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Citation: Applied Physics Letters 103, 192109 (2013); doi: 10.1063/1.4829356
View online: http://dx.doi.org/10.1063/1.4829356
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In situ growth of p and n-type graphene thin films and diodes by pulsed laser deposition

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(Received 6 September 2013; accepted 17 October 2013; published online 7 November 2013)

We report the in situ growth of p and n-type graphene thin films by ultraviolet pulsed laser deposition in the presence of argon and nitrogen, respectively. Electron microscopy and Raman studies confirmed the growth, while temperature dependent electrical conductivity and Seebeck coefficient studies confirmed the polarity type of graphene films. Nitrogen doping at different sites of the honeycomb structure, responsible for n-type conduction, is identified using X-ray photoelectron spectroscopy, for films grown in nitrogen. A diode-like rectifying behavior is exhibited by p-n junction diodes fabricated using the graphene films. © 2013 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4829356]

Graphene, a single sheet of hexagonally packed carbon atoms, has been actively studied in the past decade due to a variety of fascinating properties arising out of its highly two-dimensional structure, which holds huge promise for significant technological advances.1,2 The plethora of interesting properties which include a high surface area, high carrier mobility with large electron mean free path, and high mechanical strength make graphene a potential candidate in a variety of fields such as electronics, bio-electronics, energy conversion, energy storage, electro-catalysis, and nanocomposites for high strength mechanical applications.3–5 Recent studies show that pristine graphene can be modified chemically and structurally to suit specific needs, wherein physical and chemical properties need to be tailored.6,7 Nitrogen, for instance, is routinely doped into the graphitic structure for electronic applications, the graphene sheets are usually either transferred over a desired substrate or grown on a catalytic layer, which needs to be removed prior to building graphene based devices. For the emerging field of graphene-based electronics, it would be advantageous to develop a simple process for the growth of both p and n-type graphene films on desired substrates, without the use of catalytic layers and laborious transferring processes. Recently, we have reported22 growth of p-type graphene films using pulsed laser deposition (PLD) from highly oriented pyrolytic graphite (HOPG) directly on desired substrates without any catalytic layers. In this work, we report the growth of n-type graphene using PLD, again without the use of catalytic layers. A simple route for the development of graphene-based electronics is also demonstrated, by fabricating p-n junction diodes using the p and n-type graphene films.

Graphene films were deposited on SiN/Si substrates by pulsed laser ablation from a HOPG target (SPI Supplies, 444 HP-AB) using a KrF excimer laser (wavelength = 248 nm; pulse width = 20 ns, and repetition rate = 10 Hz). The films were grown either in high purity (5N) argon (20 mTorr) or nitrogen gas (20, 100, 250, and 500 mTorr) allowed into the chamber using a mass flow controller. The films are denoted as Ar20, N20, N100, N250, and N500, respectively. During the PLD process, the substrates were held at a temperature of 973 K and a laser fluence of 6.1 J cm−2 was used for ablation. Graphene films were analyzed using X-ray diffraction (XRD, D8 Discover, Bruker), micro-Raman spectroscopy (LabRAM ARAMIS, Horiba-Jobin Yvon), scanning electron microscopy (SEM, Nova NanoSEM 630 FESEM, FEI), and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD spectrometer). Micro-Raman spectra were acquired with notch filters cutting at ~100 cm−1 using a He-Ne laser (633 nm, 17 mW at source). A curve fitting procedure was employed to extract the peak positions, line-widths (full width at half maxima (FWHM)), and peak intensities. For XPS studies, the individual peaks were fitted by a Gaussian (70%)–Lorentzian (30%) (GL30) function, after performing a Shirley type background subtraction using the software CasaXPS. The electrical conductivity and Seebeck coefficient of the films

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were measured simultaneously using a commercial setup (RZ2001i, Ozawa Science, employing linear four-probe and differential methods, respectively. For the Seebeck coefficient measurements, a temperature difference of 2–8 K was maintained. In order to verify the application potential of the growth processes based on PLD, p-n junction diodes were fabricated using p- and n-graphene films on SiO2 covered Si substrates. The current-voltage characteristics of the films and diodes were measured at 300 K and 443 K by a semiconductor characterization system (Keithley 4200-SCS), using silver contacts.

