

# [Electronic structure and intraband health and social care essay](https://assignbuster.com/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 e#ciency compared torst generation and secondgeneration thinlm cells. In particular, hot carrier solar cells provide a pathway to high e#ciencywithout increased device complication if optimal materials can be designed with slow hot carriercooling. In this proposal, I discuss the potential for graphene quantum dots and nanoribbonsembedded in a hexagonal boron nitride matrix to act as hot carrier photoabsorbers. Densityfunctional theory is implemented to calculate the electronic structure of these systems. In addition, the theory of energy dissipation is discussed that models irreversible energysystem due to coupling with the phonon reservoir. Computational methods are used to calculatethe relaxation rate of an initially photoexcited state via electron-phonon coupling that providesa measure of hot carrier cooling in the systems of interest. Preliminary results demonstratingthe methodology are presented examining photoexcited carrier relaxation in graphene on a siliconcarbide (3C-SiC) surface. 1I. INTRODUCTIONA. Third-generation photovoltaicsGlobal oil production is expected to peak and begin declining around 2020, providing arough timeline for a transition from fossil fuels to non-conventional energy sources [1]. Ofthe 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 energyavailable in solar radiation (4. 3x1020 J/hour) compared to other sources [2]. However, recentcalculations indicate that current commercial solar cell e#ciencies, dened as maximumgenerated 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 improvementsin e#ciency and manufacturing costs are mandatory before solar cells become a commerciallyviable 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 materialand 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 depletionregion and a resulting electriceld [3]. Quasi Fermi levels can still be dened for the chargecarrier populations in each semiconductor separately. When the p-n junction is connectedto an external circuit, photoexcited electrons and the resulting holes in the depletion regionmove in opposite directions under the ineld. The photocurrent density(JPC) can be dened asJPC = qREGb(E)QE(E)dE (I. A. 1), where q is the electron charge, b(E) is the spectral photonenergy, and QE(E) is the quantum e#ciency (QE= 1 when each incident photon generatesone electron to the external circuit) [4]. The maximum possible photovoltage for a givenp-n junction is determined by di#erence in the quasi-Fermi levels of the p- and n-regions. Single junction cells, traditionally made of doped silicon or germanium, presently dom-inate commercial markets. Known asrst-generation solar cells, they have a theoreticallimiting e#ency of around 33% based on analyses done by Shockley and Queisser [5]. Thise#ciency limit results from several considerations: 1) blackbody radiation of the solar cellreduces the total possible energy capture; 2) radiative electron-hole recombination places an2upper limit on photoexcited carrier production; 3) all photons with sub-band gap energydo not contribute to electrical energy conversion; 4) each absorbed photon excites a singleelectron; 5) each excited electron (and corresponding hole) relaxes within the CB (VB) tothe 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 thegap (Shockley-Read-Hall recombination), electron-hole recombination that transfers energyto another electron (Auger recombination), and surface recombination. Due to the assump-tion that carriers relax to the band edge (5), the band gap size also plays an importantrole, as a very narrow gap leads to high photocurrent but low photovoltage whereas thereverse is true for a wider gap. For a single junction solar cell under the Shockley-Queisserassumptions, a 1. 3 eV band gap provides the optimal 33% e#ciency [5]. Decades of research intorst-generation solar cells have optimized their manufacturingmethods and researchers have achieved practical e#encies up to 28% [6], but the high ma-terial costs of the necessarily pure silicon limits the possibility of continued cost decreases. As a possible solution, second-generation solar cells that use thinlms several microme-ters thick have spurred substantial research interest. These second-generation solar cells aretypically made of copper indium gallum selenide (CIGS), cadium telluride (CdTe), or micro-morphous silicon [7{9]. Thinlm solar cells decrease costs by increasing the manufacturingunit size compared torst-generation cells, however e#ciency will likely maximize around15%, making it di#cult to compete with fossil fuels at comparable electricity costs [10]. As an approach to circumvent the e#ency limits plaguingrst- and second-generationsolar cells, third-generation cells challenge several of the Shockley-Queisser assumptionsand provide a pathway for solar cells to reach market viability. Third-generation cells aresimilar only in that their theroetical models