

Electronic structure and intraband health and social care essay



carrier relaxation in hot carrier solar cellsJ. P. TrinasticDepartment of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida, 32611, USA(Dated: March 6, 2013)AbstractThird-generation solar cells promise a higher efficiency compared to first generation and second generation thin film cells. In particular, hot carrier solar cells provide a pathway to high efficiency without increased device complication if optimal materials can be designed with slow hot carrier cooling. In this proposal, I discuss the potential for graphene quantum dots and nanoribbon embedded in a hexagonal boron nitride matrix to act as hot carrier photoabsorbers. Density functional theory is implemented to calculate the electronic structure of these systems. In addition, the theory of energy dissipation is discussed that models irreversible energy system due to coupling with the phonon reservoir. Computational methods are used to calculate the relaxation rate of an initially photoexcited state via electron-phonon coupling that provides a measure of hot carrier cooling in the systems of interest. Preliminary results demonstrating the methodology are presented examining photoexcited carrier relaxation in graphene on a silicon carbide (3C-SiC) surface. 11.

INTRODUCTIONA. Third-generation photovoltaicsGlobal oil production is expected to peak and begin declining around 2020, providing a rough timeline for a transition from fossil fuels to non-conventional energy sources [1]. Of the potential options for next-generation sources, e. g., solar, wind, geothermal, biomass, and nuclear, solar energy is a leading candidate due to the enormous amount of energy available in solar radiation (4.3×10^{20} J/hour) compared to other sources [2]. However, recent calculations indicate that current commercial solar cell efficiencies, defined as maximum generated power divided by incident power, lead to electricity prices around \$0.35

(kW-hr)?? 1 compared to \$0.02-0.05 (kW-hr)?? 1 for fossil fuels [2].

Therefore, both improvements in efficiency and manufacturing costs are mandatory before solar cells become a commercially viable renewable energy option. For a traditional single junction solar cell, the meeting of interfaces of a p-doped and n-doped material creates a depletion region that is negatively charged in the p-type material and positively charged in the n-type region. The Fermi level must match across both regions, leading to a bending of the conduction (CB) and valence (VB) bands within the depletion region and a resulting electric field [3]. Quasi Fermi levels can still be defined for the charge carrier populations in each semiconductor separately. When the p-n junction is connected to an external circuit, photoexcited electrons and the resulting holes in the depletion region move in opposite directions under the field. The photocurrent density (J_{PC}) can be defined as $J_{PC} = q \int_{E_g}^{\infty} b(E) QE(E) dE$ (I. A. 1), where q is the electron charge, $b(E)$ is the spectral photon energy, and $QE(E)$ is the quantum efficiency ($QE = 1$ when each incident photon generates one electron to the external circuit) [4]. The maximum possible photovoltage for a given p-n junction is determined by the difference in the quasi-Fermi levels of the p- and n-regions. Single junction cells, traditionally made of doped silicon or germanium, presently dominate commercial markets. Known as first-generation solar cells, they have a theoretical limiting efficiency of around 33% based on analyses done by Shockley and Queisser [5]. This efficiency limit results from several considerations: 1) blackbody radiation of the solar cell reduces the total possible energy capture; 2) radiative electron-hole recombination places an upper limit on photoexcited carrier production; 3) all photons with sub-band gap energy do not contribute to electrical energy conversion; 4) each

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absorbed photon excites a single electron; 5) each excited electron (and corresponding hole) relaxes within the CB (VB) to the band edge prior to extraction; ; and 6) non-radiative recombination is ignored. Non-radiative recombination can occur due to defects that generate impurity states within the gap (Shockley-Read-Hall recombination), electron-hole recombination that transfers energy to another electron (Auger recombination), and surface recombination. Due to the assumption that carriers relax to the band edge (5), the band gap size also plays an important role, as a very narrow gap leads to high photocurrent but low photovoltage whereas the reverse is true for a wider gap. For a single junction solar cell under the Shockley-Queisser assumptions, a 1.3 eV band gap provides the optimal 33% efficiency [5]. Decades of research in first-generation solar cells have optimized their manufacturing methods and researchers have achieved practical efficiencies up to 28% [6], but the high material costs of the necessarily pure silicon limits the possibility of continued cost decreases. As a possible solution, second-generation solar cells that use thin films several micrometers thick have spurred substantial research interest. These second-generation solar cells are typically made of copper indium gallium selenide (CIGS), cadmium telluride (CdTe), or micro-morphous silicon [7-9]. Thin film solar cells decrease costs by increasing the manufacturing unit size compared to first-generation cells, however efficiency will likely maximize around 15%, making it difficult to compete with fossil fuels at comparable electricity costs [10]. As an approach to circumvent the efficiency limits plaguing first- and second-generation solar cells, third-generation cells challenge several of the Shockley-Queisser assumptions and provide a pathway for solar cells to reach market viability. Third-generation cells

