# Spectroscopic ellipsometry on Si/$SiO_2$/graphene tri-layer system exposed to downstream hydrogen plasma: Effects of hydrogenation and chemical sputtering

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# Spectroscopic ellipsometry on Si/$SiO_2$/graphene tri-layer system exposed to downstream hydrogen plasma: Effects of hydrogenation and chemical sputtering

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In this work, the optical response of graphene to hydrogen plasma treatment is investigated with spectroscopic ellipsometry measurements. Although the electronic transport properties and Raman spectrum of graphene change after plasma hydrogenation, ellipsometric parameters of the Si/SiO2/graphene tri-layer system do not change. This is attributed to plasma hydrogenated graphene still being electrically conductive, since the light absorption of conducting 2D materials does not depend on the electronic band structure. A change in the light transmission can only be observed when higher energy hydrogen ions (30 eV) are employed, which chemically sputter the graphene layer. An optical contrast is still apparent after sputtering due to the remaining traces of graphene and hydrocarbons on the surface. In brief, plasma treatment does not change the light transmission of graphene; and when it does, this is actually due to plasma damage rather than plasma hydrogenation. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4905597]

Ever since its first isolation, graphene has attracted tremendous scientific interest, thanks to its unusual electronic and mechanical properties.[1,2] A new perspective is the chemical modification of graphene by attaching atomic hydrogen or fluorine to both sides of the graphene lattice to produce graphane or fluorographene. Fluorographene can be successfully obtained in a reactive gas environment, which was shown to result in prominent changes in graphene's electronic structure that opens an optical bandgap of ~3 eV.[3,4] An alternative method is "plasma fluorination" which results in "fluoroninated graphene" with 1 fluorine atom per 6 carbon atoms at saturation.[5,6] A similar system is "hydrogenated graphene" that has a different charge carrier mobility and lattice parameter than that of pristine graphene.[7] However, there is still no method which results in full hydrogenation of graphene, i.e., graphane formation.[8] We have previously shown that plasma hydrogenation results in certain changes in the electronic structure,[9] work function,[10] and the adhesion properties of graphene.[11]

In this work, we employ the ellipsometry technique and investigate the optical changes of graphene after treating it with hydrogen plasma. Multi-angle reflectance measurements with polarized light were performed with a Sentech SE850 ellipsometer with a spot diameter of ≈1 mm for a wavelength range of 300–2300 nm at the incidence angles of $\theta = 45°$, 55°, and 65°. Ellipsometry measures the change in the polarization state of light which is related to the optical properties of the media.[12] The actual measured quantity from the outside is the complex reflectance ratio $\rho = r_s/r_p$. $\rho$ is parametrized as $\rho = \tan(\Psi)\exp(i\Delta)$, where $\tan(\Psi)$ is the amplitude ratio and $\Delta$ is the phase shift. Ellipsometry is widely considered to have a better resolution than simple reflection measurements and, therefore, is a more efficient way for the analysis of single layer films.[13]

Graphene was grown by the chemical vapor deposition (CVD) technique on a copper foil and was then spin coated with PMMA. After etching of copper in an iron nitrate solution, graphene with a PMMA supporting layer was transferred onto Si/$SiO_2$. PMMA was then removed in boiling acetone and a tri-layer system of Si/$SiO_2$/G was obtained (Fig. 1(a)).[14,15] Hydrogenation of graphene was achieved by exposing an electrically floating sample to downstream hydrogen plasma for 5 min (ion impact energy is 10–15 eV).[9] Raman spectrum map of the plasma hydrogenated graphene reveals an I(D)/I(G) ratio of 4–4.5 at 532 nm excitation, typical of atomic buckling induced by hydrogenation[10] (Fig. 1(b)). This is the maximum ratio observed so far in the literature[16,17] (same for plasma fluorination[5,6]), and longer plasma treatment does not result in any further changes in the Raman spectrum.[9,10] Some regions in Fig. 1(b) reveal an I(D)/I(G) ratio lower than 4, which are the graphene ripples and the parts covered with large PMMA agglomerates. With our transport measurements presented in Fig. 1(c), we have also confirmed the 3–5 times reduction in the carrier mobility at RT, together with $T^{1/3}$ dependence of the maximum electrical resistivity which is a signature of variable-range hopping in 2D materials.[7]

Fig. 1(d) top panel shows the difference in ellipsometric parameters of Si/$SiO_2$/graphene tri-layer system at $\theta = 45°$ before and after plasma hydrogenation, which appears very close to 0° both for $\Psi$ and $\Delta$. Similar to this, no significant differences could be observed for other incident angles both in the visible and infrared range (not shown). Light transmission can be approximated to be independent of the electronic

