

Interface-localized states mediate ultrafast cooling of hot electrons in epitaxial graphene

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In this study, we use time- and angle-resolved photoelectron spectroscopy to investigate electron relaxation dynamics in an epitaxially grown graphene monolayer on SiC. Our findings reveal significantly faster relaxation of photoexcited electrons in non-hydrogen-intercalated epitaxial graphene compared to that for previously reported hydrogen-intercalated graphene structures. The differences in relaxation time are modeled by a combination of density function theory in conjunction with *ab initio* nonadiabatic molecular dynamics, providing a comprehensive explanation of electron relaxation pathways. This study highlights the critical influence of substrate interactions on the relaxation mechanisms in graphene, offering different perspectives for tailoring graphene electronic properties through controlled intercalation techniques.

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I. INTRODUCTION

Nearly two decades of graphene research have revealed extraordinary properties [1–3] that enable the observation of phase-coherent quantum transport [2,3], room temperature ballistic transport [2], and outstanding spin communication in graphene [3,4]. Beyond its equilibrium transport properties, graphene shows interesting nonequilibrium charge dynamics with implications for spin-dependent interfacial transfer on femtosecond timescales [5,6]. Following photoexcitation, carrier-carrier scattering rapidly establishes a hot electronic distribution [7,8], which cools through optical- and acoustic-phonon emission, disorder-assisted supercollisions, and substrate-mediated processes [9–12]. Thus, the resulting relaxation time depends on carrier density, disorder, excitation conditions, and coupling to the substrate on which graphene is realized. Epitaxial graphene is a large-scale form of graphene that exhibits a high-quality single-crystal graphene layer on SiC, obtained through graphitization. In the past few decades, epitaxial graphene has been established as a high-quality material for electrical high-frequency transistors

[13–15] and metrological resistance sensors [16]. Graphitization involves the sublimation of the Si atoms through the annealing of SiC(0001) either in ultrahigh-vacuum conditions or in an argon environment [17]. Typically, an intrinsic electron doping of $n \sim 10^{13} \text{ cm}^{-2}$ is observed in epitaxial graphene prepared using graphitization under vacuum conditions [18,19]. Hydrogen intercalation is an additional step in graphitization, in which the sample is annealed in a hydrogen environment and is often employed to manipulate graphene doping and optimize the graphene sheet's isolation from the substrate [19]. Interface-mediated carrier relaxation is pertinent to graphene/SiC. Previous experimental and theoretical studies showed that interlayer Coulomb coupling, interlayer phonons, and electronic hybridization can introduce additional cooling pathways in graphene-based systems [20–23]. In non-hydrogen-intercalated graphene/SiC, covalent buffer-layer bonding creates corrugation and hybridized states that open additional nonadiabatic relaxation pathways [24–28]. Hydrogen intercalation passivates and decouples the interface, suppressing these pathways [18,29,30]. Understanding charge transfer dynamics in graphene and at its interfaces is crucial for many electrical and optoelectronic applications involving graphene and other two-dimensional (2D) materials. Femtosecond pump-probe measurements have provided insights into charge dynamics in materials and interfaces [31,32], as well as ferromagnetic thin films [7] and materials involving the insulator-metal transition [33]. In the case of graphene, most pump-probe studies have focused on hydrogen-intercalated (HI) epitaxial graphene, using time- and angle-resolved photoelectron spectroscopy (tr-ARPES)

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[8,30,34–40]. A few studies have been performed on non-hydrogen-intercalated (NHI) epitaxial graphene [40,41]. However, the ultrafast charge dynamics has not been discussed in relation to buffer-layer/SiC hybridized states providing additional relaxation pathways. In this paper, we report on tr-ARPES experiments on NHI epitaxial graphene using femtosecond extreme ultraviolet (XUV) light pulses from high harmonic generation (HHG). HHG is a nonlinear frequency up-conversion of optical laser radiation to the XUV range [42–45]. The increased photon energy allows us to probe the entire Brillouin zone (BZ), and the XUV radiation retains both the polarization and the short-pulse structure of the fundamental driving laser [46,47]. Our results show that NHI graphene exhibits extremely short lifetimes in both the population of hot carriers above the Fermi level and the Fermi-Dirac (FD) temperature compared to HI graphene on SiC. To model the observed differences in the relaxation dynamics, we used density functional theory (DFT) combined with nonadiabatic molecular dynamics (NAMD) simulations. This model provides deep insight into the role of substrate interactions in defining relaxation pathways in graphene, shedding light on how modifications at the graphene-substrate interface can dramatically influence the material's electronic structure and consequent charge transfer dynamics.

