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► **To cite this version:**

Chanan Euaruksakul, Hideki Nakajima, Arunothai Rattanachata, Muhammad y Hanna, Ahmad. R. T. Nugraha, et al.. Electronic and Thermoelectric Properties of Graphene on 4H-SiC (0001) Nanofacets Functionalized with F4-TCNQ. *Journal of Electronic Materials*, 2020, 49, pp.6872-6880. 10.1007/s11664-020-08201-y . hal-02884010

HAL Id: hal-02884010

<https://hal.sorbonne-universite.fr/hal-02884010>

Submitted on 29 Jun 2020

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1 Electronic and thermoelectric properties of graphene on 4H- 2 SiC (0001) nanofacets functionalized with F4-TCNQ

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18 **ABSTRACT**

19 The functionalization of graphene is a well-established route for modulating its optoelectronic
20 properties for a wide range of applications. Here, we studied using photoemission spectroscopies and
21 synchrotron radiation the band structure upon evaporation of a p-type dopant tetrafluoro-
22 tetracyanoquinodimethane (F4-TCNQ) molecules and determined the work function (WF) shift over a
23 large area of epitaxial graphene grown on 4H-SiC (0001) silicon carbide substrate. This system
24 exhibits peculiar nanostructures composed of mono and multilayers, notably at the step edges where
25 the electronic properties differ from the terraces. We observed, owing to the high spatial resolution of
26 photoemission electron microscopy (PEEM), that after the adsorption of F4-TCNQ, multilayer
27 graphene on step edges was subjected to less charge transfer as opposed to the monolayer graphene on
28 terraces, making their final WF smaller. We calculated the thermoelectric properties of this
29 functionalized graphene system by using density functional theory and Boltzmann transport
30 formalism within the range of the Fermi level (E_F), and the carrier concentration which was

31 experimentally determined. We show that the *Seebeck* coefficient (S) on the nanofacets is 25% larger
32 than on the monolayer terraces, and the maximum power factor (PF) is in the order of 10^{-2} W/K²m.
33 This order of magnitude is comparable to the PF of commercial thermoelectric material such as bulk
34 bismuth telluride.

35
36 Keywords — epitaxial graphene, nanofacets, photoemission spectroscopy, work function,
37 thermoelectric properties.

38 39 INTRODUCTION

40 Graphene grown on silicon carbide (SiC) substrate remains an interesting template for both
41 fundamental studies and applications because it is monolithic to the substrate and does not require any
42 transfer. The synthesized material comprises monolayer graphene on large terraces of several microns
43 in both length and width, and step edges or nanofacets with multilayer graphene ribbons [1,2]. Owing
44 to the tunability of electronic properties, graphene and 2D analogues have been considered to be
45 potential candidates for thermoelectric applications [3–6]. However, in its 2D sheet configuration,
46 graphene presents a thermal conductivity and a zero bandgap that are detrimental for the
47 thermoelectric figure of merit (ZT) [7,8]. Interestingly, in a multilayer [9], under specific stacking
48 configuration [10] or patterned into nanoribbons [11,12], owing to confinement effects, graphene
49 exhibits a finite bandgap [13]. Moreover, these structures, when functionalized by heteroatoms,
50 undergo substantial variation of their electronic and thermal properties. The doping level can be
51 tailored to increase the electrical conductivity (σ) and hence the PF . The ambipolar transport in
52 graphene implies positive (holes) or negative (electrons) S coefficients adjusting the E_F position by
53 chemical doping or field-effect gating [14]. Therefore, E_F can then be located anywhere in the
54 electron dispersion spectra of graphene yielding to n - or p -type material. This feature allows unipolar
55 carrier transport that prevents S being compensated for by the contribution of both carrier types. WF
56 and barrier height at the interface of a heterostructure are modulated, and the carrier injection
57 mechanism can be judiciously controlled. There have been numerous studies on the functionalization
58 of monolayer graphene using various adsorbates, notably F4-TCNQ, an effective p -type dopant
59 [15,16]. This molecule is a strong electron acceptor that compensates for the natural n -type doping of

60 pristine graphene grown on SiC substrates. Much less work has focused on the electronic properties at
61 the step edges or nanofacets. These nanostructures, which exhibit a structure different from the
62 terraces, cannot be effectively probed using spatially averaged techniques [17,18]. Angle-resolved
63 photoemission electron spectroscopy (ARPES) is a powerful tool that reveals the electron-dispersion
64 spectrum as well as the overall impact of any adsorbate onto graphene [19]. However, it is not
65 possible to isolate the local electronic variations with a typical micron size probe of $\sim 100 \mu\text{m}$. On the
66 other hand, PEEM provides localized information as well as the topography of the material.
67 In this work, we have investigated functionalized epitaxial graphene on SiC and probed its electronic
68 properties at the step edges using PEEM mapping. We determined that the WF variation between the
69 step edges and monolayer terraces is as high as 0.7 eV after doping. We calculated S and σ within the
70 range of the experimental E_F and carrier density achieved and estimated the resulting PF for both
71 monolayer terrace and the nanofacets. The results showed an optimum $S \sim 100 \mu\text{V/K}$ and $S \sim 125$
72 $\mu\text{V/K}$ for monolayer and bilayer graphene, respectively with a PF of $\sim 10^{-2} \text{ W/K}^2\text{m}$.

73 74 **EXPERIMENTAL**

75 **Materials**

76 The graphene was grown on *n*-type 4H-SiC (0001) substrates. The substrate was first heated to
77 1000 °C in an ultra-high vacuum (UHV) chamber and up to 1525 °C in an argon (Ar) atmosphere to
78 favour the formation of a large and homogeneous graphene layer. The sample was then cooled from
79 1525 °C to room temperature. A homogenous topography showed several $\sim \mu\text{m}$ wide terraces on
80 average, separated by step edges [1,3]. The F4 – TCNQ molecules with 97% purity were sourced
81 from Sigma-Aldrich. The material was placed in a crucible in an *in-situ* effusion cell fitted to the
82 ARPES and PEEM systems.

83 **Instrumentations and measurements**

84 The band structure of the sample was measured around the K-point of the graphene Brillouin zone
85 (BZ) using a synchrotron radiation-based ARPES beamline 3.2Ua: PES of the Synchrotron Light
86 Research Institute (SLRI). The spectra were averaged over a $100 \mu\text{m}^2$ probe diameter and acquired
87 using a Scienta R4000 analyzer. The sample was placed in the 6-axis manipulator at room

88 temperature at a photon energy of 40 eV with an energy resolution of ~ 130 meV [20]. PEEM was
89 performed at the beamline 3.2Ub:PEEM with an Elmitec LEEM PEEM III [21]. The imaging electron
90 energy analyzer was utilized for the *WF* mapping and micro-XPS (the description of *WF* mapping by
91 PEEM is provided in the Supplementary Material). The *in-situ* LaB₆ electron gun was used as a
92 source for low-energy electron microscopy (LEEM). PEEM and LEEM could be switched so that the
93 analyses by both techniques could be carried out on the same microscopic area. The *WF* mapping in
94 PEEM was measured at 110 eV photon energy.

