Modelling ultrafast non-equilibrium carrier dynamics and relaxation processes upon irradiation of hexagonal Silicon-Carbide with femtosecond laser pulses

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We present a theoretical investigation of the yet unexplored dynamics of the produced excited carriers upon irradiation of hexagonal Silicon Carbide (6H-SiC) with femtosecond laser pulses. To describe the ultrafast behaviour of laser induced out-of-equilibrium carriers, a real time simulation based on Density Functional Theory (DFT) methodology is used to compute both the hot carrier dynamics and transient change of the optical properties. A Two-Temperature model (TTM) is also employed to derive the relaxation processes for laser pulses of wavelength 401 nm, duration 50 fs at normal incidence irradiation which indicate that surface damage on the material occurs for fluence $\sim$1.88 Jcm$^{-2}$. This approach of linking, for the first time, real time calculations, transient optical properties and TTM modelling, has strong implications for understanding both the ultrafast dynamics and relaxation processes and providing a precise investigation of the impact of hot carrier population in surface damage mechanisms in solids.

I. INTRODUCTION

Over the past decades, the advances of ultra-short pulsed laser technology have emerged as a powerful tool for many technological applications, in particular in industry and medicine [1-13]. To this end, understanding of laser driven physical phenomena such as electron excitation, scattering processes, relaxation mechanisms, phase transitions, ablation are important to elucidate many fundamental properties of solids that can lead to enhanced control of the laser energy for numerous potential applications.

One of the most challenging issues that influences laser driven phenomena in solids is the response of excited carriers scattering processes in a femtosecond time window. A better description of those mechanisms is crucial for a detailed knowledge of laser induced ultrafast processes. On the other hand, the investigation of the ultrafast electron dynamics within the electron gas in a laser-heated material is a real challenge. In principle, the extremely small electron-electron collision time (~10 fs), associated with the generation of highly hot (nonthermal) electron distribution during excitation, complicate direct observation [14]. Nevertheless, advances in laser technology have allowed generation of non-equilibrium electron distributions while they have enabled observation of their relaxation in real time, through predominantly the response of the material’s optical constants [15-17].

To model laser-matter interaction and describe material’s response, a common approach that has been widely used is the traditional two temperature model (TTM) which, however, ignores the formation of nonthermal electron populations [18]. While this assumption yields precise quantitative results for the electron dynamics that agree with pump-probe and reflectivity experiments for pulse durations longer than 100 fs [14, 19], inconsistencies have been observed at shorter pulses for which a strong presence of nonthermal electron is expected [15, 20, 21].

To overcome the limitations originating from the overestimation of the electron energy due to the assumption of the instantaneous electron thermalisation, various revised models have been proposed based on: (i) Boltzmann’s transport equations [22], (ii) three temperature models [17, 21], (iii) two temperature models with the introduction of two source terms [20, 23].

The above approaches described successfully both the ultrafast dynamics and thermal response of the irradiated material in many physical systems [16, 17, 21, 22, 24]. Nevertheless, although those methodologies appeared to illustrate efficiently the role of the nonthermal electrons in the subsequent relaxation processes, some of the above models were applied only for metals (i.e. consideration of an infinitesimal nonthermal, steplike change of the electronic distribution due to the irradiation and promotion of electrons to the unoccupied states above the Fermi energy) [15, 16, 20, 21, 23-27]. One very intriguing challenge is whether similar models can be developed for other materials (i.e. semiconductors or dielectrics) where excitation and relaxation processes include more complex mechanisms such as multiphoton/tunnelling and impact ionisation as well as carrier recombination. It is evident that a revision to existing models is required to account for the behaviour of hot (nonthermal) carriers in the conduction band and their interaction with thermalised carriers and lattice when the processes are considered. However,
validity of a simplistic extension of the aforementioned models is rather questionable. By contrast, due to the complexity of the physical mechanisms that are involved, an approach based on quantum mechanical principles is regarded as a more precise technique to describe the underlying ionisation processes and ultrafast dynamics. Simulations based on Density Functional Theory (DFT) have been applied in various systems [28, 29] and the impact of out of equilibrium electrons in relaxation processes has been successfully evaluated. Nevertheless, one still not explored process in these approaches is that they do not consider potential temporal variation of the optical properties (and therefore energy absorption) of the irradiated material induced by the presence of hot carriers, which becomes significant at extremely short pulses.

One very promising wide-band gap material is SiC and its polymorphs due to its impact to numerous technological applications. More specifically, the advantages of SiC devices are opening up for advanced applications in the most important fields of electronics while its properties allow the performance of existing semiconductor technology to be extended [30, 31]. Although the properties of this material have been widely explored, response upon extreme heating is an area that has yet to be investigated.

