Characterization of graphene-on-insulator films formed using plasma based surface chemistry

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ABSTRACT

This research explores the surface chemistry of halogen based plasmas on silicon carbide and is aimed at the synthesis of large area graphene-on-insulator films. In these studies, 6H-SiC (0001) substrates were etched using either CF₄ and Cl₂ based plasmas and then thermally annealed. The resulting surfaces were analyzed using x-ray photoelectron spectroscopy, reflection high energy electron diffraction, atomic force microscopy, and Raman spectroscopy. The analyses showed that the etching process selectively etched silicon to produce carbon rich surface layers on the silicon carbide substrate, and when annealed, these carbon rich layers formed graphene films with halogen- and oxygen-based defects. The thickness of the graphene was controlled by the plasma etch parameters. Two point current-voltage measurements were used to characterize the electrical properties of the films. The current-voltage plots exhibited back-to-back Schottky behavior which suggests that the defects open a band gap in these films. Current-voltage data were used to determine the Schottky barrier height, carrier density, and the upper limit for the film resistivity.

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1. INTRODUCTION

Driven by immense technological implications, the growth and preparation of graphene as well as the fabrication of graphene based devices have received considerable attention in recent years. Graphene synthesis routes reported to date include mechanical¹ and chemical² exfoliation, chemical vapor deposition,^{3,4} thermal sublimation of Si from SiC under ultrahigh vacuum^{5,6} and atmospheric pressure,⁷ and selective etching of Si from SiC by molecular Cl₂ at high temperature.⁸ The studies described in this paper focus on the latter approach and are part of a broader research effort to develop a practical method of wafer scale graphene-on-insulator synthesis using process tools currently available in the semiconductor industry. Motivated initially by Cl₂ etching studies of SiC and the wide spread use CF₄ and Cl₂ based plasmas in the semiconductor industry, this research has focused on the use of halogen based (CF₄ and Cl₂) inductively coupled plasma-reactive ion etching (ICP-RIE) of SiC as a potential route to the synthesis of graphene-on-insulator films.

The observations of Zinovev et al.⁸ clearly suggest that Cl₂ preferentially etches Si from the SiC surface at elevated temperatures. Consequently, the working hypothesis for the present studies was that halogen based plasmas could selectively etch Si from the near surface layers of SiC, and that the resulting C-layers could be annealed to form the graphene film. This paper reviews the results of the initial studies which demonstrated the feasibility of this approach⁹ and provides a more detailed characterization of the films. Specifically this includes a discussion of chemical structure of the films as well as the defect species. In addition, the effects of plasma power on film thickness, and measurements of the electrical properties are described. Overall, the results discussed here suggest that it may be possible to use this ICP-RIE, a conventional semiconductor processing tool, to synthesize graphene-on-insulator films.

2. EXPERIMENTAL

The samples used in these studies were 1 cm x 1 cm squares diced from chemo-mechanically polished on axis ($\pm 0.5^\circ$) 6H-SiC(0001) n-doped wafers purchased from CREE. The nominal resistivity of these wafers was quoted as 0.020 – 0.200 Ω -cm. The nominal surface roughness for these wafers was less than 5 nm RMS. In all reported cases, films were formed on the Si-surface. Comparable wafers from other vendors (e.g., University Wafer, Inc.) were also used. Prior to use, the samples were degreased using trichloroethylene, acetone, and methanol. This was followed by blow drying in ultrahigh purity N₂. These samples were plasma etched using a Trion Technologies Minilock-Phantom III ICP-RIE system using either a CF₄ or Cl₂ based plasma. The ICP power was maintained at 400 W, while the RIE power was set at values ranging from 3 to 300 W. Typical flow conditions were 20 sccm and 25 mTorr pressure. An etch time of 12 minutes was found to give reproducible results in all cases. Following the plasma etch, the samples were transferred to an ultrahigh vacuum (UHV) system and annealed at 970 °C for 60 minutes to desorb volatile halogenated surface species and reconstruct the crystal structure of the near surface layers.

After each process step, samples were analyzed using x-ray photoelectron spectroscopy (XPS), reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM) and Raman spectroscopy. The XPS measurements were performed using monochromated Al-K α x-rays using a PHI 5700 system with an Omni Focus V lens. RHEED patterns were obtained using a Staib Instruments model RH-15 system. The AFM measurements were obtained using an Agilent (formerly Molecular Imaging) model 5500. Raman spectra were taken using a Renishaw micro-Raman system with a 532 nm laser having a power level was 450 mW and spot size of 1 μ m.

As described in detail elsewhere,^{9,10} attenuation of the SiC substrate C 1s photoelectron

peak by the graphene overlayer was used to determine the thickness of the graphene. This was accomplished using a simple layer model described previously by Yates and coworkers.¹¹

The XPS analyses utilized two different modes. In the first, referred to as the normal or bulk analysis mode, the exit angle of the photoelectrons was 45° relative to the surface normal. In the second mode, referred to as the surface sensitive mode, an exit angle of 75° was used. Although varying the exit angle alone does not produce truly angle resolved spectra, increasing the exit angle does enhance spectral components associated with surface species.

