Low-temperature, site selective graphitization of SiC via ion implantation and pulsed laser annealing

Maxime G. Lemaitre, Sefaattin Tongay, Xiaotie Wang, Dinesh K. Venkatachalam, Joel Fridmann et al.

Citation: *Appl. Phys. Lett.* **100**, 193105 (2012); doi: 10.1063/1.4707383

View online: <http://dx.doi.org/10.1063/1.4707383>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v100/i19>

Published by the [American Institute of Physics](http://www.aip.org).

Related Articles

Screened hybrid density functional study on Sr₂Nb₂O₇ for visible light photocatalysis

Appl. Phys. Lett. **100**, 181903 (2012)

Role of donor-acceptor complexes and impurity band in stabilizing ferromagnetic order in Cu-doped SnO₂ thin films

Appl. Phys. Lett. **100**, 172402 (2012)

Single atom identification by energy dispersive x-ray spectroscopy

Appl. Phys. Lett. **100**, 154101 (2012)

Modification of the electrical properties of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) upon doping of ZnO nanoparticles of different content

J. Appl. Phys. **111**, 073712 (2012)

S doping effect on the properties of double perovskite La₂FeMoO₆

Appl. Phys. Lett. **100**, 132404 (2012)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT

COMSOL
CONFERENCE
WORLDWIDE
2012
USER PRESENTATIONS AND PROCEEDINGS CD
EDITION

FREE CD with 700 Multiphysics Presentations

GET YOUR
COPY TODAY >>

Low-temperature, site selective graphitization of SiC via ion implantation and pulsed laser annealing

Maxime G. Lemaitre,¹ Sefaattin Tongay,^{1,2,3,4} Xiaotie Wang,⁵ Dinesh K. Venkatachalam,⁶ Joel Fridmann,^{4,7} Brent P. Gila,^{1,4} Arthur F. Hebard,² Fan Ren,^{1,5} Robert G. Elliman,⁶ and Bill R. Appleton^{1,4,a)}

¹Department of Materials Science & Engineering, University of Florida, Gainesville, Florida 32601, USA

²Department of Physics, University of Florida, Gainesville, Florida 32601, USA

³Department of Materials Science & Engineering, University of California, Berkeley, California 94720, USA

⁴Nanoscience Institute for Medical and Engineering Technology, University of Florida, Gainesville, Florida 32601, USA

⁵Department of Chemical Engineering, University of Florida, Gainesville, Florida 32601, USA

⁶Department of Electronic Materials Engineering, Australian National University, Canberra, ACT 0200, Australia

⁷Raith USA, Incorporated, Ronkonkoma, New York 11779, USA

(Received 1 February 2012; accepted 11 April 2012; published online 8 May 2012)

A technique is presented to selectively graphitize regions of SiC by ion implantation and pulsed laser annealing (PLA). Nanoscale features are patterned over large areas by multi-ion beam lithography and subsequently converted to few-layer graphene via PLA in air. Graphitization occurs only where ions have been implanted and without elevating the temperature of the surrounding substrate. Samples were characterized using Raman spectroscopy, ion scattering/channeling, SEM, and AFM, from which the degree of graphitization was determined to vary with implantation species, damage and dose, laser fluence, and pulsing. Contrasting growth regimes and graphitization mechanisms during PLA are discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4707383>]

