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Environment-Induced Effects on the Temperature Dependence of Raman Spectra of Single-Layer Graphene

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Environment-induced effects on the E_{2G} G-band and A_1' 2D-band Raman spectral features of single-layer graphene provide insights on the intrinsic and extrinsic dependences of the phonon energy and line width on temperature. Graphene prepared via mechanical exfoliation in air exhibits a G-band line width that increases with temperature between 298 and 573 K but shows an opposite trend after annealing under Ar. The opposing temperature dependences are considered within the context of Kohn anomaly induced phonon softening and broadening. The primary cause of the changes in the E_{2G} phonon energy and the electron-phonon coupling is attributed to ambient O_2 shifting the Fermi level away from the Dirac point. Our results emphasize the need to carefully consider the sample environment when investigating electronic and vibrational properties of graphene.

Having one of the highest carrier mobilities ever reported,^{1,2} integration of single-layer graphene (SLG) in electronic devices is of pronounced interest. Raman spectroscopy has proven to be a key tool for characterization of SLG doping and the vibrational band structure,³⁻⁷ which are arguably the most important characteristics governing electronic transport; doping determines the carrier type and concentration, and the phonon band structure determines the vibrational modes that cause carrier scattering. Though the response of graphene to various gas atmospheres has been considered for sensor applications,^{8,9} there has been a limited number of studies addressing the effects that an ambient air environment have on the Fermi level position and phonon modes of this all-surface material.¹⁰⁻¹² Carbon nanotubes exhibit significant changes in electrical and optical characteristics due to ambient air.13-17 These effects of the ambient surrounding are important to consider since SLG would undergo processing, such as lithography, for use in devices or even be operated in contact with various materials (such as top gate dielectrics for transistors or low-k material for interconnects) that may compromise its supposed high performance.

Our Raman spectroscopy study elucidates the differences between "air-altered" and "intrinsic" behavior of SLG on SiO₂ substrates. By intrinsic, we refer to the behavior observed under Ar atmosphere after minimizing the effects of ambient air by thermal annealing under Ar. A primary cause of these discrepancies is shown to be the effects of O₂ from ambient air. With this knowledge, we then proceed to investigate the temperature dependence of the G-band (occurring at ~1585 cm⁻¹) and the 2D-band (~2680 cm⁻¹) peak frequencies and line widths of intrinsic SLG. This information is valuable in understanding electron-phonon coupling (EPC) and anharmonic phononphonon interactions in graphene and is also useful for predicting the performance of graphene-based electronic devices operating at elevated temperatures.

Graphene samples were made via mechanical exfoliation of highly oriented pyrolytic graphite on SiO₂/Si substrates with 300 nm thick oxide.^{18,19} Raman spectra were acquired on a Jobin Yvon LabRam HR 800 micro-Raman spectrometer with a 532 nm laser excitation and a $100 \times \log$ working distance air objective providing a spot size of $\sim 1 \,\mu$ m. Power at the objective is ~3 mW. In situ Raman measurements were carried out in an airtight heating stage having an inlet and exhaust for gas flow. All Ar annealing was carried out with a flow rate of 20 cm³/ min and heating and cooling rates of 10 K/min. Spectra were collected 10 min after each temperature of interest was reached (298, 373, 473, and 573 K). Unlike heating SLG under an O_2 rich atmosphere, which has been shown to lead to a large D-band appearance and observable etch pits,¹¹ our mild thermal treatment under inert atmosphere does not create an observable D-band.

Effects of an Ambient Environment on Single-Layer Graphene. Figure 1 shows the Raman spectra and corresponding fitting curves for the G- and 2D-bands of a SLG sample (referred to from here on as sample S1) as prepared in air, after Ar annealing at 573 K, and after subsequent exposure to O_2 flow of 10 cm³/min for 5 min at 298 K. Fits are composed of a single Lorentzian curve for both G- and 2D-bands, the latter being evidence that S1 is SLG.^{20–22} Spectra for another sample (S2, discussed later) are shown in Figure 3, which confirms that it is SLG also. The inset of Figure 1 shows the absence of the D-band (expected at ~1340 cm⁻¹).³ Even with an extended collection time and averaging giving a signal-to-noise ratio of ~60 or better for the 2D-band peak, no D-band is observed at the same baseline noise level. None of the spectra taken for S1 and S2, independent of the temperature and sample environment,