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are similar only in that their theoretical models all predict maximum efficiencies higher than the Shockley and Queisser limit. Blackbody radiation and radiative carrier recombination will always bracket efficiency limits, however each third-generation design attempts to improve one of the other cell limitations. One alternative, the tandem cell, aims to eliminate loss mechanisms due to carrier relaxation by stacking cells of increasingly larger band gaps [11]. Since electrons are still assumed to relax to the band edge prior to extraction, each cell then extracts electrons at a specific band gap energy. The combined cell results in an overall higher efficiency due to the wider possible range of photoexcited electron energies. These cells can reach theoretical efficiencies as high as 68% using four-stack cells [12], however the increased amount of materials required to reach these efficiencies limits their potential cost reductions. Intermediate band (IB), multiple exciton generation (MEG), and hot carrier (HC) solar cells are more promising third-generation designs because device fabrication would be less costly than tandem cells once optimal materials have been determined. Intermediate band designs use wide band gap semiconductors with deep level impurities to allow transitions at a wider range of photon energies. Photoexcitations can then occur from VB to IB, IB to CB, or VB to CB. If carriers are only extracted from the VB or CB, this increases the photovoltage due to the large band gap without sacrificing photocurrent, leading to efficiencies as high as 66% [13]. Multiple exciton generation (MEG) cells rely on the generation of multiple photoexcited carriers from a single photon ($QE > 1$ in Eq. 1), a mechanism recently achieved in quantum dots [10, 14] and in graphene [15]. Although both of these technologies show promise, this proposal will focus on HC solar cells and use computational methods to assess the electronic

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structure and carrier relaxation in novel materials to determine their potential use. B. Hot carrier solar cells Hot carrier cells challenge the Shockley-Queisser assumption that carriers must relax to the band edge prior to extraction to the external circuit [16]. In a traditional solar cell, photoexcited electrons undergo a series of relaxations to the band edge. Initially, electrons form a peaked excited distribution in the CB, however elastic electron-electron interactions broaden the distribution on the femtosecond (fs) timescale. This elastic interaction conserves the total energy of the photoexcited carriers, and thus no photoexcitation energy is lost. However, subsequent inelastic interactions with high-energy optical phonons on a picosecond (ps) time scale transfer energy from electrons to phonons through lattice vibrations, and the HC distribution shifts to lower energies near the band gap. In this process, the electrons then lose energy equal to the difference between their initial excitation energy and the conduction band edge, thus decreasing photovoltage and overall cell efficiency [11]. Hot carrier cells aim to extract electrons prior to this phonon-induced cooling phase by designing materials that either have low electron-phonon coupling or a large phonon band gap between the acoustic and optical phonon spectrum [17]. Since carriers are extracted prior to relaxing to the band edge, ideal absorber materials would also exhibit a minimal electronic band gap around 0.5 eV to allow maximum photoabsorbance [18]. The most common HC cooling mechanism in semiconductors is the interaction of an excited electron with a high energy optical phonon that results in two longitudinal acoustic (LA) phonons of equal energy and equal and opposite momenta, known as the Klemens mechanism [19]. If the phononic band gap between the highest LA phonon and the lowest optical phonon is greater than the

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optical phonon energy, the Klemens mechanism is inhibited and electron cooling significantly reduced. Density functional theory (DFT) studies have explored possible materials meeting the small electronic and large phononic band gap requirements, usually a result of the large difference between cation and anion masses. As an example, indium nitride (InN) meets both requirements and has also shown a slower HC cooling rate compared to gallium arsenide (GaAs) in experiment [20, 21]. However, most optimal materials require rare elements (e. g., In) that make large scale applications untenable [17]. As an alternative, recent studies [14, 22-24] have applied quantum dots (QD) as HC phot absorbers that use more earth-abundant elements. In a traditional semiconductor, a minimum photoexcitation greater than the material's band gap creates an electron-hole pair, called an exciton. These carriers, being oppositely charged, feel a weak Coulomb attraction due to dielectric screening proportional to the material's dielectric constant. The distance between the electron and hole is a material-dependent quantity known as the exciton Bohr radius, denoted as $r_e = \frac{\hbar^2 \epsilon}{e^2 (m_e + m_h)}$ (Eq. 1), where ϵ is a material's dielectric constant and m_e and m_h are the effective masses of the electron and hole, respectively [25]. If a semiconductor's radius R is now reduced to be comparable to r_e , the confinement of the charge carriers leads to discrete energy levels akin to a particle in a box. Confinement leads to an increase in the charge carriers' kinetic energy, and when the radius is small enough ($R \approx 2r_e$), the kinetic energy contributions dominate and electron-hole correlation effects can be neglected [25]. This discretization of energy levels provides a robust environment to slow hot carrier cooling due to minimal overlap between electronic states. In addition, when QDs are embedded in a host

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matrix material, the weak coupling of phonons at the interface between the matrix and embedded QD lead to miniature gaps in the phonon density of states (DOS) that can further prevent electron-phonon coupling. [17]. An important secondary component of the HC solar cell is an energy selective contact (ESC) that extracts carriers only at the average energy of the HC distribution. This allows hot carriers to cool isentropically in the ESC prior to moving to the external circuit, preventing energy loss that destroys the hot carrier effect [26]. Initial ideas for such a contact have been wide band gap semiconductors with narrow conduction and valence bands or QDs that provide a resonant tunneling mechanism for electron extraction [27]. Recent experiments have demonstrated hot carriers in a variety of QDs, including lead selenide (PbSe) nanocrystals to a titanium oxide (TiO₂) substrate [28] as well as photovoltages up to 1 volt using InAs/GaAs QDs [29]. Despite these recent successes, fundamental research into almost every part of the hot carrier design is needed to reach practical applications, specifically in the identification of earth-abundant materials that demonstrate slow carrier cooling and hot absorber-ESC tandems that can be economically manufactured. Of particular interest, studies have synthesized colloidal graphene QDs with tunable band gap and reported slow carrier cooling on the picosecond time scale [30, 31].

