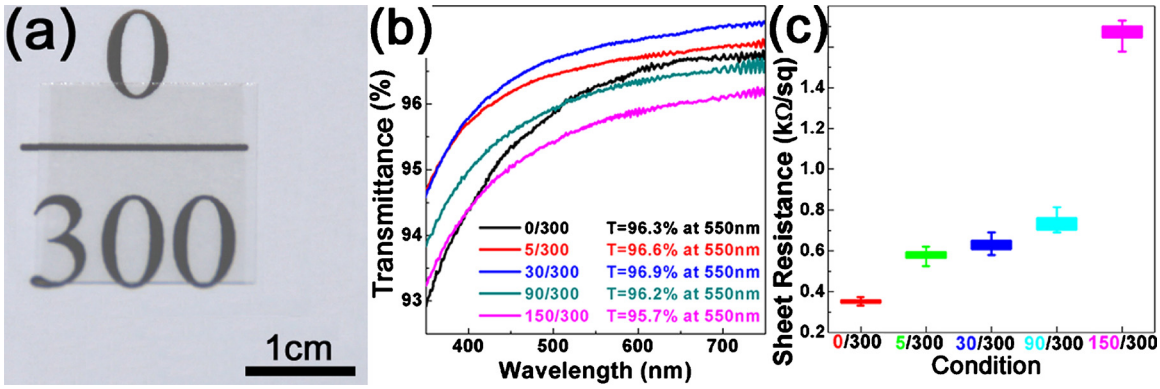


FIG. 2. (Color online) Optical and electrical properties of different graphene films. (a) Photograph of a transferred graphene film on a glass substrate. (b) Typical light transmittance of graphene films on glass. (c) The sheet resistance of different graphene films, showing strong dependence on H_2 concentration. Five samples were measured for each preparation condition, and the obtained sheet resistance is given with error bars.

ibility for the graphene films prepared using the same conditions. Figures 2(a) and 2(b) show a graphene film transferred on a glass substrate and the light transmittance of graphene films prepared by different H_2 flow rates. It is found that the transmittance of all the graphene films at 550 nm is ~96%. The slight difference in transmittance for different samples is attributed to the different concentrations and distribution of few-layer graphene sheets and wrinkles in the films. Since the light transmittance of monolayer graphene is ~97.7%,[17] such transmittance values further confirm that these graphene films should be predominantly monolayer. This result also indicates that the H_2 concentration has marginal effect on the number of layers, proving that the growth of graphene on Cu is a self-limiting process.[18] Consistent with the Raman measurements, the sheet resistance of graphene films remarkably increases with H_2 concentration at the similar transmittance (~96%), as shown in Fig. 2(c). The graphene films prepared without the use of H_2 shows the best macroscopic electrical property among all the samples, with a mean sheet resistance of $<350\ \Omega/\mathrm{sq}$ and a mean light transmittance of 96.3% at 550 nm.

Recently, the dc to optical conductivity ratio (σ_{dc}/σ_{OP}) was proposed to evaluate the optoelectrical properties of conductive films (a higher value represents higher transmittance and/or lower sheet resistance).[19] The calculated mean σ_{dc}/σ_{OP} values for different graphene films are shown in Fig. 3, and the reported values of graphene films on Ni (Refs. 4 and 5) and Cu (Refs. 9 and 10) are also listed for comparison. The mean σ_{dc}/σ_{OP} value decreases with increasing H_2 concentration, indicating that lower H_2 concentration is favorable for the growth of high-quality graphene films by ambient pressure CVD process. Except for the recently reported super-large graphene films made by improved transfer method and HNO_3 doping,[11] our graphene film prepared without the use of H_2 shows the highest value of 28, which beats the upper limit of $\sigma_{dc}/\sigma_{OP}=11$ for single crystalline graphite and approaches to the minimum industry standard for indium tin oxide replacement materials.[19] These comparisons strongly indicate that the quality of our graphene films grown on Cu foils by ambient pressure CVD is higher than those grown on Ni films, and comparable to the best one grown on Cu foils by low pressure CVD. We believe that the optoelectrical properties of our graphene films can be further improved by appropriate modifications on the transfer and doping processes.

For large scale production of graphene films, the growth rate is another important factor to determine their final cost. The Cu surface can be fully covered by graphene films within about 1 min without the use of H_2 during the growth based on scanning electron microscopy (SEM) observations and Raman measurements [Fig. 4(a)], which is much shorter than those for the preparation of continuous graphene films with the use of H_2 and those reported for low pressure CVD.[8–11] The morphology evolution of the graphene films was investigated as a function of time for the case of 150 SCCM H_2 and 150 SCCM Ar flow. It takes about 10 min for graphene films to fully cover the Cu surface, and no distinguishable difference is found if further prolonging the growth time to 30 min [Figs. 4(b)–4(d) and Ref. 14]. These results indicate that the growth rate of graphene films is dramatically decreased with increasing H_2 concentration. Moreover, it is worth noting that the density and height of wrinkles, which are usually observed in the CVD grown graphene films, are also increased with H_2 concentration.