all predict maximum e#ciencies higher than theShockley and Queisser limit. Blackbody radiation and radiative carrier recombination willalways bracket e#ciency limits, however each third-generation design attempts to improveone of the other cell limitations. One alternative, the tandem cell, aims to eliminate loss mechanisms due to carrier relax-ation by stacking cells of increasingly larger band gaps [11]. Since electrons are still assumedto relax to the band edge prior to extraction, each cell then extracts electrons at a specicband gap energy. The combined cell results in an overall higher e#ciency due to the widerpossible range of photoexcited electron energies. These cells can reach theoretical e#ciences3as high as 68% using four-stack cells [12], however the increased amount of materials requiredto reach these e#ciencies limits their potential cost reductions. Intermediate band (IB), multiple exciton generation (MEG), and hot carrier (HC) solarcells are more promising third-generation designs because device fabrication would be lesscostly than tandem cells once optimial materials have been determined. Intermediate banddesigns use wide band gap semiconductors with deep level impurities to allow transitions at awider range of photon energies. Photoexcitations can then occur from VB to IB, IB to CB, orVB to CB. If carriers are only extracted from the VB or CB, this increases the photovoltagedue to the large band gap without sacricing photocurrrent, leading to e#ciencies as highas 66% [13]. Multiple exciton generation (MEG) cells rely on the generation of multiplephotoexcited carrier from a single photon (QE > 1 in Eq I. A. 1), a mechanism recentlyachieved in quantum dots [10, 14] and in graphene [15]. Although both of these technologiesshow promise, this proposal will focus on HC solar cells and use computational methods toassess the electronic structure and carrier relaxation in novel materials to determine theirpotential use. B. Hot carrier solar cellsHot carrier cells challenge the Shockley-Queisser assumption that carriers must relax tothe 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, electronsform a peaked excited distribution in the CB, however elastic electron-electron interactionsbroaden the distribution on the femtosecond (fs) timescale. This elastic interaction con-serves the total energy of the photoexcited carriers, and thus no photoexcitation energy islost. However, subsequent inelastic interactions with high-energy optical phonons on a fs topicosecond (ps) time scale transfer energy from electrons to phonons through lattice vibra-tions, and the HC distribution shifts to lower energies near the band gap. In this process, the electrons then lose energy equal to the di#erence between their initial excitation energyand the conduction band edge, thus decreasing photovoltage and overall cell e#ciency [11]. Hot carrier cells aim to extract electrons prior to this phonon-induced cooling phase by de-signing materials that either have low electron-phonon coupling or a large phonon band gapbetween the acoustic and optical phonon spectrum [17]. Since carrier are extracted prior torelaxing to the band edge, ideal absorber materials would also exhibit a minimal electronic4band gap around 0. 5 eV to allow maximum photoabsorbance [18]. The most common HC cooling mechanism in semiconductors is the interaction of an ex-cited 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 Klemensmechanism [19]. If the phononic band gap between the highest LA phonon and the lowestoptical phonon is greater than the optical phonon energy, the Klemens mechanism is in-hibited and electron cooling signicantly reduced. Density functional theory (DFT) studieshave explored possible materials meeting the small electronic and large phononic band gaprequirements, usually a result of the large di#erence between cation and anion masses. Asan example, indium nitride (InN) meets both requirements and has also shown a slowerHC 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 applicationsuntenable [17]. As an alternative, recent studies [14, 22{24] have applied quantum dots (QD) as HCphotabsorbers that use more earth-abundant elements. In a traditional semiconductor, aminimum 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 attractiondue to dielectric screening proportional to the material's dielectric constant. The distancebetween the electron and hole is a material-dependent quality known as the exciton bohrradius, dened asre = #h2#e2 ( 1me+ 1mh) (I. B. 1), where # is a material's dielectric constant and me and mh are the e#ective masses ofthe electron and hole, respectively [25]. If a semiconductoR2s radius R is now reduced tobe comparable to re, the connement of the charge carriers leads to discrete energy levelsakin to a particle in a box. Connement leads to an increase in the charge carriers2 kineticenergy, and when the radius is small enough (R # 2re), the kinetic energy contributionsdominate and electron-hole correlation e#ects can be neglected [25]. This discretizationof energy levels provides a robust environment to slow hot carrier cooling due to minimaloverlap between electronic states. In addition, when QDs are embedded in a host matrixmaterial, the weak coupling of phonons at the interface between the matrix and embeddedQD lead to miniature gaps in the phonon density of states (DOS) that can further preventelectron-phonon coupling. [17]. 