Transient dynamics of the electronic subsystem of semiconductors irradiated with an ultrashort vacuum ultraviolet laser pulse

N Medvedev¹ and B Rethfeld¹

Department of Physics and OPTIMAS Research Center, Technical University of Kaiserslautern, Erwin Schroedinger Strasse 46, D-67663 Kaiserslautern, Germany
E-mail: medvedev@physik.uni-kl.de and rethfeld@physik.uni-kl.de

Abstract. The irradiation of semiconductors with ultrashort laser pulses causes excitation of electrons from bound states (the valence band and deep atomic shells) to the conduction band, which produces non-equilibrium highly energetic free electrons. We apply a Monte-Carlo simulation technique to study the ionization and excitation of the electronic subsystem of a solid silicon target irradiated with a femtosecond laser pulse, obtaining the transient distribution of electrons within the conduction band. We take into account the electronic band structure and Pauli’s principle for excited electrons. Secondary excitation and ionization processes induced by electrons in the conduction band and holes in the valence band were also included and simulated event by event. The temporal distributions of the density and the energy of excited electrons are calculated and discussed. We demonstrate that, due to the energy used to overcome the ionization potential, the final kinetic energy of the free electrons is significantly less than the total energy provided by the laser pulse. We extend the concept of an ‘effective energy gap’ for multiple electronic excitations, which can be applied to estimate the free-electron density after high-intensity vacuum ultraviolet (VUV) laser pulse irradiation. The effective energy gap depends on both the properties of the material and the laser pulse parameters. The concept provides a fundamental understanding of the experimentally accessible pair creation energy measured in the limit of long times.

¹ Authors to whom any correspondence should be addressed.
1. Introduction

Experiments with lasers in the visible range have shown that the ultrashort laser irradiation of semiconductors produces observable modifications of the material’s surface, such as the formation of nanobumps and the creation of molten regions [1]–[4]. With the invention of femtosecond lasers, which have a pulse duration comparable with characteristic times for processes in the electronic subsystem of the material, nanometric spatial and femtosecond temporal scales have created new possibilities for nanotechnologies, micromachining and medical surgery. The many potential uses of intense femtosecond laser pulses in applications have stimulated fundamental theoretical and experimental investigations of strongly non-equilibrium states of matter [5]–[15]. The first experiments with the free-electron laser in Hamburg (FLASH), a laser that provides pulses of femtosecond duration in the vacuum ultraviolet (VUV) to extreme ultraviolet (EUV) energy regime, has opened up a pathway to promising new areas of fundamental research and technical applications [16]–[20].

In this new range of photon energies that was not previously accessible to experiments, there remains a lack of data about the primary response of the material to irradiation. Therefore, theoretical investigations are necessary to predict and interpret experimental observations. Such theoretical investigations must consider the range from the very first energy absorption event to the final phase transitions and structural modifications of the target.

Ultrashort laser pulses allow access to fundamental electronic processes in the solid because the pulse duration is comparable to the characteristic femtosecond timescale for collisional processes such as electron–electron interactions and electron–lattice collisions. The kinetics of the excitation and relaxation of the target can be divided into a set of processes separated temporally. Due to the mass difference between electrons and ions, excitation of the electronic subsystem by a laser pulse and the subsequent creation of second-generation free electrons occur much faster (some femtoseconds, $\sim 10^{-15}$ s, or the duration of a pulse) [14, 21] than other processes, such as energy exchange with the lattice and the cooling of excited electrons, which both take up to $\sim 10^{-11}$ s [22]–[27]. The processes in the electronic subsystem play a fundamental role because they provide the initial conditions for subsequent energy
dissipation. Thus, these processes are of essential interest for all material behaviour—from the initial light absorption to further energy dissipation and the eventual phase transitions of the target in the form of melting or a transformation to warm dense matter [5, 10, 14, 23, 24].

In our studies, a Monte-Carlo method with binary collision approximation [15], [28]–[32] is applied to describe the kinetics of electronic excitation in a semiconductor that is irradiated with a femtosecond laser pulse. The number of excited and ionized electrons, the energy of these free electrons and the energy distribution function were calculated as a function of time for a 10 fs full-width at half-maximum (FWHM) Gaussian laser pulse in solid silicon. Laser and target parameters were chosen according to experiments performed with FLASH at DESY in Hamburg [20].