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Figure 1. G- and 2D-band behavior of single-layer graphene (sample S1) as prepared, after Ar annealing, and after subsequent O_2 exposure. The middle spectrum labeled "Ar Ann." corresponds to measurement at room temperature (the same temperature as the other two spectra) after Ar annealing at 573 K. The inset is of the D-band region showing no peak intensity. Lorentzian fits are in gray within the actual data. Peak positions, ω , and the full width at half-max, Γ , are indicated.



Figure 2. G-band and 2D-band peak frequencies (ω_G , ω_{2D}) and full width at half-max values (Γ_G , Γ_{2D}) for the O₂-exposed sample S1 and the air exposed sample S2 during the first Ar annealing cycle after doping. Initial data points prior to heating are taken under O₂ for S1 and air for S2, while all others are under Ar. Forward arrows indicate heating, and reverse arrows indicate cooling in (a), (b), and (d). The line for ω_{2D} is a guide to the eye.

exhibit any detectable D-band, which is indicative of the quality of our samples.

Ar annealing causes a downshift in the G-band peak position $(\omega_{\rm G})$ of ~4 cm⁻¹ and a fwhm ($\Gamma_{\rm G}$) increase of ~11 cm⁻¹, both of which indicate that the Fermi level $(E_{\rm F})$ shifts toward the charge-neutral Dirac point energy (E_0) .^{3,4,23} We note that similar spectral changes have been observed even under milder Ar annealing temperatures of 393 K.12 Both graphene and metallic carbon nanotubes are known to exhibit strong electron-phonon coupling (EPC) as $E_{\rm F}$ approaches $E_{\rm o}$, causing the G-band to broaden due to this additional scattering process.3-6,22 A reduction in carrier concentration also causes the Fermi surface wavevector, $k_{\rm F}$, to decrease and $\omega_{\rm G}$ to soften by the Kohn anomaly condition $q = 2k_{\rm F}$, with q being the wavevector of phonons susceptible to EPC. Both behaviors are understood to be symmetric about $E_{\rm o}$ (i.e., the values of $\omega_{\rm G}$ and $\Gamma_{\rm G}$ are only dependent on doping magnitude, not type).⁴ Recent electrical measurements have shown that graphene transistors in ambient air exhibit p-type doping.²⁴ In fact, most, if not all, measurements reported to date require an external gate potential to shift $E_{\rm F}$ to E_{0} .^{3,4} Raman, near-IR absorption, photoluminescence, and electrical measurements and theoretical considerations of carbon nanotubes have shown the same p-type doping effects, with O₂ specifically being considered as the cause. $^{16,25-32}$ Therefore, we Letters

100 573K 473K 473K 0 473K 298K 1550 1600 2800 Wavenumber (cm⁻¹)

150

Figure 3. Progression of the Raman spectrum with temperature while cooling during the last Ar annealing cycle of sample S2. Lorentzian fits to each peak are in gray within the actual data.

suspect the observed changes in the G-band upon Ar annealing to arise from a reduction in p-type doping by thermal removal of oxygen-containing species from SLG. The spectral progression of S1 after exposure to pure O_2 supports this explanation since opposite behaviors in ω_G and Γ_G (i.e., upshifting and narrowing) are seen relative to Ar annealing.