5An 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 allowshot carriers to cool isentropically in the ESC prior to moving to the external circuit, pre-venting energy loss that destroys the hot carrier e#ect [26]. Initial ideas for such a contacthave been wide band gap semiconductors with narrow conduction and valence bands or QDsthat provide a resonant tunneling mechanism for electron extraction [27]. Recent experiments have demonstrated hot carriers in a variety of QDs, including leadsu(CdSe) [24]. In addition, hot electron transfer has been shown from lead selenide (PbSe)nanocrystals to a titanium oxide (TiO2) substrate [28] as well as photovoltages up to 1 voltusing InAs/GaAs QDs [29]. Despite these recent successes, fundamental research into almostevery part of the hot carrier design is needed to reach practical applications, specically inthe identication of earth-abundant materials that demonstrate slow carrier cooling andhot absorber-ESC tandems that can be economically manufactured. Of particular interest, studies have synthesized colloidal graphene QDs with tunable band gap and reported slowcarrier cooling on the picosecond time scale [30, 31]. II. STUDY PROPOSALAlthough initial research into hot carriers suggests great potential to improve e#ciency, fundamental research into new materials and interfaces is required tond better methodsto exploit slow carrier cooling while keeping costs low. In this proposal, I will explore theelectronic structure and intraband carrier relaxation in graphene and graphene/hexagonalboron nitride (h-BN) hybrids as potential hot carrier photoabsorbers. In addition, I willexamine the potential for photoexcited carrier extraction from these materials by examiningcarrier relaxation and transfer from these materials to a silicon carbide (SiC) interface, acommon substrate used to create the monolayer graphene/h-BN materials. Graphene consists of a two-dimensional honeycomb lattice of sp2-bonded carbon atoms. The linear dispersion of the band structure for low energies near the K-point in the Bril-louin Zone (BZ) leads to electrons with zero e#ective mass and a host of favorable electronicproperties 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 conducting6electrode (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 per-sist into the picosecond regime, suggesting graphene could be a viable photoabsorber forhot carrier cells if its optical absorption could be improved [15, 33]. Methods for achiev-ing this suggest that sandwiching monolayer graphene between highly contrasted dielectriclayers or through chemically doping its surface can theoretically lead to 50-100% opticalabsorption [34], however these methods are still largely theoretical. Another possibility of improving optical absorption is through the use of graphene QDsor nanoribbons. Graphene is a desirable QD materials because its high dielectric constantand zero e#ective mass leads to an innite exciton bohr radius [35], indicating that quantumconnement e#ects could occur at any size and electron-hole correlations are minimal. A newmethod of creating graphene QDs has arisen due to the recent production of graphene andhexagonal boron nitride (h-BN) hybrid monolayerlms. Hexagonal BN has the same two-dimensional hexagonal structure as graphene, a similar lattice constant (2. 51 #Avs. 2. 47 #Aingraphene), 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 grapheneor h-BN on the nanometer scale. Of particular interest to the current proposal, the hybridmonolayers demonstrate higher optical absorbance compared to pristine graphene and a widerange of band gaps, indicating that this hybrid material could be used as a photoabsorberin solar cells [36]. Graphene nanoribbons with widths in the nanometer scale have alsobeen embedded in a h-BN matrix [37]. Given these recentndings, this proposal aims tounderstand photoexcitd carrier relaxation in graphene QDs and nanoribbons within a h-BNmatrix usingrst-principles calculations. Once we have examined intraband carrier relaxation in graphene QDs and nanoribbonsin the h-BN matrix, it is important to understand the photoexcited electron transfer atinterfaces that could be used in optoelectronic applications. Many experiments have demon-strated the simple and cost-e#ective 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 andextraction. Silicon carbide is a wide band gap semiconductor that can occur in a variety ofpolymorphs, all of which have tetragonally coordinated Si and C atoms. Each Si or C layeris geometrically identical, however each polymorph di#ers by shifts of the relative positionsof alternating Si and C layers. Graphene has been epitaxially grown on two polymorphs, 74H-SiC (3. 