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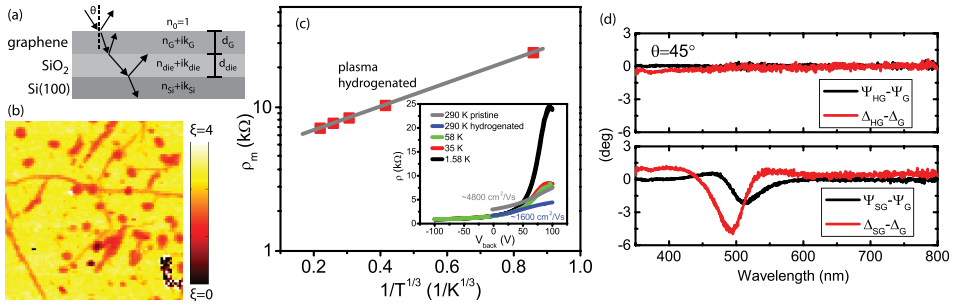


FIG. 1. (a) The tri-layer system: $Si/SiO_2/G$. (b) $\xi = I(D)/I(G)$ map ($20 \times 20\,\mu m^2$) of plasma hydrogenated graphene. (c) Transport measurements presented as maximum resistivity vs. temperature performed on hydrogenated graphene with $\xi \approx 2.5$. As a comparison, the maximum resistivity of pristine graphene was recorded to increase only 1.5 times with decreasing temperature from 70 to 1.6 K. The inset shows the actual conductance measurements. (d) Change in the ellipsometric parameters of plasma hydrogenated (top panel) and plasma sputtered (bottom panel) graphene in the visible range for $\theta = 45°$. G, die, HG, and SG stand for graphene, dielectric, hydrogenated graphene, and sputtered graphene, respectively.

band structure in conducting 2D materials,[13,18] i.e., absorbance(E) $\approx \pi\alpha$, where $\alpha = e^2/\hbar c$ is only a function of known universal constants. For energies above 2.5 eV ($\lambda \lesssim 500$ nm), this universal relation does not hold anymore for graphene because of the van Hove singularity, effects from the hydrocarbon contamination and/or excitonic effects.[13,19,20] In the case of a semiconducting 2D material, this equation is valid only above the optical band gap.[13] Theoretical calculations of graphane predict a prominent band gap in the blue,[21–23] and this directly implies that the optical properties also have to change. Thus, we can conclude with the ellipsometry measurements that plasma hydrogenated graphene is not graphane and it still is a conductive material at RT, in accordance with the electrical conductance measurements (Fig. 1(c)).

A possible way to increase the number of hydrogenated carbon atoms might be increasing the impact energy of the hydrogen ions. In order to test this, a second sample was intentionally electrically grounded during the plasma treatment. The plasma particles consist of neutral species ($H_3$, $H_2$, and H), electrons, photons, metastable negative ions, molecular ($H_3^+$ and $H_2^+$), and atomic ($H^+$) positive ions. When the sample is grounded, the ion impact energy is equal to the plasma potential which is ~30 V in the present case. The molecular ions ($H_3^+$ and $H_2^+$) dissociate during the impact and deposit energies of 10 and 15 eV/H on the surface, while the atomic hydrogen ions (protons) deposit an energy of 30 eV/H.[24] 5 min of plasma treatment under these conditions resulted in significant changes in the ellipsometric parameters (Fig. 1(d) bottom panel). The nature of such changes was investigated with scanning electron microscopy (SEM) images obtained after plasma treatment with electrically floating (Fig. 2(a)) and grounded samples (Fig. 2(b)). The image in Fig. 2(a) has the typical features of graphene such as the ripples, remaining traces of the PMMA agglomerates appearing as brighter features and multilayer (two or more) graphene appearing as darker features. In Fig. 2(b), only large PMMA agglomerates and some of the ripples are left on the $SiO_2$ surface, which suggests that graphene was effectively sputtered after 5 min of plasma treatment. 30 eV is slightly lower than the physical sputtering threshold of graphene with hydrogen,[25,26] which indicates chemical sputtering.[27] It is indeed well-established in literature that hydrogen ions sputter carbon materials chemically either through $CH_3$ creation with one bond remaining to graphene lattice that reduce sputtering threshold[28] or through supersaturation of hydrogen at the immediate surface.[29]

Finally, ellipsometric measurements were used for extracting the optical contrast and graphene's transmission (optical contrast is defined as the change of amplitude reflectivity (R) measured from the outside after introducing a new layer onto the system. In the case of graphene covering a $Si/SiO_2$ scaffold, it is $(R(Si/SiO_2)\text{-}R(Si/SiO_2/G))/R(Si/SiO_2))$. Cauchy layer models $(n(\lambda) = B_n + \frac{C_n}{\lambda^2}, k(\lambda) = B_k + \frac{C_k}{\lambda^2})$ with typical values of $C_n = 3000$ and $C_k = 1500$[30–32] were used for fitting, while $d_G$ and $d_{die}$ were fixed to 0.34 nm and 292 nm, respectively. The obtained optical contrast (Fig. 2(c)) and transmission are (Fig. 2(d)) very similar to values obtained in the literature.[13,30–34] After graphene was chemically sputtered, light was still being absorbed at $\lambda \lesssim 500$ nm that resulted in an optical contrast which could even be perceived by the naked eye or under optical microscope (Figs. 2(c) and 2(d)). We attribute this observation to the typical light absorption spectrum of hydrocarbons (in the current case, remainders of graphene and PMMA left overs) that has a peak around 4.5 eV.[19]