95 Graphene on *n*-type 4H-SiC (0001) was degassed at 400 °C overnight and then left to cool to room
96 temperature. After the degassing, the graphene layer was checked by LEEM, LEED and XPS for its
97 structural integrity and cleanliness. F4-TCNQ was then evaporated from a low-temperature effusion
98 cell (NTEZ - MBE Komponenten). The material was degassed at ~ 80 °C in a quartz crucible and for
99 a few hours while the gate valve was closed. The temperature was then raised to 100 °C for the
100 deposition, and when the gate valve opened, the pressure in the analysis chamber rose from $\sim 10^{-10}$
101 mbar to low 10^{-9} mbar. The distance from the crucible lip to the sample is approximately 25 cm in the
102 PEEM chamber and 10 cm in the ARPES chamber. *In-situ* LEEM observation during F4-TCNQ
103 deposition and XPS result after the deposition are shown in supplementary Figures SI 1&2.

104 The near-edge X-ray absorption fine structure (NEXAFS) was measured at the ARPES chamber in
105 the total electron yield mode, which monitors the drain current from the sample as a function of the
106 photon energy over the nitrogen K edge. The energy resolution of the NEXAFS N K edge is 0.4 eV.

107

108 **RESULTS AND DISCUSSION**

109 Figure 1 shows the Raman spectrum of the *as*-deposited sample. For clarity, the SiC Raman signature
110 has been subtracted to reveal the main features of graphene G ~ 1570 cm⁻¹ and 2D ~ 2700 cm⁻¹. The
111 D peak ~ 1350 cm⁻¹ could be assigned to structural defects, such as Si clusters from broken Si-C
112 bonds that are typically formed during the high-temperature graphitization.

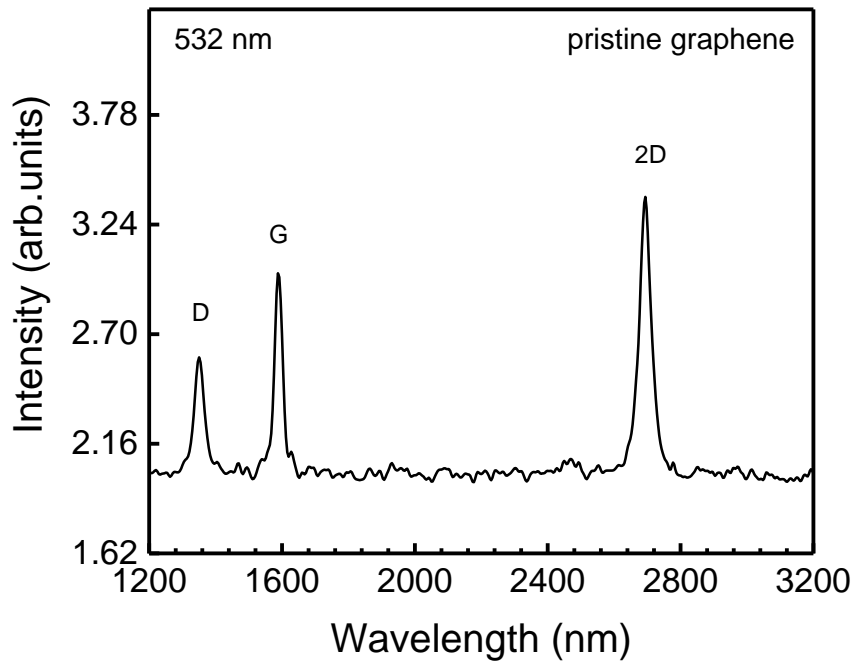


Fig. 1. Raman spectrum of as-grown graphene. The presence of the G and 2D bands across the overall area indicates homogeneous growth of graphene, but a D peak indicates the presence of defects.

113 **Photoemission characterization**

114 Figure 2a displays a LEEM image of graphene on 4H-SiC (0001) and the intensity-voltage (I-V)
 115 profiles on different marked areas. The number of dips in the I-V profiles correlates with the number
 116 of graphene layers [22]. In Figure 2, for the 10 μm field of view (start voltage = 3.8 eV), there are
 117 three different domains with one, two and three dips in the I-V curves, which indicates that the
 118 domains are monolayer, bilayer and trilayer graphene, respectively.

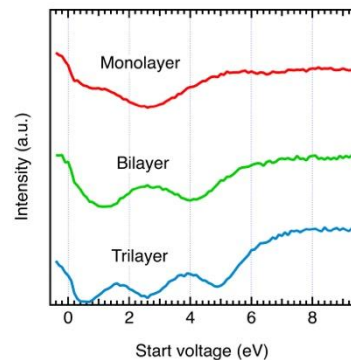
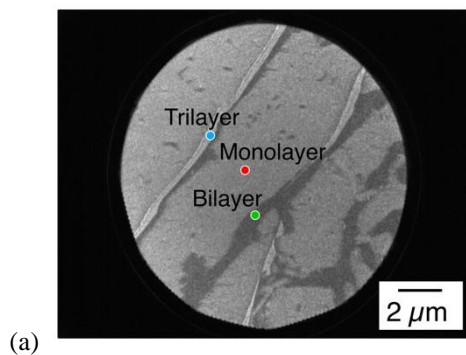


Fig. 2. a) LEEM image at the start voltage of 3.8 eV showing flat terraces with monolayer graphene and strips representing nanofacets containing bilayer and trilayer graphene. b) LEEM-IV curves of graphene before F4-TCNQ deposition. The number of dips in each plot corresponds to the number of graphene layers.

119 The LEEM image indicates that 76% of the area comprises monolayer graphene, whereas the bilayer
 120 and trilayer graphene occupy approximately 17% and 7% of the total area, respectively. These bilayer
 121 and trilayer graphene appear as narrow ribbons above the nanofacets all over the surface [23] of SiC
 122 substrate, where graphene grows thicker near kinks and defects [24,25]. Figure 3a shows the electron
 123 dispersion $E(k)$ for the pristine sample along the perpendicular to the ΓK graphene Brillouin zone,
 124 with a residual n -type doping with E_F lying at ~ 0.43 eV above the Dirac point E_D yielding a charge
 125 carrier concentration of $n \sim 1.36 \times 10^{13} \text{ cm}^{-2}$. Figure 3(b–d) represent the $E(k)$ for the doped sample
 126 with an increasing number of molecules while the spectra are accumulated.

