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# Suppression of conductivity deterioration of copper thin films by coating with atomic-layer materials

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Theoretical calculations are performed to explore the electronic structures and electron conducting properties of copper (Cu) thin films coated with graphene or *h*-boron-nitride (*h*-BN) layers. The Shockley surface states of Cu surfaces are preserved by the graphene and *h*-BN coatings which prevent the surface oxidation of Cu because of the weak interaction between the Cu surface and graphene or the *h*-BN layers. Furthermore, the Shockley surface states in Cu thin films possess quasi-two dimensional free-electron characteristics and exhibit a high conductivity of  $1.62 \times 10^7$  ( $\Omega\text{m}$ )<sup>-1</sup> at room temperature. These hybrid structures may be suitable as interconnects in memory devices that can stably store data for long periods. *Published by AIP Publishing.*  
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The increased volume of information in current and future social activity demands the further miniaturization of memory devices, which requires further device integration and the size of metal interconnects to be decreased. However, as interconnects are made smaller, their conductivity and long-term reliability are lower.<sup>1</sup> Therefore, it is necessary to explore novel stable interconnect materials with high conductivity to allow further downsizing of devices. Copper (Cu) is a crucial material in highly efficient interconnects in semiconductor integrated circuits. However, Cu nanowires are usually oxidized in the ambient environment, which drastically lowers their electrical and thermal conductivity.<sup>2</sup> Upon further miniaturization, oxidation crucially deteriorates the conductivity of metal interconnects because of the increase in the ratio of the surface oxidized area to the bulk. To overcome this problem, it is important to prevent the surface oxidation of Cu interconnects.

Surface scattering is an important phenomenon in which electrons undergo either elastic or inelastic scattering depending on the local surface states obtained upon miniaturizing devices and interconnects.<sup>2</sup> Furthermore, the surface electron density located near the nanowire surface makes a large contribution to the total conduction electron density. Therefore, surface states play an important role in the electrical conductivity of Cu nanowires on the nanometer scale. It is well known that noble metal surfaces possess electron states called Shockley surface states,<sup>3–5</sup> which have a quasi-two-dimensional (2D) free-electron-like nature. A recent study demonstrated that the Shockley surface states of noble metal surfaces could be interpreted as topological states.<sup>6</sup> Therefore, Shockley surface states are expected to lead to high electrical conductivity in Cu nanowires. However, these surface states are sensitive to surface oxidation and adsorption of metal atoms. Therefore, it is important to explore materials that prevent the surface degradation of Cu wires

induced by the adsorption of foreign materials to obtain efficient, stable nanoscale interconnects using noble metals.

Recently, atomic-layer materials, such as graphene and boron nitride (*h*-BN), have been suggested as promising coating materials for various materials because of their exceptional geometric and electronic properties, and high corrosion/oxidation resistance.<sup>7–9</sup> Indeed, the electrical conductivity of Cu nanowires with graphene as a coating layer was enhanced by 7% to 15% compared with that of bare Cu nanowires.<sup>1,2</sup> Furthermore, coating Cu films with graphene also improved their thermal conductivity.<sup>10</sup> However, the physical origin of the high conductivity of graphene-coated Cu nanowires is still unclear. Here, we present a theoretical investigation of the electronic structure and transport properties of heterostructures consisting of Cu thin films and the 2D layered materials graphene and *h*-BN physisorbed on the Cu surfaces based on the density functional theory (DFT) and semiclassical Boltzmann transport theory.

All theoretical calculations were performed based on DFT<sup>11,12</sup> as implemented in the Quantum ESPRESSO code.<sup>13</sup> Projector augmented wave pseudopotentials were used to describe the electron-ion interaction.<sup>14</sup> The valence wave functions and augmented charge density were expanded using a plane-wave basis set with cutoff energies of 60 and 540 Ry, respectively. We used the van der Waals corrected density functional for the exchange-correlation energy to accurately describe the weakly bonded layered materials, including graphene or *h*-BN and Cu surfaces.<sup>15–17</sup> All atoms were fully optimized until the remaining force acting on each atom was less than 0.0001 Ry/Bohr. Brillouin-zone integration was performed with a  $\Gamma$ -centered uniform *k*-mesh<sup>18</sup> with a  $0.009 \text{ \AA}^{-1}$  grid in self-consistent electronic structure calculations.