0 eV band gap) and 3C-SiC (2. 3 eV). Wide gap semiconductors such as these areideal for contacts to extract hot carriers at higher energy levels. First-principles calculations along with experiment have shown that a single layer ofgraphene binds to the SiC surface and does not demonstrate any traditional graphene-likeelectronic properties, however a second monolayer recovers the Dirac point and linear disper-sion, and the third layer demonstrates a 0. 3 eV band gap [38, 41, 42]. In addition, graphenegrown on Si-terminated SiC is n-doped [42]. Previous studies have shown photoexcitedelectron transfer from graphene to rutile titanium oxide (TiO2). SiC has a similar electrona#nity to TiO2 [43], but the previous study indicated partial chemical bonding betweenthe graphene and TiO2 atoms. Since the second graphene layer on the SiC surface appearsto be physisorbed with van der Waals interactions, it will be important to understand thephotoexcited transfer behavior with this di#erent type of bonding to therst graphene layerand SiC bulk. Finally, preliminary studies will be done to assess potential energy selectivecontacts (ESC) for carrier extraction by examining the binding energies and band structureof various QDs on the graphene/h-BN surface. We can determine optimal ESC materialsby matching discrete energy levels in the ESC QD to the average hot carrier energy in thegraphene QD prior to electron-phonon relaxation. This analysis could provide a guide forexperimentalists to test specic material combinations. In review, the current proposal will examine the role of graphene and graphene/h-BNcomposites as potential photoabsorbers by: 1) comparing photoexcited carrier relaxation inpristine graphene to graphene QDs and nanoribbons embedded in a BN matrix; 2) examinephotoexcited electron and hole relaxation in pristine graphene and graphene/h-BN compos-ites to the 3C-SiC substrate; and 3) determine preliminary candidate materials for ESC forcarrier extraction. III. METHODSA. Density Functional TheoryElectronic structure calculations for the graphene, graphene/h-BN, SiC, and combinedsystems will be carried out within the density functional theory (DFT) formalism [44]. Be-ginning from the Born-Oppenheimer approximation, we assume that the electrons readjust8instantaneously and adiabatically to any nuclear motion due to the comparably larger nu-clear mass. Under this approximation, we can uncouple the nuclear and electron wavefunc-tions and treat the electrons as an interacting electron gas moving within a static potentialfrom the nuclei. We can write the ground-state energy of a stationary electronic state as (inatomic units):[-#Ni(1/2)r2i+ #Niv(ri) + #Ni ... R\*(r... rN)(r... rN)dr2... drN (III. A. 2), such that if either n or is known, the other quantity can be found. Hohenberg andKohn originally proved that if two systems have the same n(r), then the potentials they feelmust only di#er by a constant, which does not a#ect the physics [45]. This important resultdemonstrates that the total energy is a unique functional of electron density, and for a givenexternal potential, we cannd a unique density that minimizes the energy. We can thenwrite the expectation value of the energy as a functional of n: E[n] = T[n] + Vnuc[n] + Vee[n] (III. A. 3). The kinetic energy T[n] and electron-electron Vee[n] functionals are universal, thus theo-retically we only need to know the nuclear potential for a given system tond the electron9density and wavefunction. However, T and Vee, contain complicated many-body physicsthat cannot be modeled precisely and must be dealt with using approximations. To makethis situation more tractable, Kohn and Sham introduced a method that maps the interact-ing electron gas onto the non-interacting homogeneous electron gas, a system for which thekinetic energy, Tnonint is known exactly [46]. We can then write the electron wavefunction asa determinant of single-particle wavefunctions, #i, known as the Kohn Sham orbitals, eachwith energy #i such that#i(-(1/2)r2 + Vks)#i = #i#i#i (III. A. 4), whereVks = Vnuc + VCoul + Vxc (III. A. 5), VCoul is the electronic Coulomb repulsion and Vxc includes all the many-body exchangeand correlation e#ects. The Kohn-Sham orbitals are the eigenvalues of a Hamiltonian thatincludes the kinetic energy of a homogeneous electron gas and actitious e#ective potential; thus, the Kohn-Sham orbitals themselves are nonphysical. However, by solving EquationIII. A. 4, we can construct the electron density asn(r) = #Nij#i(r)j2 (III. A. 6), and based on the Hohenberg-Kohn Theorem discussed above, by minimization we cannd the unique density for a given external potential Vnuc. By placing all the unknownmany-body physics in Vxc, the Kohn-Sham equations allow us to use approximations for theexchange and correlation terms and minimize the energy tond the ground state electrondensity. The ground state energy is then written asE[n] = Tnonint[n] + Vnuc[n] + VCoul[n] + Vxc[n] = Tnonint[n] +Rn(r)v(r)d(r) +R