The electrical properties of the films produced here were characterized using two point¹² current-voltage (I-V) measurements.¹³ For these measurements, equally spaced Ti/Au electrical contacts (200 nm Au / 10 nm Ti) were deposited using a Temescal BJD-2000 electron beam evaporator and a shadow mask prepared by Photo Sciences Inc. These contacts led to larger Au pads which were wire bonded to feedthrough posts on 16 pin transistor outline (TO) headers (Spectrum Semiconductor Materials, Inc.). The I-V measurements were made using a Tektronix 4200 Semiconductor Characterization System.

3. RESULTS AND DISCUSSION

Figure 1 shows the Si 2s, C 1s, O 1s, and F 1s XPS peaks for the 6H-SiC (0001) surface after an HF dip to remove the native oxide layer and after CF₄ based ICP-RIE and UHV annealing. It should be noted that the spectra have been normalized to yield the same C 1s intensity. The relative intensities of the Si 2p and C 1s peaks before plasma etching and annealing are representative of a near-stoichiometric SiC surface with a C/Si ratio of 1.2/1 after taking into account relative atomic sensitivity factors.¹⁴ After etching and annealing, it is evident that the Si has been significantly depleted with respect to C. In this case, the C/Si ratio has increased to 7.0/1.

In other words, the surface goes from being slightly C-rich (as is generally the case after the removal of the native oxide using an HF acid etch) to being extremely C-rich after the ICP-RIE and anneal. Low levels of oxygen and fluorine are observed on the etched and annealed surface. The significance of these species will be discussed more fully below. Overall, the atomic concentrations of Si, C, O, and F species present on the etched and annealed surface shown here are 22.3%, 68.4%, 3.3%, 6.0%, respectively.

The XPS sampling depth (nominally three times the electron mean free path^{15,16}) is on the order of ten or so C-Si bilayers.¹⁷ Consequently, these spectra clearly demonstrate the selective removal of Si-atoms from the near surface layers of the SiC lattice leaving a C-rich overlayer. As shown below, similar results are obtained in our work using Cl₂ based ICP-RIE and UHV annealing. This observation for both Cl₂ and CF₄ based etching precludes the possibility that the CF₄ based results represent C deposition from the CF₄ plasma. This observation is consistent with the high temperature Cl₂ based etching reported by Zinovev et al.⁸

The surface chemistry associated with the synthesis process can be understood by analysis of the C 1s and Si 2p XPS peaks. Figure 2 shows the C 1s peak for the surface produced by CF₄ based etching (400W ICP / 3W RIE) and UHV annealing at 970 °C. This peak was obtained using the bulk analysis mode and has four dominant contributions to the overall line shape. The peak at 282.5 eV is attributed to C-atoms bound as SiC in the substrate,¹⁸ while the peak at 284.1 eV is attributed to graphene.¹⁹ Two additional peaks identified as D₁ and D₂ are located at 285.7 eV and 288.4 eV, respectively. For comparison, the inset shows the effect of annealing at 970 °C alone is to produce a relatively low intensity peak at 284.5 eV due to “graphitization” of the SiC surface.²⁰

Figure 3 shows the corresponding C 1s spectrum obtained in the surface analysis mode. This spectrum is also comprised of the same four components identified in Figure 2. Here, the

increase in intensity of the three peaks identified as graphene, D₁, and D₂ (relative to the substrate peak) indicates that they are indeed associated with the surface film. The C 1s peaks identified as D₁ and D₂ are attributed to fluorine and oxygen based defects. Fluorine based defects have been previously identified by Sato *et al.*²¹ in fluorinated graphite. More recently Friedrich *et al.*²² have also observed similar defect species in XPS studies of plasma brominated graphite surfaces. Oxygen based defects are well understood from studies of graphene oxide. For example, Stankovich *et al.*²³ have used XPS to identify a variety of oxygen functionalities on graphene oxide and reduced graphene oxide surfaces.

As illustrated by Figure 4 (a), the fluorinated defect has two components. The first component is due to two coupled sp³ hybridized C-atoms each bound to a F-atom, one of which is above the surface and the other is below the surface. These are labeled as C_F-atoms, and they correspond to the high binding energy peak identified as D₂ in the spectrum. The second component is associated with the four sp² hybridized C-atoms bound to the two C_F-atoms. These are identified as C_C-atoms in the figure, and they correspond to the C 1s peak identified as D₁. These atoms are sp²-hybridized like the remainder of the graphene lattice, but have slightly less electronic charge in their bonding orbitals which gives rise to their slightly higher binding energy relative to the graphene peak.