II. EXPERIMENTAL PROCEDURE

The experimental setup consists of a commercial laser system (Coherent Elite Duo) which outputs 800 nm light at 5 kHz, with a pulse duration of 32 fs (FWHM $\text{sech}^2(\omega t)$ as measured using an autocorrelator) and pulse energy of 2 mJ that was split using an 80:20 beam splitter. The 80% component was focused into the HHG chamber, which contained a 1 mm long gas cell filled with approximately 400 mbar of argon, using a 500 mm plano-convex lens. The fundamental laser is blocked by a 200 nm thick aluminum filter that transmits approximately 50% of the XUV. An individual harmonic was then chosen using a time-preserving monochromator [48]. At the sample position, the XUV beam was focused to a spot size of approximately 200 μm using an off-axis parabolic mirror. The spot size was measured using the visible fluorescence from P43 powder during XUV illumination. The remaining 20% of the laser transmitted by the beam splitter was used as an optical pump (800 nm) for the pump-probe measurement. The delay between the pump and the probe was controlled via a retroreflector with silver mirrors mounted on a high-precision delay stage in the pump line. The power of the pump pulses was adjustable between 0 and 0.2 mJ with the use of neutral-density filter wheels. The spot size of the pump on the sample was approximately 600 μm . Both the pump and probe were horizontally polarized, with the plane of incidence aligned with that of the spectrometer. The source was described in detail in Refs. [48–52].

The experiment was performed in an ultrahigh-vacuum chamber that maintains a pressure of 5×10^{-10} mbar while coupled to the rest of the HHG system. The sample was mounted onto a four-axis (X, Y, Z, θ) manipulator stage. The ARPES measurements were performed using an angle-resolved time of flight (ARTOF) photoelectron spectrometer [53,54] which inherently measures a solid angle of 30° (two

momentum axes and one energy). Although the ARTOF allows for high resolution in both energy and angle, the data reported in this paper are limited by both the bandwidth of the HHG source and the focal spot size. An energy step size of approximately 29 meV and k -space step size of approximately $0.006 \text{ \AA}^{-1}$ were used for binning to allow for higher statistics without loss of information.

To clean adsorbates from the NHI graphene surface, it was annealed to 500°C (as measured by an R-type thermocouple) and allowed to cool below 80°C before the measurements. The annealing process was repeated once every 24 h. The sample's integrity was checked periodically by observing the Fermi edge's shape, and no signs of sample degradation were observed between the annealing processes Supplemental Material [55]. For the high-quality ARPES data shown in Fig. 1, the 15th ($\sim 23 \text{ eV}$) harmonic was used, the resolution was set to $174 \pm 22 \text{ meV}$, and each spectrum was measured for 15 min. The data accumulated over many delays [Figs. 2 and 3(a)] were measured with the 25th ($\sim 38.5 \text{ eV}$) harmonic with a resolution of $174 \pm 22 \text{ meV}$, and each spectrum was measured for 2 min. The sample was optically (800 nm) pumped in both datasets by an incidence fluence of $\sim 94 \mu\text{J}/\text{cm}^2$. The high-quality monolayer graphene sample was purchased from Graphensic and has a buffer layer with a $(6\sqrt{3} \times 6\sqrt{3}R30^\circ)$ unit cell [24,25].

III. THEORETICAL METHODS

To determine the structural and electronic properties of epitaxially grown graphene/SiC, we employed DFT calculations as implemented in the Vienna *Ab initio* Simulation Package (VASP) [56,57], utilizing the generalized gradient approximation Perdew-Burke-Ernzerhof exchange functional [58]. We modeled the graphene/SiC(0001) interface using a slab geometry with periodic boundary conditions. The supercell consists of five layers of SiC plus one layer of buffer carbon (or graphene in the case of hydrogen intercalation) plus one layer of graphene. We considered experimental system features of complex $(6\sqrt{3} \times 6\sqrt{3}R30^\circ)/\text{graphene}$ and simplified $(4 \times 4)/\text{graphene}$ models with ~ 1850 and ~ 320 atoms per cells, respectively. A plane wave cutoff energy of 400 eV, in conjunction with the projector augmented wave method [59], was utilized. van der Waals interactions were accounted for with Grimme's D3 correction [60]. The Brillouin zone integration employed the Γ -centered Monkhorst-Pack scheme with a $12 \times 12 \times 1 k$ -point grid. Electronic relaxation was considered converged when the energy change was below 10^{-5} eV, and atomic positions were optimized until the Hellmann-Feynman forces were smaller than $0.01 \text{ eV}/\text{\AA}$. To prevent artificial interactions along the z direction between neighboring images, a vacuum region of at least $15 \text{ \AA}$ was introduced. For the NAMD simulations, the hefei-namd code was employed [61]. It utilizes time-dependent DFT calculations in a surface hopping scheme based on the so-called classical path approximation to describe the observed dynamics [62,63]. The phonon contribution is included through *ab initio* molecular dynamics using a supercell. In this case, the k points of the primitive cell BZ are folded to the supercell BZ. The electron-phonon coupling is implicitly accounted for through the time-dependent nonadiabatic couplings that govern the

