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Changes in structural and electronic properties of graphene grown on 6H-SiC(0001) induced by Na deposition

S. Watcharinyanon, L. I. Johansson, C. Xia, and C. Virojanadara

Department of Physics, Chemistry, and Biology, Linköping University, S-58183 Linköping, Sweden

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The effects of Na deposited on monolayer graphene on SiC(0001) were investigated by synchrotron-based photoelectron spectroscopy and angle resolved photoelectron spectroscopy. The experimental results show that Na prefers to adsorb on the graphene layer after deposition at room temperature. Nonetheless, part of the Na atoms are able to intercalate in between the graphene and the buffer layer and some go even further into the substrate interface as indicated by the shift of the bulk SiC component in the C 1s and Si 2p core level spectra. The ARPES spectrum exhibits a lowering of the Dirac point indicating increased *n*-type doping of the monolayer graphene induced by the deposited Na atoms. Upon subsequently heating the sample, we found that a slightly elevated temperature is essential in order to promote Na intercalation. A fully Na intercalation at the graphene-SiC interface is obtained after heating at a temperature of about 75 °C. The intercalated Na decouples the buffer layer and transforms it into a second graphene layer so two π -bands are observed in the ARPES spectra. Interestingly, the two bands show different locations of the Dirac point but both exhibit linear dispersion in the vicinity of the $\bar{K}$ point and not the hyperbolic dispersion observed for AB stacked bi-layer graphene. When heating the sample to about 125 °C or higher, Na is found to leave the interface and the second graphene layer is transformed back to the carbon buffer layer.

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I. INTRODUCTION

Heating a SiC(0001) substrate to high temperature is well known to produce a carbon-rich surface with a $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ structure, a so-called buffer layer, and with graphene layers on top upon further heating.^{1,2} Graphene is a two-dimensional structural material with sp^2 bonded carbon in a honeycomb network. The unique electronic structure of graphene with a linear dispersion of the π -bands around the $\bar{K}$ points of the hexagonal Brillouin zone gives rise to effectively massless charge carriers with extremely high mobilities.^{3–5} In the recent years, graphene, especially grown epitaxially on SiC(0001), has drawn a lot of research interest since it was proposed to be the new material for high performance electronic devices.⁴ However, the carbon buffer layer that exists for epitaxial graphene grown on SiC(0001) forms strong covalent bonds to the SiC substrate and does not exhibit graphitic electronic properties. ARPES data show that the buffer layer does not exhibit any valence band states within some a few tenths of an eV from the Fermi level of the linear band structure close to the $\bar{K}$ point characteristic of graphene.⁶ The existence of the carbon buffer layer in the case of graphene grown on the SiC(0001) surface is considered to hinder a development of graphene-based electronic devices. Nonetheless, earlier studies have demonstrated that hydrogen (H),^{7–10} gold (Au),¹¹ fluorine (F),¹² lithium (Li),^{13,14} and silicon (Si) (Ref. 15) can intercalate and decouple the buffer layer from the SiC substrate. However rubidium (Rb) and cesium (Cs) (Ref. 16) do not intercalate and decouple the buffer layer and, apparently, neither the potassium (K).^{17,18} Intercalation has been shown to provide the ability to modify the charge carrier density and the electronic structure of graphene. The band structure

of graphene in the vicinity of the $\bar{K}$ point after H (Refs. 8 and 10) and Li (Ref. 13) intercalation shows a splitting of the π -band and a shift of the Dirac point contributing from charge carrier doping. Moreover, the decoupled graphene sheet(s) exhibit π -bands with a hyperbolic dispersion at the $\bar{K}$ point, indicating formation of AB stacking similar to that of as grown bi-layer graphene. In the case of Rb and Cs deposition on monolayer graphene sample,¹⁶ the π band does not split after deposition but the Dirac point has been shown to move down from the Fermi level.