To address the above challenges, a real time simulation is presented to compute the ultrafast dynamics of the excited carriers as well as the induced optical constants after irradiating hexagonal Silicon-Carbide (6H-SiC) with single femtosecond laser pulses (Section II). A TTM for semiconductors is employed to provide a description of the temporal evolution of the temperatures of the carriers/lattice population and recombination process for the thermalised population of excited carriers. A detailed analysis of the results the theoretical model yields is presented in Section III for various values of the laser fluence while an estimation of the surface damage threshold is calculated. Concluding remarks follow in Section IV.

II. THEORETICAL MODEL

a. Structure of 6H-SiC

Silicon carbide is a unique material as it occurs in some 250 polymorphs. A particular kind of polymorphism which is called polytypism, occurs in certain close-packed structures: two dimensions of the basic repeating unit cell remain constant for each crystal structure while the third dimension is a variable of a common unit perpendicular to the planes with the closest packing. Polytypes consist of layers with specific stacking sequence where the atoms of each layer can be arranged in three configurations in order to maximize the density [32]. The fundamental structural unit is a covalently bonded tetrahedron of four Carbon (C) atoms with a single silicon (Si) atom at the centre. On the other hand, each C atom is surrounded by four Si atoms. Among the various polytypes of SiC, the hexagonal 6H\(^1\) configuration is one of the most widely studied [32, 33] and it will be the focus of this work. In Fig.1, the unit cell of 6H-SiC is shown which has a complex structure with 12 atoms (Fig.1).

![Figure 1: Structure of 6H-SiC](image)

Figure 1: Structure of 6H-SiC: Silicon atoms are represented by large spheres (in red) corresponds while Carbon atoms are represented by small spheres (in blue) The cell parameters are \(a=b=3.095\ \text{Å},\ c=15.18\ \text{Å}\ [34].

b. First principles calculation

Polytypism has a strong influence on the material physical and chemical properties. In particular, the optical properties of SiC and their relation to the polytypic character have been extensively investigated [35-38]. These studies include measurements of the dielectric constant, the refractive index, as well as the determination of the frequency-dependent dielectric function, optical absorption and reflectivity spectra and are connected with the band structure of the material. The latter, may be obtained either from model Hamiltonians or with advanced \textit{ab-initio} techniques. A precise evaluation, however, of the optical properties for systems in nonequilibrium states due to excitation conditions require also consideration of correlation effects, (i.e. excitonic effects due to electron-hole Coulomb interaction) or plasmons. A consistent estimation of the role of excitonic effects can be derived from the solution of the Bethe–Salpeter (BS) equation for the electron–hole Green’s function, within the many-body perturbation theory (MBPT) framework [35]. MBPT is a rigorous approach based on Green’s function method and constitutes a proper framework for accurately computing excited state properties.

In this work, Yambo, a software package will be used to address the above issues [39]. Yambo is a consistent \textit{ab initio} code for calculating quasiparticle energies [40] and

\(^1\) Here, the Ramsdell classification scheme is used where the number indicates the number of layers in the unit cell and the letter indicates the Bravais lattice (\(H\) stands for hexagonal)
optical properties of electronic systems within the framework of MBPT and time-dependent density functional theory. In general, first-principle calculations are performed by employing a plane wave expansion of the wavefunction [37]. One advantage of the methodology is that it can provide a consistent description of the dynamics of out-of-equilibrium carriers and it can allow an accurate evaluation of the optical properties that involves consideration of correlation effects.

The reference noninteracting system is the starting point in a many body perturbative expansion procedure [39]. Within the above framework, the properties of the noninteracting system are derived via the solution of the DFT Kohn–Sham (KS) equations [39] which correspond to single particle levels \([n\mathbf{k}^>, n]\) being the band index and \(\mathbf{k}\) the wavevector used for the sampling of the Brillouin Zone (BZ). In Yambo, the KS equations and energy functionals are evaluated self-consistently. The noninteracting Green’s function \(G_0\) is given by the expression

\[
G_0^{\mathbf{k}k}(\omega) = \frac{f_{\mathbf{k}k}}{\omega - e_{\mathbf{k}k} - i0^+} + \frac{1-f_{\mathbf{k}k}}{\omega - e_{\mathbf{k}k} + i0^+}
\]

(1)

where \(f_{\mathbf{k}k}\) stands for the occupation factor while \(e_{\mathbf{k}k}\) are the KS energies. The following Dyson equation is used to relate the bare Green’s function \(G_0\) and the exact Green’s function

\[
G_{\mathbf{k}k}(\omega) = \left[\left(G_0^{\mathbf{k}k}(\omega) - \Sigma_{\mathbf{k}k}(\omega) + V_{\mathbf{k}k}^{xc}\right)\right]^{-1}
\]

(2)

where \(V_{\mathbf{k}k}^{xc}\) is the exchange-correlation potential and \(\Sigma\) is the self-energy.