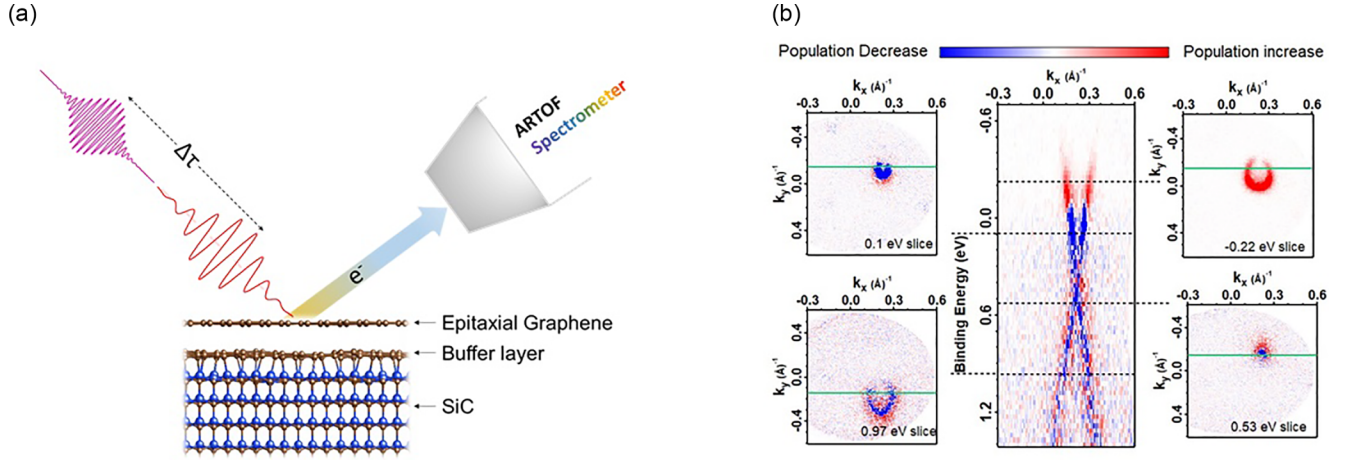


FIG. 1. (a) A schematic of the pump-probe experiment, illustrating the pump-probe time delay $\Delta\tau$, the epitaxially grown graphene sample, and the ARTOF spectrometer. (b) Difference spectra between the -530 and 10 fs data. The green lines in the corner plots indicate the constant $k_y = 0.145 \text{ \AA}^{-1}$ value used in the center E - K diagram. The red and blue points indicate an increase and decrease in electron population, respectively, comparing the unpumped and pumped cases. The data here were measured using the 25th (~ 38.5 eV) harmonic and were optically (~ 1.55 eV) pumped with a fluence of $\sim 94 \mu\text{J}/\text{cm}^2$.

electronic transitions during the dynamics. In NAMD calculations, the increased computational requirements for the large $\text{SiC}(6\sqrt{3} \times 6\sqrt{3}R30^\circ)$ model made simulating band hopping unfeasible. Therefore, only the simplified (4×4) /graphene

models were considered. While not as computationally demanding, the smaller models preserve the key interactions and capture the essential physics governing carrier relaxation. Structures were plotted using the Visualization for Electronic and Structural Analysis (VESTA) software [64]. Postprocessing