We used a slab model in which the Cu thin film was simulated as a Cu(111) thin film with seven atomic layers. We simulated the oxidation of the Cu thin film in the ambient environment by considering two main experimental structures:<sup>19,20</sup> adsorption of an O atom on both top and

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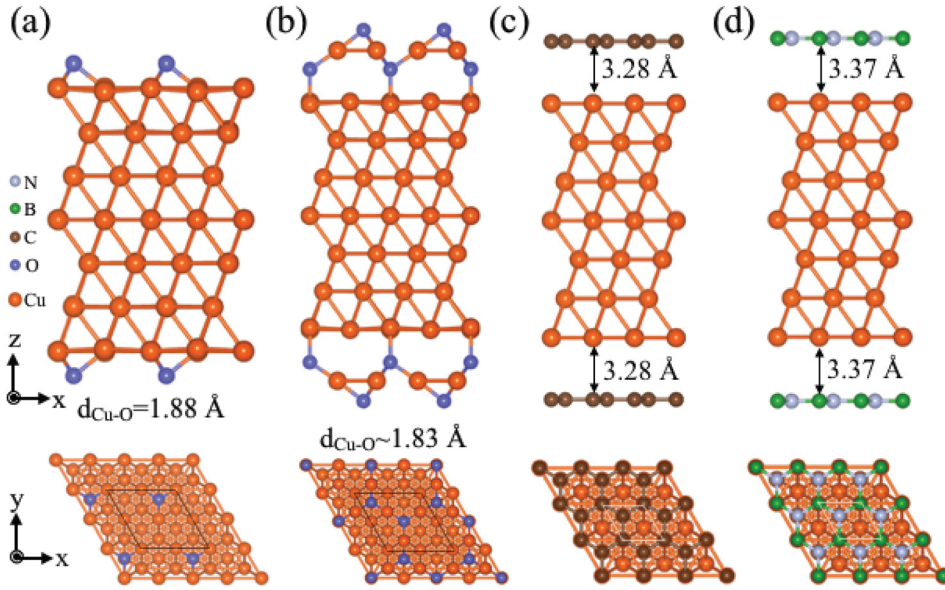


FIG. 1. Side and top views of the optimized structures of (a) a Cu(111)-(2 × 2) thin film with an adsorbed oxygen coverage of 0.25 monolayers, (b) a Cu(111)-(2 × 2) thin film with Cu<sub>1.5</sub>O layers on both sides, (c) a Cu(111)-(1 × 1) thin film with graphene coating layers, and (d) a Cu(111)-(1 × 1) thin film with *h*-BN coating layers. The surface unit cell is indicated by solid lines.

bottom surfaces of a Cu(111)-(2 × 2) thin film to give 0.25-monolayer oxygen coverage for the structure with a low adsorbed O concentration [Fig. 1(a)] and a Cu<sub>1.5</sub>O layer on both the top and bottom surfaces of a Cu(111)-(2 × 2) thin film for the structure with a high adsorbed oxygen concentration [Fig. 1(b)]. The Cu thin films were coated by adsorbing graphene or *h*-BN layers on both the top and bottom of the Cu surfaces to form graphene-Cu(111)-graphene and BN-Cu(111)-BN hybrid structures, respectively, as shown in Figs. 1(c) and 1(d). The Cu(111) thin films coated with graphene or *h*-BN were modeled using a 1 × 1 lateral periodicity, in which the lateral lattice parameters of graphene or *h*-BN were fixed to the optimized lattice parameter of the Cu(111) surface of 2.546 Å. Furthermore, to avoid spurious electrostatic interactions with the periodic images in the slab calculations, we used the effective screening medium method<sup>21,22</sup> with a vacuum region of 16 Å.