Thermal desorption of other molecules could accompany the removal of oxygen species when heating. Thus, the density of adsorbed oxygen-containing groups (and therefore p-type doping) after pure O₂ exposure may be greater since the surface is "cleaned" by Ar annealing. The larger value of $\omega_{\rm G}$ under O₂ with respect to that for as-prepared in air supports this idea. Our spectrometer resolution of ~0.5 cm⁻¹ is not sufficient to resolve the difference in $\Gamma_{\rm G}$ between the two cases. The similar values arise possibly because SLG under both conditions is doped enough not to be significantly affected by the Kohn anomaly induced broadening ($\Gamma_{\rm G}$ values converge to ~8 cm⁻¹ for $|E_{\rm F} - E_{\rm o}| > ~400$ meV).⁴

The fwhm of the 2D-band (Γ_{2D}) does not exhibit broadening due to EPC because the associated phonons are too high in energy.⁴ This explains the relatively small differences in Γ_{2D} observed under the three conditions. On the other hand, this peak is still susceptible to frequency downshifts due to removal of p-type doping, but unlike $\omega_{\rm G}$, $\omega_{\rm 2D}$ remains approximately constant at 2682 cm⁻¹. On the basis of the experimental report, we expect ω_{2D} to remain approximately constant between $E_{\rm F}$ $-E_{o}$ values of -200 and +400 meV and then begin to decrease with further n-type doping.⁴ $E_{\rm F} - E_{\rm o}$ values up to -200 meVhave been shown to be typical of air doping of carbon nanotubes.³³ This may explain why Ar annealing leaves ω_{2D} practically unchanged at $\sim 2682 \text{ cm}^{-1}$ even though it does lead to a Fermi level shift according to changes in the G-band. Only upon pure O_2 exposure after annealing does ω_{2D} finally increase, indicating that $E_{\rm F} - E_{\rm o} < -200$ meV. This provides additional evidence that Ar annealing may induce desorption of other molecules in addition to oxygen-containing species, as mentioned above.

The details of the subsequent Ar annealing cycle of O₂exposed S1 (Ar annealed and exposed to O₂ prior to temperature dependence measurements) as well those as of air-exposed sample S2 (Ar annealed and exposed to air overnight prior to temperature dependence measurements) are now discussed. The values of ω_G , Γ_G , ω_{2D} , and Γ_{2D} during this annealing cycle are shown in Figure 2 for both samples. G-band trends upon heating are consistent with the removal of oxygen species causing a loss in p-type doping, as considered above. An interesting point to note is the difference in temperatures at which ω_G and Γ_G (of both samples) begin to follow their cooling curves. This may indicate that Γ_G provides a more sensitive measurement of doping. The ω_{2D} does not show much difference between heating and cooling cycles because of the range of $E_F - E_o$ between \sim -200 and +400 meV, where it is nearly independent



Figure 4. Temperature dependence of ω_G , Γ_G , ω_{2D} , and Γ_{2D} of sample S1 after minimizing the effects of ambient air by Ar annealing. The $\omega_G(T)$ and $\omega_{2D}(T)$ are fitted to a linear relationship (solid lines, black) as in refs 34 and 35, and a polynomial fit (dashed line, blue) for $\omega_G(T)$ is also included as in ref 36. Γ_G is fitted to $\Gamma_G^{e-p}(T) + 2 \text{ cm}^{-1}$, as described in the text, while the line for Γ_{2D} is simply a guide to the eye. Data points in each plot are an average of three cooling cycles with the standard deviation as error bars.

of doping. Γ_{2D} stays within ~ 2 cm⁻¹ while heating, which, again, is because EPC does not affect Γ_{2D} . Explanations of intrinsic trends in ω_G , Γ_G , ω_{2D} , and Γ_{2D} observed during sample cooling are considered below. The two critical points that Figure 2 relays are (1) that the ambient environment of SLG greatly affects the sample doping level and must be taken into account not only in Raman investigations but also in electrical and optical studies where EPC and E_F position dictate many properties of interest and (2) that upon cooling, values of ω_G , Γ_G , ω_{2D} , and Γ_{2D} all begin to converge, implying that SLG becomes intrinsic after Ar annealing, independent of sample history (excluding intentional harsh oxidative or other covalent bond forming/breaking processes). This simple Ar annealing approach may be used to eliminate large variations in doping levels observed across as-prepared SLG samples.¹⁰