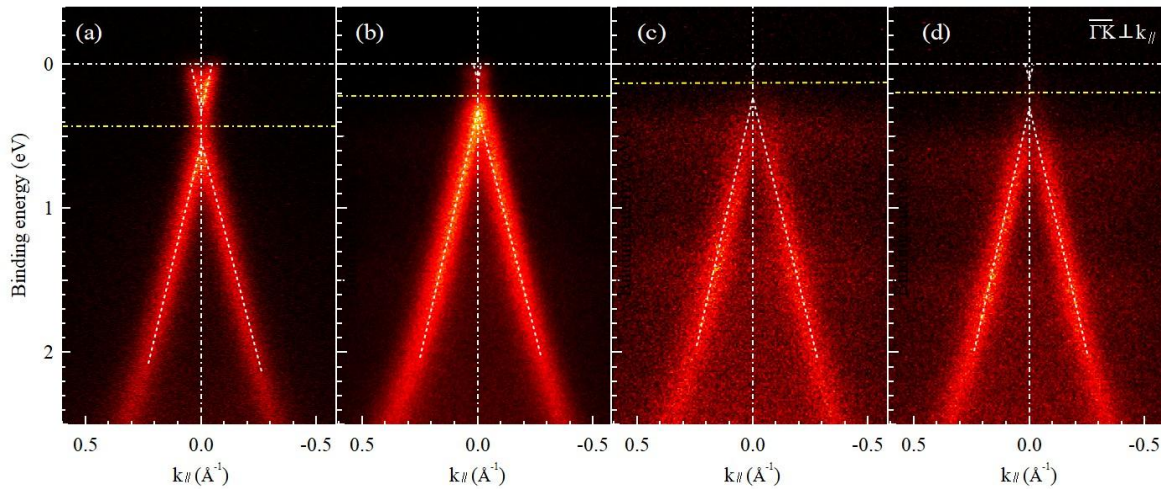


Fig. 3. ARPES measurement of graphene/4H-SiC (0001). (a) Pristine graphene, (b) after heating and opening the shutter, (c) after 2 min of deposition and (d) after 12 min. Spectra were recorded continuously. Table I shows the F4 TCNQ coverage and the carrier concentrations calculated from these ARPES plots (see supplementary Figs. SI3 and SI4 for detailed evaluation of E_D).

127 As displayed in figure 3 (b–d), E_F shifts downward towards E_D , implying a charge transfer of holes
 128 into the graphene compensating the initial n -type doping; the $E_F - E_D \sim 0.13$ eV. However, beyond
 129 0.74 nm of molecules estimated from the angle-resolved XPS (N1s, F1s and Si2p) and the attenuation

130 length of Si2p, the charge transfer saturates, and $E_F - E_D \sim 0.2$ eV. The ARPES clearly reveals the
 131 charge transfer and the relative change in E_F and therefore the WF . The charge-carrier concentration n
 132 was derived from the slope of the $E(k)$ branches [15,26], Table I. The flat bands distributed at 0.5–0.7
 133 and 1.3–1.5 eV in Fig. 3(c–d) correspond to the partially filled lowest-unoccupied molecular orbital
 134 (LUMO) and relaxed highest-occupied molecular orbital (HOMO) of F4-TCNQ resulting from the
 135 electron transfer [27,28], respectively.

	a	b	c	d
Deposition time (min)	pristine	0	2	12
F4-TCNQ (nm)	0	0.58	0.74	0.74
Dirac point (eV)	0.43	0.22	0.13	0.2
Carrier concentration (10^{12} cm^{-2})	13.6	3.55	1.24	2.94

136 **Table I:** Dirac point and charge carrier concentration for each deposition time of F4 TCNQ.

137 Figure 4 shows the near edge X-ray absorption fine structure (NEXAFS) of the nitrogen K edge on
 138 F4-TCNQ/graphene (corresponding to the panel Fig. 3d conditions). The NEXAFS spectra were
 139 measured in the total electron yield mode with three different incident angles of linearly polarized
 140 light. The angular dependence of peaks observed in the energy range below 404 eV resulted from the
 141 molecular orientation of F4-TCNQ on the graphene substrate.

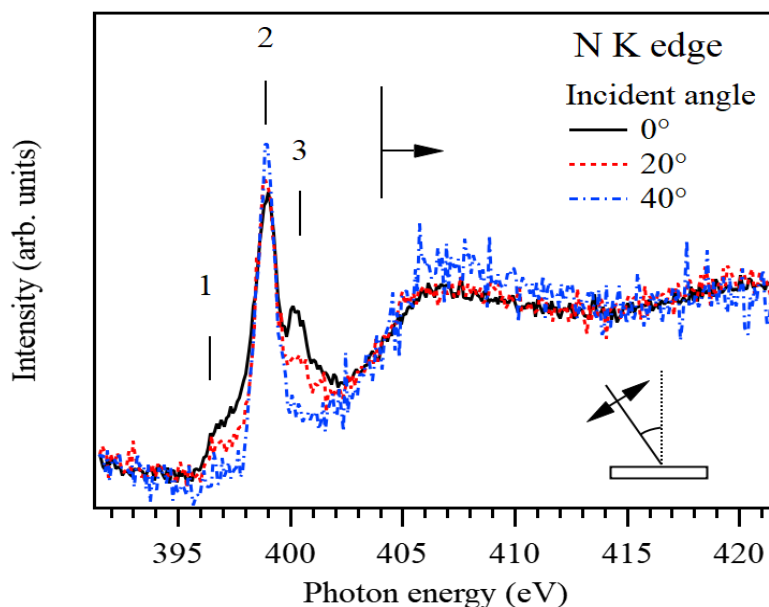


Fig. 4. Angular-dependent N K edge NEXAFS spectra of F4-TCNQ on graphene measured for different incidence angles of the linear polarized synchrotron light ($\theta = 0^\circ, 20^\circ$ and 40°). Inset

illustrates the NEXAFS geometry: θ represents the angle between the polarization vector \vec{E} and the surface normal \vec{n} .