The structure of fluorinated defect suggests that the intensity ratio for the D₁/D₂ peaks should be 2/1. The observed value for both the bulk and surface spectra is closer to 3/1. This may be due to the fact that the C_C type defects extend beyond the immediate vicinity of the C_F defects due to the large electronegativity of fluorine. Alternatively, this may be due to the fact that slightly more surface fluorine atoms desorb during the annealing process. Molecular level modeling²⁴ was used by Friedrich *et al.*²² to demonstrate that insertion of halogenated sp³ defects leads to the

buckling of planar sp^2 bound graphene sheets. This is most likely the case for the films described in the present work as well.

Structures associated with oxygen based defects are illustrated in Figure 4 (b).²⁵ As discussed by Stankovich et al.,²³ oxygen based defects include carbon atoms within the graphene plane which are either bridged by oxygen atoms (epoxide groups) or attached to hydroxide groups. Collectively, these are designated as C-O defects and give rise to a C 1s peak at 286.2 eV. Edge (carbon) atoms doubly bound to oxygen give rise to carbonyl groups. These are designated as C=O defects and give rise to a C1s peak observed at 287.8 eV. Finally, carboxyl groups designated as CO₂H give rise to a C 1s peak at 289.0 eV. These species are also thought to be attached primarily at edge sites.

Even a cursory review of the literature reveals that reported values for these binding energies may vary by several tenths of an electron volt.^{26,27,28} Consequently, it is possible that the C-O and C=O defects contribute to the peaks marked D₁ and D₂, respectively, in Figures 2 and 3. In any case, there does not appear to be a significant contribution from CO₂H defect species.

The thickness of the graphene film can be estimated using the relative intensities (areas) of the surface and substrate C 1s peaks. Specifically, the ratio of the sum of the peak intensities for the graphene, D₁ and D₂ C 1s peaks to the intensity of the substrate (SiC) C 1s peak can be directly related to the film thickness using a simple Beers law relationship.⁹ For the film depicted in Figure 2, the graphene thickness is approximately two layers. Based on the intensities of the graphene, D₁ and D₂ peaks for the film represented in Figure 2, approximately 24% of the C-atoms in the film are associated with defect states. The situation is, however, most likely more complicated than this since both oxygen and halogen based defects are likely to be present.

The results for Cl₂ based processing yield a similar physical picture. Figure 5 shows the C 1s XPS peak obtained for Cl₂ based etching and annealing at 970 °C. The plasma power in this case was 400 W ICP and 200 W RIE. As in the previous example for CF₄ based etching, the C 1s peak also has four primary components. The peak at 282.5 eV is again due to the underlying SiC substrate. Graphene is seen at 284.4 eV, while the components of the defect states are observed at 285.7 eV for D₁ and 288.4 eV for D₂.

There is a 0.3 eV up-shift in the binding energies for the graphene peak for the films produced by Cl₂ based etching (compared to those produced by CF₄ based etching). The reason for this is presently unclear, but may be due to different doping effects of fluorine and chlorine. Additionally, in the case of Cl₂ based etching, the full width at half max (FWHM) of the SiC component (1.4 eV) is somewhat greater than that for the CF₄ etched surface (0.8 eV) which is essentially the same as that for the annealed SiC surface (inset Figure 2). In contrast, the FWHM of the graphene peaks on both surfaces is essentially the same (i.e, 1.4 eV vs 1.3 eV). This broadening of the C 1s peak indicates that the chemical environment of the C-atoms in the Cl₂ etched substrate is somewhat more diverse than that of the corresponding CF₄ etched substrate.

Using the relative intensities of the surface and substrate C 1s peaks, the thickness of the graphene overlayer can be estimated at two layers for the film depicted in Figure 5.⁹ Based on the relative intensities of the graphene and defect peak intensities, approximately 25% of the C-atoms in the film are associated with defect states. This is comparable to the case for the CF₄ based films. The ratio of the D₁/D₂ peaks for this film is on the order of 5/1. This ratio is even higher than that observed for the CF₄ etched surface. If the defects are due primarily to halogenated species, this is may be due to greater desorption of surface Cl-atoms because of the weaker C-Cl bond strength (compared with the C-F bond).

Figure 6 shows a representative Si 2p XPS peak for a film which has been produced using a CF₄ based plasma (400W ICP / 3W RIE in this case) followed by annealing at 970 °C. This peak consists of four components. The peaks at 100.3 eV and 100.9 eV correspond to the Si 2p_{3/2} and 2p_{1/2} peaks, respectively, and are associated with Si-atoms bound as SiC (i.e., the substrate).^{18,29} The second set of peaks located at 101.3 eV and 101.9 eV may correspond to the Si 2p_{3/2} and 2p_{1/2} peaks for either a fluorinated silicon species^{30,31} or a non-stoichiometric Si-O_x or oxycarbide interface species.³² For both sets of peaks, the 2p_{3/2} – 2p_{1/2} splitting (0.6 eV), FWHM (0.8 eV), and intensity ratio (2/1) were the adopted from the work of Roos et al.³³