The design and synthesis of two-dimensional (2D) materials has recently inspired its own branch of materials science. Since its discovery,^{1–4} graphene has been at the forefront of this latest discipline and is emerging as a promising material system.⁵ Graphene has demonstrated exceptional electrical,⁶ optical,^{7,8} chemical,^{9,10} and mechanical properties,^{11,12} including carrier mobilities greater than 100 000 cm²/V·s,¹³ and unlike the other well-studied carbon allotropes—nanotubes and fullerenes—graphene is compatible with planar processing technologies developed for silicon. Some formidable obstacles remain before graphene devices will compete with their silicon counterparts. So far, the highest quality devices have been fabricated on small flakes exfoliated from graphite,^{1,2} but this approach is not suitable for wafer-scale device integration. Large-area graphene has been grown on various metals using chemical vapor deposition (CVD); however, this technique requires the transfer of the graphene onto insulating substrates.^{14–16} A promising technique for forming large-area graphene directly on insulating substrates is to anneal SiC single crystals at high temperatures (~1400 °C) in ultra-high vacuum (UHV).^{17,18} This results in Si sublimation, leaving behind a C-rich interface leading to the growth of graphene suitable for the fabrication of electronic devices.^{17,19} This process is, however, a costly and time-consuming method for producing electronically isolated graphene. Since graphene is a zero-gap semimetal, graphene devices rely on quantum confinement,^{20,21} strain,²² doping,^{23–25} or perpendicular electric field modulation²⁶ to achieve desired performances, but these require additional and often complicated processing steps. Currently, conventional processing technologies such as pho-

tolithography, e-beam lithography, and dry etching (O₂) are used to fabricate devices. This exposes the graphene sheets to various polymers and harsh chemical/mechanical treatment, thus leading to reduced mobility and unintentional doping of the graphene. Because of graphene's 2D structure, preservation of the surface and interface properties is essential for maximizing device performance.

There have also been promising reports of graphene synthesized on SiC by pulsed laser annealing (PLA). For example, Perrone *et al.*²⁷ used a q-switched Nd:YVO₄ to anneal the C-face of 4H-SiC in Ar and reported evidence for graphene formation, and Lee *et al.*²⁸ have shown that graphene can be grown on SiC single crystals in vacuum when irradiated with 500 pulses from a KrF excimer laser at a fluence of 1–1.2 J/cm².

In this paper, we report on a processing approach (see Figure 1(a)) we have developed that integrates ion implantation (II) with thermal or PLA to selectively graphitize SiC only where ions have been implanted.^{29–31} This approach is capable of producing arbitrary patterns of few-layer graphene (FLG) over large areas with nanoscale precision, at low processing temperatures, and in a variety of environments including air. Patterning of nanoscale graphene features was accomplished using a multi-ion beam lithography (MIBL), nanofabrication, and engineering (MionLiNE) system. The MionLiNE utilizes a variety of quick-change, liquid metal-alloy ion sources (LMAIS), and an ExB filter to produce scanned, nanometer-dimension, mass-selected ion beams (single, or multiply charged ions or ion clusters) accelerated through 15–40 kV and directed onto a sample stage that uses a laser interferometer and a 20 MHz, 16 bit pattern generator, and integrated software for lithographic patterning over 100 mm × 100 mm areas.³²

^{a)} Author to whom correspondence should be addressed. Electronic mail: applet@eng.ufl.edu.

FIG. 1. Characterization of a selectively graphitized region of SiC after 50 ArF pulses at 1 J/cm^2 . (a) Schematic of the two-step ion implantation and pulsed laser annealing graphitization process. (b) Raman spectra comparing a region of FLG (blue) and unannealed SiC (black). INSET: Zoom plot of 2D-band. (c) SEM (scale bar = $10 \mu\text{m}$) and (d) Raman G-band map of PLA spot indicating graphitization, and (e) AFM (scale bar = $1 \mu\text{m}$) of the annealed region.

We have previously reported that graphene nanoribbons with dimensions ranging from 20–200 nm in width can be selectively grown on SiC crystals by maskless ion implantation of Au or Si and thermal annealing in 1×10^{-6} Torr vacuum to temperatures at least 100°C below that required to graphitize unimplanted SiC.²⁹ The advantage of thermal annealing implanted SiC is that graphene forms only in the implanted regions, while the surrounding and underlying SiC recovers its crystallinity. Here, we show that it is also possible to grow graphene only in implanted areas by PLA with an ArF laser. The attractiveness of this alternative is that PLA is a non-equilibrium, rapid annealing method that maintains the substrate surface near room temperature and can be performed with short processing times in a variety of environments including air.