n(r)n(r2)jr?? r2j drdr2

## +

Rn(r)vxc(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, vxc. This termincludes the di#erence in kinetic energy between the interacting and non-interacting gas aswell as the exchange and correlation electron-electron interactions. Various approximationshave been developed for vxc to account for exchange and correlation e#ects. The local densityapproximation (LDA) uses a functional that is proportional to the electron density [44]. This approximation can overestimate binding energies, and more recently a generalizedgradient approximation (GGA) has been developed that depends on both the density andits gradient [44, 47]. Both methods have been successful in providing accurate groundstate energies, band structure, and other quantum mechanical phenomena, however both10underestimate band gaps in semiconducting and insulating materials. For the current proposal, DFT electronic structure calculations will be carried out us-ing VASP [48, 49], a code using a plane-wave basis set to construct the Kohn-Sham or-bitals. Projector augmented-wave (PAW) potentials [50, 51] will be implemented that lin-early transform the quickly oscillating all-electron wavefunctions of core electrons to smoothpseudo-wavefunctions to improve computational e#ciency. The PBE generalized gradientapproximation [52] will be used to approximate exchange and correlation e#ects. Forma-tion energies and band structure will be compared between graphene armchair QDs, zigzagQDs, and nanoribbons in a h-BN matrix both freestanding and epitaxially on the 3C-SiCinterface. B. Intraband carrier relaxationTo assess photoexcited intraband carrier relaxation in graphene and graphene/h-BN hy-brids alone and at the SiC interface, we will employ a rate equation that accounts fornonadiabatic coupling between electronic states and electron-phonon interactions that me-diate the relaxation process. The following discussion generally follows the physics of systemrelaxation and energy dissipation described in [53]. Since we are primarily concerned with electron and hole relaxation, we consider theelectrons as the relevant system of interest and phonons as the reservoir. In this case, wecan separate the Hamiltonian asH = HS + HS?? R + HR (III. B. 1)where HS is the electronic system Hamiltonian, HR is the reservoir (phonons) Hamilto-nian, and HS?? R represents the coupling between the two systems. Within the density matrixformalism, we can consider the state of the total system and reservoir at any time t as amixture of pure states n(t), given by the density operator as^#(t) = #npnjn(t)> , respectively, we can write the density operator matrix elements as11Since we are not interested in the reservoir dynamics, we integrate over the reservoircoordinates to dene a reduced density matrix #^R(s, s2; t) that only depends on system co-ordinates. This is the same as taking the trace of the density operator over the reservoircoordinates (or any basis set in the reservoir space): Taking the time derivative of #^R(s, s2; t) and using Equation III. B. 3 above, we can writean equation of motion for the reduced density matrix:@#^R(t)@t = - i#h[HS,#^R(t)] - i#htrR([HS?? R, ^#(t)]) (III. B. 6). where we have taken trR([HR, ^#(t)]) = 0 and used the fact that HS is independent ofthe trace over reservoir coordinates so the commutator can be expressed with respect tothe reduced density operator. We can rewrite this in the interaction representation where agiven operator A^ is transformed as A^I = Uy0(t-t0)AU0(t-t0), and the time evolution operatorU0(t-t0) = US(t-t0)UR(t-t0). Then the equation of motion can be rewritten as@ ^#IR(t)@t = - i#htrR([HIS?? R, ^#I (t)]) (III. B. 7). This equation demonstrates that we only need to calculate the commutation betweenthe system-reservoir coupling and the density operator to describe the system equationof motion. To do this, we approximate the commutation using second-order perturbationtheory. We consider a separable HS?? R interactionHS?? R = V(s)#(R) (III. B. 8), where V(s) and #(R) are the system and reservoir parts of the interaction. We implementtwo projector operators, ^ P and ^Q, related by ^ P = 1 - ^Q. The operator ^ P is designed toseparate the density operator ^#(t) into its system and reservoir components,^ P ^#(t) = ^R#^R(t) (III. B. 9), where we assume the reservoir component ^Ris in thermal equilibrium and time-independent. If we apply both projection operators to the equation of motion for ^#I(t)and take the trace over reservoir coordinates, the result provides a set of coupled equationsin terms of #I(t) and ^Q^WI (t):@#^RI (t)@t = - i#htrR([HIS?? R, ^R#^RI + ^Q^#I ] (III. B. 10), and@ ^Q^#I@t = i#h^Q([HIS?? R, ^R#^RI + ^Q^#I ] (III. B. 11). We can examine therst order approximation using Eq III. B. 10 if we ignore ^Q^#I , howeverthis term only leads to an energy shift and does not introduces relaxation dynamics. We can12obtain the second-order perturbation by integrating therst-order of approximation (^Q^#I! 