In summary, hydrogen plasma treatment of an electrically floating $Si/SiO_2$/graphene tri-layer system results in partial hydrogenation of graphene. Plasma hydrogenated graphene exhibits different electronic properties from its pristine counterpart, but it is still a conductive material at RT. The optical absorption of 2D conducting materials is universal and, therefore, no change in the optical contrast of the $Si/SiO_2$/graphene tri-layer system can be observed after plasma hydrogenation. When the sample is left electrically grounded during the plasma treatment, hydrogen ions chemically sputter graphene; leaving only some of the ripples and some portions protected by the large PMMA agglomerates behind. A change in the optical contrast can only be recorded when graphene layer was destroyed in this way. Ellipsometry or other optical methods which cannot detect plasma hydrogenation of graphene can be efficiently used to predict plasma damage. A possible prospect is to implement *in situ* optical techniques during plasma treatment to account for such damages.

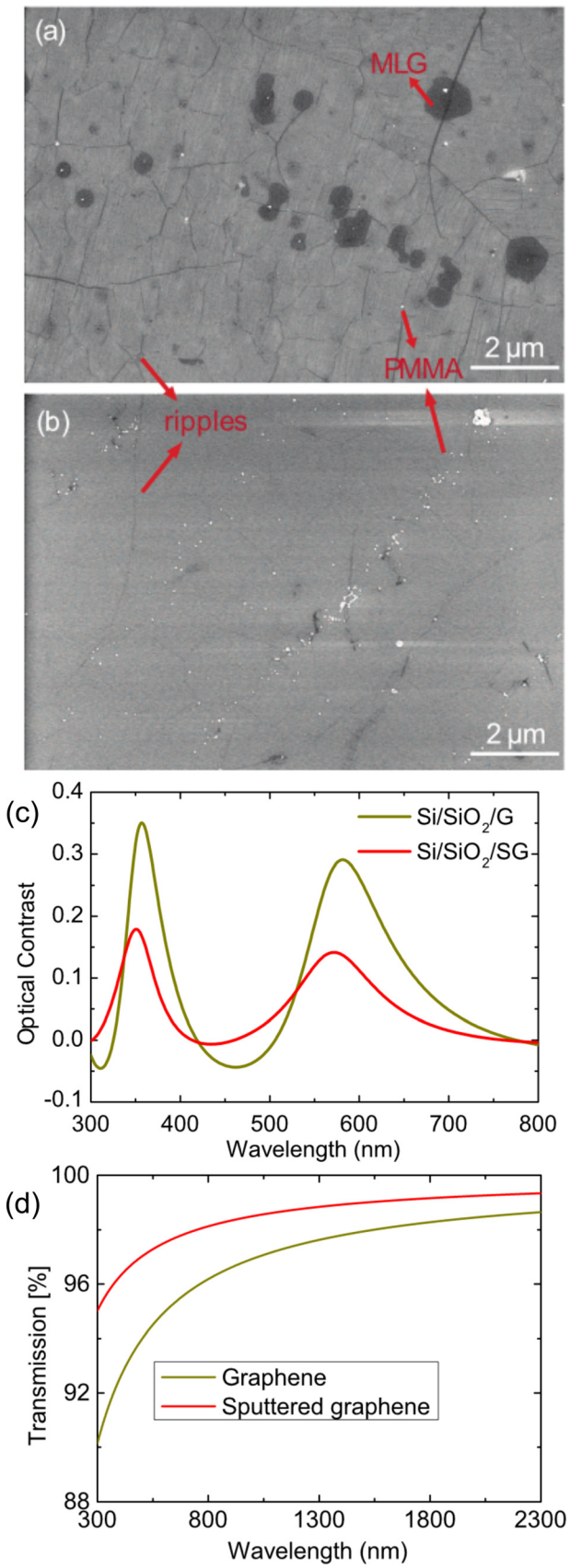


FIG. 2. SEM images of the (a) $Si/SiO_2/G$ and (b) $Si/SiO_2/SG$ tri-layer systems. (c) Optical contrast and (d) transmission of graphene. $d_{die} = 292$ nm, $B_{n_G} = 2.458$, $B_{k_G} = 1.439$, $C_{n_G} = 3000$, $C_{k_G} = 1500$, $d_G = 0.34$, $B_{n_{SG}} = 3.255$, $B_{k_{SG}} = 2.253$, $C_{n_{SG}} = 3000$, $C_{k_{SG}} = 1500$, $d_{SG} = 0.34$. $Si/SiO_2/HG$ system has the same optical properties as the $Si/SiO_2/G$ system. G, MLG, HG, and SG stand for graphene, multilayer graphene, hydrogenated graphene, and sputtered graphene, respectively.

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