To establish the PLA parameters, a 4 H-N type SiC single crystal was implanted over broad areas using the accelerator facilities at the Australian National University. The implant conditions and retained dopant concentrations as measured by ion scattering were 60 keV Au at $3.6 \times 10^{16} \text{ Au/cm}^2$, 40 keV Cu at $8.0 \times 10^{16} \text{ Cu/cm}^2$, and 40 keV Ge at $3.5 \times 10^{16} \text{ Ge/cm}^2$. Each implanted area as well as the unimplanted regions of the crystal were then annealed using a JPSATM IX-260 ArF excimer laser system with 193 nm wavelength, 25 ns pulse duration, and 20 Hz repetition rate. Metal masks were inserted into the laser beam and imaged on the sample as $45 \mu\text{m} \times 45 \mu\text{m}$ squares. Eight $45 \mu\text{m} \times 45 \mu\text{m}$ square areas were sequentially annealed with 500, 300, 100, 50, 10, 5, 2, and 1 pulses, in each region, at various fluences ranging from 0.1 – 1.2 J/cm^2 per pulse. The PLA regions were analyzed using micro-Raman with a 532 nm green laser, scanning electron microscopy

(SEM), atomic force microscopy (AFM), and optical microscopy. Raman spectroscopy is ideal for distinguishing single-layer graphene from multi-layer graphene and graphite³³ and to characterize disorder, stacking symmetry, and doping of the graphitic films.³⁴ Figures 1(b)–1(e) shows Raman, SEM, and AFM analyses for one such window, where unimplanted SiC was laser annealed with 50 pulses at 1.0 J/cm^2 per pulse. A region of FLG on SiC was compared to an unannealed area (Figure 1(b)), illustrated by appearance of the so-called D-, G-, and 2D-bands in the Raman spectrum.³⁵ The presence of a large D-band, comparable in intensity to the G-band is consistent with previous reports of both thermal and laser annealing of the C-face of SiC.^{28,29} The relative intensity of the G-band with respect to the silicon carbide transverse optical phonon overtone ($\text{SiC}_{\text{TO(X)}}$) at 1520 cm^{-1} , and the single-peak Lorentzian fit of the 2D-band (position and FWHM of 2679 cm^{-1} and 138 cm^{-1} , respectively) indicate the presence of FLG.³⁵ A Raman map of the G-peak (Figure 1(d)) confirms that the presence of graphitic carbon at the surface is constrained to the PLA-exposed area. The patchy appearance of the Raman map may be due to surface melting of the unimplanted SiC at this high laser fluence. The SEM and AFM (Figures 1(c) and 1(e), respectively) measurements indicate an increase in roughness of the sample ($R_{\text{RMS}}[\text{PLA}] = 2.2 \pm 0.4 \text{ nm}$ versus $R_{\text{RMS}}[\text{Virgin}] = 0.95 \pm 0.02 \text{ nm}$).

Figure 2 summarizes the laser fluence thresholds for the onset of graphitization (Φ_G) induced by PLA in air for pristine as well as ion implanted SiC. The implantation of SiC with Si (self-dopant), Ge (isoelectronic), Au (noble/catalytic), and Cu (catalytic) provided a comparison for the effect of various types of dopants and is seen to have a significant effect on the threshold-fluence for graphitization, Φ_G . It is clear from the data in Figure 2 that while graphitization of unimplanted SiC has a $\Phi_G \sim 0.8 \text{ J/cm}^2$ (indicated by the shaded region in Figure 2(a)), the thresholds for ion-implanted SiC occur at fluences as low as 0.1 J/cm^2 (Figure 2(b)). No graphitization was observed for the as-implanted and unannealed regions.