The recently introduced concept of an effective energy gap (EEG) [15] makes it possible to estimate the free-electron density created due to high-intensity, high-energy laser pulse irradiation. In contrast to previous models, which applied only to long-timescale experiments [34]–[40], our concept focuses on the statistical behaviour of quasiparticles on ultrashort timescales.

Here, we extend and generalize the EEG concept, analysing the influence of different processes involved for different photon energies and intensities, and give the limits of the validity of the concept.

2. Model

In our model, we consider the following electronic processes: photoabsorption by bound electrons, impact ionization by free electrons and Auger-like processes within the valence band (the so-called Coster–Kronig transitions or impact ionization by holes). We neglect the radiative decay of electronic vacancies and electron–hole recombinations because they usually require longer times than those allowed by the timescales investigated here [41, 42]. Interactions among ionized electrons were also neglected because their typical density is low in comparison with the electron density in the valence band [28, 29, 31].

The basic idea of the numerical model is as follows. Firstly, we simulate the penetration of the photons with a density corresponding to the intensity envelope of the laser pulse. For each photon, the penetration depth is calculated. If this penetration depth is within our simulation box, the photon is considered to be absorbed and to have given its energy to a randomly chosen electron. Secondly, this ionized electron can then perform secondary ionizations. To simulate this process, the free path is calculated according to the ionization cross-section. At the end of this free path, the traced electron exchanges energy with a randomly chosen valence electron. This process proceeds by ionization of the second electron, which can then also travel further and perform secondary ionizations itself as long as it has a sufficiently high energy. At the same time, the holes that remained after the ionization can decay by Auger-like processes and also create free electrons. We simulate these three main processes by following each particle, event by event, during and slightly after the laser pulse.

2.1. Target and photoionization processes

In the present work, the solid silicon target is considered to be a homogeneous isotropic arrangement of atoms with a density of \( n_{\text{at}} = 4.5 \times 10^{28} \, \text{m}^{-3} \) and with an electronic density of states (DOS) corresponding to solid silicon [43, 44] (see figure 1). Note in figure 1 that the deep atomic shells \( L_1, L_{2,3} \) and \( K \) have energies of 100, 148 and 1839 eV [45], respectively. These
Figure 1. DOS of solid silicon as given in [43, 44]. The deep atomic shells considered in this work ($L_1$, $L_{2,3}$, and $K$, with energies of 100, 148 and 1839 eV, respectively) are not shown in this figure.

Figure 2. Attenuation length of the photon inside a solid silicon target. The low-energy data are taken from the Virginia Semiconductor Inc. (see footnote 2) and the high-energy data are extracted from [46].

shells are not shown. We chose a Gaussian shape for the temporal intensity distribution of the laser pulse. Further excitation parameters of the laser pulse were chosen to mimic experimental data [20]: the energy of the photons was $\bar{h}\nu = 38$ eV, the intensity of the laser pulse was $2 \text{ J cm}^{-2}$ (unless otherwise indicated) and the FWHM of the duration of the laser pulse was $\tau_L = 10$ fs with a total duration numerically cut off at 25 fs.

The number of absorbed photons can be calculated if the fluence and the attenuation length for a photon travelling in solid silicon (presented in figure 2) are known. The data were extracted from [46]².

² The compilation of experimental data was done by Virginia Semiconductor Inc., see www.virginiasemi.com and references therein.
The probability of multiphoton absorption is proportional to $J_l^2(e\overline{E}_L\overline{q}/(m_e\omega^2))$ [48], where $J_l$ are the Bessel functions of the first kind, $l$ is the order of the function and indicates the number of absorbed photons (for positive integer $l$), $e$ is the electron charge, $\overline{E}_L$ is the laser field amplitude and $\overline{q}$ is the momentum change of the electron from the collision with a third partner during the photoabsorption process. The laser field amplitude can be estimated by the fluence [14]. For our range of fluences and the VUV–XUV photons, the probability of two-photon absorption is approximately two orders of magnitude lower than the probability of one-photon absorption. As fluence increases, the two-photon absorption probability increases and only approaches the one-photon absorption probability at a fluence of approximately 50 J cm$^{-2}$. Thus, in the present work, we consider only one-photon absorption process.