Figure 2(a) displays the electronic energy bands of an isolated Cu(111) thin film. We find delocalized occupied states located around -0.426 eV below the Fermi energy level at the  $\Gamma$ -point. These electron states show a quadratic dispersion relation with an effective mass of 0.38  $m_e$  around the  $\Gamma$ -point and Fermi wavelength  $\lambda_F$  of 31.88 Å. Furthermore, these states

exhibit an unusual wavefunction distribution with floating nature above the surfaces, in which maxima of the distribution are not situated at the atomic sites but in the vacuum region at a distance of about 2.0 Å from the top or bottom atomic Cu layer, as shown in Fig. 2(b). This state extends parallel to the Cu surfaces and possesses a quasi-2D free-electron-like nature. These states are classified as the Shockley surface states of metal surfaces.<sup>3</sup> These results are in good agreement with previous theoretical and experimental observations.<sup>4,5,23</sup> Moreover, our calculations also revealed that these Shockley surface states have a high density of states of  $1.47 \times 10^{13} \text{ cm}^{-2}$  at the Fermi level. Because of their high density of states and free-electron-like behavior, the Shockley states play important roles in lateral quantum confinement effects at metal surfaces, such as quantum corrals,<sup>24</sup> quantum migration,<sup>25</sup> and ballistic conduction.<sup>26</sup> Therefore, it is expected that these Shockley surface states could enhance the electrical conductivity of Cu thin films.

Cu surfaces are easily oxidized by oxygen under ambient conditions, resulting in the formation of copper oxides on the surfaces that could decrease the electrical conductivity of Cu thin films. Figure 3(a) presents the energy band dispersion of a Cu(111) thin film with an adsorbed oxygen coverage of 0.25 monolayers [Fig. 1(a)]. The oxygen atoms are chemically adsorbed on the surface with a binding energy of 100 meV/Å<sup>2</sup>, and the Cu-O bond lengths are 1.83–1.88 Å, in excellent agreement with other theoretical (1.83 Å) and experimental (1.9 Å) values.<sup>19,20</sup> The chemical bonds formed between oxygen and the Cu surface dramatically modulate the electronic structure of the Cu thin film. Detailed wavefunction distribution analysis revealed that the electron states around the Fermi level consist of hybridized 3*d*-orbitals of Cu and 2*p*-orbitals of O atoms [Fig. 3(b)], in good agreement with other theoretical results.<sup>19,27</sup> Because of this hybridization, the Shockley surface states are absent around the Fermi level, as reported in experiments.<sup>4</sup> Therefore, oxygen adsorption on the Cu surface disrupts the Shockley surface states. Furthermore, the Cu thin film coated with Cu<sub>1.5</sub>O layers [Fig. 1(b)] also exhibits highly modulated electronic properties near the Fermi level, in which the Shockley surface

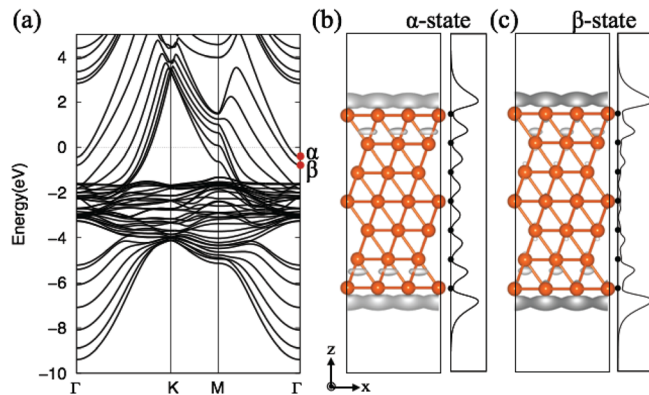


FIG. 2. (a) Electronic energy band structure of a bare Cu thin film and the square wavefunction distribution (grey) and its average on the *xy*-plane of the (b)  $\alpha$ -state and (c)  $\beta$ -state at the  $\Gamma$ -point, as denoted in (a).