Figure 7 (a) shows the F 1s XPS spectrum for a single layer film. This peak consists of two components. One is located at 685.6 eV and the other at 687.6 eV. Both peaks have a FWHM of 1.7 eV. The presence of two peaks is consistent with the picture of the halogenated defect states consisting of atoms bound both above and below the surface plane. The lower binding energy peak is associated with the subsurface F-atoms. This assignment is motivated by that fact that the highly electronegative F-atom can extract charge from C-atoms in the graphene film as well as C- and / or Si-atoms at the surface of the substrate. This additional electronic charge in the valence level of the F-atom provides shielding of the F 1s level from the positive nuclear core and, thereby, reduces the F 1s binding energy relative to those F-atoms adsorbed above the surface, which can extract electrons only from the C-atoms in the graphene film. Given this assignment one would expect the intensity of the higher binding energy peak to be greater than that of the subsurface F 1s peak. The fact that the two intensities are approximately the same, suggests that somewhat more of the surface F-atoms are desorbed than their subsurface counterparts during the annealing process. This is consistent with the relative intensities of the D₁ and D₂ peaks in Figure 2.

Figure 7 (b) shows the F 1s spectrum for a three layer film. As with the previous spectrum the FWHM for each component is 1.7 eV. Here, as observed, one expects the number of interior or subsurface F-atoms to increase relative the number of surface F-atoms, which should stay approximately the same. Figure 7 (c) shows the F 1s spectrum for a five layer graphene film after the adsorption of 4-nitrophenyl diazonium. This molecule is shown in the inset. In this case, the lower binding energy peak is shifted slightly to a lower energy and the higher binding energy peak is not observed. This suggests that the surface fluorine has been removed in the reaction. This may involve the formation of volatile NF species. The point to be made here, however, is that this observation further supports the assignment of the higher binding energy F 1s peak as the surface species, since it is not likely that the surface reaction would involve the subsurface F-atoms.

The O1s peak consists of a single broad (~ 3 eV FWHM) symmetrical peak centered at 531.7 eV. Because of its symmetry a clear-cut deconvolution is not possible; however its position and width are consistent with a variety of species including silicon oxycarbides³² as well as oxygen-based defect species.²³

Figure 8 shows a RHEED pattern obtained with the electron beam along the $[1\bar{1}00]$ of the 6H-SiC substrate after graphene growth. The vertical lines show the 0th and 1st order graphene features, while the arrows indicate features from the underlying SiC substrate. This pattern is consistent with a graphene film that is rotated by 30° relative to the substrate. This pattern is quite similar in orientation to that shown by Feenstra and coworkers³⁴ for graphene grown by UHV annealing of the SiC(0001) surface. Based on an analysis of the rotated reciprocal lattices, the fractional spacing of the graphene and 6H-SiC features is $a_G / (a_{SiC} \sqrt{3})$, while the measured spacing is 0.49. This yields a value of 2.61 nm for a_G if it is assumed that a_{SiC} is 3.08 nm. When compared with the nominal value of 2.46 nm for a_G , this shows there is approximately 6% tensile strain in

the graphene films grown here. This may seem large; however it should be noted that graphene has approximately a 20% lattice mismatch relative to 6H-SiC. The source of the 6% strain in the present case may be the buckling of the surface due to the halogen- and oxygen-based defects which are present in the film. The diffuse, spotty nature of the RHEED features may also be due to this buckling of the surface as is the surface roughness of the films.

Figure 9 (a) shows the AFM image of a typical $10\ \mu\text{m} \times 10\ \mu\text{m}$ region for a two layer film. Excluding several extraneous particles, the height range (dark to bright) was $\sim 0.8\ \text{nm}$ with an overall root mean square (RMS) roughness of $0.5\ \text{nm}$. Figure 9 (b) shows a $1\ \mu\text{m} \times 1\ \mu\text{m}$ region taken near the center of the larger image. In contrast to terraced surfaces produced by high temperature Si sublimation,^{5,6} the graphene films produced by plasma etching and annealing were essentially planar with low lying hillocks and valleys. The RMS roughness ($\sim 0.5\ \text{nm}$) of these surfaces is essentially the same as that of the SiC substrate and slightly more than twice the roughness that we have observed previously for “atomically flat” terraces on 6H-SiC produced by high temperature hydrogen etching ($0.2\ \text{nm}$)³⁵. The increase in roughness may be associated with the buckling of the surface due to the defects or may simply reflect the initial roughness of the substrate surface.