The temperature dependence of electrical conductivity of the graphene films, shown in Fig. 1(a), reveals the semiconducting nature of the films, i.e., an increase in conductivity with temperature. The films grown in nitrogen exhibit higher electrical conductivity compared to the one grown in Ar. The higher electrical conductivity is attributed to the doping of graphene with N, which donates electrons. Among the films grown in nitrogen, N250 shows the highest electrical conductivity above 300 K, indicating that the conductivity increases with partial pressure of nitrogen (Table I). The switching of the type of conductivity is evident from the temperature dependence of Seebeck coefficient of the films, shown in Fig. 1(b). While graphene grown in Ar shows a positive Seebeck coefficient, indicative of p-type conduction and a positive slope with temperature, the ones grown in N shows a negative Seebeck coefficient, at higher temperatures and a negative slope with temperature. It is to be mentioned here that our attempts at nitrogen doping of p-type films either by high temperature (500–800 °C) annealing in nitrogen gas or exposure to nitrogen plasma were unsuccessful, indicating that nitrogen doping occurs only during growth of the films.

The θ–20 XRD patterns for the films N250 and Ar20 are shown in Fig. 1(c). The broad peak is indicative of the nanostructured nature of the graphene films. The inter-planar spacing (d value) for N250 and Ar 20 are 4.32 and 4.57 Å, respectively. This is higher than the ideal value reported for graphite (3.35 Å) and is attributed to the defects in graphene.2 The crystal radius of C4+ with co-ordination number 3 is 0.06 Å while that of N5+ with the same co-ordination number is 0.044 Å. The lower d value obtained for the N doped graphene film is hence attributed to the substitutional doping of C with N atoms. The SEM images of the surface revealed a smooth morphology, and the films had to be scratched to reveal the in-plane growth of graphene sheets, as shown by the wrinkled surfaces in Fig. 1(d).

The Raman spectra obtained for the films are shown in Fig. 2. The spectra are normalized with respect to the graphitic-G band occurring at 1592 cm⁻¹. The G-band

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**TABLE I.** Intensity of D (I_D), G (I_G), and 2D (I_2D) bands of the Raman spectra of the graphene films formed using different partial pressures of nitrogen and Argon. The ratio of the intensities and the electrical conductivity of the films at 300 K are also presented.

<table>
<thead>
<tr>
<th>Sample</th>
<th>I_D (a.u)</th>
<th>I_G (a.u)</th>
<th>I_2D (a.u)</th>
<th>I_D/I_G</th>
<th>I_2D/I_G</th>
<th>Electrical conductivity at 300 K (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N20</td>
<td>1.26</td>
<td>1.00</td>
<td>0.25</td>
<td>1.26</td>
<td>0.25</td>
<td>62.54</td>
</tr>
<tr>
<td>N100</td>
<td>1.56</td>
<td>1.00</td>
<td>0.28</td>
<td>1.56</td>
<td>0.28</td>
<td>66.58</td>
</tr>
<tr>
<td>N250</td>
<td>1.52</td>
<td>1.00</td>
<td>0.16</td>
<td>1.52</td>
<td>0.16</td>
<td>70.02</td>
</tr>
<tr>
<td>Ar20</td>
<td>2.36</td>
<td>1.00</td>
<td>0.24</td>
<td>2.36</td>
<td>0.24</td>
<td>42.83</td>
</tr>
</tbody>
</table>
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confirms the formation of hexagonal graphitic lattice. The D-band, which represents the defects in the graphene films, is observed to be of higher intensity for film Ar20 compared to the N-doped films. The high intensity can be attributed to the non-sp² bonds, particularly at the edges of the nanostructured graphene. The ratio of intensity of D band to that of G band (I_D/I_G) is lower for N-doped films (Table I), implying that N-doping helps in reducing the defects. From the FWHM of XRD spectra, it is clear that both Ar20 and N250 films have the same grain size and hence the lower defect in N-doped films is not due to bonding of C atoms at the edges of the nanostructured graphene with N atoms to form hexagonal lattices with larger grain size. Evidently, the presence of N helps in quenching of defects within the nanostructured graphene framework. This is possible if N enters the lattice predominantly in the graphitic (quaternary) form or the pyridinic form (hexagonal edge substitution), which is confirmed using XPS studies detailed below.

Figure 3(a) shows the XPS survey spectra obtained for the films N250 and Ar20. The N1s peak confirms the presence of N (~2%) in N250. The high resolution N1s core level spectra of film N250 is shown in Fig. 3(b). The experimental data could be deconvoluted into five peaks corresponding to five different types of nitrogen incorporated in the planar graphene network (Fig. 3(c)). The peak assigned as N1 (binding energy of 398.2 eV) corresponds to pyridinic N, wherein N substitutes for C at the edge of the graphene crystallites, each N atom being bonded to two carbon atoms and donates one p-electron to the π system. The high intensity of N1 peak in N250 is attributed to the nanostructured nature of the film, with edge defects offering more sites for pyridinic N substitution of C atoms. The peak N2 at 399.4 eV corresponds to the nitrile (C≡N) functional group, wherein N atoms bond with C atom without substitution. This peak has also been attributed to the pyrrole-like nitrogen by few authors. A substitution of C atom within the aromatic structure by a N atom resulting in a graphite-like structure (quaternary N), where the N atom is bonded to three other C atoms, leads to peak N3, at 400.8 eV. The peaks N4 and N5 centered at 402.2 and 404.7 eV, respectively, are attributed to the pyridinic N-oxide and chemisorbed nitrogen oxide species which is responsible for the increase in oxygen content in film N250 as compared to N20. From the high intensity of N1 and N3 peaks, it is clear that substitution by N atoms which contributes additional electrons to the π-conjugated system is dominant in our films. Hence, compared to undoped graphene film (Ar20), films doped with N are expected to have higher electrical conductivity, which is indeed observed.