In this paper, we report a study of Na deposited on epitaxial graphene on SiC(0001) for the purpose to see if Na can intercalate and change the structural and electronic properties of the graphene. Core level photoelectron spectroscopy (PES) and angle resolved photoelectron spectroscopy (ARPES) of the valence band were utilized to investigate the changes induced in the monolayer graphene sample upon Na deposition and subsequent heating. In contrast to other alkali metals (Li, K, Rb, and Cs), the intercalation of Na into graphite was found to be difficult.¹⁹ Na graphite intercalation compounds were only obtained under high pressure^{20,21} or in the presence of impurities such as oxygen,²² hydrogen, or nitrogen.²³ Our study shows that in the case of graphene Na can easily intercalate into the carbon layers at an elevated temperature of about 75 °C, and that no high pressure or impurity is needed. A theoretical study of Na intercalation of epitaxial graphene on SiC by Jhi *et al.*²⁴ reported that the charge transfer and the Na binding energy are strongly depended on the Na coverage. According to calculated energetics, Na prefers to intercalate between the buffer and top graphene layer and to adsorb on top of the graphene layer. An earlier investigation of alkali

metal atoms (Na, K, and Cs) deposited on monolayer graphite grown on a Ni(111) substrate²⁵ revealed that all these alkali metal atoms penetrated under the monolayer graphite at room temperature. This results in a dilation of the monolayer graphite-Ni interlayer distance and causes changes in the electronic structure of the system. Our experiments show that directly after Na deposition on graphene on SiC(0001) at room temperature Na prefers to stay on top of the graphene layer inducing highly *n*-type doping on the monolayer graphene. The Na intercalation, similar to that observed from monolayer graphite on Ni(111), is then accomplished at an elevated sample temperature. Na intercalates in between the top graphene and the buffer layer and can even go through the buffer layer and intercalate at the SiC interface. This eliminates and transforms the buffer layer into another graphene layer. In addition, the π -bands observed after intercalation process show a linear dispersion similar to those obtained from AA stacking and not at all hyperbolic type as typically reported for the AB stacking bi-layer graphene.

II. EXPERIMENT

A *n*-type on-axis 6H-SiC(0001) wafer purchased from SiCrystal was used to prepare monolayer graphene samples. The SiC wafer has a mis-orientation error within 0.06° . It was chemically and mechanically polished on the Si face. The graphene samples were prepared by direct current heating the substrate at a temperature of 1300°C for a few minutes *in situ* at a base pressure of approximately 10^{-10} mbar. This is known to produce graphene samples with a dominant coverage of one monolayer (ML). Na deposition was performed using a SAES getter source. The samples were kept at room temperature during Na exposure for 6 min. The Na coverage was determined to be about 2 ML. After deposition, the evolution of Na intercalation was investigated upon subsequent heating of the sample at temperatures from ca. 75 to 1200°C .

PES and ARPES were utilized to investigate the sample after deposition and subsequent annealing. The experiments were carried out at beamline I311 (Ref. 26) and I4 (Ref. 27) at the MAX-lab synchrotron radiation facility in Lund, Sweden. Beamline I311 is equipped with a modified SX700 monochromator and large Scienta electron analyzer. It was utilized for high-resolution studies of the C 1s, Si 2p, and Na 2p core levels. The total energy resolution was set to ≤ 0.10 eV for photon energies from 33 to 450 eV and to ≤ 0.30 eV for higher energies up to 750 eV. Beamline I4 is equipped with a spherical grating monochromator and an angular resolved electron energy analyzer with a two-dimensional detector from SPECS. The low angular dispersion lens mode was selected for detailed ARPES studies of the valence band around the $\bar{K}$ -point in the Brillouin zone. The base pressure was about 10^{-10} mbar in both the experimental stations utilized. The sample temperature was determined using optical pyrometers in the temperature range 250 – 1350°C . Lower sample temperatures had to be estimated from extrapolation of the input power (current $\times$ voltage) and sample temperature relation determined over the temperature range covered by the pyro-

eters. The uncertainty in the low temperatures around 100°C is therefore as large as $\pm 25^\circ\text{C}$.