Figures 10 (a) and (b) show Raman spectra representative of the SiC substrate and a two layer graphene film, respectively. A comparison of the before (a) and after growth (b) spectra shows that the graphene film attenuates the SiC spectrum by $\sim 30\%$. Figure 10 (c), the difference spectrum, was obtained by scaling the SiC spectrum, subtracting it from the spectrum for the film, and performing a baseline operation. From Figure 10 (c), it can be seen that the Raman peaks associated with the film are located at $1352\ \text{cm}^{-1}$ ($76\ \text{cm}^{-1}$), $1597\ \text{cm}^{-1}$ ($63\ \text{cm}^{-1}$), $2689\ \text{cm}^{-1}$ ($120\ \text{cm}^{-1}$), and $2915\ \text{cm}^{-1}$ ($188\ \text{cm}^{-1}$). Here the numbers in brackets are the corresponding FWHM

values. Although there are peak shifts of up to 17 cm^{-1} , the first three peaks compare reasonably well with the D, G, and 2D regions expected for the exfoliated graphene³⁶ as well as graphene formed by sublimation of Si from SiC.³⁷ The FWHM values for these peaks are, however, considerably broader than those observed for exfoliated graphene or graphene formed by sublimation of Si from SiC. The feature at 2915 cm^{-1} is not observed for either exfoliated graphene or graphene formed by sublimation of Si from SiC. The D/G/2D ratio for the difference spectrum is 0.5/1/0.1. While the D/G ratio is comparable to what is found for graphene formed by sublimation of Si from SiC, the G/2D is not.^{37,38,39} In what follows, the reasons for these variations in D/G/2D ratio and FWHM as well as the new peak at 2915 cm^{-1} will be discussed.

Robinson et al.³⁷ studied the nucleation of graphene on SiC (0001) surfaces using the sublimation process. They observed graphene nucleation at step edges on the surface and, using 488 nm radiation, that the D/G/2D (peak height) ratio varied from 0.05/1/0.59 to 0.73/1/0.53 as the annealing temperature decreased from 1425 °C to 1225 °C. They attributed this variation to temperature dependent changes in grain size. Shivaraman et. al.³⁸ using 488 nm radiation observed a D/G/2D ratio of 0.07/1/0.73 for few layer graphene formed above 1300 °C. Finally, Röhrle *et al.*³⁹ using 532 nm radiation found a G/2D ratio of 1/0.81 for few layer graphene films formed at annealing temperatures above 1200 °C (no information on the D peak was given). Thus, the D/G ratio (0.5/1) observed in the present studies is within the range of values observed for graphene films grown on SiC (0001) surfaces by Si sublimation, but the G/2D ratio (1/0.1) is much less than expected. This issue along with the peak broadening and the new peak at 2915 cm^{-1} can be resolved by considering the effects of the fluorine- and oxygen-based defects on the Raman spectrum of graphene.^{40,41}

In studies of fluorination of graphene, Robinson *et al.*⁴⁰ show the overall effect on the Raman spectra is to enhance the intensity of the D peak and reduce the intensity of the 2D peak relative to the G peak as well as to broaden all the peaks. In addition, they observed a new peak at $\sim 2961\text{ cm}^{-1}$. Although the spectra are not of sufficient quality to allow extraction of peak intensities (particularly for the 2D) and FWHM values, qualitatively, this is qualitatively what is observed for the Raman spectra reported here. In similar fluorination studies, Nair *et al.*⁴¹ observed comparable effects using 514 nm radiation. FWHM values of $\sim 109\text{ cm}^{-1}$ for the D and G peaks and $\sim 163\text{ cm}^{-1}$ for the 2D peak, can be extracted from their spectra for graphene exposed to XF_2 for 9 hours at 70°C . The corresponding D/G/2D ratio was 1.3/1/0.2. Although the details on the kinetics of these changes to the Raman spectra are limited, it is clear that both the FWHM values and the D/G/2D ratios depend on the extent of fluorination. Further, as discussed by Nair *et al.*,⁴¹ “partially fluorinated graphene exhibits Raman spectra that resemble those of graphene oxide.” Consequently, it is highly likely that both oxygen- and fluorine-based defects play a crucial role in determining the peak position, FWHM values, and D/G/2D ratios in the present studies. It is important to note that the defect dependent broadening and reduction in the intensity of the 2D peak preclude its use in establishing the number of layers in the films produced here.

Figure 11 (a) shows the effect of RIE power on the bias voltage for both CF_4 and Cl_2 based plasma processes. For both plasma chemistries, the bias voltage depends linearly on the RIE power, and becomes increasingly negative with increasing RIE power. Consequently, the kinetic energy of the positive ions impinging on the SiC surface (e.g., CF_3^+ in the case of CF_4 plasmas^{42,43} and Cl_2^+ and Cl^+ in the case of Cl_2 based plasmas⁴⁴) increases with increasing RIE power. In general, the etching process is a combination of physical etching due energy and momentum transfer and chemical etching due to formation of volatile chemical species. Consequently,

increasing RIE power or equivalently increasing the bias voltage should increase the importance of physical etching relative to chemical etching.