Intrinsic Behavior of Single-Layer Graphene Raman Spectral Features with Temperature. With initial complications of the air environment on line widths and frequencies defined, additional heating cycles under Ar were conducted to study the response of G- and 2D-band peaks of intrinsic SLG with temperature. The spectra for cooling during the very last Ar annealing cycle of S2 are shown in Figure 3 as an example. Figure 4 shows the dependence of ω_{G} , Γ_{G} , ω_{2D} , and Γ_{2D} on temperature for S1 averaged over three sequential coolings (S2 shows the same behavior). Note that in Figure 1, $\Gamma_{\rm G} = 19.6$ cm⁻¹ for S1 after the first Ar annealing, while Figure 4b shows that it should be closer to 25.5 cm^{-1} . It is likely that S1 is not intrinsic after just one heating and cooling cycle. Therefore, only data taken after at least two complete cycles are considered here, which seems to be enough to reach intrinsic behavior (i.e., overlapping data between cycles). The $\omega_G(T)$ and $\omega_{2D}(T)$ in Figure 4 are fitted with linear relationships similar to Calizo et al.^{34,35} (solid lines, black). A polynomial fit of $\omega_{\rm G}(T)$ is also included (dashed line, blue), with fixed coefficients estimated from the ab initio results of Bonini et al.³⁶ For the linear fit of $\omega_{\rm G}(T)$, our values of the slope and intercept are expectedly larger than those of refs 34 and 35, owing to our investigation of temperatures above room temperature rather than below. For the polynomial fit, the only fitting parameter of $\omega_{\rm G}$ at T = 0 K and direct use of fixed coefficients for graphene given in footnote 31 of ref 36 give a reasonable agreement within $\sim 2 \text{ cm}^{-1}$.

While Γ_{2D} increases with increasing temperature, Γ_G shows an unusual decrease with temperature. $\Gamma_G(T)$ is determined by the sum of contributions from electron-phonon (Γ_G^{e-p}) and phonon-phonon (Γ_G^{p-p}) interaction terms. Γ_G^{p-p} is expected to vary by only ~0.5 cm⁻¹ across the temperature range considered here³⁶ and has been fixed to equal 2 cm⁻¹ for the subsequent analysis. Γ_G^{e-p} is estimated following ref 36 as

$$\Gamma_{\rm G}^{\rm e-p}(T) = \{\Gamma_{\rm G}^{\rm e-p}(T=0)\} \times \left[f\left(-\frac{\hbar\omega_0}{2k_{\rm B}T}\right) - f\left(\frac{\hbar\omega_0}{2k_{\rm B}T}\right)\right] (1)$$

where

$$\Gamma_{\rm G}^{\rm e-p}(T=0) = \frac{\sqrt{3}a_0^2\hbar^2}{4M\beta^2} \langle D_{\rm E_{2G}}^2 \rangle_{\rm I}$$

from ref 37, $f(\mathbf{x})$ is the Fermi–Dirac distribution, $a_0 = 2.46$ Å is the graphite lattice parameter, M is the mass of a carbon atom, $\beta = 5.52$ Å·eV is the calculated slope of the electron dispersion at the K-point of the Brillouin zone, $\hbar\omega_0$ is the E_{2G} phonon energy, and $\langle D_{E_{2G}}^2 \rangle_F$ is the EPC matrix element for E_{2G} phonons. Thermal smearing of the electron energy distribution increasing population above and decreasing population below the Dirac point decreases $\Gamma_G^{e^{-p}}$ (and therefore Γ_G) with increasing temperature, which is observed in Figure 4b.

Data in Figure 4b is fit using eq 1 plus a 2 cm⁻¹ offset to take Γ_{G}^{p-p} into account. Here, $\hbar\omega_{0}$ is fixed at 196 meV for simplicity since it only changes by ~1.5 meV from 298 K to 573 K. Then, the only fitting parameter is $\Gamma_{G}^{e-p}(T=0)$, and the best fit to the experimental data is obtained with Γ_{G}^{e-p} $(T=0) = 24.9 \text{ cm}^{-1}$, which is about a factor of 2 larger than the calculated value given in refs 36 and 37. We note that $\langle D_{E_{2G}}^2 \rangle_F$ has been calculated by many groups^{6,37-43} and has been predicted to have values as low as 8.5 eV²/Å², giving $\Gamma_{G}^{e-p}(T=0) = 2.1$ cm⁻¹, and as high as 86 eV²/Å², giving $\Gamma_{G}^{e-p}(T=0) = 20.7$ cm⁻¹. Given the amount of uncertainty in this value, in addition to possible variations in β , we believe that our obtained fitting parameter $\Gamma_{G}^{e-p}(T=0) = 24.9 \text{ cm}^{-1}$ is reasonable.

