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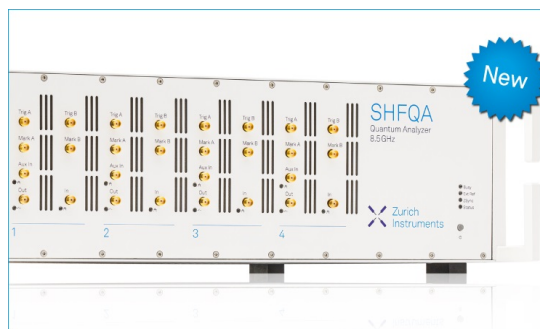
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Large area few-layer graphene/graphite films as transparent thin conducting electrodes

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By dissolving carbon atoms decomposed from methane in a metal substrate at high temperatures, large area uniform few-layer graphene (FLG)/graphite films were precipitated on metal surfaces upon cooling. The thickness could be controlled by varying the amount of carbon atoms in the metal. Such films were transferred to glass slides after dissolving the metal substrate in an aqueous solution of $\text{Fe}(\text{NO}_3)_3$. Sheet resistances as low as $200 \Omega/\square$ with a transmittance of 85% were obtained from FLG films. The resistance and transmittance can be changed over one order of magnitude, making such films potentially useful for transparent thin conducting electrodes. © 2009 American Institute of Physics. [doi:10.1063/1.3220807]

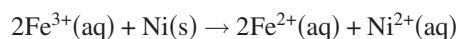
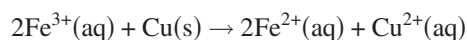
Transparent conducting films (TCFs) are used in many modern technological devices such as solar cells, displays, touch screens, etc. The current most popular TCF is indium tin oxide (ITO). There is a stated need for a substitute for ITO due to the limited supply of indium. Thin films of conductive carbon nanotube networks are a promising candidate for a cost-effective and abundant source of transparent conductor to replace ITO. However, the conductivity of carbon nanotube networks is still relatively high due to the high resistance at the nodes of the networks.¹ Recently, the isolation of graphene, a one-atom-thick planar sheet of sp^2 -bonded carbon atoms packed in a “honeycomb” crystal lattice, has been reported.² An ideal monolayer of graphene has a transmittance of 97.7%,³ with electron mobility values in excess of $15\,000 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ at room temperature.⁴ Due to the high conductivity and the high transmittance, graphene is a promising material for flexible TCF. Recently, researchers have developed a few kinds of films composed of reduced graphene oxide platelets by exposure to hydrazine vapor⁵ or annealing in hydrogen.⁶ However, these films based on reduced graphene oxide sheets show relatively poor electrical conductivity perhaps due to either structural defects formed during the oxidation and reduction process, or the fact that the reduction does not return the structure to pristine graphene, or both factors. In this paper, we present a chemical vapor deposition (CVD) technique to uniformly deposit and precipitate few-layer graphene (FLG) and graphite films with a controllable thickness range of a few to hundreds of layers for possible application as TCFs.

Graphite formation on the surface of metals, particularly transition metals, has been studied for a long time.⁷ The “metallurgical model” was used to explain the formation of graphite in such systems.^{8–10} Since carbon is being decomposed at the metal surface from hydrocarbon gas at high temperatures, the concentration gradient causes it to diffuse into the metal, with the gradient along the direction normal to the surface. A fraction of the carbon atoms in a solid solution in a metal at elevated temperatures is known to precipitate as a graphite film upon cooling. It is obvious that the thickness of the graphite film can be controlled by varying

the solubility of carbon atoms dissolved in the metal at high temperatures and by varying the thickness of the metal. Recently, submicron-thick Ni films were used to segregate large area graphene by exploiting the temperature-dependent solubility of carbon in Ni.^{9,11,12}