II. STUDY PROPOSAL

Although initial research into hot carriers suggests great potential to improve efficiency, fundamental research into new materials and interfaces is required to find better methods to exploit slow carrier cooling while keeping costs low. In this proposal, I will explore the electronic structure and intraband carrier relaxation in graphene and graphene/hexagonal boron nitride (h-BN) hybrids as potential hot carrier

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photoabsorbers. In addition, I will examine the potential for photoexcited carrier extraction from these materials by examining carrier relaxation and transfer from these materials to a silicon carbide (SiC) interface, a common substrate used to create the monolayer graphene/h-BN materials. Graphene consists of a two-dimensional honeycomb lattice of sp^2 -bonded carbon atoms. The linear dispersion of the band structure for low energies near the K-point in the Brillouin Zone (BZ) leads to electrons with zero effective mass and a host of favorable electronic properties such as high electron and hole mobility. Due to its high optical transparency (2.3% of visible light is absorbed [32]), graphene is often used as a transparent conducting electrode (TCE) in devices such as light-emitting diodes (LEDs) and solar cells. However, recent experiments have found evidence of hot photoexcited carriers in graphene that persist into the picosecond regime, suggesting graphene could be a viable photoabsorber for hot carrier cells if its optical absorption could be improved [15, 33]. Methods for achieving this suggest that sandwiching monolayer graphene between highly contrasted dielectric layers or through chemically doping its surface can theoretically lead to 50-100% optical absorption [34], however these methods are still largely theoretical. Another possibility of improving optical absorption is through the use of graphene QDs or nanoribbons. Graphene is a desirable QD material because its high dielectric constant and zero effective mass leads to an infinite exciton Bohr radius [35], indicating that quantum confinement effects could occur at any size and electron-hole correlations are minimal. A new method of creating graphene QDs has arisen due to the recent production of graphene and hexagonal boron nitride (h-BN) hybrid monolayers. Hexagonal BN has the same two-dimensional hexagonal

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structure as graphene, a similar lattice constant (2.51 Å), but has a large band gap of 5.2 eV. Films made from chemical vapor deposition (CVD) have shown hybrid layers are possible that consist of segregated regions of graphene or h-BN on the nanometer scale. Of particular interest to the current proposal, the hybrid monolayers demonstrate higher optical absorbance compared to pristine graphene and a wider range of band gaps, indicating that this hybrid material could be used as a photoabsorber in solar cells [36]. Graphene nanoribbons with widths in the nanometer scale have also been embedded in a h-BN matrix [37]. Given these recent findings, this proposal aims to understand photoexcited carrier relaxation in graphene QDs and nanoribbons within a h-BN matrix using first-principles calculations. Once we have examined intraband carrier relaxation in graphene QDs and nanoribbons in the h-BN matrix, it is important to understand the photoexcited electron transfer at interfaces that could be used in optoelectronic applications. Many experiments have demonstrated the simple and cost-effective growth of both graphene and h-BN layers on SiC [38-40], and therefore it is of great importance to understand its potential for carrier transfer and extraction. Silicon carbide is a wide band gap semiconductor that can occur in a variety of polymorphs, all of which have tetragonally coordinated Si and C atoms. Each Si or C layer is geometrically identical, however each polymorph differs by shifts of the relative positions of alternating Si and C layers. Graphene has been epitaxially grown on two polymorphs, 4H-SiC (3.0 eV band gap) and 3C-SiC (2.3 eV). Wide gap semiconductors such as these are ideal for contacts to extract hot carriers at higher energy levels. First-principles calculations along with experiment have shown that a single layer of graphene binds to the SiC

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surface and does not demonstrate any traditional graphene-like electronic properties, however a second monolayer recovers the Dirac point and linear dispersion, and the third layer demonstrates a 0.3 eV band gap [38, 41, 42]. In addition, graphene grown on Si-terminated SiC is n-doped [42].

Previous studies have shown photoexcited electron transfer from graphene to rutile titanium oxide (TiO₂). SiC has a similar electron affinity to TiO₂ [43], but the previous study indicated partial chemical bonding between the graphene and TiO₂ atoms. Since the second graphene layer on the SiC surface appears to be physisorbed with van der Waals interactions, it will be important to understand the photoexcited transfer behavior with this different type of bonding to the first graphene layer and SiC bulk. Finally, preliminary studies will be done to assess potential energy selective contacts (ESC) for carrier extraction by examining the binding energies and band structure of various QDs on the graphene/h-BN surface. We can determine optimal ESC materials by matching discrete energy levels in the ESC QD to the average hot carrier energy in the graphene QD prior to electron-phonon relaxation. This analysis could provide a guide for experimentalists to test specific material combinations. In review, the current proposal will examine the role of graphene and graphene/h-BN composites as potential photoabsorbers by: 1) comparing photoexcited carrier relaxation in pristine graphene to graphene QDs and nanoribbons embedded in a BN matrix; 2) examine photoexcited electron and hole relaxation in pristine graphene and graphene/h-BN composites to the 3C-SiC substrate; and 3) determine preliminary candidate materials for ESC for carrier extraction. III. METHODSA.