For the simulation, we chose a cube of silicon with a size of $10 \times 10 \times 10$ nm$^3$. The considered cube is assumed without free surfaces. Thus we use periodical boundary conditions. It should be noted that electron emission from the surface might change the transient number of free electrons and their energy distribution. However, the mean free path for electrons with energies of the order of tens of eV in silicon is typically on the sub-nanometre scale [47]. Thus, our assumption of periodic boundaries for the simulation box means that we do not consider the effect of a several nanometres thick surface; we are instead interested in the general processes that occurred in the bulk.

The initial energy distribution of electrons was chosen to be represented by an empty conduction band and a completely filled valence band, which corresponds to the given DOS in figure 1 [43, 44]. The energy scale for free-electron kinetic energy starts at the bottom of the conduction band ($E = 0$ eV in figure 1). All electrons above the final ‘outermost’ state of the conduction band (~7 eV, figure 1) are treated as free electrons (i.e. as belonging to the continuum but still inherently in the crystal). All free electrons within the conduction band and the continuum are treated with the parabolic dispersion law with all effective masses equal to the free-electron mass. Thus, we explicitly include the DOS of the material but not the detailed band diagram itself. The main influence on the results presented below comes from Pauli blocking. Therefore, we account for the real DOS of silicon in detail, while the band structure is used only for the preliminary analysis (described in section 2.2) and does not enter the modelling. This approximation also considerably simplifies the numerics and makes the calculations significantly less time-consuming.

Interactions of every single photon with bound electrons were simulated event by event. The probability of interaction with every single electron from different energy states is determined from the relative cross-section. The details of the numerical algorithm can be found in [28].

The pure cross-sections for photoionization of electrons in different energy levels within the valence band are considered to be equal, which is a fairly good approximation in this energy interval [46]. Differences were introduced only by having different densities of electrons in different levels, according to the DOS function: the valence band was discretized and each discrete interval was normalized according to the total number of electrons, which yields the relative concentration values for electrons in different discrete energy intervals in the valence band. The conduction band was discretized in the same manner. $L$ and $K$ atomic shells are represented as delta-function energy levels containing a corresponding number of electrons.
2.2. Band structure analysis of secondary processes: impact ionization and Auger decay

Secondary electrons are ionized by impact ionizations and Auger decays to deeper shells (i.e. the Coster–Kronig transitions) within the valence band. For these processes, momentum and energy conservation are simultaneously taken into account in accordance with the real dispersion laws of the material. Conserving these quantities leads to a strong reduction in the probability of secondary electron ionization. Thus, to analyse the processes of secondary electron excitation, the electronic band structure of the material must be taken into account. The band diagram [44] and examples of energy- and momentum-conserving secondary processes are shown in figure 3.

An analysis of the impact ionization process corresponding to an initial state with one electron each in the conduction and valence bands and a final state with two electrons in the conduction band (see figure 3, where an electron \( e_1 \) ionizes a second electron \( e_2 \), dashed arrows) shows that this process required a minimum kinetic energy for the initially free electron of \( E_{\text{min}}^e = 1.2 \) eV. This energy is approximately equal to the indirect energy gap of silicon, \( E_{\text{gap}} = 1.15 \) eV, as shown previously in [49]. Electrons with energies less than the value of \( E_{\text{min}}^e \) cannot initiate impact ionization. Therefore, an electron with energy \( E^e > E_{\text{min}}^e \) can only perform secondary ionizations until its energy becomes less than the minimum energy of this process, which, in this case, is the real indirect energy gap of the material, \( E_{\text{gap}} \).

Similarly, for an Auger-like (Coster–Kronig) secondary electron creation corresponding to an initial state with one hole and one electron in the valence band and a final state with one electron in the conduction band and a hole with higher energy in the valence band (see figure 3, where a hole \( h \) in the valence band ionizes an electron \( e_A \) to the conduction band, solid arrows), we obtain a minimum initial energy for a hole in the valence band of \( E_{\text{min}}^h = -3 \) eV, as measured from the bottom of the conduction band. Therefore, holes of higher energies than \(-3 \) eV cannot create a secondary electron and will remain stable on femtosecond timescales.