Yambo uses the GW approximation for the calculation of the electronic self-energy \(\Sigma\) [41] (\(G\) stands for the one-body Green’s function and \(W\) for the dynamically screened Coulomb interaction) to obtain the quasiparticle correction to energy levels. Yambo adopts the plasmon-pole approximation (PPA) for the evaluation of the GW self-energy which is approximated with a single pole function [39]. The calculation of the inverse microscopic dielectric function in reciprocal space

\[
\varepsilon_{G\mathbf{G'}}^{-1}(q, \omega) = \delta_{GG'} + \nu(q + G)\gamma_{G\mathbf{G'}}(q, \omega)
\]

(3)

(\(\delta_{GG'}\) is the Kronecker delta function and \(\nu(q + G)\) requires the knowledge of the reducible response function \(\chi\) in the random phase approximation (RPA) [42, 43]

\[
\chi_{G\mathbf{G'}}(q, \omega) = \left[\delta_{GG'} - \nu(q + G')\gamma_{G\mathbf{G'}}(q, \omega)\right]^{-1} \chi_{G\mathbf{G'}}^{0}(q, \omega)
\]

(4)

In the above expression, the noninteracting response function \(\chi_{G\mathbf{G'}}^{0}(q, \omega)\) is calculated through the computation of the bare Green’s function \(G_0\) [39].

c. Calculation of optical properties: the Bethe-Salpeter equation

The above discussion indicates that the evaluation of the response function is required for an accurate calculation of the inverse dielectric function \(\varepsilon^{\prime\prime}\). To compute the optical properties of the excited material, one should evaluate first the macroscopic dielectric constant that is defined in terms of the microscopic inverse dielectric function [44]

\[
\varepsilon_{mm}(\omega) = \lim_{q \to 0} \frac{1}{\varepsilon^{-1}(q, \omega)_{G=\omega=G'=0}}
\]

(5)

where \(\varepsilon\) is a matrix in reciprocal space. Although this technique appears to be a straightforward methodology to compute the optical properties, it suffers from fundamental problems due to the induced local field effects following charge redistribution during laser-matter interactions. As a result, the RPA technique is inadequate to describe efficiently electronic correlations that occur in the response function. To avoid the drawbacks of the RPA in the calculation of the dielectric constant, a more elaborate equation of motion for \(\chi\) that takes into account the effect of electron–electron correlations. This is the BS equation that is introduced by using the electron–hole Green’s function [39]. In principle, the BS equation can be reduced to an eigenvalue problem of the Hamiltonian, which in general may not be Hermitian. Yambo, adopts the standard Tamm–Dancoff approximation [45], in which only electron-hole pairs at positive energy are considered and the Hamiltonian is Hermitian. A straightforward calculation of the dielectric constant \(\varepsilon\) can be derived that is expressed in terms of the eigenstates and eigenvalues the Hamiltonian [39].

Following the calculation of \(\varepsilon(=\varepsilon_i + i\varepsilon_r)\), the optical properties such as the refractive index \(n\), extinction coefficient \(k\), and reflectivity \(R\) of the material can be derived from the following expressions

\[
n = \sqrt{\frac{\varepsilon_i^2 + \varepsilon_r}{2}}
\]

(6)

\[
k = \sqrt{\frac{\varepsilon_i^2 - \varepsilon_r}{2}}
\]

\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}
\]
d. Calculations with Yambo

In this work, the equilibrium properties were computed starting from a self-consistent calculation of the Kohn-Sham eigenvalues and eigenstates in the DFT framework within the local-density approximation. DFT calculations were performed with the Quantum-Espresso code [46] using the Perdew-Burke-Ernzerhof functional [47] and norm-conserving pseudopotentials. Compared to other polytypes of SiC, the analysis of 6H-SiC in terms of band-to-band transitions is more demanding and complex due to the large number of bands being folded into the small BZ. A shifted $8\times8\times2$ k-point sampling for the ground-state was used, while a kinetic energy cut-off of 100 Ry was considered. The quasiparticle corrections to the fundamental band gap have been calculated from the standard GW approximation with the Godby-Needs plasmon-pole model and applied as a rigid shift to all the bands (i.e. Yambo uses the $GW$ approximation for the electronic self-energy $\Sigma$ [41]). Calculations of the quasiparticle energies and optical susceptibilities have been performed using the Yambo code [39], and a total of 100 bands for Green’s function expansion was used.