Density Functional Theory Electronic structure calculations for the graphene, graphene/h-BN, SiC, and combined systems will be carried out within the <https://assignbuster.com/electronic-structure-and-intraband-health-and-social-care-essay/>

density functional theory (DFT) formalism [44]. Beginning from the Born-Oppenheimer approximation, we assume that the electrons readjust instantaneously and adiabatically to any nuclear motion due to the comparably larger nuclear mass. Under this approximation, we can uncouple the nuclear and electron wavefunctions and treat the electrons as an interacting electron gas moving within a static potential from the nuclei. We can write the ground-state energy of a stationary electronic state as (in atomic units):

$$E = \int \psi^\dagger(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') \psi(\mathbf{r}) \psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{III. A. 2})$$

such that if either n or ψ is known, the other quantity can be found. Hohenberg and Kohn originally proved that if two systems have the same $n(\mathbf{r})$, then the potentials they feel must only differ by a constant, which does not affect the physics [45]. This important result demonstrates that the total energy is a unique functional of electron density, and for a given external potential, we can find a unique density that minimizes the energy. We can then write the expectation value of the energy as a functional of n : $E[n] = T[n] + V_{\text{nuc}}[n] + V_{\text{ee}}[n]$ (III. A. 3). The kinetic energy $T[n]$ and electron-electron $V_{\text{ee}}[n]$ functionals are universal, thus theoretically we only need to know the nuclear potential for a given system to find the electron density and wavefunction. However, T and V_{ee} contain complicated many-body physics that cannot be modeled precisely and must be dealt with using approximations. To make this situation more tractable, Kohn and Sham introduced a method that maps the interacting electron gas onto the non-interacting homogeneous electron gas, a system for which the kinetic energy, T_{nonint} is known exactly [46]. We can then write the electron wavefunction as a determinant of single-particle wavefunctions, ψ_i , known as the Kohn Sham orbitals, each with energy ϵ_i such that $\left[-\frac{1}{2} \nabla^2 + V_{\text{KS}} \right] \psi_i = \epsilon_i \psi_i$

(III. A. 4), where $V_{ks} = V_{nuc} + V_{Coul} + V_{xc}$ (III. A. 5), V_{Coul} is the electronic Coulomb repulsion and V_{xc} includes all the many-body exchange and correlation effects. The Kohn-Sham orbitals are the eigenvalues of a Hamiltonian that includes the kinetic energy of a homogeneous electron gas and an effective potential; thus, the Kohn-Sham orbitals themselves are nonphysical. However, by solving Equation III. A. 4, we can construct the electron density $n(r) = \sum_i |c_i(r)|^2$ (III. A. 6), and based on the Hohenberg-Kohn Theorem discussed above, by minimization we can find the unique density for a given external potential V_{nuc} . By placing all the unknown many-body physics in V_{xc} , the Kohn-Sham equations allow us to use approximations for the exchange and correlation terms and minimize the energy to find the ground state electron density. The ground state energy is then written as $E[n] = T_{kin}[n] + V_{nuc}[n] + V_{Coul}[n] + V_{xc}[n] = T_{kin}[n] + \int n(r)v(r)d(r) + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} dr dr'$

+

$\int n(r)v_{xc}(r)d(r)$ (III. A. 7). Since each of the terms depends on the electron density, this equation can be solved self-consistently with an approximation used for the exchange-correlation term, v_{xc} . This term includes the difference in kinetic energy between the interacting and non-interacting gas as well as the exchange and correlation electron-electron interactions. Various approximations have been developed for v_{xc} to account for exchange and correlation effects. The local density approximation (LDA) uses a functional that is proportional to the electron density [44]. This approximation can overestimate binding energies, and more recently a generalized gradient approximation (GGA) has been developed that depends

on both the density and its gradient [44, 47]. Both methods have been successful in providing accurate groundstate energies, band structure, and other quantum mechanical phenomena, however both underestimate band gaps in semiconducting and insulating materials. For the current proposal, DFT electronic structure calculations will be carried out using VASP [48, 49], a code using a plane-wave basis set to construct the Kohn-Sham orbitals. Projector augmented-wave (PAW) potentials [50, 51] will be implemented that linearly transform the quickly oscillating all-electron wavefunctions of core electrons to smooth pseudo-wavefunctions to improve computational efficiency. The PBE generalized gradient approximation [52] will be used to approximate exchange and correlation effects. Formation energies and band structure will be compared between graphene armchair QDs, zigzag QDs, and nanoribbons in a h-BN matrix both freestanding and epitaxially on the 3C-SiC interface.