These limiting values of energies for electrons, \( E_{\text{min}}^e \), and holes, \( E_{\text{min}}^h \), must be taken into account in all subsequent analyses of secondary electron ionization. Obviously, they strongly depend on the band structure of the considered material.

*New Journal of Physics* 12 (2010) 073037 (http://www.njp.org/)
2.3. Modelling of secondary processes

The following algorithm was applied to determine the interaction parameters realized in a collision between a free electron in the conduction band and a bound electron in the valence band (impact ionization). First, the path lengths are determined for all possible subsequent collisions of the chosen free electron with bound electrons in different energy levels of the valence band. The bound electron to be ionized is then chosen based on the shortest length. Finally, the transferred energy is calculated. As a result, the free path, the duration of the motion and the energy loss of the chosen electron are obtained. This scheme is used to describe the dynamics of all the excited electrons.

For randomly arranged atoms, the distribution of path lengths for a series of collisions with bound electrons can be written in an exponential form \([28, 29]\). The total cross-section of impact ionization for a particle at a discretized energy interval of the valence band can be determined by the expression obtained by Gryziński \([50]\), which depends only on the ionization potential of the electron. All cross-sections \(\sigma\) of interactions are multiplied by a Pauli factor \(w \sim f_v(1 - f_c)\), where \(f_v\) is the distribution function of electrons in the valence band and \(f_c\) is the distribution function of electrons in the conduction band. Both distribution functions are taken with respect to the energy levels of electrons, which participate in the traced collision. By including this factor, the expression for the mean free path automatically takes into account Pauli’s principle: if there are no free states in the discretized interval, the cross-section is zero. In that situation, the mean free path tends to infinity, and such a collision becomes impossible \([28]\). The energy transferred to a bound electron with ionization potential \(I_e\) during an interaction with an electron of kinetic energy \(E_e\) lies within the interval \([I_e, E_e]\) and is fixed by the randomly chosen impact parameter according to the following expression:

\[
\Delta E_e = E_e\left[1 + \left(\frac{b}{a_0}\right)^2\left(\frac{E_e}{2\text{Ryd}}\right)^2\right]^{-1},
\]

where \(\Delta E_e\) is the energy transferred to the bound electron, \(b\) is the randomly chosen impact parameter between a free electron and the selected bound electron, \(a_0 = 0.53\ \text{Å}\) is the Bohr radius and \(\text{Ryd} = 13.6\ \text{eV}\) is the Rydberg constant \([32]\).

This scheme assumes that impact ionization and laser field interactions are independent processes. Generally, that might not be the case: the presence of a strong laser field can influence electron–electron collision processes \([51, 52]\). This influence is particularly important for low-frequency (i.e. visible light) very intense laser pulses where the field is so intense that it can be treated in the classical limit. However, for VUV–XUV photon energies and our analysed fluences, the laser–electron interaction is of a purely quantum nature. It is an essential point that electrons can gain energy from the laser field only in units of \(\hbar\omega\). Thus, the processes of electron–electron interactions (impact ionizations) and photoabsorption can be treated as independent \([14, 21, 48]\).

We note that, as the photon energy decreases, multiphoton absorption becomes increasingly important. For photon energies of \(\sim 10\ \text{eV}\) and a fluence of \(2\ \text{J cm}^{-2}\), the two-photon absorption probability already equals the one-photon absorption probability. Thus, even for lower photon energies, the laser field becomes classical. However, this effect is neglected in the present work because we are focusing on the VUV–XUV range.

For Auger-like processes within the valence band (the Coster–Kronig transitions), the exponential law for the decay time can be applied with characteristic times assumed to be equal to those obtained in \([53]\). The DOS and Pauli’s principle are taken into account in the same way as for the electron impact ionization process. The electron (hole) enabling the Auger-like transition and the electron being ionized are chosen randomly from among the electrons in the valence band.
Figure 4. Transient energy distribution of free electrons in the conduction band and holes in the valence band. The fluence of the laser pulse is 2 J cm$^{-2}$ and the photon energy is 38 eV.

The subsequent dynamics of the secondary electrons produced by the first generation of free electrons and holes and their interactions with the valence electrons were also taken into account in the same manner.

3. Results and discussion

3.1. Energy and density of excited electrons

As a result of the numerical algorithm described above, we obtained the transient energy distribution of electrons and holes, which enabled us to study their transient dynamics. Figure 4 represents the energy distribution of electrons in the conduction band (positive energy) and holes in the valence band (negative energy) in Si at different time points during the irradiation. Curves were normalized to the final number of absorbed photons.