The growth of graphene films starts from individual small graphene islands [Fig. 4(b)], which are randomly formed and distributed on Cu surface. These islands grow in two-dimension, and finally join together to a continuous film.[8,18] As a result, defects appear at interisland junctions

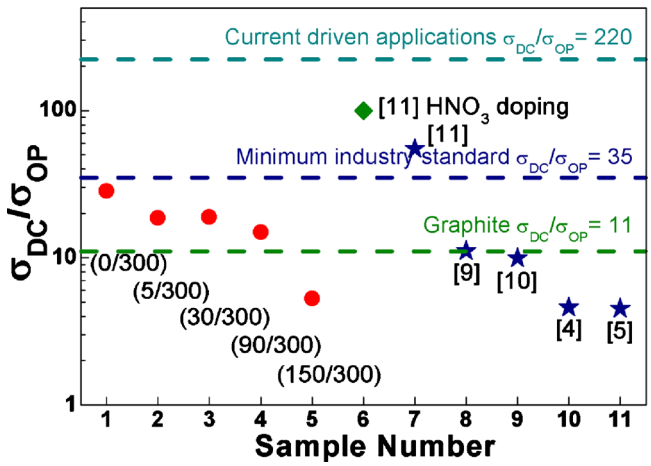


FIG. 3. (Color online) The dc to optical conductivity ratios of different graphene films. The five dots represent the mean σ_{dc}/σ_{OP} values of our graphene films prepared in different H_2 concentrations, and are marked by H_2 flow rate/total flow rate. The stars represent some reported values for graphene films grown on Ni and Cu.

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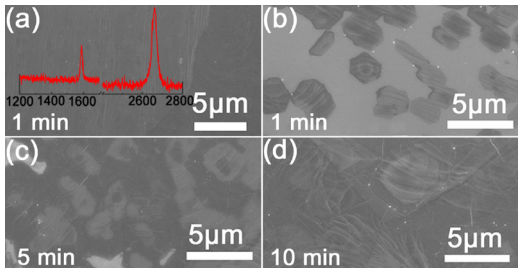


FIG. 4. (Color online) Structure evolution of the graphene films with growth time. (a) SEM image of the graphene films prepared for 1 min without the use of H_2 during the growth. The inset shows a typical Raman spectrum taken from an arbitrary position on the Cu surface, confirming the formation of monolayer graphene. (b), (c), and (d) SEM images of the graphene films prepared with a growth period of (b) 1, (c) 5, and (d) 10 min. In this case, the flow rate of both H_2 and Ar was 150 SCCM.

because of the formation of pentagonal and heptagonal arrangements of carbon atoms. We suggest that the formation of small islands and consequently more inter-island junctions for the case of high H_2 concentration are the crucial reasons for the obtained graphene of low quality, which are probably due to the low decomposition rate of CH_4 and consequent low carbon supply under such conditions. Further studies are required to elucidate this point. Another thing we need to point out is that H_2 gas can be dissolved in Cu under high temperature, with a solubility of ~0.007 at. % at 1000 °C.[20] When Cu foils cool down to room temperature, H_2 gas releases from the Cu foils because the solubility of H declines to less than 10^{-7} at. %.[20] Therefore, the wrinkles are related to not only the different thermal expansion coefficients between Cu and graphene[8] but also the degassed H_2. Based on the above results, we suggest that the presence of H_2 leads to many inter-island junctions and wrinkles, which are responsible for the observed graphene films of low quality prepared with high H_2 concentration.

In summary, we developed an ambient pressure CVD for growing high-quality graphene films on Cu foils. The quality and growth rate of graphene films is dramatically increased with decreasing H_2 concentration. Without the use of H_2, continuous high-quality graphene films are obtained within 1 min, with a sheet resistance of <350 Ω/sq at light transmittance of 96.3%, which is much better than those of graphene grown on Ni and comparable to the best optoelectrical properties reported for the graphene films prepared by low pressure CVD on Cu. We suggest that the presence of H_2 leads to a large number of inter-island junctions and wrinkles, which are responsible for the observed low quality and large sheet resistance of graphene prepared at high H_2 concentration. Because of the ambient pressure, rapid growth rate, absence of H_2 and readily available Cu foils, this CVD process enables inexpensive and high-throughput growth of high-quality graphene films over large areas, which will be helpful to facilitate a wide range of technological applications of graphene.

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