B. Intraband carrier relaxation

To assess photoexcited intraband carrier relaxation in graphene and graphene/h-BN hybrids alone and at the SiC interface, we will employ a rate equation that accounts for nonadiabatic coupling between electronic states and electron-phonon interactions that mediate the relaxation process. The following discussion generally follows the physics of system relaxation and energy dissipation described in [53]. Since we are primarily concerned with electron and hole relaxation, we consider the electrons as the relevant system of interest and phonons as the reservoir. In this case, we can separate the Hamiltonian as $H = H_S + H_{S?? R} + H_R$ (III. B. 1) where H_S is the electronic system Hamiltonian, H_R is the reservoir (phonons) Hamiltonian, and $H_{S?? R}$ represents the coupling between the two systems. Within the density matrix formalism, we can consider the state of the total system and reservoir

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at any time t as a mixture of pure states $n(t)$, given by the density operator as $\hat{\rho}(t) = \sum_n p_n |n(t)\rangle \langle n(t)|$, respectively, we can write the density operator matrix elements as $\rho_{ij}(t)$. Since we are not interested in the reservoir dynamics, we integrate over the reservoir coordinates to define a reduced density matrix $\hat{\rho}^R(s, s'; t)$ that only depends on system coordinates. This is the same as taking the trace of the density operator over the reservoir coordinates (or any basis set in the reservoir space): Taking the time derivative of $\hat{\rho}^R(s, s'; t)$ and using Equation III. B. 3 above, we can write an equation of motion for the reduced density matrix: $\frac{d}{dt} \hat{\rho}^R(t) = -i \text{tr}_R([\hat{H}_S, \hat{\rho}^R(t)] - i \text{tr}_R([\hat{H}_S, \hat{\rho}^R(t)])$ (III. B. 6). where we have taken $\text{tr}_R([\hat{H}_R, \hat{\rho}^R(t)]) = 0$ and used the fact that \hat{H}_S is independent of the trace over reservoir coordinates so the commutator can be expressed with respect to the reduced density operator. We can rewrite this in the interaction representation where a given operator \hat{A} is transformed as $\hat{A}^I = U^\dagger(t-t_0) \hat{A} U(t-t_0)$, and the time evolution operator $U(t-t_0) = U_S(t-t_0) U_R(t-t_0)$. Then the equation of motion can be rewritten as $\frac{d}{dt} \hat{\rho}^I(t) = -i \text{tr}_R([\hat{H}_S, \hat{\rho}^I(t)])$ (III. B. 7). This equation demonstrates that we only need to calculate the commutation between the system-reservoir coupling and the density operator to describe the system equation of motion. To do this, we approximate the commutation using second-order perturbation theory. We consider a separable $\hat{H}_S \hat{H}_R$ interaction $\hat{H}_S \hat{H}_R = V(s) \hat{\rho}(R)$ (III. B. 8), where $V(s)$ and $\hat{\rho}(R)$ are the system and reservoir parts of the interaction. We implement two projector operators, \hat{P} and \hat{Q} , related by $\hat{P} = 1 - \hat{Q}$. The operator \hat{P} is designed to separate the density operator $\hat{\rho}(t)$ into its system and reservoir components, $\hat{P} \hat{\rho}(t) = \hat{\rho}^S \hat{\rho}^R(t)$ (III. B. 9), where we assume the reservoir component $\hat{\rho}^R$ is in thermal equilibrium and time-independent. If we apply

both projection operators to the equation of motion for $\hat{\rho}(t)$ and take the trace over reservoir coordinates, the result provides a set of coupled equations in terms of $\hat{\rho}(t)$ and $\hat{Q}^W(t)$:

$$\frac{d}{dt} \hat{\rho}(t) = -i \text{tr}_R [\hat{H} S^R, \hat{\rho} S^R + \hat{Q}^W] \quad (\text{III. B. 10}),$$

$$\frac{d}{dt} \hat{Q}^W(t) = i \text{tr}_R [\hat{H} S^R, \hat{Q}^W + \hat{Q}^W] \quad (\text{III. B. 11}).$$

We can examine the first order approximation using Eq III. B. 10 if we ignore \hat{Q}^W , however this term only leads to an energy shift and does not introduce relaxation dynamics. We can obtain the second-order perturbation by integrating the first-order approximation ($\hat{Q}^W|_0$) of Eq III. B. 11 and plugging it into Eq III. B. 10. After simplification, the second-order equation of motion can be written in the Schrodinger representation as

$$\frac{d}{dt} \hat{\rho}(t) = -i \text{tr}_R \int_0^t dt' C(t-t') [V, U S^R(t-t') \hat{\rho}(t-t') U^\dagger S^R(t-t')] - C(t) [V, U S^R(t) \hat{Q}^W(t) U^\dagger S^R(t)] \quad (\text{III. B. 12}),$$