The first curve shows a time $t = 0$ fs, which corresponds to the absorption of the very first photon. One can see that, before secondary processes start (just after absorption of the first photon), this distribution reflects the band structure of the material: electrons from the valence band are shifted to the continuum by adding the photon energy ($E_{ph} = 38$ eV in the presented case), while at the same time holes appear at the corresponding energy in the valence band. Then, electrons and holes start to redistribute their energy.

There are two competing mechanisms of energy redistribution: the absorption of photons during the laser pulse, which increases the total energy and the number of free electrons and holes, and secondary ionizations, which are responsible for decreasing the energy of free electrons and shifting the distribution to low-energy states, just as Auger processes shift the distribution of holes to lower absolute values of energy. The spikes on the curves show that the DOS influences the energy distribution at all times during irradiation.

By integrating over all positive energies, we obtain the total kinetic energy of the electron gas during the laser pulse irradiation (figure 5). The energy shown in this figure is normalized to
Figure 5. The total energy of free electrons in the conduction band normalized for the total absorbed energy (right ordinate). The number of free electrons created by different processes during the laser pulse irradiation and normalized per number of absorbed photons is also presented (left ordinate). The intensity envelope of the laser pulse is added as a dashed line in arbitrary units.

The total energy provided by the absorbed photons. The shape of the curve reflects the two competing mechanisms mentioned above. During the laser pulse, electron energy increases due to photoabsorption, while impact ionizations and Coster–Kronig decays decrease the energy—even for times longer than the pulse duration of 25 fs. Figure 5 demonstrates that the final kinetic energy of the free electrons is much less than the total energy provided by the laser pulse. An essential part of the energy (≈ 65%) is spent to overcome the ionization potential and is held as potential energy (i.e. the energy of holes).

Figure 5 also shows the transient number of free electrons during the irradiation together with the laser pulse intensity envelope in arbitrary units. We calculated the temporal evolution of the number of free electrons ionized by direct photon absorption, electron impact and Auger-like processes, respectively. The number of electrons increased very quickly during the laser pulse because the time between two impact ionization events is much shorter than the characteristic time of the problem. The collision time for an impact ionization can be estimated as \( t_{\text{e-e}} \sim l_e / \langle v_e \rangle \sim (n_e \sigma \langle v_e \rangle)^{-1} \sim 10^{-16} \text{s} \), where \( l_e \) is the mean free path of excited electrons, \( n_e \) is the density of bound electrons in the valence band, \( \sigma \) is the cross-section of impact ionization and \( \langle v_e \rangle \) is the mean velocity of free electrons. Therefore, the maximum increase occurs exactly when the laser intensity (and thus the photoionization probability) has its maximum. Electron–electron impact ionization is the dominant process for free-electron generation, which differs from the irradiation of dielectrics with visible light [6, 14]. Auger-like processes also play a significant role in secondary electron production, as shown in the same figure. Due to these secondary processes, each photon excites about \( N_{\text{e/ph}} = 15 \) electrons (cf figure 5, where the primary excited electrons create around ten secondary electrons by impact ionization and four secondary electrons by Auger-like transitions).
To estimate the number of ionized electrons, it is commonly assumed that each electron within or above a certain critical energy performs an impact ionization. Using the band gap of the material considered here, this assumption leads to $N_{\text{est}} = \hbar \omega / E_{\text{gap}} = 32.6$ electrons per photon, which drastically overestimates the number of excited electrons compared to the present calculation. Such an overestimation was also found experimentally decades ago [34], and several models were proposed for a better estimation of the number of free electrons (see the description of theoretical models in [37] and numerical models in [33] and the references therein). One of the most common models involves the application of the direct band gap of the material [35]. However, impact ionization, as well as Auger-like processes, are restricted by energy and momentum conservation [14]. Therefore, they generally take place as indirect transitions, as shown in figure 3. Thus, the direct band gap has no physically justified meaning for impact ionization and appears as a fit parameter. Our calculations reveal that the discrepancy in earlier estimations is caused by the fact that electrons are located in more than just the highest state of the valence band and are ionized into more than just the lowest state of the conduction band. To calculate the number of ionized electrons, we introduced the concept of an EEG [15]. For the present case of solid silicon irradiated by a laser pulse with a photon energy of 38 eV, it can be estimated as $E_{\text{EEG}} = \hbar \omega / N_{e/\text{ph}} = 2.62$ eV.