0) of Eq III. B. 11 and plugging it into Eq III. B. 10. After simplication, the second-orderequation of motion can be written in the Schrodinger representation as@#^R(t)@t = - i#h2R t?? t00 d# (C(# )[V, US(# )V#^R(t - # )UyS(# )] - C#(# )[V, US(# )#^R(t- #)VUyS(# )]) (III. B. 12), III. B. 12 is known as the Quantum Master Equation. Therst term reiterates the mean-eldcontribution fromrst-order perturbation theory. The second term describes energy dissipa-tion and the inclusion of C(t) introduces memory e#ects that disappear after a characteristictime #M that depends on the system of interest. We next rewrite the Quantum Master Equation in an energy representation and applyseveral approximations that will allow its use in computational analyses. If we choose= < aj#^R(t)j b> and Vab = < ajVj b>. In this basis, the equation simplies by using?? iEa##h . The equation of motion for the reduced densitymatrix elements becomes@#ab@t = - i! ab#ab + i@t (diss) (III. B. 13), where@#ab@t (diss) = -#cdR t?? t00 d# ( 1#h2 C(-#)VbcVcdei! da##ac(t - # ) - 1#h2 C(#)VacVcd(# )ei! db##db(t - # ) -[ 1#h2 C(-#)VcaVbdei! db# + 1#h2 C(#)VdbVacei! ca# ]#cd(t - # )) (III. B. 14). This last term denes the dissipative behavior of the equation of motion and will be ourcentral concern moving forward in discussing carrier relaxation. For a given system, wecan dene a time scale with minimum time step #t to coarse-grain our time axis for theprocesses in which we are interested. If #t is much larger than the memory time #M, we areessentially probing the system at long enough time intervals so that the correlation e#ectscan be neglected. In this case, known as the Markov approximation, we can extend theintegral limit in Equation III. B. 14 to innity without a#ecting its value and approximate#ab(t - # ) = #ab(t). The real parts of each term in the integral of Eq III. B. 14 represent the energy dissipationof the density matrix elements relevant to the discussion of carrier relaxation. We can rewritethis equation in di#erent notation to eventually dene the relaxation rate term for an initialphotoexcited state:@#ab@t (diss) = -#cdRab; cd#cd(t) (III. B. 15), 13whereRab; cd = #ac#eReR10 d# ei! de# 1#h2 C(#)VbeVed + #bd#eReR10 d# ei! ce# 1#h2 C(#)VaeVec -ReR10 d# ei! db# 1#h2 C(#)VcaVbd - ReR10 d# ei! ca# 1#h2 C(#)VdbVac (III. B. 16). Equation III. B. 16 is known as the Redeld equation, where Rab; cd is the Redeld ten-sor [54]. We are interested in electron relaxation, which is represented by population trans-fer between the eigenstates. This case corresponds to a= b and c= d in the Redeld tensorrepresentation, such that the Redeld tensor reduces toRaa; cc = 2#ac#eReR10 d# ei! ae# 1#h2 C(#)VaeVea - 2ReR10 d# ei! ca# 1#h2 C(#)VcaVac = #ac#ekae - kca(III. B. 17). the principle of detailed balance such that kab = e#h! ab= kBT kba, however we are only concernedwith therst rate describing transitions out of the initial state. If we split therst termof Eq III. B. 17 into two integrals andnity to zero whiletaking the complex conjugate of the integrand, we can combine the two into an integralfrom negative to positive innity. Taking the Fourier transform, the transition rate iskab = Re 1#h2VabVbaC(! ab) = Re 1#h2 jVabj2C(! ab) (III. B. 18). A second case exists when a 6= b, a = c, and b = d, which represents damping ratesfor the o#-diagonal matrix elements of #ab(t). These o#-diagonal elements represent phasedi#erences between the energy eigenstates and are referred to as coherences, however they wilnot be the focus of the current proposal. We also assume that there is no coupling betweenpopulation transfer and coherence processes, known as the secular approximation. Finally, we treat the correlation function C(! ab) within the harmonic oscillator approximation suchthat the reservoir coupling component is#(Z) = #lclql (III. B. 19), where ql are harmonic coordinates and cl are the coupling constants. Using this formu-lation, it can be shown [53] that the reservoir correlation function reduces toC(! ab) = 2##h[n(! ab)+1][P(#h! ab)] (III. B. 20), where n(! ab) is the Bose-Einstein distribution function and P(! ab) is the phonon densityof states (DOS). Substituting this expression into Eq III. B. 18, the rate equation becomeskab = 2##h jVabj2(n(! ab) + 1)P(#h! ab) (III. B. 21), which is the central equation we will be using in the current proposal. Since we are only14interested in the diagonal terms of density matrix when considering popuulation transfer, we can write a simple di#erential equation@#aa@t = -#bkab#bb(t) (III. B. 22). Equations III. B. 21 and III. B. 22 provide an intuitive interpretation of how intrabandphonon-asisted relaxation is calculated. For two given states, the nonadiabatic system-coupling term jVabj2 provides a measure of state overlap that will increase the likelihoodof 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 ! ab for the giventransition to occur. If we consider an initial photoexcitation as a pure state in the densitymatrix formalism, then we canx our initial condition