III. B. 12 is known as the Quantum Master Equation. The first term reiterates the mean-field contribution from first-order perturbation theory. The second term describes energy dissipation and the inclusion of $C(t)$ introduces memory effects that disappear after a characteristic time τ_M that depends on the system of interest. We next rewrite the Quantum Master Equation in an energy representation and apply several approximations that will allow its use in computational analyses. If we choose $\rho_{ab}(t) = \langle a | \hat{\rho}(t) | b \rangle$ and $V_{ab} = \langle a | V | b \rangle$. In this basis, the equation simplifies by using $\hat{H} = \sum_i \epsilon_i |i\rangle \langle i|$. The equation of motion for the reduced density matrix elements becomes

$$\frac{d}{dt} \rho_{ab}(t) = -i \rho_{ab}(t) + i \int_0^t dt' (\text{diss})_{ab}(t-t') = -i \text{tr}_R \int_0^t dt' C(t-t') [V_{bc} V_{cd} \rho_{ca}(t-t') - V_{ca} V_{bd} \rho_{cb}(t-t')] - [V_{db} V_{ac} \rho_{ca}(t-t') - V_{ca} V_{db} \rho_{cb}(t-t')] \quad (\text{III. B. 14}).$$

This last term denotes the dissipative behavior of the equation of motion and will be our central concern moving forward in discussing carrier

relaxation. For a given system, we can define a time scale with minimum time step Δt to coarse-grain our time axis for the processes in which we are interested. If Δt is much larger than the memory time τ_M , we are essentially probing the system at long enough time intervals so that the correlation effects can be neglected. In this case, known as the Markov approximation, we can extend the integral limit in Equation III. B. 14 to infinity without affecting its value and approximate $\rho_{ab}(t - \tau) = \rho_{ab}(t)$. The real parts of each term in the integral of Eq III. B. 14 represent the energy dissipation of the density matrix elements relevant to the discussion of carrier relaxation. We can rewrite this equation in different notation to eventually define the relaxation rate term for an initial photoexcited state: $\frac{d\rho_{ab}}{dt}(\text{diss}) = -\frac{1}{\hbar} \sum_{cd} R_{ab; cd} \rho_{cd}(t)$ (III. B. 15), where $R_{ab; cd} = \frac{1}{\hbar} \sum_{ei} C_{ei}^{(a)} V_{be} V_{ed} + \frac{1}{\hbar} \sum_{ei} C_{ei}^{(b)} V_{ae} V_{ec} - \frac{1}{\hbar} \sum_{ei} C_{ei}^{(c)} V_{ca} V_{bd} - \frac{1}{\hbar} \sum_{ei} C_{ei}^{(d)} V_{db} V_{ac}$ (III. B. 16). Equation III. B. 16 is known as the Redfield equation, where $R_{ab; cd}$ is the Redfield tensor [54]. We are interested in electron relaxation, which is represented by population transfer between the eigenstates. This case corresponds to $a = b$ and $c = d$ in the Redfield tensor representation, such that the Redfield tensor reduces to $R_{aa; cc} = \frac{1}{\hbar} \sum_{ei} C_{ei}^{(a)} V_{ae} V_{ea} - \frac{2}{\hbar} \sum_{ei} C_{ei}^{(c)} V_{ca} V_{ac} = \frac{1}{\hbar} \sum_{ei} C_{ei}^{(a)} \omega_{ae} - \frac{1}{\hbar} \sum_{ei} C_{ei}^{(c)} \omega_{ca}$ (III. B. 17). the principle of detailed balance such that $k_{ab} = e^{-\beta \hbar \omega_{ab}} k_{ba}$, however we are only concerned with the rate describing transitions out of the initial state. If we split the first term of Eq III. B. 17 into two integrals and go to zero while taking the complex conjugate of the integrand, we can combine the two into an integral from negative to positive infinity. Taking the Fourier transform, the transition rate is $k_{ab} = \text{Re} \frac{1}{\hbar} \sum_{ei} V_{ab} V_{ba} C_{ei}^{(a)}(\omega_{ab}) = \text{Re} \frac{1}{\hbar} \sum_{ei} V_{ab} V_{ba} C_{ei}^{(a)}(\omega_{ab})$

$\frac{1}{2} \sum_{ab} |V_{ab}|^2 C_{ab}(t)$ (III. B. 18). A second case exists when $\omega_a = \omega_b$, $\gamma_a = \gamma_b$, and $\omega_a = \omega_b$, which represents damping rates for the off-diagonal matrix elements of $\rho_{ab}(t)$. These off-diagonal elements represent phase differences between the energy eigenstates and are referred to as coherences, however they will not be the focus of the current proposal. We also assume that there is no coupling between population transfer and coherence processes, known as the secular approximation. Finally, we treat the correlation function $C_{ab}(t)$ within the harmonic oscillator approximation such that the reservoir coupling component is $\rho(Z) = \sum_l |c_l|^2 \rho_l(Z)$ (III. B. 19), where q_l are harmonic coordinates and c_l are the coupling constants. Using this formulation, it can be shown [53] that the reservoir correlation function reduces to $C_{ab}(t) = \frac{2}{\hbar} \sum_{\mathbf{h}} \frac{P(\mathbf{h})}{\omega_{\mathbf{h}}}$ (III. B. 20), where $n(\omega)$ is the Bose-Einstein distribution function and $P(\omega)$ is the phonon density of states (DOS). Substituting this expression into Eq III. B. 18, the rate equation becomes $\dot{\rho}_{ab} = \frac{2}{\hbar} \sum_{\mathbf{h}} |V_{ab}|^2 (n(\omega_{\mathbf{h}}) + 1) P(\omega_{\mathbf{h}})$ (III. B. 21), which is the central equation we will be using in the current proposal. Since we are only interested in the diagonal terms of density matrix when considering population transfer, we can write a simple differential equation $\dot{\rho}_{aa} = -\rho_{ab} \gamma_{bb}(t)$ (III. B. 22). Equations III. B. 21 and III. B. 22 provide an intuitive interpretation of how intraband phonon-assisted relaxation is calculated. For two given states, the nonadiabatic system-coupling term $\frac{1}{2} \sum_{ab} |V_{ab}|^2$ provides a measure of state overlap that will increase the likelihood of such a transition occurring. However, this is weighted by the phonon density of states, such that there must be an available phonon equal to the transition energy ω_{ab} for the given transition to occur. If we consider an initial photoexcitation as a pure state in the density matrix formalism, then we can set our initial condition by setting the