Figure 11 (b) shows the overall effects of bias voltage on the number of graphene layers formed using both CF_4 and Cl_2 based plasma processes. In both cases, the UHV annealing temperature was 970 °C. For Cl_2 based plasma process, the number graphene layers increases nearly linearly with bias voltage. This strongly suggests that physical rather than chemical mechanisms dominate the etching process for Cl_2 based plasmas. For the CF_4 based process, the behavior is more complex. The non-linear dependence at low bias voltage suggests that chemical etching may dominate the process for these conditions. However, the near linear increase in the number of layers for bias voltages above -100 V suggests that physical etching processes begin to dominate for higher bias voltages. In the bias voltage regime where physical etching dominates chemical etching (i.e. above -100 V), the fact that the CF_4 based plasma produces a greater number of layers than the Cl_2 based process suggest that chemistry, though not the dominant factor, still contributes and that fluorine is more active than chlorine in this regard. A critical point which should be emphasized here, regardless of the complexity of the etch mechanism, is that in the one to three layer range RIE power (i.e., bias voltage) can be used to tailor the graphene film thickness.

Electrical properties of the graphene films were characterized using two point measurements. Here, the primary focus was on films produced using CF_4 based process; however, the films produced using Cl_2 based process yielded generally comparable results.¹² Figure 11 shows typical two point I-V plots for one, two, and three layer films produced using the CF_4 based etching and annealing at 970 °C. In addition, the corresponding I-V plot for the SiC substrate is also shown. From these data, it is evident that the graphene on SiC film exhibits back-to-back

Schottky characteristics. Moreover, for the voltage range considered, the predominant conduction channel is through the graphene film with very limited participation of the SiC substrate.

Generally, Ti/Au contacts on graphene produced by other synthesis methods exhibit Ohmic behavior.^{45,46} In every instance studied here, the Ti/Au contacts exhibited Schottky characteristics. This is consistent with the observations of Wu and co-workers⁴⁷ for graphene oxide, and it suggests that the halogen- and oxygen-based defects open up a band gap in the normally semi-metallic graphene electronic structure. This assertion is motivated by several experimental and computational results. Bekyarova *et al.*⁴⁸ functionalized the graphene surface with aryl groups and observed a doubling of the room temperature resistance. This was attributed to conversion of sp²-C to sp³-C, and it was further proposed that functionalization opened a band gap which allowed the formation of insulating and semiconducting regions on the graphene film. More recently, Ribas *et al.*⁴⁹ computationally demonstrated the conversion of sp²-C to sp³-C due to fluorine addition and the consequent opening of a band gap in the graphene. In addition, they demonstrated that band gap energy was a function of fluorine surface coverage. Finally, Robinson *et al.*⁴⁰ and Nair *et al.*⁴¹ have investigated the fluorination of graphene. Both groups observed that thermally activated fluorination of graphene using XeF₂ leads to the opening of a band gap on the order of 3 eV wide; which confirm Ribas' predictions.

Analyses of the non-linear I-V data were used to estimate the carrier density, N_d, Schottky barrier height, Φ_B, and the resistivity of the graphene films following methods used by Wu and co-workers⁴⁷ to characterize graphene oxide films. Since the graphene film is essentially two-dimensional, the measured current, I, can be expressed using Anwar's⁵⁰ modified Richardson-Dushman equation:

$$I = \frac{wq\sqrt{8\pi m^*}}{h^2} (kT)^{3/2} e^{\frac{-q\Phi_B}{kT}} e^{\frac{q\Delta\Phi_B}{kT}} \quad 2$$

where w is the contact width, q is the charge present, m^* is the charge carrier's effective mass, T is the film temperature, h is Planck's constant, k is Boltzmann's constant, Φ_B is the Schottky barrier height, and $\Delta\Phi_B$ is the barrier lowering due to the applied electric field. Following the treatment given by Wu and co-workers, $\Delta\Phi_B$ can be written

$$\Delta\Phi_B \approx \left(\frac{q^3 N_d V}{8\pi^2 (\epsilon')^2 \epsilon} \right)^{1/4} \quad 3$$

where ϵ' and ϵ are the high frequency and static permittivity of the film, respectively.

Substituting this expression into equation 2 and rearranging yields

$$\ln\left(\frac{I}{wq\sqrt{8\pi(kT)^3 m^*}/h^2}\right) = -\frac{q\Phi_B}{kT} + \left(\frac{q^7 N_d}{8\pi^2 (\epsilon'_s)^2 \epsilon_s (kT)^4}\right)^{1/4} V^{1/4} \quad 4$$

The term on the left hand side of this equation can be viewed as the natural log of a reduced current. Plotting this term as a function of $V^{1/4}$ should yield a straight line with a slope proportional to the fourth root of the carrier density and an intercept proportional to the Schottky barrier height.

Figure 13 shows a typical plot of Equation 4, in this case for the two layer I-V data shown in Figure 12. In calculating the reduced current, it was assumed that the charge carriers were electrons, so q was taken as the electron charge. Following Wu and coworkers,⁴⁷ it was further assumed that the effective mass, m^* , was numerically equal to the mass of a free electron. As they point out, the calculations are not particularly sensitive to changes in this value since variations of two orders of magnitude for m^* produce less than a 10% in the calculated value of the Schottky barrier height. Based on the data shown in Figure 13, the Schottky barrier height for the two layer film was found to be on the order of 0.52 eV. Overall, values for the Schottky barrier height ranged from 0.50 eV to 0.56 eV and showed no systematic dependence on film thickness. These values

agree quite well with those observed by Wu and coworkers⁴⁷ who found Schottky barrier heights ranging from 0.45 eV to 0.70 eV for graphene oxide.