Having established the p- or n-type nature of our graphene films, we have fabricated p-n junction diodes and studied their current-voltage (I–V) characteristics at 300 K and 443 K. Figure 4(a) shows the schematic of the p-n junction. Measurements between contacts 1 and 2, 3 and 4, and 4 and 1, respectively, provided the I–V characteristics of n-graphene, p-graphene and the p-n junction formed by the p and n-type graphene films. The top-left and right-bottom insets to Fig. 4(b) show the in-plane I–V characteristics of p-type graphene and n-type graphene films, respectively. In both the cases, the I–V characteristics showed ohmic behavior (at both 300 K and 443 K), indicating that the silver electrodes form ohmic contacts with both p-type and n-type graphene films. Since both the films act as semiconductors, as evident from Fig. 1(a), the resistivity drops as temperature increases and hence the slope of the I–V curves in the insets increases at 443 K. Interestingly, the I–V characteristics of Ar-doped graphene/N-doped graphene junction showed non-linear rectifying-like behavior, indicating the existence of p-n junction at the interface of Ar-doped (p-type) and N-doped (n-type) graphene films. The non-linear behavior of I–V characteristics is more pronounced at 443 K and is attributed to the increased difference in Seebeck coefficient of p- and n-type films with increasing temperature as evident.

FIG. 2. Raman spectra of the pristine and N-doped graphene films, normalized with respect to the graphitic G-band.

FIG. 3. (a) XPS survey spectra of the films Ar20 and N250. (b) High resolution spectra of N1s peak of the film N250, along with the deconvoluted peaks. (c) Schematic of different kinds of bonding of nitrogen in the graphene framework. N1 refers to pyridinic, N2 to nitrile, N3 to graphitic, N4 to pyridinic N-oxide, and N5 to chemisorbed nitrogen oxides.

FIG. 4. (a) Schematic of p-n junction diode measurements. (b) I–V characteristics of p-type graphene and n-type graphene films, respectively. The non-linear behavior of the p-n junction at the interface of Ar-doped (p-type) and N-doped (n-type) graphene films is shown in the insets.
where $I$ is the diode current, $I_s$ is the reverse bias saturation current, $V$ is the voltage across the diode, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $n$ is the ideality factor, which is a measure of how closely the diode follows the ideal diode behavior. The ideality factor for the current device was found to be 17.5, which is unusually high compared to that of an ideal diode ($n = 1$). Ideality factors greater than 10 have been reported for oxide based p-n diodes and such high values have been attributed to deep-level-assisted tunneling. In fact, the tunneling process may be the dominating conduction mechanism in our p-n junction due to the presence of high density of carriers in the individual p- and n-type graphene films as evident from the high reverse current, which is even higher at 443 K due to the decreased depletion layer width. In spite of the weak diode performance, the obtained results suggest that p-n diodes can be fabricated using PLD deposited n- and p-type graphene films and one can expect better performance once the thickness and conductivity of the films are optimized.

Graphene thin films of both p and n-types have been fabricated using pulsed laser deposition from a highly ordered pyrolytic graphite target, employing a KrF excimer laser, in the presence of argon and nitrogen gases, respectively. Extensive Raman analysis, electron microscopy, and x-ray diffraction studies confirmed the growth of in-plane nanostructured graphene films with defects. The majority carrier type in the films is revealed by the high temperature Seebeck coefficient studies. The electrical conductivity of films n-type graphene films increased with the nitrogen partial pressure during growth and the presence of nitrogen dopants in the n-type films, which is responsible for electron doping, is confirmed by X-ray photoelectron spectroscopy studies. p-n junction diodes fabricated using the films showed diode-like rectifying behavior. The simple growth process help deposit p and n-type graphene films on any desired substrates without the use of catalytic layers, thereby avoiding labor-intensive transferring processes usually required for developing graphene-based electronics.

Support for this work was provided by the competitive faculty-initiated collaboration (FIC) grant at KAUST.

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