III. RESULTS AND DISCUSSIONS

PES was utilized to investigate the changes in the core level spectra of monolayer graphene samples after Na deposition and subsequent heating. A series of C 1s core level spectra acquired at a photon energy of 450 eV are presented in Fig. 1(a). Before Na deposition, the C 1s spectrum of monolayer graphene is resolved into three components, i.e. bulk SiC, graphene (G), and buffer layer (B) as shown by the bottom curves in Fig. 1(a). Changes in the C 1s spectrum are observed directly after Na deposition. An additional bulk SiC component, labeled SiC', shifted by about 1.6 eV to lower binding energy is observed. Similar component shifted to smaller binding energy has been observed earlier in the C 1s spectra recorded from H (Refs. 9 and 10) and Li (Ref. 13) intercalated monolayer graphene but the actual shifts are somewhat different. The shift has been interpreted to arise from the formation of a different dipole layer at the graphene-SiC interface. This suggests that directly after deposition Na atoms can intercalate into the interface and interact with SiC substrate and modify the dipole layer. However, the unshifted SiC component is still present in the spectrum indicating that Na intercalates only partly at the interface leaving non-intercalated areas that contribute to the unshifted component. Moreover, after Na deposition the G/SiC and G/B intensity ratios extracted from the spectrum are found to decrease. This is suggested to be due to a distortion of the graphene layer induced by Na adsorption. An additional small shoulder is detected on the high binding energy tail of the spectrum. This type of shoulder has been suggested to arise from the changes in the coulomb charge density in the interface region¹³ or from the interaction of metal atoms with the buffer layer contributing to the asymmetric line shape.¹⁶

FIG. 1. C 1s core level spectra collected (a) at a photon energy of 450 eV from the monolayer graphene sample, before and after Na deposition and heating from 75 to 1200°C , (b) at different photon energies after Na deposition, and (c) after heating to 75°C .

The sample was then heated at a temperature of about 75 °C. Interestingly, at this temperature the entire bulk SiC component in the C 1s spectrum shifts to lower binding energy implying a complete Na intercalation, i.e. that Na fully occupies the substrate interface. The G/SiC intensity ratio now increases by about a factor of 3. This can be caused either by the attenuation of the SiC' signal due to a thick Na layer at the interface or by an increase of the amount of graphene after intercalation. The G/B intensity ratio is also found to increase since the amount of Na in between the graphene and the buffer layer remain similar upon heating, see below, and to a value that is even larger than obtained for the initial clean sample. We therefore suggest that the increase of the G/SiC and G/B intensity ratios is due to an increase of the amount of graphene upon Na intercalation. In this case, an elevated temperature of about 75 °C is required in order to allow the Na to go through the graphene and the buffer layer into the interface. The intercalated Na lifts up and transforms the buffer layer into another graphene layer that contributes to the increase of the G/SiC and G/B ratios. These results are in a good agreement to the observation of a splitting of the single π -band into two π -bands in the ARPES spectra after Na intercalation at 75 °C, as shown below. Moreover, the distortion of the graphene sheet induced by the Na adsorption on the surface is recovered after heating. Rising the sample temperature to 175 °C, the intensity of the shifted SiC' component decreases and the SiC component reappears in the C 1s spectrum. This indicates that the Na atoms have started to leave the interface. At the same time, the B component becomes more visible and the extracted G/SiC and the G/B ratios decrease showing that upon removal of the Na from the interface the buffer layer is recreated. At 1200 °C when Na is expected to be removed completely from the sample, the shifted SiC' component has disappeared. The shape of the monolayer graphene spectrum is restored.

The C 1s spectra recorded at photon energies from 330 eV (surface sensitive) to 750 eV (bulk sensitive) after Na deposition and after heating at about 75 °C are shown in Figs. 1(b) and 1(c), respectively. Both figures clearly show that the intensity of the shifted bulk SiC' component increases with increasing photon energy. This confirms that the shifted SiC' component originates from the interface and bulk region underneath the graphene and the buffer layer. After heating at 75 °C, Fig. 1(c), the initial SiC component has essentially vanished and only the shifted SiC' component is observed in the spectra. These results indicate that the Na intercalation has been completed at this temperature, i.e. that Na has intercalated fully into the graphene-SiC interface and produced a similar modified interface dipole layer all over the sample.