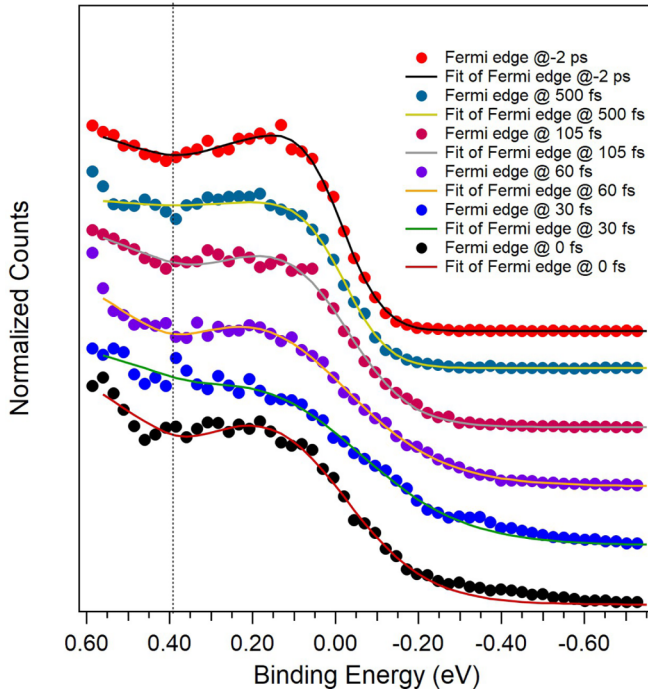


FIG. 2. The measured FD distribution for six different pump-probe delay times. The black, blue, purple, wine, turquoise, and red circles correspond to angle-integrated spectra for six different pump-probe delays: 0 , 30 , 60 , 105 , 500 , and -2000 fs, respectively. Each dataset is accompanied by corresponding fits of the FD distribution. The data here were measured using the 15th (~ 23 eV) harmonic and was optically (~ 1.55 eV) pumped with an incidence fluence of $\sim 94 \mu\text{J}/\text{cm}^2$. The vertical dotted line at 0.39 eV indicates the location of the Dirac point.

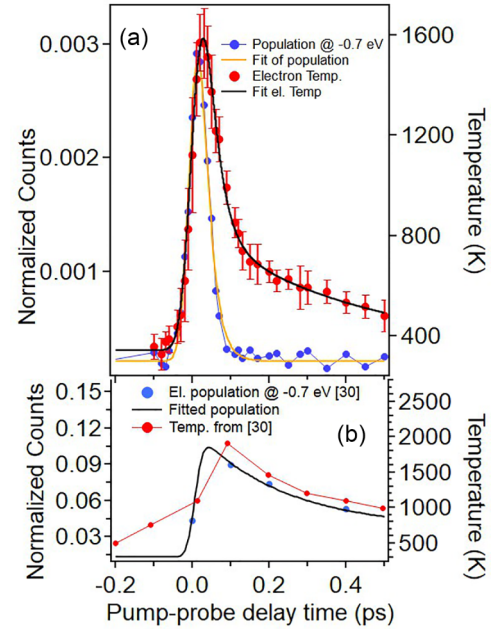


FIG. 3. (a) The blue points indicate the measured change in electron population at -0.7 eV BE with pump-probe delay. A fit of the hot carrier dynamics is shown by the orange line. The red points indicate the measured change in the FD temperature with pump-probe delay. The black line is a fit of the FD temperature (b) For comparison, we show data for HI graphene adopted from Johannsen *et al.* [30]. The blue points indicate the change in population at -0.7 eV BE with pump-probe delay. The red points indicate the change in FD temperature with pump-probe delay. The black line is a fit of the estimated population at -0.7 eV BE.

of results was carried out using the VASPKIT code [65]. A review of NAMD, which includes calculations of ultrafast electron transfer in van der Waals heterostructure interfaces, is available in Ref. [38].

IV. RESULTS

The experimental setup is illustrated in Fig. 1(a). An XUV pulse (violet wave) excites photoelectrons from the graphene surface that are subsequently collected by the ARTOF spectrometer. On the graphene, the optical pump (red wave) spatially overlaps with the probe, and its arrival time relative to the XUV probe Δt is controlled such that the evolution of the excited hot carriers can be studied. Figure 1(b) shows representative difference cuts in k space obtained by subtracting the data taken at negative time delays (-530 fs, probe before pump) from the $+10$ fs data, where the red and blue points indicate increased and decreased electron populations, respectively. The center panel in Fig. 1(b) shows the difference spectrum as an E - K plot. Here, the momentum distribution along one direction (k_x) of the electron population is shown as a function of binding energy (BE), and the other momentum axis is held constant ($k_y = 0.145 \text{ \AA}^{-1}$). The other four panels in Fig. 1(b) depict the constant energy surface (the k_x and k_y distribution) at four different binding energies. At the top dotted line in Fig. 1(b), located at -0.22 eV, an increased population of hot carriers is observed due to the presence of the optical pump. The dotted line below, located at 0.1 eV, demonstrates a decrease in electron population. Two additional horizontal dotted lines, located at 0.54 and 0.97 eV binding energy, demonstrate deeper valence bands with reduced electron population accompanied by a transient broadening of the bands. The broadening was studied in Ref. [34], where it was found that it reflects the pump-induced opening of additional decay channels for holes. These additional channels result in a reduced lifetime of excited states, which is reflected in the lifetime broadening of the photoemission spectra.