142 The first peak located at 396.5 eV decreases as the incident angle increases, and the second peak
143 located at 399.0 eV shows the highest intensity and slightly increases. The third peak located at 400.5
144 eV decreases as the incident angle increases. These three peaks are well characterized in their orbitals
145 and symmetries [29]. The first peak corresponds to π^* (a_u, b_{1u}), and the second peak consists of π^*
146 (b_{3g}, a_u) and σ^* (b_{1g}, b_{2u}). The third peak originates from π^* (b_{2g}). The π^* orbital is distributed out of
147 the F4-TCNQ molecular plane, whereas σ^* has an orbital in the molecular plane. Because resonances
148 1 and 3 are clearly observed at the normal incidence, one can assert that the molecules stand upright
149 on the terraces, in agreement with the literature [15]. Resonance 2 has two different features close to
150 each other; the intensity does not significantly change with the light polarization, as opposed to the 2
151 other resonances. The broad peak above 404 eV is assigned to σ^* orbitals, and the ionization
152 threshold is located at 404 eV. XPS analysis of the N1s peak shows the presence of anionic and
153 neutral configurations in supplementary Figure SII. N1s can be deconvoluted into 3 peaks by
154 Gaussian fitting after background subtraction. The first peak located at 397.7 eV corresponds to the
155 anionic species N^{-1} , and the second peak located at 399.6 eV is attributed to the neutral N^0 species.
156 The third peak appears at 401.5 eV and seems to be the satellite peak due to the shake-up process
157 [30,31]. The anionic species contribute to the charge transfer through the $C\equiv N$ bonds, whereas the
158 fluorine atoms remain inactive. F1s spectra (supplementary Fig. SII) present no difference
159 independently of the deposition conditions. The XPS results agree with the literature and support the
160 standing-upright orientation of F4-TCNQ molecules on the graphene substrate, a result that is also
161 consistent with our NEXAFS results. Note that it is not possible using NEXAFS to resolve the
162 nanofacets, but we believe (considering the tilted topography) that the molecules could be lying down,
163 which is the most energetically stable position, as calculated by Tian *et al.* [32].
164 Furthermore, we observed the non-homogeneous modification of electronic structure for graphene
165 functionalized with F4-TCNQ by *WF* mapping under PEEM, Fig. 5. Whereas the F4-TCNQ
166 deposition in PEEM was made on a separate setup from the PES platform, the deposition parameters

167 were identical. This ensured that F4-TCNQ molecules deposited in PEEM were in the same
 168 configuration and induced a similar effect on the electronic properties. Note that the absolute WF
 169 measurement in PEEM is tedious to perform directly due to both non-isochromaticity in the imaging
 170 XPS mode and the difficulty in determining the Fermi edge. To evaluate the absolute WF profile of
 171 pristine graphene (blue line) in Fig. 5c, the PEEM measurement before functionalization was offset by
 172 the absolute $WF \sim 4.3$ eV of the monolayer graphene measured in our previous work [1,3]. After F4-
 173 TCNQ deposition, we offset the PEEM data by the positive shift of 1.28 eV on monolayer graphene
 174 measured by PES (our WF shift measurement originated mostly from monolayer domains, which
 175 covered more than 76% of the surface, and the result also compares well with Chen *et al.* [28] and
 176 Coletti *et al.* [15] who reported shifts of WF for monolayer graphene on 6H-SiC(0001) after F4-
 177 TCNQ deposition of 1.3 eV and 1 eV, respectively).

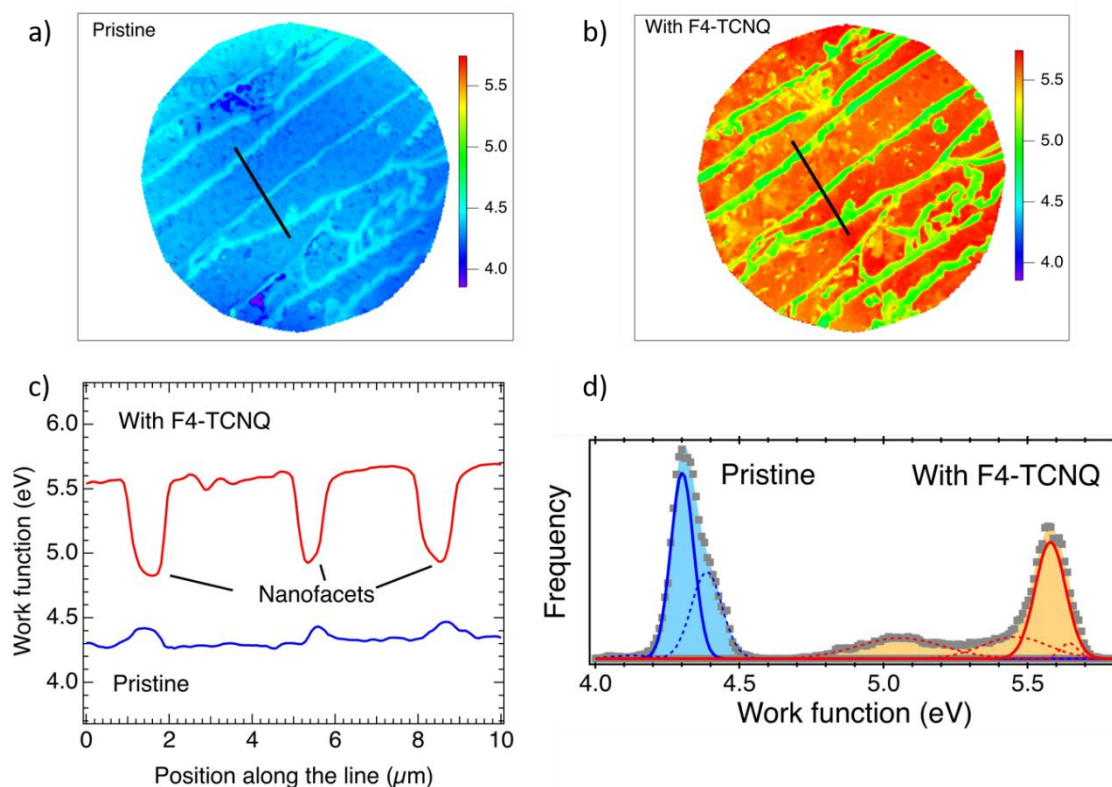


Fig. 5. Work function mapping before (a) and after (b) F4-TCNQ deposition on graphene/SiC (25 μm field of view). (c) line profiles showing work function variation across graphene on terraces and on nanofacets of SiC. (d) Histograms showing the distribution of work function from work function mapping in (a) and (b).