Results of PLA on areas patterned by MIBL are illustrated in Figure 3. The MionLiNE was used to pattern a 4 H-SiC single crystal by implanting 35 keV Au ions to a fluence of $5 \times 10^{16} \text{ Au ions/cm}^2$. The ArF laser was then used to anneal the implanted patterns with 100 pulses of 25 ns duration, at a fluence of 0.8 J/cm^2 . To demonstrate the patterning capabilities of this technique, an SEM image of two nano-scale FLG lines is presented in Figure 3(a). We also fabricated graphene micro-arrays by maskless ion-implantation that are similar to those patterned with conventional methods by Ju *et al.*³⁶ to demonstrate graphene plasmonics in the terahertz range. A periodic micro-ribbon array composed of five lines, each $2 \mu\text{m}$ wide and $10 \mu\text{m}$ long, separated by $2 \mu\text{m}$ was patterned on the sample (Figure 3(b)). The Raman map of the 2D-band intensity (Figure 3(c)) of this area shows graphitization only where the SiC was implanted.

The measurements in Figure 2(b) suggest that the onset of graphitization occurs at lower fluences for the implanted catalytic species (Au and Cu) than for isoelectronic and self-dopants like Ge and Si. It should be noted that at these implantation conditions, Au and Cu also induce more lattice damage in SiC. However, crystalline SiC (c-SiC) becomes amorphous

FIG. 2. Onset of graphitization with increasing laser fluences for various implantation species as evidenced by Raman. Relative G-band intensities (after normalization) versus, (a) laser fluences on unimplanted SiC, and (b) the graphitization onset fluence at $1 \text{ J}/\text{cm}^2$ for various implanted SiC samples. (c) The full Raman spectra for each implant condition annealed at $1 \text{ J}/\text{cm}^2$ and 50 pulses. The spectra are normalized by the shoulder at 1920 cm^{-2} to avoid interference with the large convoluting G-band. INSET: Zoom plot of the 2D-bands.

FIG. 3. Growth of FLG with nanoscale features by Au-ion beam lithography and PLA. (a) SEM of $800 \text{ nm} \times 10 \mu\text{m}$ and $400 \text{ nm} \times 10 \mu\text{m}$ lines. (b) Reproduction of a plasmonic terahertz metamaterial consisting of a micro-array of $2 \mu\text{m}$ wide lines. (c) Raman 2D-band map of the metamaterial array. Scale bars are 1, 2, and $2 \mu\text{m}$, respectively.

at quite low implant fluences $\sim 10^{14}$ – 10^{15} ions/ cm^2 compared to the doses used in our experiments,³⁷ and our implantation conditions were chosen to create comparable amorphous layer thicknesses. This suggests that ion species like Au and Cu—that behave as catalysts for CVD growth of graphene—may contribute catalytically to influence Φ_G , however a more comprehensive study is needed to confirm this.

There appears to be a number of mechanisms contributing to the onset of SiC graphitization. When heated to high temperatures in UHV for long periods Si appears to sublime, leading to graphitization.¹⁷ If instead SiC is implanted with Au or Si, the graphitization temperature is reduced significantly, the underlying SiC recrystallizes, and FLG grows selectively in only the implanted regions.²⁹ PLA in UHV with 500 pulses from a KrF laser on unimplanted SiC initiates graphitization at about 1 – $1.2 \text{ J}/\text{cm}^2$ and the authors argue that as many as 500 pulses could not thermally sublime enough Si to form even a monolayer of graphene.²⁸ They suggest that the laser induces photophysical Si-C bond breaking that allows the Si evaporation rate at the surface to exceed equilibrium effusion flux. Our PLA experiments on silicon integrated circuit (SiC) samples that are “doped” and rendered amorphous in the near-surface by ion implantation with a variety of different species, demonstrate the onset of graphitization at relatively low fluences, well below the melting threshold for c-SiC.³⁸