In our experiments, polycrystalline Cu (99.999%, 50 μm thick) and Ni (99.9%, 25 μm thick) foils from Alfa Aesar were used as substrates. Due to the different carbon solubilities in Cu (~ 0.001 at. % at 900 °C)¹³ and in Ni (~ 0.1 at. % at 900 °C),¹⁴ the thickness of FLG/graphite can be engineered over one order. Before the deposition, each substrate temperature was held at 900 °C for 30 min under 10 Torr H_2 in order to clean the surface and remove the metal oxide. During the carbon deposition, the substrate temperature was held at high growth temperatures for about 10 min and the pressure at 50 Torr. The gas used was methane (99.999%). In this work, Cu foils were held at 900 and 850 °C, respectively, and Ni foils at 950, 900, and 850 °C, respectively, in different runs. We thus label the samples as Cu-900, Cu-850, Ni-950, Ni-900, and Ni-850, respectively. After deposition, the substrate was cooled down to room temperature at a cooling rate of 10 °C/s.

After etching the substrate in an aqueous $\text{Fe}(\text{NO}_3)_3$ solution (1 M/l), the FLG/graphite film was transferred to a glass slide, an SiO_2/Si wafer, or various other substrates. In this process, the Cu or Ni foil was cut into $10 \times 10 \text{ mm}^2$ pieces and floated on the solution surface due to surface tension. The etching reaction can be represented as follows:



Overnight reaction generated two films: one film submerged in solution and “balled up” due to the hydrophobic nature of graphite and the other one floating on the solution surface owing to surface tension. Glass slides, SiO_2/Si wafer pieces, and membranes were used to capture the floating films, which were then thoroughly rinsed in de-ionized water. In order to demonstrate the homogeneity over large areas, a typical FLG film covering an area of $10 \times 10 \text{ mm}^2$ on a glass slide is shown in Fig. 1(a).

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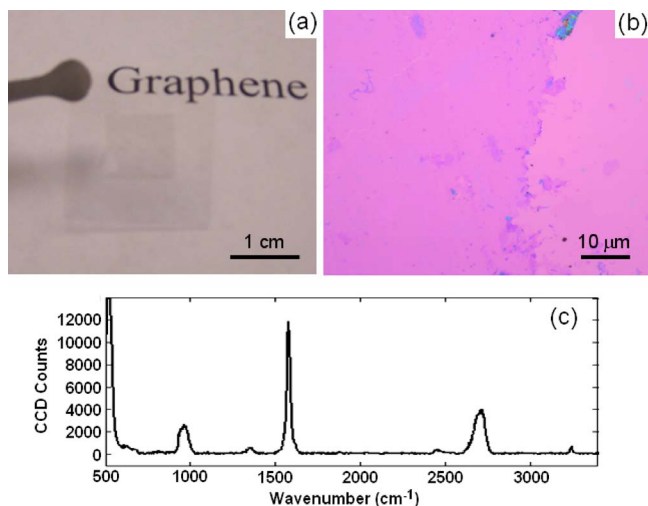


FIG. 1. (Color online) Photograph (a) and optical microscope image (b) of few-layer graphite films on glass slide and SiO_2/Si wafer, respectively. The size of the FLG film in (a) is about $1 \times 1 \text{ cm}^2$. (c) Typical Raman spectrum of FLG film taken from (b). D , G , and $2D$ bands were detected at 1350, 1582, and 2700 cm^{-1} , respectively. Silicon peaks can also be seen in the spectra at ~ 500 and 900 cm^{-1} .

SiO_2 with a thickness of 300 nm is an ideal substrate to optically image FLG. The image contrast is very sensitive to graphene thickness due to light interference on the SiO_2 layer modulated by the graphene layer.¹⁵ As an example, Figs. 1(b) and 1(c) show an optical image and a Raman spectrum (WITec, Alpha300, 532 nm laser) of the Cu-900 sample after it was transferred onto the SiO_2/Si substrate. The optical image was taken at the edge of the FLG with part of the substrate exposed. The uniformity of the color contrast in the optical image indicates the uniformity of the graphene thickness, although some small cracks formed during the transfer process. Two prominent graphene peaks appeared in the Raman spectrum [Fig. 1(c)] at ~ 1582 and $\sim 2700 \text{ cm}^{-1}$, corresponding to G and $2D$ bands, and the D -band was detected at 1350 cm^{-1} , which is due to defects or edges.¹⁶

Small D bands are seen in the Raman spectrum, but the intensity ratio of the D band to the G band is not high, especially compared to that of reduced graphene oxide, suggesting few defects and good crystal quality.