178 In the 25 μm field of view and before the onset of deposition (Fig. 5a), we observed a small *WF*
179 difference between graphene on the terraces (monolayer) and nanofacets (bilayer and trilayer), which
180 exhibit a ~ 0.1 eV larger *WF* than the monolayer areas. This observation has been reported on 6H-
181 SiC(0001) by Hibino *et al.* [33] and on 6H-SiC(000 $\bar{1}$) by Mathieu *et al.* [34,35]. We also noted
182 smaller domains within monolayer graphene scattered all over the SiC terraces, which have slightly
183 lower (less than 0.1 eV) *WF*. Figure 5b displays the mapping after 8-minute deposition of F4-TCNQ.
184 The *WF* profile dramatically changed, as shown by the line profiles in Fig. 5c. The *WF* of monolayer
185 graphene on SiC terraces became ~ 0.7 eV larger than the graphene on top of nanofacets, as shown by
186 the red line profile in Fig. 5c. The profile shows that electron transfer occurs strongly on the
187 monolayer graphene on SiC terraces and, in contrast, there is a relatively much smaller effect induced
188 by F4-TCNQ on bilayer and trilayer graphene domains on the nanofacets, where the *WF* shifts only
189 by ~ 0.5 - 0.6 eV. This functionalization also makes the *WF* of the bilayer and trilayer graphene
190 domains smaller than the monolayer graphene after F4-TCNQ doping. To provide a statistical
191 representation of the work function changes under the entire field of view in Fig. 5a and 5b,
192 histograms of the *WF* data from individual pixels of the *WF* mapping before and after F4-TCNQ
193 deposition are plotted together in Fig. 5d. Each histogram is fitted with Gaussian functions to
194 determine the number of species distinguishable by a small difference in *WF* [34,36]. The main peaks
195 before and after F4-TCNQ deposition (solid blue and red lines) represent the monolayer graphene on
196 SiC terraces that covers most of the total surface area. The histogram shows the overall shifts over the
197 entire area and a clear spreading of the work function over a wider range after doping by F4-TCNQ.
198 Shoulders are observed on both lower and higher energies of the main peak centred at 5.5 eV. This
199 also shows up as a non-uniform colour for the monolayer graphene domains in the mapping and could
200 be assigned to either the non-uniform layer of F4-TCNQ or interactions with the buffer layer at the
201 substrate interface. Note that the large full width half maximum (FWHM) of the Gaussian peaks that
202 represent the bilayer and trilayer graphene (at 0.53 eV lower than the main monolayer graphene) in
203 the histogram are assigned to the artefacts inherent to the small electric field on the surface of the
204 sample arising from the difference in *WF* itself [37].

205 To discuss the difference in charge transfers of F4-TCNQ that results in different shifts of WF on
206 monolayer graphene on terraces, and bilayer and trilayer graphene on nanofacets, we compared our
207 results with the literature. F4-TCNQ may adsorb on graphene with either standing or lying-down
208 configurations depending on the types of supporting substrates [38,39] and the surface coverage. For
209 F4-TCNQ on epitaxial monolayer graphene on SiC, the molecules lie down parallel to the surface at
210 low coverage [40]. At high coverage, the configuration switches to standing upright with the cyano
211 groups of F4-TCNQ bonding to the surface only on one side. This configuration change is evidenced
212 by the deconvolution of N 1s spectra in XPS into N^{-1} and N^0 components [6,15] and by angular-
213 dependent NEXAFS in this work (which largely measures the monolayer graphene). To our
214 knowledge, there is no report on the determination of the adsorption configurations of F4-TCNQ on
215 pure bi-layer graphene on SiC. We could not clarify the orientation of the molecules on the narrow
216 nanofacets, neither by NEXAFS nor by PEEM, due to the angle rotation constraints of our equipment.
217 However, DFT calculations by Tian *et al.* [32] have shown that the F4-TCNQ molecule lies down on
218 free-standing bi-layer graphene [32], and this is likely to occur on the bilayer and trilayer graphene
219 near the nanofacets. Although it is expected that lying down F4-TCNQ induces more charge transfer
220 per molecule (they transfer electrons with the cyano groups on both sides instead of on one side), the
221 adsorption footprint in this configuration is larger, and there could be repulsive forces between the
222 molecules that makes the packing less dense compared to that of standing F4-TCNQ on monolayer
223 graphene; hence, a lower WF shift is observed on the nanofacets.

224 **Evaluation of thermoelectric properties**

225 Functionalized graphene superlattices are thought to enhance the TE properties [41]. Considering the
226 electronic properties measured on our graphene template functionalized with F4-TCNQ, we
227 determined the TE properties of monolayer and bilayer graphene within the linear Boltzmann
228 transport theory and constant relaxation time approximation (CRTA). In this framework, one can
229 calculate S and σ assuming a phenomenological relaxation time constant τ_0 and electronic energy
230 dispersion $E_{s\mathbf{k}}$, where s denotes the band index and \mathbf{k} is the electron wave vector. The electronic
231 structure of the functionalized graphene is calculated using Quantum ESPRESSO [42,43]. We carried
232 out a geometrical optimization for the orientation of the molecule and found that the most stable

233 configuration on both monolayer, bilayer and trilayer graphene was the F4-TCNQ molecule lying
 234 down above graphene. The expressions for S and σ are [3–5,44–46]

$$235 \quad S = -\frac{1}{eT} \frac{\sum_{s,\mathbf{k}} (E_{s\mathbf{k}} - E_F) v_{s\mathbf{k}}^2 \tau_0 \frac{\partial f_{s\mathbf{k}}}{\partial E_{s\mathbf{k}}}}{\sum_{s,\mathbf{k}} v_{s\mathbf{k}}^2 \tau_0 \frac{\partial f_{s\mathbf{k}}}{\partial E_{s\mathbf{k}}}}, \quad (1)$$

236 and

$$237 \quad \sigma = -\frac{e^2}{NV} \sum_{s,\mathbf{k}} v_{s\mathbf{k}}^2 \tau_0 \frac{\partial f_{s\mathbf{k}}}{\partial E_{s\mathbf{k}}}, \quad (2)$$

238 where e is the unit electric charge (defined to be positive), T is the average temperature of the material,
 239 N is the number of \mathbf{k} in the unit cell, E_F is the Fermi energy, $f_{s\mathbf{k}}$ is the Fermi-Dirac distribution
 240 function and $v_{s\mathbf{k}}$ is the component of the electronic group velocity for a specific direction at each \mathbf{k}
 241 point. Note that the CRTA is valid for near-equilibrium transport involving elastic and isotropic
 242 scattering, which we assume in this work for simplicity. Figure 6 illustrates the model implemented.
 243 The accuracy of the calculation thus mostly depends on the choice of τ_0 parameter, which can be
 244 measured experimentally or taken from the literature. Figure 7 presents the calculated results of S , σ
 245 and PF (which is equal to $S^2\sigma$) for the functionalized monolayer and bilayer graphene as a function of
 246 Fermi energy and the carrier concentration. For each thermoelectric quantity, there are two curves
 247 shown in Figure 7 scaled with E_F and the carrier concentration, respectively for the experimental
 248 doping range achieved. The plots of σ and PF are scaled by τ_0 , where the value of this τ_0 parameter
 249 could vary depending on the sample, typically on the order of 0.5–10 ps as observed by pump probe
 250 techniques [47,48]. Note that from the formulas of S and σ , S does not depend on the relaxation time
 251 because τ_0 in the numerator will cancel with that in the denominator, as opposed to σ .