Depending on the fluence, the non-equilibrium PLA process can exclusively heat or even melt the near-surface. The effects associated with the PLA of amorphous SiC (a-SiC) have been investigated by Baeri *et al.*³⁹ who used time-resolved reflectivity to measure the surface melt thresholds of a-SiC formed by ion implantation. They created various-

thickness amorphous layers in 6H-SiC single crystals by Ar implantations and annealing the samples with a 25 ns, q-switched ruby laser (wavelength = 694 nm) to determine the laser fluences at which surface melting occurred. Our experimental conditions differ somewhat, but some of their conclusions and observations can be applied to analyze our experiments. They concluded that the melting point of a-SiC (~2445 K) is much lower than that of the crystalline phase (~3500 K), and even lower than the temperature at which peritectic decomposition occurs (~2850 K). As a consequence of the differences in the absorption, thermal conductivity, and diffusivity between a- and c-SiC, their measurements and calculations conclude that the surface melting threshold is strongly dependent on the thickness of amorphous layers, raising the possibility that this may explain the trends observed in Figure 2. Extracting fundamental parameters from their measurements, they were able to show that thin layers ~50 nm required high laser fluences ~1.3 J/cm² to melt, compared to only ~0.4 J/cm² for layers thicker than 200 nm. But our amorphous layer thicknesses—33 nm (Cu), 26 nm (Au), and 31 nm (Ge), as measured by ion scattering/channeling⁴⁰—are too thin and our Φ_G onsets begin at such low fluences compared to melting that this mechanism seems improbable. This further suggests that doping or catalytic effects may be responsible for the observed threshold reduction, and/or that the mechanism does not require surface melting. Experiments are currently underway to resolve these issues.

We have demonstrated that ion implantation combined with pulsed laser annealing offers an approach for rapid synthesis of few-layer graphene and provides great flexibility for the study of the mechanisms of SiC graphitization. We observe selective graphitization of ion implanted SiC when annealed in air with an ArF pulsed laser at onset fluences far below those for unimplanted SiC. Both the ion induced damage and the implanted species are contributing factors. The laser fluence as well as the number of pulses at a given fluence can also be used to control the amount of graphitization. Coupled with multi-ion beam lithography, these techniques provide a low-temperature approach for direct synthesis of graphene nanostructures. Future studies will concentrate on quantifying the mechanisms contributing to graphitization and optimizing the experimental conditions for producing graphene devices and structures.

We acknowledge the support of the Staff and Nanofabrication Engineers at the Nanoscale Research Facility, University of Florida. This work is supported by the Office of Naval Research (ONR) under Contract Number 00075094 (BRA) and by the National Science Foundation (NSF) under Contract Number 1005301 (AFH).

- ¹K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- ²K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 10451 (2005).
- ³Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, *Nature* **438**, 201 (2005).
- ⁴K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature* **438**, 197 (2005).
- ⁵A. K. Geim, *Science* **324**, 1530 (2009).
- ⁶A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- ⁷L. A. Falkovsky, *J. Phys.: Conf. Ser.* **129**, 012004 (2008).