by setting the matrix element cor-responding to the photoexcited state equal to one and the rest to 0. We can then solve EqIII. B. 22 with this initial condition to determine the carrier relaxation to all other states fora given photoexcited state.. We will use Eq III. B. 21 to compute relaxation rates for the systems discussed within thisproposal. Therefore, we need to compute jVabj2 and P(! ab) using computational methods. Referring to Eq III. B. 18, we determine Vab, the system coupling component, by calculat-ing the nonadiabatic coupling between electronic states. This coupling is calculated byperforming quantum molecular dynamics (MD) of the system using the Verlet velocity al-gorithm [55] in VASP and calculating the overlap of eigenstates at adjacent time steps. ForjVabj2 = #Ni#h2N j < ia(t)j @@t j ib(t)> j2 = #Ni#h2N j < ia(t)j ib(t+#t)?? ib(t)#t > j2 (III. B. 23)where #t is the simulation time step and N is the total number of time steps. The systemis annealed to 300K using an NVT ensemble and then simulated within the microcanonicalensemble until the matrix elements jVabj2 converge to stable values. The phonon DOS willbe calculated using the frozen phonon method in VASP, in which each atom is displacedby 0. 015 #Aand the resulting forces on all other atoms are calculated to calculate the forceconstants and subsequent frequencies. Gaussian broadening of the phonon DOS is used whencalculating photoexcited relaxation, which provides a rough representation of the existenceof rarer multiphonon processes that can assist relaxation at higher transition energies. Using this method, we will compare photoexcited carrier relaxation in pristine grapheneto that in graphene QDs and nanoribbons embedded in the h-BN matrix. We dene pho-toexcited states as those with the largest oscillator strengths between normalized occupied15and unoccupied states, dened as 1me#h! ab < ajpj b> 2, where me is the electron mass and pis the momentum operator. Starting from this pure photoexcited state, we then solve thedi#erential equation and measure the time taken for the excited electron and correspond-ing hole to relax to the conduction and valence band edges, respectively. After analyzingrelaxation for freestanding monolayers, we will examine the same structures at the 3C-SiCinterface to understand carrier transfer mechanisms. IV. PRELIMINARY RESULTSThe preliminary results demonstrate the feasibility of the proposed study of electronicstructure and intraband carrier relaxation in graphene-SiC structures. In particular, wereport initial results looking at photoexcited carrier relaxation in pristine graphene at theC-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-terminatedinterface has a similar structure with a 2 #Abond length between surface Si and graphene C atoms. As shown in previous studies [42], therst epitaxial graphene layer binds to the SiCsurface 1. 65 #Aabove the bulk C atom. The second graphene layer is 3. 35 #Aabove therst and recovers pristine graphene band structure, including the Dirac point at the Kpoint (Figure 2(a)). Unbonded SiC carbon atoms at the surface lead to athe 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 to2 #A. The second graphene layer again recovers its traditional band structure, however it isnow n-doped (Figure 2(b)). This di#erence in electronic structure could have a signicantimpact on dominant transition dipole moments for photoexcitation and subsequent carrier16relaxation, which will be further explored. At this time, I report carrier relaxation resultsonly for the C-terminated SiC-graphene interface that leaves the second graphene layerundoped. FIG. 2. Band structure for C- and Si-terminated graphene-SiC interface along high-symmetryk-point paths. a) C-terminated SiC; b) Si-terminated SiC. Note that thenear the Dirac point arises due to dangling bonds at the SiC surface. For the present results, we only examine photoexcitation and carrier relaxation at theK-point. Further developments in the code will allow for averaging over k-points to providea more representative picture of carrier relaxation. However, the smallest required photoex-cited energies occur at the K-point and provide an important characterization of electronrelaxation. Initial photoexcited states were chosen as those states with the largest oscillatorstrengths with the initial state at the Dirac point. Several possible photoexcitations arechosen to describe qualitative di#erences in the photoexcited states based on their localiza-tion either on the graphene or SiC. Therst photoexcited state (PE1) has the majority ofits charge density residing on the second graphene layer (Figure 3(a)), the second (PE2) ismixed between the graphene and SiC (Figure 3(b)), the third (PE3) is largely in SiC (Fig-ure 3(c)), and the last (PE4) largely resides on therst graphene layer (Figure 3(d)). Bycomparing relaxation rates between these examples, we can study the e#ect of localizationon relaxation and carrier extraction. We next calculate the carrier relaxation for each