The angle-integrated spectra for multiple delays are shown in Fig. 2. The fits shown in Fig. 2 were achieved using the same procedure as that used by Someya *et al.* [41]. Briefly, the angle-integrated density of states was modeled by a linearly increasing amplitude for energies above the Dirac point (DP). The state filling was modeled by an FD distribution, using both the temperature and chemical potential as fitting parameters. Finally, the model was convoluted by a Gaussian distribution which corresponds to the 174 meV energy bandwidth of the XUV source. The chemical potential for the unpumped system defines the 0 eV binding energy in both Figs. 1(b) and 2.

Comparing these results to studies of HI graphene, we see a similar increase in both electron temperature and electron population in the conduction band due to electrons being promoted from the valence band into the π^* bands by the optical pump (see, e.g., [34,36]). The FD fit (green and wine curves in Fig. 2) deviates from the measured distribution (blue and black points in Fig. 2) up to 60 fs and at energies high in the conduction band (~ 0.2 – 0.6 eV). However, the amplitude close to the Fermi level appears to closely follow a FD distribution at all times, suggesting a very fast thermalization

process for electrons and holes close to the Fermi level for both NI and NHI graphene.

The temporal behavior of the hot carriers is presented in Fig. 3(a), where we show the time-dependent FD temperature and the electron population high up in the conduction band (-0.7 eV), well above the Fermi level but accessible by the (~ 1.55 eV) optical pump. Both the temperature and electron population were fitted with exponential functions, and the details of the fit can be found in the Supplemental Material [55] (and Refs. [41,66–68] therein). The decay of the FD temperature was fitted with a double exponential and revealed a sharp initial decay constant of 31 fs. The corresponding fit of the electron population measured at -0.7 eV BE gave a falling edge with a decay constant of 10 fs, which is on the same order as the fall in temperature. It should be noted that these decay constants are smaller than the temporal widths of the pump and probe, which makes properly accounting for the convolution of the pulse lengths important. We obtained accurate measurements of the convolution using above threshold ionization of helium (see the Supplemental Material [55] and Refs. [41,66–68] therein). The rise times of both the FD temperature and the electron population at -0.7 eV BE correlate well with the temporal cross-correlation of the pump-probe system (~ 59 fs, as verified by the above threshold ionization of helium). The second decay constant of the temperature was found to be 451 fs. In Fig. 3(b) we adopt data from Johannsen *et al.* [30] showing both the time-dependent FD temperature and the electron population at -0.7 eV BE for HI graphene. Johannsen *et al.* also reported a double exponential decay of the temperature, with decay constants of 150 and 3050 fs. This represents an order of magnitude increase in the time it takes for the graphene to cool down compared to the NHI case [30]. The decay constant of the electron population at -0.7 eV BE is 235 fs [30], which, again, is an order of magnitude slower than for the NHI case presented here. The time dependence of the FD temperature in HI graphene is within the realm of what can be expected from electron-phonon interactions [30], where the electron temperature decreases by the energy flow into the phonon system. Also, the electron population decay in the conduction band [see Fig. 3(b)] can be related to phonon scattering in HI graphene due to its relatively slow decay [41]. However, the ultrafast cooling of NHI is an order of magnitude faster than what is commonly expected from electron-phonon interactions [8,19].

To understand the differences between the relaxation dynamics observed in Figs. 3(a) and 3(b), we developed three models of SiC/graphene based on two possible unit cell configurations of the substrate. They are shown in the top panels of Fig. 4 and correspond to a smaller SiC(4×4) unit cell without and with hydrogen intercalation [SiC(4×4)/graphene and SiC(4×4)_H/graphene, respectively] and to a larger unit cell [SiC($6\sqrt{3} \times 6\sqrt{3}R30^\circ$)/graphene]. The latter represents the structure found in our sample as verified by low-energy electron diffraction (see Fig. S2 in the Supplemental Material [55] and Refs. [41,66–68] therein), which is typically seen in experiments [24,29,30,34]. In all models, two graphene layers (a top layer and a buffer layer) sit on top of the substrate. The atoms of the bottom layer of the substrate slab were passivated by hydrogen in all three models. The relaxation of the smaller SiC(4×4) model with a SiC surface intercalated by hydrogen