Similar changes are observed in the Si 2p core level spectra shown in Fig. 2, which were collected at a photon energy of 190 eV. Before Na deposition, the spectrum of monolayer graphene shows a Si 2p doublet that originates from the bulk SiC substrate. Directly after deposition, two extra components are detected that are labeled SiC' and S' and shifted by about 1.6 and 2.4 eV from the main bulk SiC doublet to lower binding energy. Since the shift of the SiC'

FIG. 2. Si 2p core level spectra collected at a photon energy of 190 eV from the monolayer graphene sample, before and after Na deposition and heating from 75 to 1200 °C.

component corresponds well to the shift observed for the SiC substrate peak in the C 1s spectrum after Na deposition, the SiC' component is interpreted to originate from the bulk SiC and the S' component from the uppermost Si-C bilayer in the intercalated areas where the modified dipole layer, induced by Na-SiC interaction, has formed. After heating the sample to 75 °C, the shifted SiC' and S' components are found to dominate the Si 2p spectrum and indicate a full intercalation of Na at the interface. These shifted components have almost disappeared after heating at a temperature of about 175 °C when the initial SiC component again dominates which suggests that most of the Na has already left the interface. Further heating at 1200 °C results in a complete disappearance of the shifted components and a Si 2p peak shapes very similar to the one obtained from the clean sample before Na deposition.

Figure 3 presents a set of Na 2p core level spectra acquired at a photon energy of 140 eV. It should be noted that also these spectra are plotted with the same peak height so only relative intensities within each spectrum can be directly compared. A curve fitting was applied in an effort to resolve the components in these spectra. A spin orbit splitting of 0.16 eV and a branching ratio ($\text{Na } 2p_{1/2}/\text{Na } 2p_{3/2}$) of 0.5 are used to fit the Na 2p spectra. After Na deposition the spectrum exhibits a dominant Na 2p doublet, labeled N1, at a binding energy of 30.8 eV that is attributed to Na atoms adsorbed on the sample surface. The doublet is accompanied by a small/weak shoulder on each side. The shoulders are decomposed into three components, labeled N2 at lower binding energy and N3 and N4 at higher binding energy, respectively. The N2 component is assigned to intercalated Na atoms at the

FIG. 3. Na 2p core level spectra collected at a photon energy of 140 eV from the monolayer graphene sample, before and after Na deposition and heating from 75 to 1200 °C.

interface, i.e., Na atoms that go through the graphene and the buffer layer and terminate at the interface. The N3 component is suggested to relate to Na atoms that are situated in between carbon layers, i.e., between the graphene sheet and the buffer layer. Finally, the N4 component is assigned to Na clusters on the surface.²⁸ After heating at 75 °C, the intensity of N1 component decreases by a factor of about 25 compared with that before heating. The Na 2p spectrum becomes considerably broader and the N2/N1 (as well as N2/N3 and N3/N1) peak intensity ratio increases significantly. Considering the C 1s and Si 2p spectra, the increasing of the N2/N1 (and N2/N3) ratio is an evidence of an increase of Na intercalation into the interface between the SiC substrate and the carbon buffer layer. Heating at 75 °C thus promoted Na intercalation at the interface. Further heating at 175 °C, however, results in a pronounced decrease of the N2/N1 (and N2/N3) ratio indicating a decrease of Na at the interface. This corresponds well to the pronounced decrease in relative intensity of the shifted/intercalated components (SiC' and S') in the C 1s and Si 2p spectra. The N3 component assigned to Na situated in between carbon layers and the weak N4 assigned to Na clusters are observed directly after deposition as well as after heating at temperatures from 75 to 175 °C. A model for the Na intercalation of monolayer graphene is suggested and illustrated in Fig. 4. An epitaxial monolayer of graphene grown on SiC(0001) is known to have an ordered carbon buffer layer that is strongly bound to the SiC substrate^{1,7,29} as illustrated in Fig. 4(a). Upon Na deposition on monolayer graphene, Fig. 4(b), most of the Na atoms adsorb on the sample surface (N1), some form surface clusters (N4), and they induce distortions of the graphene layer. However, part of the Na atoms is able to intercalate in between the gra-