chosen PE state. As shown in Figure4, we can visualize the relaxation in both real (top row) and energy (bottom row) for eachphotoexcitation. In real space, the intitial and subsequent states are projected along thez-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 at least17FIG. 3. Charge density isosurfaces (yellow) and cross-sections (red) for sampled photoexcitedstates (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 torstgraphene layer (PE4). partially on the second graphene layer. As seen in the energy space, these photoexcitationsbroaden to include other available bands in the femtosecond time range, which corresponds tothe renormalization of the hot carrier distribution [11] and has been experimentally identiedpreviously 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. Theseresults indicate the potetntial for hot carrier extraction prior to phonon-initiated carriercooling. Photoexcited states localized either on the SiC orrst graphene layer (Figures4(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 foreach of the chosen photoexcited states. The graphene-SiC structure on the right aligns with thez-axis of the graphs in therst row to help visualize the electrion relaxation pathway. a) PE1; b)PE2; c) PE3; and d) PE4. 18Across all PE states, the photoexcited electron relaxes to the second graphene layer beforerelaxing to the impurity state, indicating that 3C-SiC does not act as an electron acceptorat this interface. However, the graphene hot carrier distribution does persist long enoughthat, if an ESC material were adsorbed to the graphene surface, these hot carriers may beextracted prior to phonon cooling. This situation requires further investigation and will beincluded in the proposed study. In addition, current analyses are being done to determinephotoexcited hole behavior at the interface. V. CONCLUSIONS AND FUTURE WORKIn conclusion, the proposed study aims to understand photoexcited electron and hole relax-ation in pristine graphene as well as graphene QDs and nanoribbons embedded in a hexgonalboron nitride matrix. The study will use computational methods based on energy dissipationtheory to model electron-phonon coupling and to calculate relaxation rates for photoexcitedcarriers. Photoexcited carrier relaxation will be examined on freestanding graphene QD/h-BN surfaces and subsequently at the SiC interface to determine photoexcited charge transfermechanisms. 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 actas an electron acceptor, and therefore electron accepting materials will be initially studiedas ESC candidates. It is important to note that the current computational methodology does not take intoaccount all relaxation methods and does not explicitly account for multiphonon processes. As discussed in the proposal, electron-hole correlation e#ects should be minimal in grapheneQDs, however an inclusion of this interaction could conrm this and extend the methodol-ogy to QDs where this coupling is important. Other future work in this area could includeaccounting for explicit multiphonon processes, electron-phonon interactions that change theelectron's momentum, and extending this methodology to include photoexcitation and relax-ation at multiple k-points. In addition, the inclusion of other electron-electron interactionssuch as impact ionization would provide a more complete analysis of electron relaxation andallow the study of multiple exciton generation within the same framework. Finally, the graphene-SiC interface is a prime candidate for intermediate band (IB) solarcell design when SiC is doped with boron, aluminum, or nickel to create deep donor and19acceptor levels. Therefore, future research will include examining the electronic structureof the doped SiC-graphene interface and calculating electron relaxation and charge transfer. Non-radiative recombination via the impurity states is an important limiting relaxationprocess 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. AcknowledgmentsI am extremely grateful to Dr. Hai-Ping Cheng for her guidance and support in the devel-opment of this proposal and to Dr. Dmitri Kilin for his guidance in using the nonadiabaticcoupling code. I would also like to thank The Quantum Theory Project, University ofFlorida High Performance Computing (UFHPC), and The National Energy Research Scien-tic Computing Center (NERSC) for computational resources.[1] D. L. Greene, J. L. Hopson, and J. Li, Energy Policy 34, 515 (2006), Hong KongEditorial Board meeting presentations Hong Kong Editorial Boardmeeting presentations .[2] N. S. Lewis and D. G. Nocera, Proceedings of the National Academy of Sciences 103, 15729(2006), http://www. pnas. org/content/103/43/15729. full. pdf+html.[3] S. M. Sze and K. K. Ng, Physics of semiconductor devices (Wiley-interscience, 2006).[4] J. Nelson, The Physics of Solar Cells, 1st ed. (Imperial College Press, 2003).[5] W. Shockley and H. J. Queisser, Journal of Applied Physics 32, 510 (1961).[6] M. 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