In Yambo, the ground state energy of the system, the expectation value of any single-particle observable in the ground state and the excitation spectra can be derived through the detailed knowledge of the Green's function. As described above, when the Green's function and self-energy of the non-interacting system are known, the corresponding Green's function of the interacting system can be calculated by solving the Dyson equation [39]. Thus, the macroscopic computation of the dielectric function is obtained by including local field effects in the calculation of the response function. Within the MBPT formalism, this is achieved by the employment of Yambo code by solving the Dyson equation for the susceptibility $\chi$ [39].

e. Real time simulations

Following the evaluation of the ground state properties, performance of real time (RT) simulation involves some preliminary steps: (a) firstly, the electron-phonon matrix elements are created using Quantum Espresso, (b) secondly, removal of all symmetries due to the existence of the pumping field that breaks the symmetry of the system is considered. This is done in connection with the polarization of the incident field.

Upon implementing all the above steps, the real-time simulation proceeds at different run levels. More specifically, the collision files are initially calculated choosing a suitable potential approximation. In this work, a Hartree potential is used while the matrix elements related with the electronic correlation are calculated [48]. It is noted that lattice is considered frozen, as the pulse duration is at the order of the phonon cycle period.

Figure 2: Simulated results for the real and imaginary part of dielectric constant (a,b) and (c) reflectivity at various photon energies assuming longitudinal and transverse dielectric constant components.
The static dielectric function is firstly computed before the calculation of the Kernel components for the electron-hole states of interest. Several parameters have to be adjusted at this run level, such as the cut-off energy of the dielectric function, the number of bands included in the calculation, the states participating in the dynamics, the Hartree-Fock and correlation terms.

In this work we consider the laser irradiation as a single shot laser pulse impinging normally to the sample. For the pulse simulation, it is important to set precisely the propagation variables such as the time interval, the duration of the simulation, the integrator and the pulse intensity. In regard to the laser pulse shape and polarisation, a linearly polarized Gaussian pulse has been chosen that is centered at the fundamental absorption peak in order to generate a significant amount of carriers. The number of carriers is expected to increase as long as the pulse intensity is nonzero.

Simulation results for the optical properties of the irradiated material derived from the above real time simulation are illustrated in Fig.2 for various photon energies that correspond to laser wavelengths in the range [73 nm, 12μm] at 300 K. Results show the frequency dependence of the real and imaginary parts of the dielectric constant along the transverse and longitudinal directions, respectively (Fig.2a,b). A comparison with theoretical and measured values for the longitudinal component of the dielectric function ε (Fig.2a,b) reported in previous works shows a remarkable agreement that illustrates the validity of the approach [35, 37, 49]. It is noted that while there is a discrepancy between ε values between the two polarization directions, there is no difference in ε for the transverse and longitudinal components for the photon energy used in this work (3.09 eV). An interesting aspect is the ‘metallic’ behaviour (i.e. $Re(ε)<0$) that is exhibited in both transverse and longitudinal spectra by the irradiated material at laser wavelengths $λ<179$ nm (photon energies larger than 6.9 eV).

f. Energy and Particle Balance equations

To describe the carrier excitation and relaxation processes for semiconductors, the relaxation time approximation to Boltzmann’s transport equation is widely employed [18, 50-56] to determine the spatial ($F=(x,y,z)$) and temporal dependence ($t$) of the carrier density number, carrier energy and lattice energy. The carrier system is assumed to be non-degenerate (i.e. Maxell-Boltzmann distributed) as the adoption of a more rigorous approach is not expected to lead to substantial differences in the evaluation of the main observable effects (i.e. damage thresholds [53]). Based on this picture, the following set of coupled (nonlinear) energy and particle balance equations are used to derive the evolution of the carrier density number $N_c$, carrier temperature $T_c$ and lattice temperature $T_L$ [51, 53, 54]:

$$C_c \frac{dT_c}{dt} = \frac{C_c}{\tau_c} (T_c - T_L) - \frac{\partial N_c}{\partial t} (E_r + 3k_B T_c) - N_c \frac{\partial E_r}{\partial T_c} \frac{dT_c}{dt}$$

$$C_L \frac{dT_L}{dt} = \nabla \cdot \left( K_L \nabla T_L \right) + \frac{C_c}{\tau_c} (T_c - T_L)$$