FIG. 4. Schematic representation of monolayer graphene sample (a) before and (b) after Na deposition, (c) after heating at 75, and (d) at 175 °C.

phene and the buffer layer (N3) and some go even further into the interface between the buffer layer and the substrate (N2). Increasing the sample temperature to about 75 °C, Fig. 4(c), allows more Na atoms to intercalate in between the carbon layers and into the interface to interact with the SiC substrate and modify the interface dipole layer. Moreover the distorted graphene sheet seems to recover at this temperature as observed in the C 1s spectrum in Fig. 1(a). At the interface, Na decouples the buffer layer and transforms it into a second graphene layer. The monolayer graphene and carbon buffer layer now converts into bi-layer graphene with Na at the graphene-SiC interface and in between the graphene layers. At a temperature of about 175 °C, the intercalated Na has mainly been removed from the interface and the second graphene layer has been transformed back to carbon buffer layer.

ARPES is utilized to investigate changes induced in the electronic band structure by Na deposition. The band structure probed close to the $\bar{K}$ point in the Brillouin zone in the direction perpendicular to $\bar{\Gamma} \rightarrow \bar{K}$ is shown in Fig. 5. Before Na deposition, the monolayer graphene sample shows a single π -band with a linear dispersion and a Dirac point located at about 0.4 eV below the Fermi level, as illustrated in Fig. 5(a). Charge transfer from the substrate, i.e. substrate-graphene interaction,^{6,30} causes this shift of the Dirac point. Deposition of Na on the graphene sample induces pronounced changes in the band structure, as seen in Fig. 5(b). The Dirac point is shifted down to a binding energy of 1.4 eV below the Fermi level. This indicates additional n -type doping, i.e. that electrons from Na are released and injected into empty states in the π -band of the graphene layer. Based on the linear dispersion near the Dirac point, the charge concentration is estimated³¹ to be of about $1.3 \times 10^{14} \text{ cm}^{-2}$. The single π -band is seen to become somewhat broader and more diffuse after Na deposition. This is interpreted as caused by distortions in the graphene layer

FIG. 5. π -band dispersion around the $\bar{K}$ point recorded from the monolayer graphene sample (a) before and (b) after Na deposition, (c)-(f) after heating at 75, 125, 270, and 1200 °C.

induced by the adsorbed Na, as also indicated in the C 1s spectrum where the G/SiC (G/B) intensity ratio reduced after Na deposition. After heating at 75 °C, the single π -band splits into two. The presence of two π -bands indicates the formation of bi-layer graphene. This is supported by the earlier observations made after similar heating: the increase of the G/SiC and G/B intensity ratios in the C 1s spectrum, the dominance of the shifted SiC' and S' components in the C 1s and Si 2p spectra and the significant increase in the N2/N1 (as well as N2/N3 and N3/N1) peak intensity ratio in the Na 2p spectrum that all pointed to Na intercalation at the interface. Unlike Li on monolayer graphene¹³ that directly splits the π -band into two bands after deposition at room temperature, an elevated temperature of about 75 °C is required in order to allow Na deposited on monolayer graphene to fully intercalate into the interface, decouple the buffer layer and transform it into a second graphene layer. Interestingly, the two π -bands then show the Dirac points at different energies suggesting a different amount of doping on each layer, i.e. one highly *n*-doped (lower band) and one with a lower doping concentration (upper band). The two π -bands with different Dirac points are similar to the π -bands obtained after heating the Rb and Cs (Ref. 16) deposited on monolayer graphene samples. However, in the Rb, Cs, and K (Ref. 17) cases none of them do intercalate into the graphene and decouple the buffer layer. The two π -bands with different Dirac point in the case of Rb and Cs show a large variation of the band intensity caused by an inhomogeneous doping of monolayer graphene. In the Na case, an equivalent intensity of the two π -bands indicating two decoupled graphene layers after intercalation corresponds well to the increase of the graphene component in the C 1s spectra. Interestingly, the π -band dispersion in the vicinity of the $\bar{K}$ point after Na intercalation looks different from that of H- (Refs. 8 and 10) and Li-intercalated (Ref. 13) bi-layer graphene, which exhibits a hyperbolic dispersion similar to that of the as grown bi-layer graphene with an AB stacking. Instead, the dispersion observed after the intercalation is similar to the calculated Dirac-type linear dispersion relation results for AA stacking.^{32,33} After heating at about 125 °C, the highly doped band has almost faded away suggesting that most Na atoms have left the interface. After heating the sample at 270 °C, only a weak trace of the highly doped π -band is still detectable so most of the second graphene layer has been transformed back into a carbon buffer layer. Further heating up to 1200 °C results in a complete elimination of Na from the sample and the single π -band of monolayer graphene is re-established.