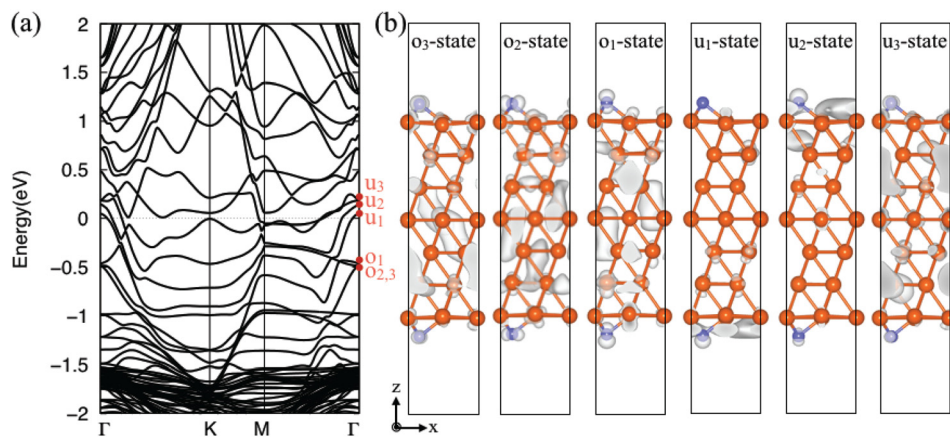


FIG. 3. (a) Electronic energy band structure of a Cu thin film with an adsorbed oxygen coverage of 0.25 monolayers and (b) square wavefunction distribution of the  $o_1$ ,  $o_2$ ,  $o_3$ ,  $u_1$ ,  $u_2$ , and  $u_3$  states around the Fermi level at the  $\Gamma$ -point, as denoted in (a).

states are also absent (Fig. S1, [supplementary material](#)). The strong perturbation of the electronic structure at the Fermi level could increase the number of scattering centers that influence the electron transfer on the Cu surface during oxidation, causing the electrical conductivity of the Cu thin films to decrease.<sup>28</sup>

Next, we show that graphene and *h*-BN adsorbed on Cu surfaces protect the Shockley surface states from surface oxidation. As shown in Figs. 1(c) and 1(d), graphene and *h*-BN monolayers bound weakly to the Cu surface via van der Waals interactions with an interlayer spacing of about 3.3 Å. The calculated binding energies for the interaction of the Cu surface with graphene and *h*-BN layers were 21 and 19 meV/Å<sup>2</sup>, respectively. Although these binding energies are smaller than those of conventional chemical bonds, they are still comparable to or larger than those of other layered compounds such as BN, graphite, or MoS<sub>2</sub> crystals.<sup>29</sup> Therefore, it is expected that graphene and *h*-BN layers are unlikely to peel off Cu surfaces in actual device structures. In addition, we estimated the possibility of O atom diffusion through defect-free graphene and *h*-BN monolayers. The energy barrier for this process is extremely high (over 20 eV), indicating that the diffusion of O atoms through the graphene and *h*-BN layers to oxidize the Cu surface is unlikely to happen (Fig. S2, [supplementary material](#)). In other words, the defect-free graphene and *h*-BN monolayers act as excellent protecting layers for oxidation. For a graphene monolayer with a single vacancy, the O atoms preferably adsorb at C atoms with dangling bonds or vacancy site (Fig. S3, [supplementary material](#)). Previous theoretical

calculations also showed that O atoms need to overcome an energy barrier of about 1.5 eV to penetrate through this vacancy.<sup>30</sup> This decreasing energy barrier implies that the efficiency of the protecting layer could decrease. However, this limitation could be suppressed by coating with few-layer graphene or *h*-BN. Recent experiments have demonstrated that graphene or *h*-BN on Cu and Ni readily prevents surface oxidation at not only room temperature but also at high temperatures of up to 1100 °C and long-term passivation.<sup>7,8,31</sup> Therefore, our results suggest that graphene and *h*-BN layers could act as ideal ultrathin barriers to prevent the oxidation of Cu surfaces.