matrix element corresponding to the photoexcited state equal to one and the rest to 0. We can then solve Eq III. B. 22 with this initial condition to determine the carrier relaxation to all other states for a given photoexcited state. We will use Eq III. B. 21 to compute relaxation rates for the systems discussed within this proposal. Therefore, we need to compute $\langle j | V_{ab} | j \rangle$ and $P(|ab\rangle)$ using computational methods. Referring to Eq III. B. 18, we determine V_{ab} , the system coupling component, by calculating the nonadiabatic coupling between electronic states. This coupling is calculated by performing quantum molecular dynamics (MD) of the system using the Verlet velocity algorithm [55] in VASP and calculating the overlap of eigenstates at adjacent time steps. For $\langle j | V_{ab} | j \rangle = \frac{1}{N} \sum_{i=1}^N \langle \psi_i^j(t) | \psi_i^j(t+\Delta t) \rangle$ (III. B. 23) where Δt is the simulation time step and N is the total number of time steps. The system is annealed to 300K using an NVT ensemble and then simulated within the microcanonical ensemble until the matrix elements $\langle j | V_{ab} | j \rangle$ converge to stable values. The phonon DOS will be calculated using the frozen phonon method in VASP, in which each atom is displaced by 0.015 Å and the resulting forces on all other atoms are calculated to calculate the force constants and subsequent frequencies. Gaussian broadening of the phonon DOS is used when calculating photoexcited relaxation, which provides a rough representation of the existence of rarer multiphonon processes that can assist relaxation at higher transition energies. Using this method, we will compare photoexcited carrier relaxation in pristine graphene to that in graphene QDs and nanoribbons embedded in the h-BN matrix. We define photoexcited states as those with the largest oscillator strengths between normalized occupied and unoccupied states, defined as $\frac{1}{\sqrt{2}} \langle \psi_i^a | \hat{p} | \psi_j^b \rangle$

$b > 2$, where m_e is the electron mass and \hat{p} is the momentum operator.

Starting from this pure photoexcited state, we then solve the differential equation and measure the time taken for the excited electron and corresponding hole to relax to the conduction and valence band edges, respectively. After analyzing relaxation for freestanding monolayers, we will examine the same structures at the 3C-SiC interface to understand carrier transfer mechanisms.

IV. PRELIMINARY RESULTS

The preliminary results demonstrate the feasibility of the proposed study of electronic structure and intraband carrier relaxation in graphene-SiC structures. In particular, we report initial results looking at photoexcited carrier relaxation in pristine graphene at the C-terminated 3C-SiC interface (Figure 1).

FIG. 1. Interface between the C-terminated, 3C silicon carbide polymorph and two graphene layers. Small, brown sphere and large, blue spheres represent C and Si, respectively. The Si-terminated interface has a similar structure with a 2 Å bond length between surface Si and graphene C atoms. As shown in previous studies [42], the first epitaxial graphene layer binds to the SiC surface 1.65 Å above the bulk C atom. The second graphene layer is 3.35 Å above the first and recovers pristine graphene band structure, including the Dirac point at the K point (Figure 2(a)). Unbonded SiC carbon atoms at the surface lead to the Fermi level. For Si-terminated 3C-SiC surfaces, a similar physical structure results, however the bond length between the Si surface atom and the graphene C atom extends to 2 Å. The second graphene layer again recovers its traditional band structure, however it is now n-doped (Figure 2(b)). This difference in electronic structure could have a significant impact on dominant transition dipole moments for photoexcitation and subsequent carrier relaxation, which will be further explored. At this