$$\frac{dN_c}{dt} = -\int \gamma N_c^3 dt + PE$$

where $k_B$ stands for the Boltzmann constant, $C_c$ is the carrier heat capacity $(C_c = 3N_c k_B)$, $C_L$ is the lattice heat capacity [57], $\gamma$ stands for the Auger recombination coefficient (for 6H-SiC, $\gamma = 7 \times 10^{-31}$ cm$^6$/s [58]), $\tau_c$ is the carrier-phonon energy relaxation time (~300-500 fs in semiconductors [51, 53, 56]) and $E_r$ corresponds to the $T_L$ dependent energy band gap of 6H-SiC ($E_r = 3.01 - 6.5 \times 10^{-4} \times (T_c - 1200)$ eV [59, 60]). Finally, $K_L$ is the lattice heat conductivity of 6H-SiC ($K_L = 611/(T_c - 115)$ Wcm$^{-1}$K$^{-1}$ [57]. In previous works, an anisotropic heat conductivity was reported for various polytypes of SiC including 6H-SiC in which it was shown that the cross-plane thermal conductivity $K^{(x)}$ (perpendicular to the hexagonal planes) of 6H-SiC is 30% lower than its in-plane thermal conductivity $K^{(z)}$ (parallel to the hexagonal planes) [61, 62]. Experimental observations suggest that the anisotropy in the thermal conductivity 6H-SiC is expected due to the hexagonal Bravais lattice structure which suggests that in general this difference should not be ignored in a rigorous investigation. Nevertheless, it is assumed that for the purposes of this study, the computation of the damage thresholds, results are not expected to be remarkably sensitive to the 3D character of the heat diffusion. Certainly, a more precise exploration of the impact of the anisotropy on thermal effects could provide a more detailed account of the role of directional heat diffusivity, however, this investigation is beyond the scope of the present study. Therefore, for the sake of simplicity, a bulk material is considered while the laser spot radius is taken to be substantially larger than the thickness of the material and, thereby, a 1-d solution is considered to sufficiently determine the carrier dynamics and thermal response of the system.

In contrast to the traditional methodology where laser intensity was included in the TTM equations to generate carrier excitation, in this approach, carrier excitation and their internal thermal energy have been calculated through the employment of DFT approaches. Therefore, Eqs.7 are used at $r=6\tau_p$ ($\tau_p$ stands for the laser pulse duration) when laser is considered to have been switched off. One assumption that is made is that carriers are considered to thermalize instantaneously (i.e. a delta function thermalisation is assumed) after the end of the pulse and, thus, Eqs.1 do not involve interaction of nonthermalised
population with the lattice system [20, 23]. The rapid development of $T_e$ is also expected at higher fluences due to enhanced excitation levels and shorter carrier-carrier

\[
\pi \frac{I}{2} \ln 2
\]

and it is similar to the rate of the carrier energy density. On the other hand, the last equation in Eqs.7 indicates the gradual reduction of the excited carrier population through an Auger recombination process. Notably, the carrier density evolution contains also an additional term $PE$ that is attributed to polarization effects (see next section). This term is not included in the traditional TTM. Furthermore, no carrier current or heat current density is included in Eqs.7 (in previous studies, simulations manifested that neglecting heat dissipation and particle transport are not expected to produce substantial changes to the material response [50, 51, 53]).

III. RESULTS AND DISCUSSION

A quantitative description of carrier excitation, relaxation processes, and thermal response of both the carrier and lattice systems is provided through the use of the aforementioned DFT+TTM combined model. To highlight the contribution of the nonthermal carriers to the transient dynamics of the system, pulsed beams of duration, significantly smaller than the carrier-phonon energy relaxation time, are assumed ($\tau_p \approx 50 \text{ fs}$). The photon energy of the laser beam is $\hbar \omega = 3.09 \text{ eV}$ which corresponds to laser beam wavelength $\lambda_L$ equal to 401 nm and it is similar to the size of the material’s energy band gap ($\pm 3 \text{ eV}$).

The initial conditions are $T_e(t=0) = T_i(t=0) = 300 \text{ K}$, and $N_e = 10^{23} \text{ cm}^{-3}$ at $t=0$. The (peak) fluence is $E_p = \sqrt{\pi \tau_p I_0 / (2 \ln 2)}$, where $I_0$ stands for the peak intensity. To solve Eqs.1, an explicit forward time centered space finite difference scheme is used [56].