IV. SUMMARY

PES and ARPES were utilized to investigate the influence of Na deposited on monolayer graphene grown on SiC(0001). After Na deposition with the sample at room temperature, we found that Na adsorbs on the graphene surface and also form clusters. This induces a distortion of the graphene layer as indicated by a lowering of the G/SiC and G/B intensity ratio in the C 1s spectra collected after Na deposition. Moreover the appearance of a shifted bulk SiC compo-

nent in the C 1s and Si 2p spectra suggests that some Na atoms are able to penetrate into the interface, interact with the SiC substrate, and contribute to a partial intercalation. Other Na atoms are found to intercalate in between the graphene and the buffer layer. Increasing the sample temperature to about 75 °C recovers the distorted graphene sheet and promotes the Na intercalation, i.e., more Na atoms go through the graphene and the buffer layer into the interface. This decouples the buffer layer from the SiC substrate and transforms it into a second graphene layer. The monolayer graphene sample is now converted into two graphene layers as indicated by the observed splitting of the single π -band into two π -bands in the ARPES spectra. The sample now has Na at the graphene-SiC interface and also in between the graphene layers contributing to a different amount of doping on each layer as seen from the different energies of the Dirac point of the two π -bands. Moreover, the two graphene layers exhibit a linear dispersion in the vicinity of $\bar{K}$ point and not the hyperbolic dispersion observed for the AB stacking of the as grown bi-layer graphene. The intercalated Na starts to be removed from the sample already at a temperature of 125 °C when the second graphene layer is observed to transform back to a carbon buffer layer.

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- ¹F. Owman, L. I. Johansson, and P. Mårtensson, "Silicon carbide and related materials 1995," In *Proceedings of the Sixth International Conference* (IOP, Bristol, UK, 1996), p. 477.
- ²W. A. de Heer, C. Berger, X. Wu, P. N. First, E. H. Conrad, X. Li, T. Li, M. Sprinkle, J. Hass, M. L. Sadowski, M. Potemski, and G. Martinez, *Solid State Commun.* **143**, 92 (2007).
- ³A. K. Geim and K. S. Novoselov, *Nature Mater.* **6**, 183 (2007).
- ⁴C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, *J. Phys. Chem. B* **108**, 19912 (2004).
- ⁵J. Jobst, D. Waldmann, F. Speck, R. Hirner, D. K. Maude, T. Seyller, and H. B. Weber, *Phys. Rev. B* **81**, 195434 (2010).
- ⁶K. V. Emtsev, F. Speck, T. Seyller, L. Ley, and J. D. Riley, *Phys. Rev. B* **77**, 155303 (2008).
- ⁷C. Virojanadara, R. Yakimova, A. A. Zakharov, and L. I. Johansson, *J. Phys. D* **43**, 374010 (2010).
- ⁸C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, *Phys. Rev. Lett.* **103**, 246804 (2009).
- ⁹C. Virojanadara, A. A. Zakharov, R. Yakimova, and L. I. Johansson, *Surf. Sci.* **604**, L4 (2010).
- ¹⁰S. Watcharinyanon, C. Virojanadara, J. R. Osiecki, A. A. Zakharov, R. Yakimova, R. I. G. Uhrberg, and L. I. Johansson, *Surf. Sci.* **605**, 1662 (2011).
- ¹¹I. Gierz, T. Suzuki, R. T. Weitz, D. S. Lee, B. Krauss, C. Riedl, U. Starke, H. Höchst, J. H. Smet, C. R. Ast, and K. Kern, *Phys. Rev. B* **81**, 235408 (2010).
- ¹²A. L. Walter, K.-J. Jeon, A. Bostwick, F. Speck, M. Ostler, T. Seyller, L. Moreschini, Y. S. Kim, Y. J. Chang, K. Horn, and E. Rotenberg, *Appl. Phys. Lett.* **98**, 184102 (2011).
- ¹³C. Virojanadara, S. Watcharinyanon, A. A. Zakharov, and L. I. Johansson, *Phys. Rev. B* **82**, 205402 (2010).
- ¹⁴C. Virojanadara, A. A. Zakharov, S. Watcharinyanon, R. Yakimova, and L. I. Johansson, *New J. Phys.* **12**, 125015 (2010).
- ¹⁵C. Xia, S. Watcharinyanon, A. A. Zakharov, R. Yakimova, L. Hultman, L. I. Johansson, and C. Virojanadara, *Phys. Rev. B* **85**, 045418 (2012).
- ¹⁶S. Watcharinyanon, C. Virojanadara, and L. I. Johansson, *Surf. Sci.* **605**, 1918 (2011).