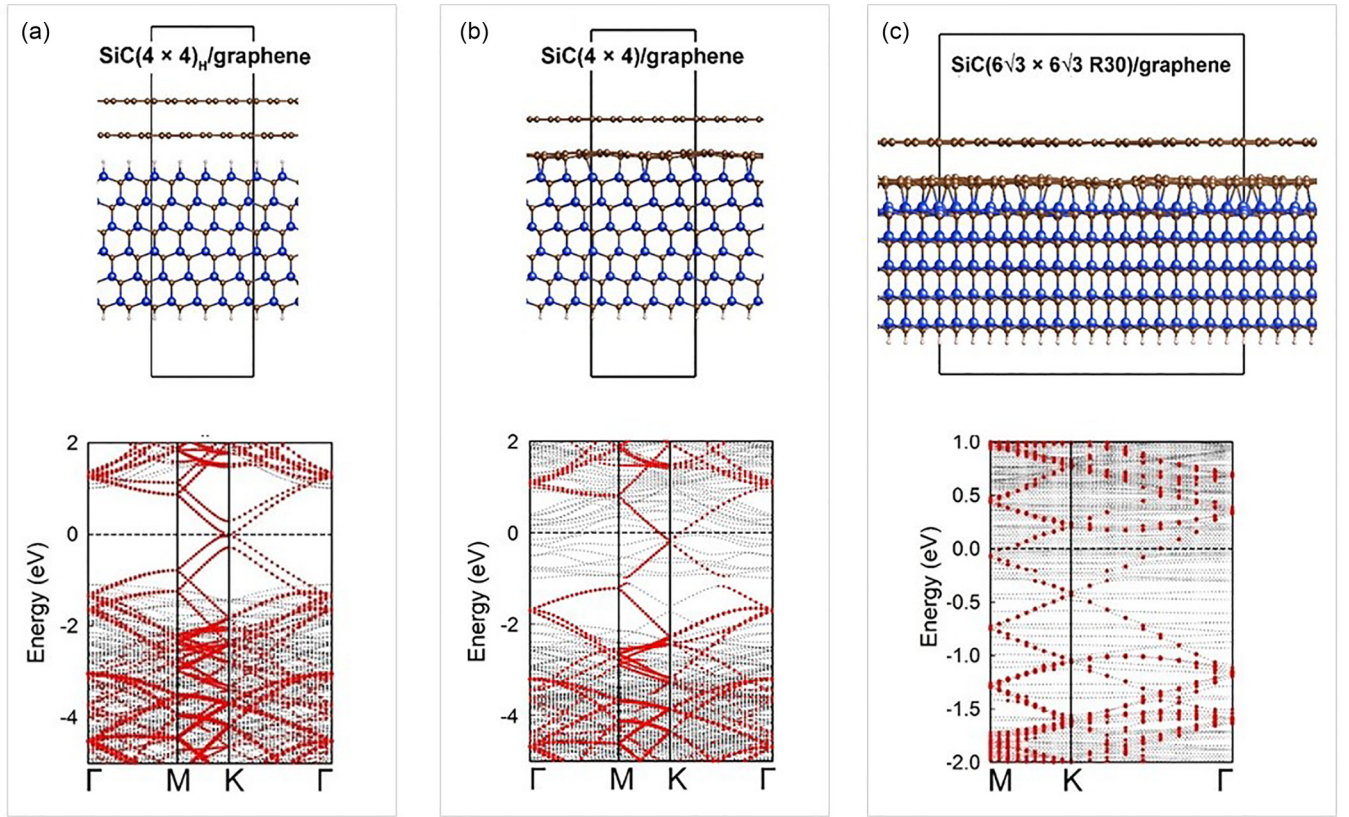


FIG. 4. Side views of the different SiC/graphene models and corresponding band structures: (a) SiC(4×4)_H/graphene model with the SiC surface intercalated by hydrogen at the interface, (b) SiC(4×4)/graphene model without intercalated hydrogen, and (c) the large SiC($6\sqrt{3} \times 6\sqrt{3}R30^\circ$)/graphene model without intercalated hydrogen. The blue, brown, and beige atoms represent Si, C, and H, respectively. The solid black line shows a unit cell. All three panels show the corresponding calculated band structures at the bottom of each plot. The red and black dots represent graphene and SiC/buffer-layer bands, respectively. The Fermi level is set to 0 eV. The density of the SiC bands (shown as black dotted lines) reflects the size of the respective unit cells.

atoms at the interface [Fig. 4(a)] demonstrates the absence of any chemical interaction between the graphene layers (top and buffer) and the SiC surface. Under this configuration both the graphene top layer and the buffer layer are flat. The SiC(4×4) and SiC($6\sqrt{3} \times 6\sqrt{3}R30^\circ$) models without hydrogen intercalation reveal significant corrugation of the buffer layers [Figs. 4(b) and 4(c)] caused by covalent bonding with the substrate, while the top graphene layer is not completely flat, revealing some interaction with the buffer layer. The deviation from the perfect flat plane reaches $\pm 0.14 \text{ \AA}$ for SiC($6\sqrt{3} \times 6\sqrt{3}R30^\circ$), while it is only $\pm 0.04 \text{ \AA}$ in the case of the smaller (4×4) model. This indicates that the larger model provides enhanced interaction between graphene and the buffer layer compared to the smaller model.