The optical properties evolution (real and imaginary part of dielectric constant, and reflectivity $R$) are illustrated in Fig.3 for six various fluence (peak) values, 0.45, 0.6, 0.75, 0.9, 1.05, and 1.88 J/cm$^2$. For all fluence values, DFT calculations showed a decreasing reflectivity reaching a minimum at $t=6\tau_p$ before a relaxation to the initial reflectivity value ($\approx 0.401 \text{ nm}$) $\approx 8.9+0.15i$ shown also in Fig.2). This behavior resembles that demonstrated by lower band-gap semiconductors upon irradiation with laser pulses of duration that is comparable with $\tau_c$, and fluences that are not high enough to induce ‘metallisation’ ($\text{Re} (\varepsilon) < 0$ [55, 56]) of the irradiated material. Interestingly, both for the fluences studied in this work as well as for even larger that correspond to intensities $\approx 300 \text{ TW/cm}^2$ where the material appears to undergo phase transformation or even ablation, $\text{Re} (\varepsilon)$ never becomes negative (Fig.3a).

On the other hand, a noticeable variation of the imaginary

![Figure 3: Evolution of (a) real part, (b) imaginary part of dielectric constant, (c) reflectivity. ($\lambda_L = 401 \text{ nm}$, $\tau_p = 50 \text{ fs}$).](image-url)
part of the dielectric constant $\varepsilon$ is predicted (Fig. 3b) that is also related to the free electron absorption coefficient and significant response of the excited electron system. Furthermore, transient reflectivity calculations (Fig. 3c) illustrate a substantially large drop during the pulse duration that further increases the laser energy absorption. The decrease of reflectivity with increase of the laser energy is reflected on the excited carrier density as it leads to higher excitation conditions (Fig. 4a). By contrast, larger laser energies allow increase excitation at larger depths (Fig. 3b).

To quantify the carrier population in the simulations, it is defined temperature that further increases the laser energy absorption. Furthermore, transient reflectivity calculations (Fig. 3c) demonstrate that after the end of the pulse the carrier density evolution remains constant unlike an anticipated decrease in other semiconductors in different conditions semiconductors [50, 53, 55, 56]. The absence of a decreasing behaviour is due to the fact that (Auger or radiative) recombination processes have not been included in the DFT model. Certainly, the incorporation of such processes in the quantum mechanical approach would allow a more precise description of carrier transient evolution. Recombination and other scattering processes could be introduced by selecting appropriate approximations for the self-energy and updating self-energy during the real-time simulations (i.e. dynamical self-energy). These additions, though, would make the approach more demanding which is beyond the scope of the present study [64]. It is noted that, the initial decrease (from a peak value) of carrier density that is shown in Fig. 4a is due to some kind of polarisation effects ($PE$) in the third equation in Eqs. 1 describes these processes) which are usually small at resonances but it becomes more important outside the resonance regimes. Similar behaviour has been reported in previous works in which the decrease of carrier density is attributed to recombination effects [29].

On the other hand, the model presented in the previous section is aimed to combine the DFT-based calculations and TTM model results by linking the description in the two different regimes where nonthermal (Regime I) and thermal (Regime II) carriers are present. Therefore, to allow an efficient description of carrier dynamics, some physically consistent methodology is required to link the two regimes. To correlate the carrier temperature of a thermalized population with their density, it is assumed that after the end of the pulse, the carriers have reached their maximum thermal energy (i.e. $\frac{dT_e}{dt}$ = 0) as until that moment they continue to receive energy from the laser source [50, 51, 55]. Furthermore, it is assumed that at the end of the pulse, through scattering processes, carriers have thermalised and a Fermi-Dirac distribution with a well-defined temperature has been re-established [14].

Given the anticipated insignificant variation of the lattice temperature within the pulse duration due to the small $\tau_p$ and the large heat capacity of the lattice system for semiconductors compared to $C_v, T_L$ is approximately equal to $T_L^0 = 300 K$ at the end of pulse. It is noted that in other materials such as metals with smaller heat capacity, hot carrier-phonon scattering processes lead to a rather substantial increase of the lattice temperature within the pulse duration [23, 25]. By contrast, similar notable increase of $T_L$ is not expected for 6H-SiC; however, a more thorough investigation that provides a more conclusive estimation of the lattice temperature is beyond the scope of the present work.