To summarize, we have described the p-type doping effect that ambient O_2 has on the Raman spectrum of air-exposed single-layer graphene. The ability to remove these environmental effects has allowed for the direct experimental observation of the temperature-enhanced reduction of EPC in intrinsic graphene due to electron energy smearing leading to a decreasing G-band phonon mode line width with increasing temperature. Both ambient air doping and the temperature effects on Raman spectra have been explained within the context of the strong EPC near the Dirac point.

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References and Notes

(1) Du, X.; Skachko, I.; Barker, A.; Andrei, E. Y. Nat. Nanotechnol. 2008, *3*, 491.

(2) Morozov, S. V.; Novoselov, K. S.; Katsnelson, M. I.; Schedin, F.; Elias, D. C.; Jaszczak, J. A.; Geim, A. K. *Phys. Rev. Lett.* **2008**, *100*, 016602.

(3) Pisana, S.; Lazzeri, M.; Casiraghi, C.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Mauri, F. *Nat. Mater.* **2007**, *6*, 198.

(4) Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; Sood, A. K. *Nat. Nanotechnol.* **2008**, *3*, 210.

(5) Lazzeri, M.; Mauri, F. Phys. Rev. Lett. 2006, 97, 266407.

(6) Piscanec, S.; Lazzeri, M.; Mauri, F.; Ferrari, A. C.; Robertson, J. *Phys. Rev. Lett.* **2004**, *93*, 185503.

(7) Maultzsch, J.; Reich, S.; Thomsen, C.; Requardt, H.; Ordejón, P. Phys. Rev. Lett. 2004, 92, 075501.

(8) Wehling, T. O.; Novoselov, K. S.; Morozov, S. V.; Vdovin, E. E.; Katsnelson, M. I.; Geim, A. K.; Lichtenstein, A. I. *Nano Lett.* **2008**, *8*, 173.

(9) Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 652.

(10) Casiraghi, C.; Pisana, S.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C. *Appl. Phys. Lett.* **2007**, *91*, 233108.

(11) Liu, L.; Ryu, S.; Tomasik, M. R.; Stolyarova, E.; Jung, N.; Hybertsen, M. S.; Steigerwald, M. L.; Brus, L. E.; Flynn, G. W. *Nano Lett.* **2008**, *8*, 1965.

(12) Haluska, M.; Obergfell, D.; Meyer, J. C.; Scalia, G.; Ulbricht, G.; Krauss, B.; Chae, D. H.; Lohmann, T.; Lebert, M.; Kaempgen, M.; Hulman, M.; Smet, J.; Roth, S.; von Klitzing, K. *Phys. Status Solidi B* **2007**, *244*, 4143.

(13) Gaur, A.; Shim, M. Phys. Rev. B 2008, 78, 125422.

(14) Heinze, S.; Tersoff, J.; Martel, R.; Derycke, V.; Appenzeller, J.; Avouris, Ph. Phys. Rev. Lett. **2002**, *89*, 106801.

(15) Shim, M.; Siddons, G. P. Appl. Phys. Lett. 2003, 83, 3564.

(16) Dukovic, G.; White, B. E.; Zhou, Z.; Wang, F.; Jockusch, S.; Steigerwald, M. L.; Heinz, T. F.; Friesner, R. A.; Turro, N. J.; Brus, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 15269.

(17) Nguyen, K. T.; Gaur, A.; Shim, M. Phys. Rev. Lett. 2007, 98, 145504.

(18) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451.

(19) Zhang, Y.; Tan, Y. W.; Stormer, H. L.; Kim, P. Nature 2005, 438, 201.

(20) Bunch, J. S.; van der Zande, A. M.; Verbridge, S. S.; Frank, I. W.; Tanenbaum, D. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. *Science* **2007**, *315*, 490.