The weak interaction between the graphene or *h*-BN monolayer and Cu surface suggests that the electronic structure of these hybrid materials should be the simple sum of that of each constituent. Figures 4(a) and 4(c) depict the electronic energy band structures of Cu thin films coated with graphene and *h*-BN, respectively. In both structures, the electronic states around the  $\Gamma$ -point exhibit similar characteristics to those of the isolated Cu thin film [Fig. 2(a)]. Quadratic dispersion bands emerge at the  $\Gamma$ -point and Fermi level, indicating that the states retain the Shockley surface state nature of a bare Cu film [Figs. 4(b) and 4(d)]. Therefore, the Shockley surface states of the Cu surface are preserved under the graphene or *h*-BN coating. However, the Shockley surface states hybridized with the  $\pi$ -states of graphene and *h*-BN, leading to upward shifts of 0.146 and 0.086 eV for graphene and *h*-BN, respectively. The existence of Shockley surface states was indeed experimentally observed in graphene grown on the Cu(111) surface.<sup>32–34</sup>

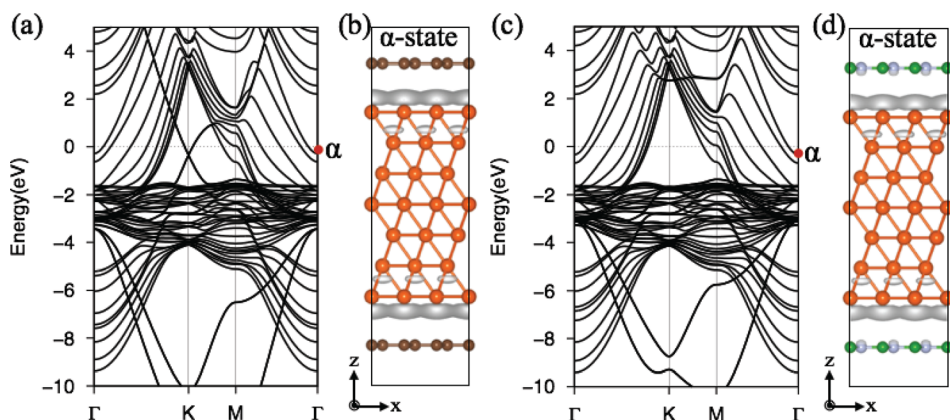


FIG. 4. (a) Electronic energy band structure and (b) square wavefunction distribution of the  $\alpha$ -state at the  $\Gamma$ -point of a Cu thin film with a graphene coating layer. (c) Electronic energy band structure and (d) square wavefunction distribution of the  $\alpha$ -state at the  $\Gamma$ -point of a Cu thin film with a *h*-BN coating layer.

Our results demonstrate that graphene and *h*-BN prevent oxidation of Cu surfaces and allow them to retain their Shockley surface states.

It is important to clarify the modulation of the electric conductivity of Cu thin films after oxidation or coating with a graphene or a *h*-BN layer. To this end, we computed electrical conductivities by solving the semiclassical Boltzmann transport equation within the constant scattering time approximation on the basis of the energy band structures obtained by DFT calculations, as implemented in the BoltzTrap code.<sup>35</sup> The computational details are described in the [supplementary material](#). Table I lists the electrical conductivity of Cu thin films with and without the adsorbates. It should be noted that the conductivities of Cu hybrid materials have been normalized to the electron relaxation time. A Cu thin film with clean surfaces exhibits a high electrical conductivity of  $0.441 \times 10^{21} (\Omega\text{ms})^{-1}$  at room temperature. The electrical conductivity of the oxidized Cu thin film decreased by about 0.1–0.2 times compared with that of the bare Cu thin film. The conductivity deterioration of the oxidized Cu thin film could be ascribed to the formation of copper oxides on the Cu surface. As discussed above, the adsorbed O atoms modify the electron states at the Fermi level of the Cu film because of the strong hybridization between O and Cu atoms. These localized states could act as scattering centers for electron transport. This result is consistent with previous experimental work.<sup>28,36,37</sup> In contrast, the Cu thin films coated with graphene or *h*-BN layers display high conductivity of about  $0.438 \times 10^{21} (\Omega\text{ms})^{-1}$ . Mehta *et al.*<sup>2</sup> recently showed that the electrical conductivity of graphene-coated Cu nanowires was 15% higher than that of Cu nanowires without a graphene coating. Furthermore, they also demonstrated experimentally that the graphene-coated Cu nanowires did not have an oxidation layer, while the Cu nanowires without graphene possessed Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> oxidation layers. We found that the Shockley surface states exhibited a large conductivity of  $1.62 \times 10^7 (\Omega\text{m})^{-1}$  at room temperature (Fig. S5, [supplementary material](#)). In addition, the electronic thermal conductivity (electron contribution) of Cu thin films (Table I) was also enhanced by graphene or *h*-BN coating, in good agreement with recent experiments.<sup>2,10</sup> These results indicate the contribution of Shockley surface states to both the electrical and thermal conductivities of Cu nanowires.