In regard to the carrier density evolution that is derived from the DFT approach, a correction to the carrier density evolution to account for Auger recombination is introduced.
The third equation of Eqs.7 can be used to produce the rate of the carrier density while the initial carrier density to derive \( T^\text{max}_c \) corresponds to the value of \( N_c \) at \( t=6\tau_p \) (for which DFT calculations predict a constant carrier density). It is noted that \( PE \) are considered to represent the predominant process for carrier density decrease while after the end of the pulse Auger recombination mechanisms start to become significant. Considering the above assumptions, the maximum carrier temperature \( T^\text{max}_c \) is calculated by Eqs.5 and the condition \( \frac{\partial T_c}{\partial t} = 0 \). Considering the above assumption the maximum carrier temperature \( T^\text{max}_c \) is calculated through the expression

\[
T^\text{max}_c \approx -\frac{T_{L}^0}{\gamma N_c^3 E_g} \frac{(C_c + \frac{N_c C_c}{C_L} \frac{\partial E_g}{\partial T_L})}{(C_c + \frac{N_c C_c}{C_L} \frac{\partial E_g}{\partial T_L} - 3k_N \chi N_c^3)} \quad (8)
\]

Consideration of the conditions described above and the use of Eqs.7-8 allow the calculation of the evolution of the carrier densities (including the correction due to Auger recombination), as well as the temporal dependence of the carrier and lattice. Results and correction to the carrier density evolution profile are shown in Fig.4b for 1.88 J/cm\(^2\) (similar behavior is predicted for other fluences) while the inset depicts the transient dynamics of \( N_c \) at larger timepoints. Notably, the significant decrease of \( N_c \) resulting from the contribution of recombination processes is manifestly illustrated in Fig.4b which indicates the Auger recombination role should not be ignored. The significance of Auger recombination in both the carrier dynamics [65] and surface modification processes have been also revealed in previous reports [66].

On the other hand, the thermal response of the carrier and lattice systems at various fluences is summarised in the inset of Fig.5. It is evident that a maximum carrier temperature occurs at \( t=6\tau_p \), that is subsequently followed by a decrease due to carrier-lattice heat transfer and relaxation of the system. Relaxation processes and exchange of energy between the carrier and lattice subsystems yield a similar behaviour to what is observed in other materials [50, 53, 55, 56]. Furthermore, the simulated maximum \( T_L \) values allow an estimation of the damage threshold of the material (~1.88 J/cm\(^2\)). It is noted that damage threshold is associated to the fluence value at which the surface lattice temperature exceeds the melting point of the material [23, 54, 67, 68] \( (T_{\text{melting}}=3100 \text{ K for 6H-SiC}) \) [69].

Certainly, the aforementioned methodology and predictions that are used to provide an estimate for the damage thresholds require validation of the model with experimental results; to the best of our knowledge, there are not similar reports with experimental observations for the pulse duration and laser wavelengths considered in this work. Nevertheless, experimental measurements for damage thresholds illustrated in Fig.6 at various laser wavelengths and pulse durations indicate that the theoretical value for the critical fluence for the simulations conditions represents a reasonable prediction: experimental measurements at various wavelengths (Fig.6) show a dispersion of the damage threshold estimations while the simulated value appears to be within the range of the measured values [70-74]. Certainly, other effects should also be taken into account to provide a conclusive picture such as reflectivity changes at different wavelengths (Fig.2b) and role of multiphoton absorption.

On the other hand, there is a number of reports about uniform laser induced periodic surface structures (LIPSS) which are formed on 6H-SiC crystal irradiated by femtosecond laser pulses at various wavelengths [75]. Experimental results for irradiation with multishot laser pulses at 400 nm indicate a measured fluence threshold for laser induced periodic surface structure (LIPSS) formation which is approximately equal to 0.49 J/cm\(^2\) [75] while the model yields a fluence threshold approximately equal to 1.88 J/cm\(^2\) for one shot simulations. Similarly, bulk ablation of 6H-SiC at 785 nm takes place at a fluence of 1.4 J/cm\(^2\) [76] while nanoripples have lower damage threshold than bulk single crystals which has also been observed in other studies [75]. A possible reason can be attributed to the fact that, in principle, an experimentally observed formation of LIPSS requires irradiation with multiple number of pulses \( (NP>10 \text{ shots}) \) [77]). By contrast, it is known that in transparent materials and semiconductors [78, 79], the damage threshold for surface modification at increasing \( NP \) drops substantially (more than \( \frac{1}{4} \) of the value for \( NP=1 \)) compared to the measured value for one shot experiments due to the presence of defects and incubation.

Figure 5: Evolution of electron and lattice temperature (\( \lambda_e = 401 \text{ nm, } \tau_p=50 \text{ fs} \)).
This is expected to provide a satisfactory agreement between the predicted one laser shot-based result with the measured value (i.e., deduction of a predicted multi-shot damage threshold around 0.4 J/cm² which appears to agree with the experimental value).