(21) Graf, D.; Molitor, F.; Ensslin, K.; Stampfer, C.; Jungen, A.; Hierold, C.; Wirtz, L. *Nano Lett.* **2007**, *7*, 238.

(22) Ferrari, A. C. Solid State Commun. 2007, 143, 47.

(23) Yan, J.; Zhang, Y.; Kim, P.; Pinczuk, A. Phys. Rev. Lett. 2007, 98, 166802.

(24) Romero, H. E.; Shen, N.; Joshi, P.; Gutierrez, H. R.; Tadigadapa, S. A.; Sofo, J. O.; Eklund, P. C. ACS Nano **2008**, *2*, 2037.

(25) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. Science 2000, 287, 1801.

(26) Sumanasekera, G. U.; Adu, C. K. W.; Fang, S.; Eklund, P. C. *Phys. Rev. Lett.* **2000**, *85*, 1096.

(27) Shim, M.; Back, J. H.; Ozel, T.; Kwon, K.-W. Phys. Rev. B 2005, 71, 205411.

(28) Strano, M. S.; Huffman, C. B.; Moore, V. C.; O'Connell, M. J.; Haroz, E. H.; Hubbard, J.; Miller, M.; Rialon, K.; Kittrell, C.; Ramesh, S.; Hauge, R. H.; Smalley, R. E. J. Phys. Chem. B **2003**, *107*, 6979.

(29) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell,

C.; Ma, J. P.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. Science 2002, 297, 593.
(30) Jhi, S. H.; Louie, S. G.; Cohen, M. L. Phys. Rev. Lett. 2000, 85,

(50) Jill, S. H.; Loule, S. G.; Collell, M. L. Phys. Rev. Lett. 2000, 85, 1710.

(31) Sumanasekera, G. U.; Adu, C. K. W.; Fang, S.; Eklund, P. C. *Phys. Rev. Lett.* **2000**, *85*, 1096.

(32) Froudakis, G. E.; Schnell, M.; Muhlhauser, M.; Peyerimhoff, S. D.; Andriotis, A. N.; Menon, M.; Sheetz, R. M. *Phys. Rev. B* **2003**, *68*, 115435.

(33) Shim, M.; Gaur, A.; Nguyen, K. T.; Abdula, D.; Ozel, T. J. Phys. Chem. C 2008, 112, 13071.

(34) Calizo, I.; Miao, F.; Bao, W.; Lau, C. N.; Balandin, A. A. Appl. Phys. Lett. 2007, 91, 071913.

(35) Calizo, I.; Baladin, A. A.; Bao, W.; Miao, F.; Lau, C. N. Nano Lett. 2007, 7, 2645.

(36) Bonini, N.; Lazzeri, M.; Marzari, N.; Mauri, F. Phys. Rev. Lett. 2007, 99, 176802.

(37) Lazzeri, M.; Piscanec, S.; Mauri, F.; Ferrari, A. C.; Robertson, J. *Phys. Rev. B* **2006**, *73*, 155426.

(38) Piscanec, S.; Lazzeri, M.; Robertson, J.; Ferrari, A. C.; Mauri, F. *Phys. Rev. B* **2007**, *75*, 035427.

(39) Mahan, G. D. Phys. Rev. B 2003, 68, 125409.

(40) Park, J. Y.; Rosenblatt, S.; Yaish, Y.; Sazonova, V.; Ustunel, H.; Braig, S.; Arias, T. A.; Brouwer, P. W.; McEuen, P. L. *Nano Lett.* **2004**, *4*, 517

(41) Jiang, J.; Saito, R.; Gruneis, A.; Dresselhaus, G.; Dresselhaus, M. S. Chem. Phys. Lett. 2004, 392, 383.

(42) Perebeinos, V.; Tersoff, J.; Avouris, P. Phys. Rev. Lett. 2005, 94, 086802.

(43) Koswatta, S. O.; Hasan, S.; Lundstrom, M. S.; Anantram, M. P.; Nikonov, D. E. *Appl. Phys. Lett.* **2006**, *89*, 023125.

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