Finally, the reliability of nanosized Cu interconnects is another critical issue due to the electromigration of Cu atoms. In order to clarify the effect of graphene and *h*-BN coating layers on the Cu electromigration, we investigated

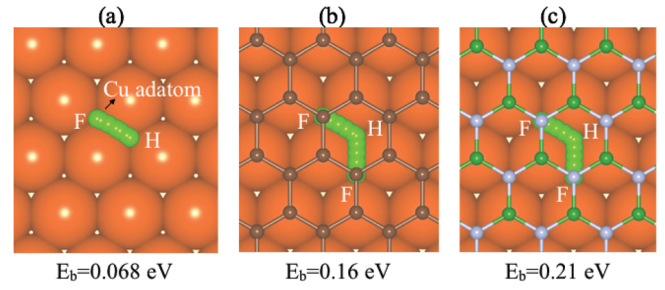


FIG. 5. Diffusion process and barrier energies ( $E_b$ ) of (a) a Cu adatom on a clean Cu(111)-(3 × 3) surface, (b) Cu adatom on a Cu(111)-(3 × 3) surface with a graphene coating layer, and (c) Cu adatom on a Cu(111)-(3 × 3) surface with a *h*-BN coating layer. The F and H symbols denote the fcc and hcp three-fold hollow adsorption sites of the Cu adatom on the Cu surfaces.

the diffusion processes between the stable adsorption sites of the Cu adatom on Cu(111) surfaces, as shown in Fig. 5. On the clean Cu(111) surface, the Cu adatom diffuses with a small energy barrier of 0.068 eV, in good agreement with a previous theoretical value of 0.07 eV.<sup>38</sup> By coating the Cu(111) surface with graphene or *h*-BN layers, the diffuse energy barrier of Cu adatoms increases about 2–3 times, compared with that on the clean Cu(111) surface. These results indicate that graphene or *h*-BN coating layers inhibit the movement of Cu adatoms on Cu surfaces. In other words, much higher external driving force is needed to migrate Cu adatoms on the graphene (or *h*-BN)-coated Cu surface than those on the clean Cu surface. Moreover, recent works<sup>39,40</sup> on Cu metal-dielectric interfaces showed that graphene barrier layers prevent Cu atoms to penetrate through the interface. These results could explain the lifetime improvement of nanosized Cu interconnects by employing the graphene barrier layers rather than the industrial standard barrier material TaN, as reported in experiments.<sup>41</sup> Therefore, the reliability of nanosized Cu interconnects could be remarkably improved by coating with graphene or *h*-BN atomic-layers.

In summary, we found that the intrinsic Shockley surface states of Cu surfaces are destroyed by oxygen gas adsorption, leading to substantial surface scattering and decreased electrical conductivity. In sharp contrast, these Shockley surface states of Cu surfaces are preserved by the presence of graphene or *h*-BN coatings because of the weak interaction between the Cu surface and graphene or the *h*-BN layer. The Shockley surface states with quasi-2D free-electron characteristics exhibited a high conductivity of  $1.62 \times 10^7 (\Omega\text{m})^{-1}$  at room temperature. Our calculations suggest a possible approach to realize high efficiency and robustness nanosized Cu interconnects by coating with atomic-layer materials for future devices.

See [supplementary material](#) for computational details and additional results.