- ⁸R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, *Science* **320**, 1308 (2008).
- ⁹D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, *Science* **323**, 610 (2009).
- ¹⁰R. R. Nair, W. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov, and A. K. Geim, *Small* **6**, 2877 (2010).
- ¹¹J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, *Nature* **446**, 60 (2007).
- ¹²J. S. Bunch, A. M. Van Der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, and P. L. McEuen, *Science* **315**, 490 (2007).
- ¹³K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, *Solid State Commun.* **146**, 351 (2008).
- ¹⁴A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, *Nano Lett.* **9**, 30 (2008).
- ¹⁵X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**, 1312 (2009).
- ¹⁶S. Lee, K. Lee, and Z. Zhong, *Nano Lett.* **10**, 4702 (2010).
- ¹⁷K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and T. Seyller, *Nature Mater.* **8**, 203 (2009).
- ¹⁸Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and P. Avouris, *Science* **327**, 662 (2010).
- ¹⁹J. Robinson, X. Weng, K. Trumbull, R. Cavaleiro, M. Wetherington, E. Frantz, M. LaBella, Z. Hughes, M. Fanton, and D. Snyder, *ACS Nano* **4**, 153 (2009).
- ²⁰M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim, *Phys. Rev. Lett.* **98**, 206805 (2007).
- ²¹B. Özyilmaz, P. Jarillo-Herrero, D. Efetov, and P. Kim, *Appl. Phys. Lett.* **91**, 192107 (2007).
- ²²Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, and Z. X. Shen, *ACS Nano* **2**, 2301 (2008).
- ²³T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, and A. I. Lichtenstein, *Nano Lett.* **8**, 173 (2007).
- ²⁴X. Wang, X. Li, L. Zhang, Y. Yoon, P. K. Weber, H. Wang, J. Guo, and H. Dai, *Science* **324**, 768 (2009).
- ²⁵S. Tongay, K. Berke, M. Lemaitre, Z. Nasrollahi, D. B. Tanner, A. F. Hebard, and B. R. Appleton, *Nanotechnology* **22**, 425701 (2011).
- ²⁶Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, and F. Wang, *Nature* **459**, 820 (2009).
- ²⁷D. Perrone, G. Maccioni, A. Chiolerio, C. Martinez de Marigorta, M. Naretto, P. Pandolfi, P. Martino, C. Ricciardi, A. Chiodoni, E. Celasco, L. Scaltrito, and S. Ferrero, in Proceedings of the Fifth International WLT-Conference on Laser Manufacturing, Munich, June 2009.
- ²⁸S. Lee, M. F. Toney, W. Ko, J. C. Randel, H. J. Jung, K. Munakata, J. Lu, T. H. Geballe, M. R. Beasley, R. Sinclair, H. C. Manoharan, and A. Salleo, *ACS Nano* **4**, 7524 (2010).
- ²⁹S. Tongay, M. Lemaitre, J. Fridmann, A. F. Hebard, B. P. Gila, and B. R. Appleton, *Appl. Phys. Lett.* **100**, 073501 (2012).
- ³⁰B. Appleton and B. Gila, U.S. patent application pct/us2010/024723 (2 February 2009).
- ³¹B. Appleton, B. Gila, M. Lemaitre, and S. Tongay, U.S. patent application 61/526,510 (8 August 2011).
- ³²B. R. Appleton, S. Tongay, M. Lemaitre, B. Gila, J. Fridmann, P. Mazarov, J. E. Sanabia, S. Bauerdick, L. Bruchhaus, R. Mimura, and R. Jede, *Nucl. Instrum. Methods Phys. Res. B* **272**, 153 (2012).
- ³³A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, *Phys. Rev. Lett.* **97**, 187401 (2006).
- ³⁴A. C. Ferrari, *Solid State Commun.* **143**, 47 (2007).
- ³⁵Z. H. Ni, W. Chen, X. F. Fan, J. L. Kuo, T. Yu, A. T. S. Wee, and Z. X. Shen, *Phys. Rev. B* **77**, 115416 (2008).
- ³⁶L. Ju, B. Geng, J. Horng, C. Girit, M. Martin, Z. Hao, H. A. Bechtel, X. Liang, A. Zettl, Y. R. Shen, and F. Wang, *Nat. Nanotechnol.* **6**, 630 (2011).
- ³⁷M. V. Rao, P. Griffiths, O. W. Holland, G. Kelner, J. A. Freitas, D. S. Simons, P. H. Chi, and M. Ghezzi, *J. Appl. Phys.* **77**, 2479 (1995).
- ³⁸T. Mizunami and N. Toyama, *Opt. Laser Technol.* **35**, 451 (2003).
- ³⁹P. Baeri, C. Spinella, and R. Reitano, *Int. J. Thermophys.* **20**, 1211 (1999).
- ⁴⁰Ion scattering/channeling measurements made at the Vanderbilt University accelerator facility in collaboration with Leonard Feldman, Sarit Dhar, and Anthony Hmelo.