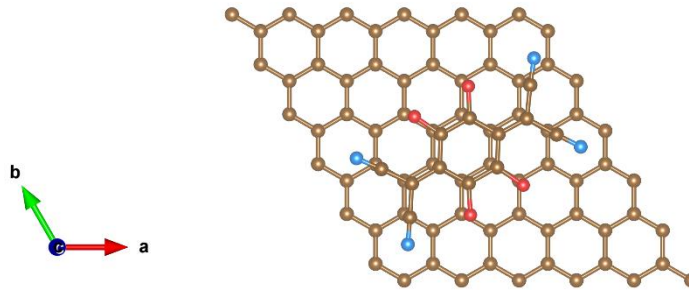
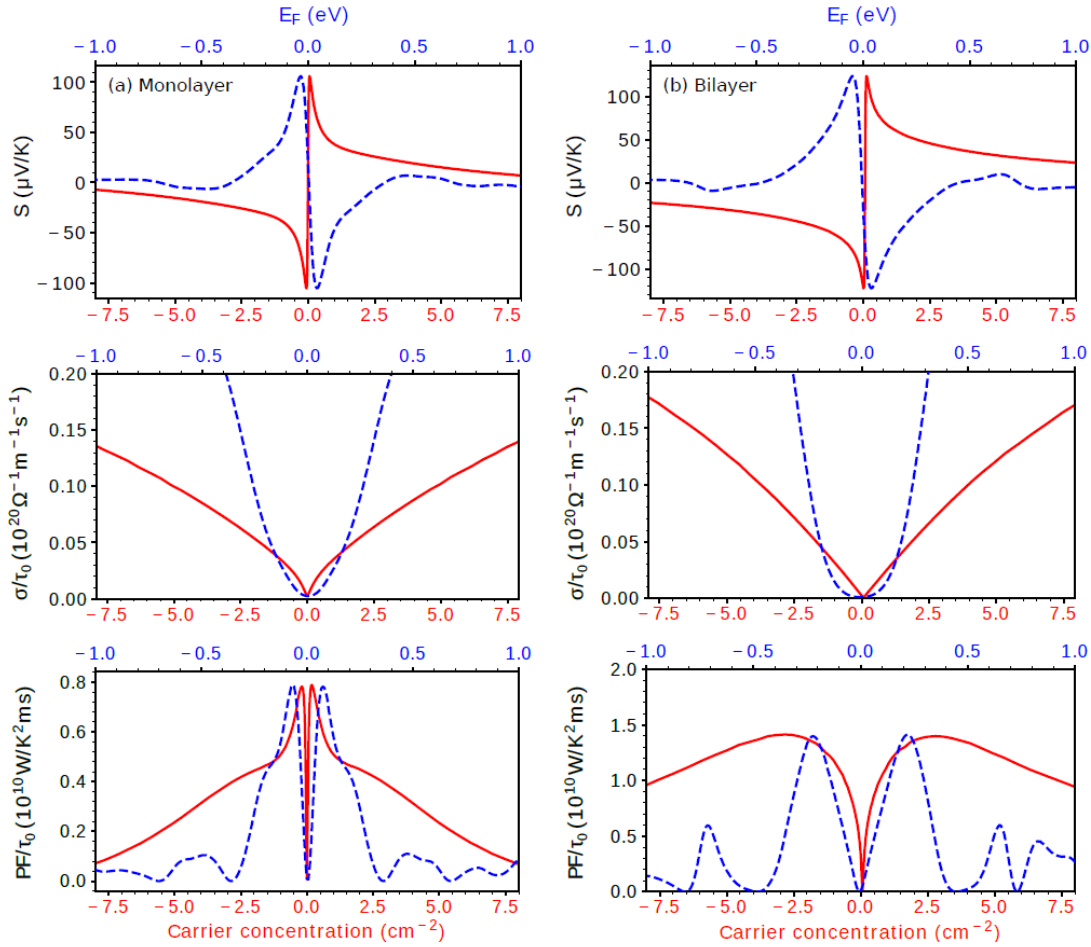


Fig. 6. F4TCNQ on free-standing graphene configuration after relaxation. The molecule is in a lie-down position, which is the most energetically favourable configuration for both low and high coverage.

252

253 In Figure 7, the maximum S values are close to $100 \mu\text{V/K}$ for functionalized monolayer graphene,
254 whereas bilayer graphene exhibits a $S \sim 125 \mu\text{V/K}$ that is higher than that of monolayer graphene
255 owing to the bandgap opening. This order of magnitude is on par with experimental data [14,49]
256 measured on flakes. We observe that upon appropriate doping within -0.5 to 0.5 eV or with a carrier
257 concentration of the order of 10^{12} cm^{-2} , which we attained experimentally (see Table I), the TE
258 properties of graphene could be enhanced significantly. There exists an optimal doping to obtain the
259 maximum PF in both p - and n -type graphene, where the p -type (n -type) corresponds to the negative
260 (positive) E_F or the positive (negative) carrier concentration. The presence of two maximum peaks in
261 PF near $E_F = 0$ is mainly due to the two peaks (negative and positive) S because the electrical
262 conductivity monotonically increases with doping. However, the values of maximum PF strongly
263 depend on the relaxation time τ_0 . Using Figure 7, and knowing τ_0 and the carrier concentration, one
264 can estimate the thermoelectric properties of one's own functionalized graphene sample. For example,
265 we can estimate by assuming the typical relaxation time within 0.5 – 10 ps, the maximum calculated
266 PF in the order of $10^{-2} \text{ W/K}^2\text{m}$, which is in the same order of magnitude as the PF of bulk bismuth
267 telluride [50], one of the most integrated TE materials available on the market. Functionalization or
268 doping of graphene multilayer nanofacets exhibit enhanced thermoelectric performance. Practically,
269 one would need to isolate the graphene patterns from the substrate to reduce heat losses.
270



271

272 **Fig. 7.** Calculated Seebeck coefficient, electrical conductivity and power factor as a function of Fermi
 273 energy (upper horizontal axis) and carrier concentration (lower horizontal axis) for (a) monolayer and
 274 (b) bilayer graphene. Note that the electrical conductivity and power factor are scaled by the
 275 relaxation time. The range of Fermi energy in this figure covers a larger range of doping than the
 276 range of carrier concentration. The blue trace is scaled with E_F , whereas the red one with the carrier
 277 concentration.