In contrast to lack of sensitivity of the Schottky barrier height to m^* , the values calculated for N_d were strongly dependent on the values used for ϵ and ϵ' . In their calculations, Wu and coworkers,⁴⁷ used approximate values based on the average of the SiC substrate and the air above. Although specific values are not known for the films produced here, given their defect nature (~25% fluorine- and oxygen-based defects), values similar to graphene oxide may be more appropriate. Since the studies of Wu and coworkers⁴⁷ appeared, values for both parameters have been reported for graphene oxide. Specifically, Huang et al.⁵¹ have observed values of $\epsilon \sim 10,000$ and $\epsilon' \sim 2$. Using these values, the carrier density was for the three layer film represented in Figure 12 was estimated to be $\sim 3.3 \times 10^{14} \text{ cm}^{-2}$. Assuming an areal density of $3.8 \times 10^{15} \text{ cm}^{-2}$ for carbon atoms in the graphene film, this represents a doping density $\sim 9 \%$ which is slightly less than but comparable to the magnitude of fluorine- and oxygen-based defect levels observed by XPS. This may simply reflect the fact that not all defects are active donors or acceptors. Values of the carrier density for the single and three layer films were $2.0 \times 10^{14} \text{ cm}^{-2}$ and $5.6 \times 10^{14} \text{ cm}^{-2}$, respectively. Thus, the carrier density increased with film thickness. These values are two orders of magnitude higher than those recently observed for epitaxial graphene on SiC.⁵²

The nonlinear behavior of the I-V data precludes the possibility of directly measuring the resistance of the graphene films. However, as discussed by Wu and coworkers⁴⁷ and further elaborated upon by Zhang et al.,⁵³ the linear high voltage portion of the I-V data can be used to estimate an upper limit for the film resistivity. Both groups note that the voltage drop is across both Schottky barriers and the film, but in the high voltage linear portion of the curve, the voltage drop across the film dominates. Consequently, the dynamic resistance in this portion of the I-V

curve provides an upper limit of the film resistance. Following this approach, the nominal sheet resistance for the one, two, and three layer films represented in Figures 11 were found to be 46.6 Ω per sq, 50.7 Ω per sq, and 61.5 Ω per sq, respectively. Using an average graphene layer thickness of 0.346 nm based on the measurements of Weng, et al.⁵⁴ for multi-layer epitaxial graphene films on 6H-SiC (0001), the corresponding resistivities calculated for these films are 1.6 $\mu\Omega$ -cm, 3.5 $\mu\Omega$ -cm, and 6.4 $\mu\Omega$ -cm. Likewise, the corresponding carrier mobilities are found to be 665.3 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, 377.5 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, and 176.5 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

Resistivity values for single layer exfoliated graphene⁵⁵ and epitaxial graphene on SiC⁵⁶ are nominally $\sim 1 \mu\Omega$ -cm. In addition, Yu et al.⁵⁷ have shown that the individual graphene layers in multilayer films and stacks act as parallel resistors. Consequently, the resistance of a multilayer film is less than the nominal 1 $\mu\Omega$ -cm of a single layer. The resistivity of a single layer film reported in this work is 1.6 $\mu\Omega$ -cm. While this is in reasonably good agreement with reported values for single layer graphene, the increase in resistivity with film thickness is not. The reason for this differences is not presently understood; however, it may be associated with the doping of the graphene films by fluorine- and oxygen-defects.

Given the high electronegativity of both fluorine and oxygen, it is likely that defects derived from these species serve as acceptors giving rise to p-type conductivity. Recently, the effects of doping on carrier mobility in few layer graphene have been reported by Khan, et al.⁵⁸ In their studies, increases in hole mobility by a factor of three or more were observed. Moreover, they note that for multilayer films, doping was limited to the surface. The situation is much different in the present case where dopants are most likely distributed throughout the multilayer graphene films on both sides of the carbon layers. In addition, the doping levels in the present case are much higher. These factors may give rise to increased carrier scattering with increased

film thickness and, ultimately, to electron transport between the graphene planes. Thus, high levels of dopants distributed throughout the films could produce the observed dependence of resistivity on film thickness.

The results for the non-linear I-V measurements suggest that the halogen- and oxygen-based defects open a band gap to yield semiconducting graphene. Combining this with the possible use of such defect sites to open useful reaction pathways, the defects introduced by the plasma based synthesis route may prove to be quite beneficial. In fact, Robinson et al.⁴⁰ suggest that fluorinated defects and techniques to produce them will “broaden graphene’s utility in electronic, optical, and sensing technologies.” Although systematic studies have not been performed here, XPS analyses of films annealed at lower temperatures (eg., ~500 °C) have a higher concentration of defects.¹² This observation at least opens the door to band gap tuning using the present synthesis approach. Moreover, these surfaces with their fluorine- and oxygen-based defects may prove quite amenable to functionalization, which is a critical step in many applications.