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time, I report carrier relaxation results only for the C-terminated SiC-graphene interface that leaves the second graphene layer undoped. FIG. 2. Band structure for C- and Si-terminated graphene-SiC interface along high-symmetry k -point paths. a) C-terminated SiC; b) Si-terminated SiC. Note that the near the Dirac point arises due to dangling bonds at the SiC surface. For the present results, we only examine photoexcitation and carrier relaxation at the K -point. Further developments in the code will allow for averaging over k -points to provide a more representative picture of carrier relaxation. However, the smallest required photoexcited energies occur at the K -point and provide an important characterization of electron relaxation. Initial photoexcited states were chosen as those states with the largest oscillator strengths with the initial state at the Dirac point. Several possible photoexcitations are chosen to describe qualitative differences in the photoexcited states based on their localization either on the graphene or SiC. The first photoexcited state (PE1) has the majority of its charge density residing on the second graphene layer (Figure 3(a)), the second (PE2) is mixed between the graphene and SiC (Figure 3(b)), the third (PE3) is largely in SiC (Figure 3(c)), and the last (PE4) largely resides on the first graphene layer (Figure 3(d)). By comparing relaxation rates between these examples, we can study the effect of localization on relaxation and carrier extraction. We next calculate the carrier relaxation for each chosen PE state. As shown in Figure 4, we can visualize the relaxation in both real (top row) and energy (bottom row) for each photoexcitation. In real space, the initial and subsequent states are projected along the z -axis of the structure to visualize localization at each layer over time. Figures 4(a) and 4(b) show similar relaxation patterns since both PE states (PE1 and PE2) are localized

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at least 17 FIG. 3. Charge density isosurfaces (yellow) and cross-sections (red) for sampled photoexcited states (PE) overlaid on the graphene-SiC structure. a) PE localized to graphene layers (PE1); b) PE spread across graphene and SiC (PE2); c) PE localized to SiC (PE3); d) PE localized to the first graphene layer (PE4). partially on the second graphene layer. As seen in the energy space, these photoexcitations broaden to include other available bands in the femtosecond time range, which corresponds to the renormalization of the hot carrier distribution [11] and has been experimentally identified previously in graphene [56]. This hot carrier distribution persists into the picosecond range, at which point they relax to the SiC surface and the dangling bond impurity state. These results indicate the potential for hot carrier extraction prior to phonon-initiated carrier cooling. Photoexcited states localized either on the SiC or the first graphene layer (Figures 4(c)-(d)) do not demonstrate a similar hot carrier distribution across the femtosecond timescale and relax more quickly to the SiC surface. FIG. 4. Photoexcited carrier relaxation within real (top row) and energy (bottom row) space for each of the chosen photoexcited states. The graphene-SiC structure on the right aligns with the z-axis of the graphs in the first row to help visualize the electron relaxation pathway. a) PE1; b) PE2; c) PE3; and d) PE4. 18 Across all PE states, the photoexcited electron relaxes to the second graphene layer before relaxing to the impurity state, indicating that 3C-SiC does not act as an electron acceptor at this interface. However, the graphene hot carrier distribution does persist long enough that, if an ESC material were adsorbed to the graphene surface, these hot carriers may be extracted prior to phonon cooling. This situation requires further investigation and will be included in the proposed study. In addition, current analyses are being done to <https://assignbuster.com/electronic-structure-and-intraband-health-and-social-care-essay/>

determine photoexcited hole behavior at the interface. V. CONCLUSIONS AND

FUTURE WORK In conclusion, the proposed study aims to understand

photoexcited electron and hole relaxation in pristine graphene as well as

graphene QDs and nanoribbons embedded in a hexagonal boron nitride

matrix. The study will use computational methods based on energy

dissipation theory to model electron-phonon coupling and to calculate

relaxation rates for photoexcited carriers. Photoexcited carrier relaxation will

be examined on freestanding graphene QD/h-BN surfaces and subsequently

at the SiC interface to determine photoexcited charge transfer mechanisms.

Once this interface is well understood, energy selective contact (ESC) materi-

als will be tested at the graphene surface. Preliminary results suggest that

SiC does not act as an electron acceptor, and therefore electron accepting

materials will be initially studied as ESC candidates. It is important to note

that the current computational methodology does not take into account all

relaxation methods and does not explicitly account for multiphonon

processes. As discussed in the proposal, electron-hole correlation effects

should be minimal in graphene QDs, however an inclusion of this interaction

could confirm this and extend the methodology to QDs where this coupling is

important. Other future work in this area could include accounting for explicit

multiphonon processes, electron-phonon interactions that change

the electron's momentum, and extending this methodology to include

photoexcitation and relaxation at multiple k-points. In addition, the inclusion

of other electron-electron interactions such as impact ionization would

provide a more complete analysis of electron relaxation and allow the study

of multiple exciton generation within the same framework. Finally, the

graphene-SiC interface is a prime candidate for intermediate band (IB)

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solarcell design when SiC is doped with boron, aluminum, or nickel to create deep donor and acceptor levels. Therefore, future research will include examining the electronic structure of the doped SiC-graphene interface and calculating electron relaxation and charge transfer. Non-radiative recombination via the impurity states is an important limiting relaxation process in IB cells, and therefore we will use DFT calculations to understand the non-radiative transition energies using various dopants to determine optimal doping materials. Acknowledgments I am extremely grateful to Dr. Hai-Ping Cheng for her guidance and support in the development of this proposal and to Dr. Dmitri Kilin for his guidance in using the nonadiabatic coupling code. I would also like to thank The Quantum Theory Project, University of Florida High Performance Computing (UFHPC), and The National Energy Research Scientific Computing Center (NERSC) for computational resources.

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