278

279 CONCLUSION

280 Substrate-graphene interaction always plays an important role in determining the electronic structure
 281 of graphene. In this work, we demonstrated that surface-transfer doping is also affected by different
 282 graphene thicknesses, particularly on the nanofacet structures of the substrate. This difference results
 283 in non-homogeneous charge transfers across the graphene layer. This inhomogeneity may either be
 284 detrimental to device performance or, on the other hand, be used as a bottom-up approach to control
 285 the energy level and create different graphene electronic structures suitable for TE applications. Here,
 286 we observed a direct change in the electronic properties and band structure of graphene upon *in-situ*
 287 functionalization by F4-TCNQ molecules. We have also mapped the *WF* across the sample and

288 observed a significant difference in the charge transfers from F4-TCNQ doping on the monolayer
289 graphene on terraces as opposed to bilayer and trilayer graphene on nanofacets. Considering the
290 electronic properties measured under the synchrotron beamline and a relaxation time range 0.5–10 ps,
291 we obtained a maximum thermoelectric power factor PF in the order of 10^{-2} W/K²m, comparable to
292 commercial thermoelectric materials. Interestingly, we observed that the graphene on nanofacets
293 located at the edges exhibits a PF nearly as high as the monolayer graphene on the terraces and a
294 *Seebeck* coefficient 25 % larger. This improvement suggests that functionalization is an effective
295 route to enhance the thermoelectric properties of nanostructured materials.

296

297 ACKNOWLEDGMENT

298 The authors would like to thank Dr Abdelkarim Ouerghi for providing high quality epitaxial graphene
299 samples. M.B. would like to thank the Centre National de la Recherche Scientifique (CNRS) for their
300 financial support through the JRP program grant number 1630 as well as Professor Songphol
301 Kanjanachuchai (Chulalongkorn University) for fruitful discussions. M.Y.Y. and A.R.T.N.
302 acknowledge Mahameru Grid LIPI for their high-performance computing facilities. C.E. would like to
303 thank Pat Photongkam and Thipusa Wongpinij for assisting in LEEM/PEEM operations.

304 REFERENCES:

- 305 1. M. Boutchich, H. Arezki, D. Alamarguy, K.-I. Ho, H. Sediri, F. Gunes, Fethullah, J.
306 Alvarez, J. Kleider, C. Lai, and A. Ouerghi, *Appl. Phys. Lett.* **105**, 233111 (2014).
- 307 2. E. Pallecchi, F. Lafont, V. Cavaliere, F. Schopfer, D. Mailly, W. Poirier, and A. Ouerghi,
308 *Sci Rep* **4**, 4558 (2014).
- 309 3. F. Günes, H. Arezki, D. Pierucci, D. Alamarguy, J. Alvarez, J.-P. Kleider, Y. J. Dappe, A.
310 Ouerghi, and M. Boutchich, *Nanotechnology* **26**, 445702 (2015).
- 311 4. Z. Han, A. Kimouche, D. Kalita, A. Allain, H. Arjmandi-Tash, A. Reserbat-Plantey, L.
312 Marty, S. Pairis, V. Reita, N. Bendiab, J. Coraux, and V. Bouchiat, *Adv. Funct. Mater.* **24**,
313 964 (2014).
- 314 5. K.-I. Ho, M. Boutchich, C.-Y. Su, R. Moreddu, E. S. R. Marianathan, L. Montes, and C.-S.
315 Lai, *Adv. Mater.* **27**, 6519 (2015).
- 316 6. L. Khalil, D. Pierucci, E. Papalazarou, J. Chaste, M. G. Silly, F. Sirotti, M. Eddrief, L.
317 Perfetti, E. Lhuillier, and A. Ouerghi, *Phys. Rev. Mater.* **3**, 084002 (2019).
- 318 7. T. A. Amollo, G. T. Mola, M. S. K. Kirui, and V. O. Nyamori, *Crit. Rev. Solid State Mater.*
319 *Sci.* **43**, 133 (2018).
- 320 8. V.-T. Tran, J. Saint-Martin, P. Dollfus, and S. Volz, *Sci. Rep.* **7**, 2313 (2017).
- 321 9. L. I. Johansson, R. Armiento, J. Avila, C. Xia, S. Lorcy, I. A. Abrikosov, M. C. Asensio,
322 and C. Virojanadara, *Sci. Rep.* **4**, 4157 (2015).