4. CONCLUSIONS

The production of graphene films using both CF₄ and Cl₂ based ICP-RIE has been studied. The resulting surfaces were analyzed using XPS, RHEED, and Raman spectroscopy. Both plasma types were seen to selectively etch Si from the near surface layers of 6H-SiC. Subsequent annealing of these carbon rich surfaces at 970 °C leads to the formation of few layer graphene films in which the number of layers were controlled using through the plasma parameters. Specifically, films ranging from one to three layers were formed by controlling the RIE power, which in effect controlled the kinetic energy of the incident ions. RHEED patterns were consistent with films of reasonably high crystal quality, while XPS revealed the presence of both halogen-

and oxygen-based defects. The Raman spectra were very similar to those for fluorinated graphene and graphene oxide, and this is attributed to the fluorine- and oxygen-based defects in the film.

Current-voltage measurements exhibited back-to-back Schottky characteristics. This suggests that the fluorine- and oxygen-based defects have opened a band gap in the graphene. The Schottky barrier heights of the films produced here were between 0.45 eV and 0.70 eV and were comparable to those for multi-layer graphene oxide films. The carrier densities for these films were between $2.0 \times 10^{14} \text{ cm}^{-2}$ and $5.6 \times 10^{14} \text{ cm}^{-2}$ and increased with film thickness. This represents a doping density of ~9% which is roughly comparable to defect density measured by XPS. The resistivity of the films produced here ranged from 1.6 $\mu\Omega\text{-cm}$ to 6.4 $\mu\Omega\text{-cm}$ and increased with film thickness. The single layer resistivity values were comparable to graphene formed by Si sublimation from SiC.

The defect structures of the films produced here were similar to those of graphene oxide and fluorinated graphene as evidenced by the XPS and Raman analyses, although the XPS analyses indicated that the defect levels were considerably lower. The RHEED and electrical measurements, however, indicated more graphene like characteristics. Consequently, these results are of significance for several reasons. First, these films, as grown, may prove very useful in applications where the thermal management and chemical inertness of the SiC substrate are required in conjunction with a low resistivity surface film. Second, these results point the way toward a scalable surface chemical route to graphene-on-insulator films. Much work remains, however, to fully demonstrate a manufacturing technology based on this approach. Key issues that will need to be considered include growth on 4H-SiC and semi-insulating 4H-SiC substrates as well as the control of defect/doping densities.

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FIGURE CAPTIONS

Figure 1. XPS survey spectra for the 6H-SiC (0001) surface a) after an HF dip to remove the native oxide and b) after CF₄ based ICP-RIE and annealing at 970 °C.

Figure 2. C 1s XPS spectrum for a graphene film produced by CF₄ based ICP-RIE and annealing at 970 °C. The inset illustrates the effect of simply annealing at 970 °C.

Figure 3. C 1s XPS spectrum acquired in the surface mode a graphene film produced by CF₄ based ICP-RIE and annealing at 970 °C.

Figure 4. Schematic of a) fluorine- and b) oxygen-based defect states (from ref. 25).

Figure 5. C 1s XPS spectrum for a graphene film produced by Cl₂ based ICP-RIE and annealing at 970 °C.

Figure 6. Si 2p XPS spectrum for a graphene film produced by CF₄ based ICP-RIE and annealing at 970 °C.

Figure 7. F 1s XPS spectra for single (a) and three layer (b) graphene films produced by CF₄ based ICP-RIE and annealing at 970 °C, and (c) a similarly produced five layer graphene after reaction with diazonium. The inset illustrates the diazonium molecule.

Figure 8. RHEED patterns obtained for the $[1\bar{1}00]$ azimuth for a) the substrate, b) a two layer graphene film, and c) a three layer film.

Figure 9. AFM images of a two layer film showing a) a typical 10 μm x 10 μm region and b) a 1 μm x 1 μm region taken near the center of the larger area. Excluding several extraneous particles, the height range for these images is ~0.8 nm.

Figure 10. Raman spectra for a) the 6H-SiC substrate, b) a two layer graphene film, and c) the difference spectrum after scaling and subtracting the a and b.

Figure 11. a) Plot of bias voltage versus RIE power for the CF₄ and Cl₂ based plasmas. b) Corresponding plot of graphene thickness versus bias voltage.

Figure 12. I-V plot for a) one, b) two, and c) three layer graphene on SiC films and d) the corresponding response for the SiC substrate.

Figure 13. Richardson-Dushman analysis of the two layer data I-V shown in Figure 11.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 6. Si 2p XPS spectrum for a graphene film produced by CF₄ based ICP-RIE and annealing at 970 °C.

Figure 7

Figure 8

Figure 9 (New)

Figure 10

Figure 11

Figure 12

Figure 13

Figure 13. Richardson-Dushman analysis of the two layer I-V data shown in Figure 12.