- ¹⁷A. L. Walter, A. Bostwick, K.-J. Jeon, F. Speck, M. Ostler, T. Seyller, L. Moreschini, Y. J. Chang, M. Polini, R. Asgari, A. H. MacDonald, K. Horn, and E. Rotenberg, *Phys. Rev. B* **84**, 085410 (2011).
- ¹⁸E. Rotenberg, Personal communication (2011).
- ¹⁹M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **51**, 1 (2002).
- ²⁰V. V. Avdeev, V. A. Nalimona, and K. N. Semenenko, *Synth. Met.* **38**, 363 (1990).
- ²¹I. T. Belash, A. D. Bronnikov, O. V. Zharikov, and A. V. Palnichenko, *Solid State Commun.* **64**, 1445 (1987).
- ²²M. E. Gardi, A. Herold, P. Lagrange, M. Lelaurain, and J. F. Mareche, *Mol. Cryst. Liq. Cryst.* **244**, 29 (1994).
- ²³D. Billaud and A. Herold, *Carbon* **16**, 301 (1978).
- ²⁴S.-M. Choi and S.-H. Jhi, *Appl. Phys. Lett.* **94**, 153108 (2009).
- ²⁵A. Nagashima, N. Tejima, and C. Oshima, *Phys. Rev. B* **50**, 17487 (1994).
- ²⁶R. Nyholm, J. N. Andersen, U. Johansson, B. N. Jensen, and I. Lindau, *Nucl. Instrum. Methods Phys. Res. A* **467–468**, 520 (2001).
- ²⁷B. N. Jensen, S. M. Butorin, T. Kaurila, R. Nyholm, and L. I. Johansson, *Nucl. Instrum. Methods Phys. Res. A* **394**, 243 (1997).
- ²⁸Y.-C. Chao, L. S. O. Johansson, and R. I. G. Uhrberg, *Surf. Sci.* **391**, 237 (1997).
- ²⁹C. Virojanadara, M. Syväjärvi, R. Yakimova, L. I. Johansson, A. A. Zakharov, and T. Balasubramanian, *Phys. Rev. B* **78**, 245403 (2008).
- ³⁰T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, and E. Rotenberg, *Phys. Rev. Lett.* **98**, 206802 (2007).
- ³¹A. H. Castro Neto, F. Guinea, M. N. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- ³²J. Borysiuk, J. Soltys, and J. Piechota, *J. Appl. Phys.* **109**, 093523 (2011).
- ³³C. L. Lu, C. P. Chang, Y. C. Huang, J. H. Ho, C. C. Hwang, and M. F. Lin, *J. Phys. Soc. Jpn.* **76**, 024701 (2007).