323 10. W. Bao, L. Jing, J. Velasco, Y. Lee, G. Liu, D. Tran, B. Standley, M. Aykol, S. B. Cronin,
324 D. Smirnov, M. Koshino, E. McCann, M. Bockrath, and C. N. Lau, *Nat. Phys.* **7**, 948 (2011).
325 11. K.-P. Chang, K.-I. Ho, M. Boutchich, Julien Chaste, H. Arezki, and C.-S. Lai, *Semicond.*
326 *Sci. Technol.* **35**, 015005 (2019).
327 12. T. Fang, A. Konar, H. Xing, and D. Jena, *Phys. Rev. B* **78**, 205403 (2008).
328 13. E. H. Hasdeo, L. P. A. Krisna, M. Y. Hanna, B. E. Gunara, N. T. Hung, and A. R. T.
329 Nugraha, *J. Appl. Phys.* **126**, 035109 (2019).
330 14. Y. M. Zuev, W. Chang, and P. Kim, *Phys. Rev. Lett.* **102**, 096807 (2009).
331 15. C. Coletti, C. Riedl, D. S. Lee, B. Krauss, L. Patthey, K. Von Klitzing, J. H. Smet, and U.
332 Starke, *Phys. Rev. B* **81**, 235401 (2010).
333 16. H. Pinto, R. Jones, J. P. Goss, and P. R. Briddon, *J. Phys. Condens. Matter* **21**, 402001
334 (2009).
335 17. C. Chen, J. Avila, H. Arezki, F. Yao, V. L. Nguyen, Y. H. Lee, M. Boutchich, and M. C.
336 Asensio, *J. Phys. Conf. Ser.* **864**, 012029 (2017).
337 18. H. Henck, Z. Ben Aziza, D. Pierucci, F. Laourine, F. Reale, P. Palczynski, J. Chaste, M.
338 G. Silly, F. Bertran, P. Le Fèvre, E. Lhuillier, T. Wakamura, C. Mattevi, J. E. Rault, M.
339 Calandra, and A. Ouerghi, *Phys. Rev. B* **97**, 155421 (2018).
340 19. P. Ayria, S. Tanaka, A. R. T. Nugraha, M. S. Dresselhaus, and R. Saito, *Phys. Rev. B* **94**,
341 075429 (2016).
342 20. H. Nakajima, A. Tong-on, N. Sumano, K. Sittisard, S. Rattanasuporn, C. Euaruksakul, R.
343 Supruangnet, N. Jearanaikoon, P. Photongkam, N. Chanlek, and P. Songsiriritthigul, *J. Phys.*
344 *Conf. Ser.* **425**, 132020 (2013).
345 21. C. Euaruksakul, N. Jearanaikoon, W. Bussayaporn, N. Kamonsutthipajit, P. Photongkam,
346 S. Tunmee, and P. Songsiriritthigul, *J. Phys. Conf. Ser.* **425**, 182011 (2013).
347 22. H. Hibino, H. Kageshima, F. Maeda, M. Nagase, Y. Kobayashi, and H. Yamaguchi, *Phys.*
348 *Rev. B - Condens. Matter Mater. Phys.* **77**, 075413 (2008).
349 23. D. Pierucci, H. Sediri, M. Hajlaoui, E. Velez-Fort, Y. J. Dappe, M. G. Silly, R. Belkhou,
350 A. Shukla, F. Sirotti, N. Gogneau, and A. Ouerghi, *Nano Res.* **8**, 1026 (2015).
351 24. M. L. Bolen, S. E. Harrison, L. B. Biedermann, and M. A. Capano, *Phys. Rev. B* **80**,
352 115433 (2009).
353 25. J. Osaklung, C. Euaruksakul, W. Meevasana, and P. Songsiriritthigul, *Appl. Surf. Sci.*
354 **258**, 4672 (2012).
355 26. S. Y. Zhou, G.-H. Gweon, A. V. Fedorov, P. N. First, W. A. de Heer, D.-H. Lee, F.
356 Guinea, A. H. Castro Neto, and A. Lanzara, *Nat. Mater.* **6**, 770 (2007).
357 27. N. Koch, S. Duhm, J. P. Rabe, A. Vollmer, and R. L. Johnson, *Phys. Rev. Lett.* **95**,
358 237601 (2005).
359 28. W. Chen, S. Chen, D. C. Qi, X. Y. Gao, and A. T. S. Wee, *J. Am. Chem. Soc.* **129**, 10418
360 (2007).
361 29. J. Fraxedas, Y. J. Lee, I. Jiménez, R. Gago, R. M. Nieminen, P. Ordejón, and E. Canadell,
362 *Phys. Rev. B - Condens. Matter Mater. Phys.* **68**, 195115 (2003).
363 30. J. M. Lindquist and J. C. Hemminger, *J. Phys. Chem.* **92**, 1394 (1988).
364 31. P. Persson, S. Lunell, A. Szöke, B. Ziaja, and J. Hajdu, *Protein Sci.* **10**, 2480 (2009).
365 32. X. Tian, J. Xu, and X. Wang, *J. Phys. Chem. B* **114**, 11377 (2010).
366 33. H. Hibino, H. Kageshima, M. Kotsugi, F. Maeda, F.-Z. Guo, and Y. Watanabe, *Phys. Rev.*
367 *B* **79**, 125437 (2009).
368 34. C. Mathieu, N. Barrett, J. Rault, Y. Y. Mi, B. Zhang, W. A. De Heer, C. Berger, E. H.
369 Conrad, and O. Renault, *Phys. Rev. B - Condens. Matter Mater. Phys.* **83**, 235436 (2011).
370 35. J. Hicks, A. Tejada, A. Taleb-Ibrahimi, M. S. Nevius, F. Wang, K. Shepperd, J. Palmer, F.
371 Bertran, P. Le Fèvre, J. Kunc, W. A. De Heer, C. Berger, and E. H. Conrad, *Nat. Phys.* **9**, 49
372 (2013).

- 373 36. N. Barrett, O. Renault, H. Lemaître, P. Bonnaillie, F. Barcelo, F. Miserque, M. Wang, and
374 C. Corbel, *J. Electron Spectrosc. Relat. Phenom.* **195**, 117 (2014).
- 375 37. J. Jobst, L. M. Boers, C. Yin, J. Aarts, R. M. Tromp, and S. J. van der Molen,
376 *Ultramicroscopy* **200**, 43 (2019).
- 377 38. S. Yoshimoto, K. Kameshima, T. Koitaya, Y. Harada, K. Mukai, and J. Yoshinobu, *Org.*
378 *Electron.* **15**, 356 (2014).
- 379 39. H.-Z. Tsai, A. A. Omrani, S. Coh, H. Oh, S. Wickenburg, Y.-W. Son, D. Wong, A. Riss,
380 H. S. Jung, G. D. Nguyen, G. F. Rodgers, A. S. Aikawa, T. Taniguchi, K. Watanabe, A. Zettl,
381 S. G. Louie, J. Lu, M. L. Cohen, and M. F. Crommie, *ACS Nano* **9**, 12168 (2015).
- 382 40. W. Chen, D. Qi, X. Gao, and A. T. S. Wee, *Prog. Surf. Sci.* **84**, 279 (2009).
- 383 41. J. Y. Kim and J. C. Grossman, *Nano Lett.* **15**, 2830 (2015).
- 384 42. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L.
385 Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R.
386 Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari,
387 F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G.
388 Sciauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.*
389 *Condens. Matter* **21**, 395502 (2009).
- 390 43. P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra,
391 R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S.
392 de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R.
393 Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E.
394 Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A.
395 Otero-de-la-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P.
396 Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni,
397 *J. Phys. Condens. Matter* **29**, 465901 (2017).
- 398 44. H. J. Goldsmid, *Introduction to Thermoelectricity* (Springer, Berlin, 2009).
- 399 45. B. Liao, J. Zhou, B. Qiu, M. S. Dresselhaus, and G. Chen, *Phys. Rev. B - Condens.*
400 *Matter Mater. Phys.* **91**, 235419 (2015).
- 401 46. W. Li, *Phys. Rev. B - Condens. Matter Mater. Phys.* **92**, 075405 (2015).
- 402 47. P. A. George, J. Strait, J. Dawlaty, S. Shivaraman, M. Chandrashekar, F. Rana, and M.
403 G. Spencer, *Nano Lett.* **8**, 4248 (2008).
- 404 48. K. Fukumoto, M. Boutchich, H. Arezki, K. Sakurai, D. Di Felice, Y. J. Dappe, K. Onda,
405 and S. Koshihara, *Carbon* **124**, 49 (2017).
- 406 49. Y. Anno, Y. Imakita, K. Takei, S. Akita, and T. Arie, *2D Mater.* **4**, 025019 (2017).
- 407 50. O. Yamashita, S. Tomiyoshi, and K. Makita, *J. Appl. Phys.* **93**, 368 (2003).
- 408