The band structures of SiC/graphene are shown in the bottom panels of Fig. 4. The band structure of the hydrogenated SiC(4×4)_H/graphene heterostructure shown in Fig. 4(a) has the DP at the Fermi level, and therefore, the graphene and the buffer layer can be considered quasifreestanding bigraphene. The band structure agrees with previous theoretical and experimental data demonstrating a double Dirac cone [69]. The band structure of the SiC(4×4)/graphene model without hydrogen intercalation [Fig. 4(b)] results in n doping with the DP shifted to -0.18 eV . The doping effect, however, is significantly smaller than that observed in the experimental data

shown in Fig. 1(b). The large SiC($6\sqrt{3} \times 6\sqrt{3}R30^\circ$)/graphene model without hydrogen intercalation that contains 1864 atoms [Fig. 4(c)] gave results more in line with the experimental data, with a DP at -0.42 eV [Fig. 1(b)], and previous theoretical results [26]. In Figs. 4(b) and 4(c) we also observe several new bands forming around the Dirac crossing which are not present in the hydrogen-intercalated case in Fig. 4(a). These additional bands arise from the covalent interaction between SiC and the corrugated buffer layer, which does not exist in the hydrogen-intercalated case. These bands can serve as extra deexcitation pathways, allowing the non-hydrogen-intercalated sample to cool faster.

To further investigate this possible mechanism, we simulate hot carrier dynamics using NAMD simulations and observe the possible electron hopping dynamics in the SiC(4×4)_H/graphene and SiC(4×4)/graphene models (Fig. 5) containing 324 and 308 atoms, respectively. Following geometry optimization, the system was heated to 300 K using the velocity rescaling algorithm, ensuring thermal equilibrium before initiating the carrier relaxation simulations. A 5 ps microcanonical *ab initio* molecular dynamics trajectory was then generated using a 1 fs time step, allowing for a detailed examination of electron relaxation over relevant timescales. To ensure statistical reliability, the calculations were averaged over 100 different initial configurations, with

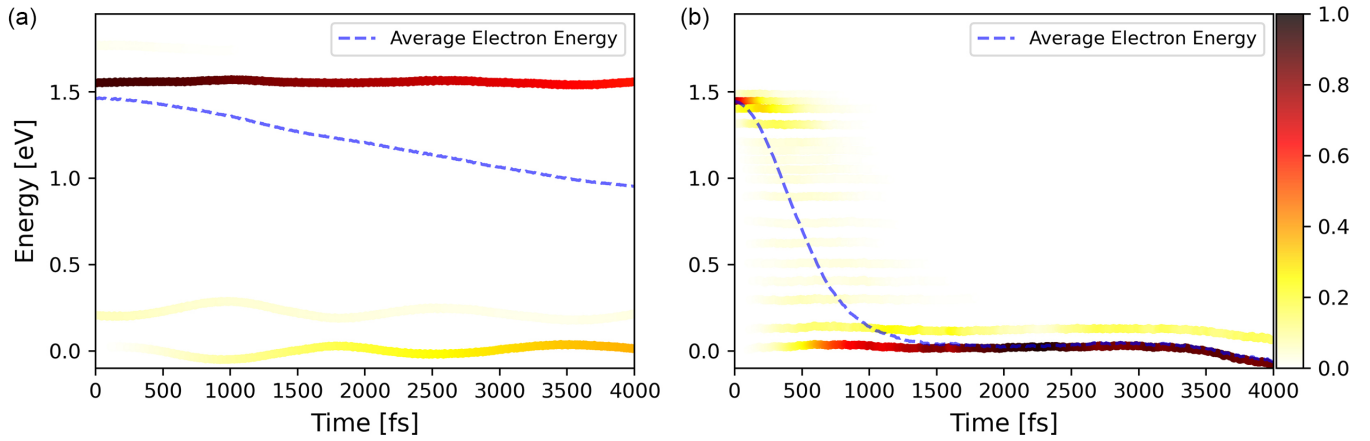


FIG. 5. The time-dependent electron energy changes at 300 K in the models (a) with and (b) without a hydrogen-intercalated $\text{SiC}(4 \times 4)$ surface. The horizontal colored lines indicate the electron population in different energy states (the scale is in the right panel), and the blue dashed lines represent the average electron energy. The energy scale is relative to the ground state energy of the electron in the valence band Dirac cone at the $(0.174 \text{ \AA}^{-1}, 0.174 \text{ \AA}^{-1}, 0)$ k point.