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TABLE I. Theoretical electrical conductivities  $\sigma/\tau$  [ $10^{21} (\Omega\text{ms})^{-1}$ ] and electronic thermal conductivities  $\kappa^0/\tau$  [ $10^{16} (\text{W/mKs})$ ] of a bare Cu thin film (Cu), a Cu thin film with an adsorbed oxygen coverage of 0.25 monolayers (Cu-O), a Cu thin film with a Cu<sub>1.5</sub>O layer (Cu-Cu<sub>1.5</sub>O), a Cu thin film with a graphene coating layer (Cu-Graphene), and a Cu thin film with a *h*-BN coating layer (Cu-BN) at room temperature.

T (300 K)	Cu	Cu-O	Cu-Cu <sub>1.5</sub> O	Cu-graphene	Cu-BN
$\sigma/\tau$	0.441	0.056	0.095	0.437	0.439
$\kappa^0/\tau$	0.323	0.04	0.06	0.319	0.321

Simulator (SGI ICE X) supercomputer at the National Institute for Materials Science (NIMS) and the Hitachi 8000 Supercomputer at the Research Institute for Information Technology, Kyushu University.

- <sup>1</sup>C. G. Kang, S. K. Lim, S. Lee, S. K. Lee, C. Cho, Y. G. Lee, H. J. Hwang, Y. Kim, H. J. Choi, S. H. Choe, M.-H. Ham, and B. H. Lee, *Nanotechnology* **24**, 115707 (2013).
- <sup>2</sup>R. Mehta, S. Chugh, and Z. Chen, *Nano Lett.* **15**, 2024–2030 (2015).
- <sup>3</sup>W. Shockley, *Phys. Rev.* **56**, 317–323 (1939).
- <sup>4</sup>P. O. Gartland and B. J. Slagsvold, *Phys. Rev. B* **12**, 4047–4058 (1975).
- <sup>5</sup>F. Schiller and C. Laubschat, *Phys. Rev. B* **74**, 085109 (2006).
- <sup>6</sup>B. Yan, B. Stadtmüller, N. Haag, S. Jakobs, J. Seidel, D. Jungkenn, S. Mathias, M. Cinchetti, M. Aeschlimann, and C. Felser, *Nat. Commun.* **6**, 10167 (2015).
- <sup>7</sup>S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Kang, J. Park, and R. S. Ruoff, *ACS Nano* **5**, 1321–1327 (2011).
- <sup>8</sup>Z. Liu, Y. Gong, W. Zhou, L. Ma, J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, and P. M. Ajayan, *Nat. Commun.* **4**, 2541 (2013).
- <sup>9</sup>V. G. Kravets, R. Jalil, Y.-J. Kim, D. Ansell, D. E. Aznakayeva, B. Thackray, L. Britnell, B. D. Belle, F. Withers, I. P. Radko, Z. Han, S. I. Bozhevolnyi, K. S. Novoselov, A. K. Geim, and A. N. Grigorenko, *Sci. Rep.* **4**, 5517 (2014).
- <sup>10</sup>P. Goli, H. Ning, X. Li, C. Y. Lu, K. S. Novoselov, and A. A. Balandin, *Nano Lett.* **14**, 1497–1503 (2014).
- <sup>11</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864–B871 (1964).
- <sup>12</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133–A1138 (1965).
- <sup>13</sup>P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- <sup>14</sup>A. D. Corso, *Comput. Mater. Sci.* **95**, 337–350 (2014).
- <sup>15</sup>T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, *Phys. Rev. B* **76**, 125112 (2007).
- <sup>16</sup>I. Hamada and M. Otani, *Phys. Rev. B* **82**, 153412 (2010).
- <sup>17</sup>I. Hamada, *Phys. Rev. B* **89**, 121103 (2014).