In regard to the employment of the aforementioned approach to describe LIPSS formation and the correlation of periodic structure patterning with the interference of laser pulses with Surface Plasmon waves (SP) that are excited as a result of laser irradiation, special attention is required: according to well established theories, SP are linked to excited carrier densities that lead to \( \text{Re}(\varepsilon) < -1 \). However, according to the simulation results in Fig.3a, despite the large decrease of \( \text{Re}(\varepsilon) \) for 1.88 J/cm², this parameter does not drop to sufficiently low values that can induce SP excitation although very high carrier densities are produced (\( \sim 8 \times 10^{21} \text{ cm}^{-3} \)). This can be attributed firstly to the need to revise the dispersion relation that is required for SP excitation [54, 56, 80]; more specifically, the Drude-model-based dielectric function expression differs if nonthermal contributions are included that indicates that appropriate corrections have to be included. Therefore, the carrier densities evaluation for which \( \text{Re}(\varepsilon) < -1 \) is expected not to be the correct condition to determine the onset of SP excitation. Secondly, given the significance of the incubation effects, the precise role of defects in multipulse experiments (that lead to SP excitation and LIPSS formation [54, 81, 82]) and the variation caused to an effective dielectric constant should be also taken into account. These are some issues that need to be elaborated on to determine the contribution of hot electrons in incubation-related processes and surface modification mechanisms.

Certainly, a more accurate conclusion will be drawn if more appropriately developed experimental (for example, time-resolved experimental) protocols are also introduced to evaluate the damage thresholds at the onset of the phase transition; similarly, pump-probe experiments could be used to validate the reflectivity changes. Furthermore, the aforementioned potential impact of anisotropy-related effects on damage thresholds should be further explored. Anisotropies in visible pump probe experiments have been previously reported by pumping at 800 nm [83].

The DFT-based methodology presented to calculate the optical properties of the irradiated material can also been used to cover a wider range of potential photon energies extending to 100 eV (i.e., wavelength ~12 nm) (Fig.7). The latter corresponds to a spectral region in which Free Electron Lasers (FEL) can be used to enable unique ultrafast scientific research [84]. At the same time, the unique output characteristics of X-ray FEL present severe requirements on the optics used to guide and shape the x-ray pulses, and the detectors used to characterize them [84, 85]. To avoid damage, it is important to know the conditions under which materials undergo damage and the
multiscale model presented in this work is aimed to be used to determine those conditions in a systematic way. One interesting characteristic that is deduced from Fig.7 about the optical properties of the material at very large photon energies is that the solid exhibits negligible extinction ($\text{Im}(\varepsilon) \approx 0$) while it also allows almost all laser energy to pass through the material (negligible reflectivity) at room temperature.

Although several parameters (including a more rigorous description of the thermalisation process of the carriers, influence of scattering processes in the induced thermal effects, microscopic analysis of non-equilibrium phase transition mechanisms through the use of hybrid Molecular Dynamics-TTM models [28, 86, 87] and a complete parametric investigation for the impact at a large range of photon energies and pulse durations) should be considered towards providing a complete picture of the ultrafast processes, the aforementioned framework is designed to provide, for the first time, a satisfactory methodology to link processes at two very small timescales (some hundreds of fs).

IV. CONCLUSIONS

A theoretical framework was presented that describes both the ultrafast dynamics and thermal response following irradiation of 6H-SiC with ultrashort pulsed lasers of duration that is too short to assume an instantaneous thermalisation of excited carriers. The dynamics of nonthermal electrons and thermalisation process is described through a quantum mechanical approach and real time simulations. Equilibration of the thermalised carrier population with the lattice through carrier-phonon scattering processes is presented via a revision of the classical TTM that allows also a reduction of the carrier density which is not appropriately accounted for in real time simulations. Results predict the temporal variation of the optical constants and allow an estimation of the surface damage threshold. The theoretical framework is expected to enable a systematic analysis of the impact of the yet unexplored hot (nonthermal) carriers on surface (or even structural effects) on semiconductors through a combined RT+TTM methodology. Predictions resulting from the above theoretical approach demonstrate that elucidating ultrafast phenomena in the interaction of matter with very short pulses (<100 fs) can potentially set the basis for the development of new tools for non-linear optics and photonics for a large range of applications.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from Nanoscience Foundries and Fine Analysis (NFFA)-Europe H2020-INFRAIA-2014-2015 (under Grant agreement No 654360), HELLAS-CH project (MIS 5002735), implemented under the “Action for Strengthening Research and Innovation Infrastructures,” funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” and co-financed by Greece and the EU (European Regional Development Fund), and COST Action TUMIEE (supported by COST-European Cooperation in Science and Technology). We would also like to acknowledge fruitful discussions with Davide Sangalli and Andrea Marini.
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