each structure undergoing 50 000 trajectories over 4.0 ps. The simulation is performed at a single k point $(0.174 \text{ \AA}^{-1}, 0.174 \text{ \AA}^{-1}, 0)$ corresponding to excitation from the Dirac cone valence band to the conduction band. This k point is chosen because it roughly represents the experimental laser excitation of 1.55 eV. To model the intercalated systems, we included double Dirac cone bands. Note that only vertical transitions within the wave vector are allowed in these simulations. We can see that the electron population probability of the higher-energy Dirac cone in the conduction band is extremely low, and electrons drop immediately to the lower-energy conduction band, which is a bottleneck due to the energy gap down to the valence band that plays a significant role in the phonon bottleneck effect [70]. The only relaxation path here could be phonons. However, due to the practical computational limitations, such calculations were inaccessible. Simulations suggest that the average electron energy slowly decreases but does not reach complete relaxation within 4 ps, which is behavior similar to that of the hydrogen-intercalated measurements [30]. In Fig. 5(b), we model similar excitation and decay for the non-hydrogen-intercalated graphene [whose band structure is shown in Fig. 4(b)]. The initial excitation was chosen similarly to that in the previous case. In contrast to Fig. 5(a), we can see an extremely fast relaxation back to the Dirac cone in the valence band, which is almost complete after ~ 600 fs. In the absence of hydrogen intercalation, the large number of bands at high energies supports a fast decay back to the ground state. These bands are characteristic of the buffer layer, which facilitates charge transfer between graphene and SiC, leading to quicker energy dissipation. Since this model considers only the $\text{SiC}(4 \times 4)$ unit cell, the interaction between graphene and the buffer layer is limited and would probably significantly increase if we could model the dynamics using $\text{SiC}(6\sqrt{3} \times 6\sqrt{3}R30^\circ)$ shown in Fig. 4(c). Due to the increased computational requirements for simulating band hopping with an increased number of bands, calculating time-dependent electron energy changes for the large $\text{SiC}(6\sqrt{3} \times 6\sqrt{3}R30^\circ)$ model was not feasible.

V. CONCLUSIONS

In this study, we investigated the ultrafast relaxation dynamics in epitaxially grown graphene using time-resolved ARPES. Our results show a significantly faster electron relaxation in NHI graphene samples compared to other studies of HI SiC-grown structures. There appears to be a very fast thermalization process for electrons and holes close to the Fermi level for both HI and NHI graphene since there is excellent fitting of the Fermi-Dirac distribution at low binding energies during pump-probe overlap [36]. The cooling of electrons in HI samples was previously assigned to electron-phonon scattering [9], and the few existing tr-ARPES studies of NHI graphene assigned the faster electron dynamics to increased electron-phonon scattering due to n doping [34,40]. However, a recent study concluded that doping has no effect on the decay constant [71]. Fast dynamics can also be found for graphene on metal substrates, which is usually assigned to hybridization [23,72]. It has been suggested that the main scattering mechanism is driven by out-of-plane acoustic and optical phonon modes [27]. Therefore, one can expect that corrugations of $\pm 0.14 \text{ \AA}$ ($\sim 4\%$ of the layer thickness), which are directly tied to substrate coupling, enhance scattering because of changes in interatomic distances and angles between bonds, while interface-induced states provide an additional relaxation pathway. This is supported by the earlier theoretical formulation proposed by Katsnelson and Geim [28]. Our measurements show that the cooling is even faster than found previously for NHI graphene, and it is unlikely that the electron-phonon interaction is strong enough to explain this result. However, our experimental results correlate well with nonadiabatic molecular dynamics simulations, showing an order of magnitude faster electron relaxation time for NHI systems than for HI systems. The faster relaxation in the NHI graphene is attributed to additional deexcitation pathways introduced by the bands created by the interaction between the buffer layer and the SiC substrate. The buffer layer facilitates charge transfer between graphene and SiC, leading to quicker energy dissipation. This allows for more rapid

electron cooling, as reflected in both the occupied density of states and Fermi-Dirac temperature measurements. From a device perspective, this increased coupling can serve as an opportunity by facilitating faster electron transport through a graphene layer, which could enhance the speed of existing 2D heterostructure layers. These findings enhance our understanding of the role of substrate interactions in defining the electron and phonon dynamics of graphene and hint at a possible advantage in combining SiC graphitization with existing 2D heterostructure growth techniques.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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