Scanning electron microscopy (SEM, FEI Quanta-600) and high-resolution transmission electron microscopy (HR-TEM, JEM-2010F) were used to study the structures of these samples. Figure 2(a) shows an SEM image of a FLG (Cu-900) on a silicon nitride “holey membrane” support. The platform for this holey film is a low stress 300 nm SiN film with an area of $0.5 \times 0.5 \text{ mm}^2$ on a circular 3 mm silicon frame. The diameter of the holes is $2.5 \mu\text{m}$ with a pitch of $10 \mu\text{m}$ in an array of 100×100 in a hexagonal arrangement. The SEM image in Fig. 2(a) shows a FLG film suspended on these holes. The edges of broken film always fold back, allowing for an observation of the cross section of the film to obtain the number of layers by counting the fringes. Such images of Cu-900 and Ni-950 [Figs. 2(b) and 2(c)] show the perfect layer structure and the typical thickness ranging from 3 to 50 nm with a d -spacing of 3.35 \AA .¹⁰

The sheet resistance and the transmittance of these samples were measured by the van der Pauw four probes method (Keithley, 6221 and 6514) and a spectroscopic ellipsometer system (JA Woollam M2000), respectively. Figure 3(a) shows the sheet resistance versus transmittance curve for FLG/graphite films with varying thicknesses. Sheet resistances as low as $200 \Omega/\square$ with a corresponding transmittance of 85% were obtained from sample Cu-900. According to the Beer-Lambert law, the transmittance of light (T) through a homogeneous material is $T = e^{-\alpha d}$, where α is the effective absorption coefficient $\alpha = 4\pi k/\lambda$, d is the film thickness, k is the extinction coefficient, and λ is the wavelength of incident light. The sheet resistance is defined as $R = 1/Gd$, where G is the material conductivity. Combining these two equations yields

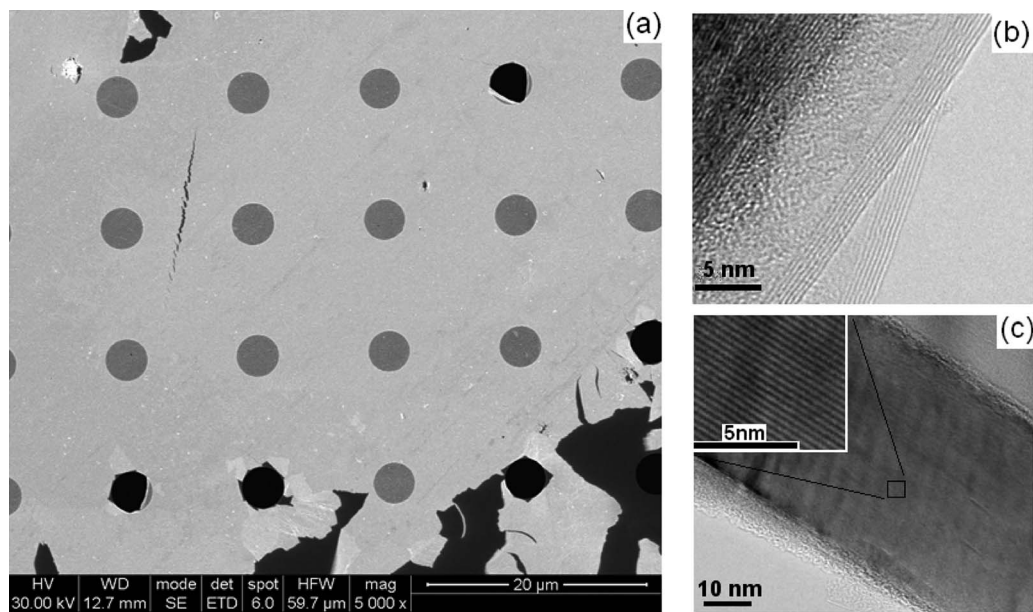


FIG. 2. SEM image (a) of FLG on SiN support membranes and HRTEM images of sample Cu-900 (b) and Ni-950 (c). The inset of (c) shows the high magnification image taken on the square region.