- <sup>18</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188–5192 (1976).
- <sup>19</sup>A. Soon, M. Todorova, B. Delley, and C. Stampfl, *Phys. Rev. B* **73**, 165424 (2006).
- <sup>20</sup>T. Matsumoto, R. Bennett, P. Stone, T. Yamada, K. Domen, and M. Bowker, *Surf. Sci.* **471**, 225–245 (2001).
- <sup>21</sup>M. Otani and O. Sugino, *Phys. Rev. B* **73**, 115407 (2006).
- <sup>22</sup>I. Hamada, M. Otani, O. Sugino, and Y. Morikawa, *Phys. Rev. B* **80**, 165411 (2009).
- <sup>23</sup>K. Berland, T. L. Einstein, and P. Hyldgaard, *Phys. Rev. B* **85**, 035427 (2012).
- <sup>24</sup>M. F. Crommie, C. P. Lutz, and D. M. Eigler, *Science* **262**, 218–220 (1993).
- <sup>25</sup>H. C. Manoharan, C. P. Lutz, and D. M. Eigler, *Nature* **403**, 512–515 (2000).
- <sup>26</sup>K. Kobayashi, *Phys. Rev. B* **66**, 085413 (2002).
- <sup>27</sup>A. Soon, M. Todorova, B. Delley, and C. Stampfl, *Surf. Sci.* **601**, 5809–5813 (2007).
- <sup>28</sup>J. S. Chawla, F. Zahid, H. Guo, and D. Gall, *Appl. Phys. Lett.* **97**, 132106 (2010).
- <sup>29</sup>T. Björkman, A. Gulans, A. V. Krashenninnikov, and R. M. Nieminen, *Phys. Rev. Lett.* **108**, 235502 (2012).
- <sup>30</sup>M. Topsakal, H. Şahin, and S. Ciraci, *Phys. Rev. B* **85**, 155445 (2012).
- <sup>31</sup>R. S. Weatherup, L. D’Arsié, A. Cabrero-Vilatela, S. Caneva, R. Blume, J. Robertson, R. Schloegl, and S. Hofmann, *J. Am. Chem. Soc.* **137**, 14358–14366 (2015).
- <sup>32</sup>C. Jeon, H.-N. Hwang, W.-G. Lee, Y. G. Jung, K. S. Kim, C.-Y. Park, and C.-C. Hwang, *Nanoscale* **5**, 8210–8214 (2013).
- <sup>33</sup>S. Pagliara, S. Tognolini, L. Bignardi, G. Galimberti, S. Achilli, M. I. Trioni, W. F. van Dorp, V. Ocelik, P. Rudolf, and F. Parmigiani, *Phys. Rev. B* **91**, 195440 (2015).
- <sup>34</sup>S. Gottardi, K. Müller, L. Bignardi, J. C. Moreno-López, T. A. Pham, O. Ivashenko, M. Yablonskikh, A. Barinov, J. Björk, P. Rudolf, and M. Stöhr, *Nano Lett.* **15**, 917–922 (2015).
- <sup>35</sup>G. K. Madsen and D. J. Singh, *Comput. Phys. Commun.* **175**, 67–71 (2006).
- <sup>36</sup>J. S. Chawla, F. Gstrein, K. P. O’Brien, J. S. Clarke, and D. Gall, *Phys. Rev. B* **84**, 235423 (2011).
- <sup>37</sup>A. Sanchez-Soares, S. L. T. Jones, J. J. Plombon, A. P. Kaushik, R. E. Nagle, J. S. Clarke, and J. C. Greer, *Phys. Rev. B* **94**, 155404 (2016).
- <sup>38</sup>C. Yu, J. Liu, H. Lu, and J. Chen, *Appl. Surf. Sci.* **253**, 8652–8656 (2007).
- <sup>39</sup>J. H. Bong, S. J. Yoon, A. Yoon, W. S. Hwang, and B. J. Cho, *Appl. Phys. Lett.* **106**, 063112 (2015).
- <sup>40</sup>Y. Zhao, Z. Liu, T. Sun, L. Zhang, W. Jie, X. Wang, Y. Xie, Y. H. Tsang, H. Long, and Y. Chai, *ACS Nano* **8**, 12601–12611 (2014).
- <sup>41</sup>L. Li, X. Chen, C.-H. Wang, J. Cao, S. Lee, A. Tang, C. Ahn, S. S. Roy, M. S. Arnold, and H.-S. P. Wong, *ACS Nano* **9**, 8361–8367 (2015).