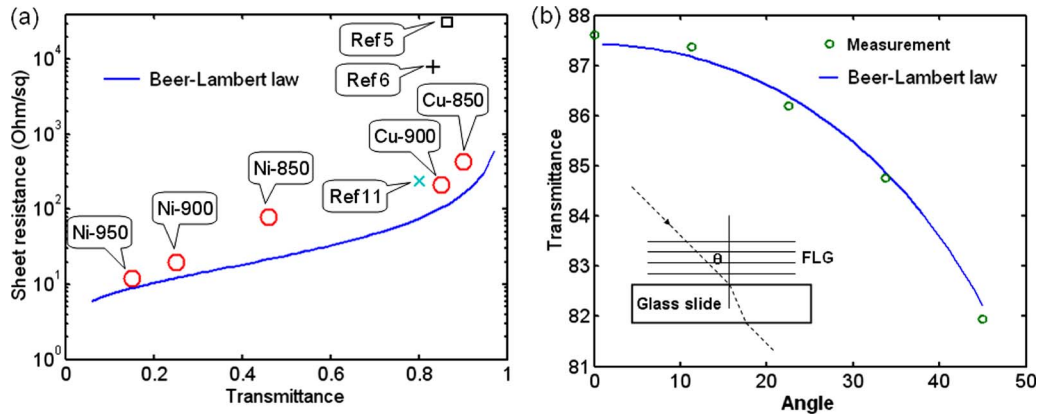


FIG. 3. (Color online) (a) Plots of sheet resistance as a function of transmittance at 550 nm, in comparison with other TCF. \times : FLG (see Ref. 11); $+$: reduced graphene oxide (see Ref. 6); and \square : reduced graphene oxide (see Ref. 5) from references. (b) The transmittance of Cu-900 as a function of incidence angle.

$$R = \frac{-4\pi k}{G\lambda \ln T}, \quad (1)$$

where k is 1.3 and G is taken as 2.1×10^6 S/m for graphite in the hexagonal plane.¹⁷ The calculated sheet resistance as a function of transmittance by Eq. (1) was plotted in Fig. 3(a) (solid line) for comparison to the experimental results. It clearly shows that the experimental results from the FLG/graphite films in this study are qualitatively consistent with the prediction of this model. Compared with the theoretical values from Eq. (1), the higher experimental sheet resistances could be due to the small cracks formed during the transfer process.

In order to further demonstrate the optical anisotropy in the film, the optical transmittance of the FLG as a function of incidence angle is shown in Fig. 3(b). The transmittance at 550 nm wavelength is about 87% for light incident perpendicular to the sample and about 82% for an angle of incidence 45° . We suggest that the angular effect shown in Fig. 3(b) may be due to the effective thickness change when samples tilt. As shown in the inset of Fig. 3(b), the effective thickness of FLG l is $d/\cos(\theta)$ for light with the angle of incidence of θ . Thus, for the limit of $al \ll 1$, the transmittance T can be expressed as

$$T = e^{-al} \approx 1 - al = 1 - \alpha d/\cos(\theta). \quad (2)$$

The calculated transmittance values using Eq. (2) are shown in Fig. 3(b) as well. It can be seen that the transmittance as a function of incident angle is in good agreement with this theoretical prediction and the influence of off-normal angles on the percent of light transmitted is smaller, relatively, than for that of single wall carbon nanotube thin films.¹⁸

In summary, thermal CVD was used to deposit large area FLG and graphite films with the thickness ranging from a few layers to hundreds of layers on metal substrates, and the films were transferred to other substrates after dissolving the metals in an aqueous solution of iron chloride. The optical and electrical properties as a function of FLG/graphite thick-

ness were systematically studied. Sheet resistances as low as $200 \Omega/\square$ for a transmittance of 85% were obtained on FLG, and the dependence of the transmittance on the angle of incidence of light was found to be smaller than that reported for single wall carbon nanotube thin films.

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