Using the above-described Monte-Carlo approach, we calculated the number of ionized electrons at different photon energies of the incident laser pulse (figure 6). For comparison, we also present the experimental results for similar parameters taken from [34] (red circles) and a
typical numerical model [33] (green triangles). As one can see, our calculations coincide well with the experimental results, while the difference between the experimental data and other models is significant (it can be seen even more clearly in figure 7, which will be introduced below). This discrepancy is due to the fact that earlier theoretical works were not focused on ultrashort timescales. Previous models to calculate the ‘pair creation energy’ (PCE) neglected the temporal dependence of the free-electron density [37], which is essential in femtosecond timescales (i.e. in timescales before a detailed balance is established and while the electron density is changing significantly).

It should be noted here that, in the case of low photon energies and high intensities, the interaction with a laser field may influence the electron–electron impact ionization process and thus change the number of free electrons. Furthermore, the intense laser pulse combined with the strong degree of ionization may also influence the band structure and the DOS of the target, which, in turn, affects the electronic dynamics. Both of the mentioned effects should be treated carefully if one is interested in intense visible light irradiation. However, they may be justifiably neglected for the higher photon energies in the VUV–XUV range.

Generally, in femtosecond timescales and for VUV–XUV photon energies, the EEG can be expressed as

$$E_{\text{EEG}} = \langle E_e \rangle + E_{\text{gap}} + \langle E_h \rangle,$$

where $\langle E_e \rangle$ is the mean kinetic energy of ionized electrons and $\langle E_h \rangle$ is the mean energy of holes.

By averaging the kinetic energy of electrons over the electronic distribution presented in figure 4, we found that the mean kinetic energy at the end of the laser pulse was approximately equal to half of the band gap. This result can be understood as follows. An electron with kinetic energy higher than a certain minimum energy $E_e > E_{\text{min}}^e$ quickly performs secondary ionizations. As was shown in section 2, the minimum energy necessary for impact ionization in the case of silicon is equal to the indirect energy gap $E_{\text{min}}^e = E_{\text{gap}}$. Therefore, all electrons with energy $E_e > E_{\text{gap}}$ will produce secondary electrons until their energy falls below $E_{\text{gap}}$. On femtosecond timescales, all the electrons end up with energies between 0 and $E_{\text{gap}}$. Thus, the mean kinetic energy of a free electron after the laser pulse irradiation is roughly half of the band gap energy $\langle E_e \rangle \approx 1/2 E_{\text{gap}}$.

We should mention that, in cases with a high density of free electrons, the mean kinetic energy of electrons increases due to Pauli’s principle. $\langle E_e \rangle$ may then be larger than half of the minimum energy for secondary ionizations, which leads to a larger EEG. Cases such as this are presented below.

One must also remember that the transient mean kinetic energy of electrons is a function of time. It changes during the laser pulse irradiation and then approaches the value of $\sim 1/2 E_{\text{gap}}$ by the end of the laser pulse and stays almost constant for some time until the energy loss to the lattice via electron–phonon coupling becomes essential (typically, on timescales of 0.1–1 ps). Additionally, as mentioned above, further electron–hole recombination will change the number of free electrons and their mean kinetic energy in the picosecond timescale.

The same argument holds for the average energy of holes, which have their own minimum energy for secondary electron creation via an Auger-like process $|E_{\text{min}}^h| = 3 \text{ eV}$, as seen in the analysis of the static band structure discussed in section 2. Therefore, after losing energy due to an Auger-like process, holes will end up with an energy between the minimal energy $|E_{\text{min}}^h|$ and $E_{\text{gap}}$, i.e. $\langle E_h \rangle \approx 1/2 (|E_{\text{min}}^h| - E_{\text{gap}})$ at the end of the laser pulse, which again is confirmed by averaging over the distribution of holes presented in figure 4.
With these considerations, the EEG can be estimated as

$$E_{\text{EEG}} = \frac{1}{2} \cdot (E_{\text{gap}} + E_{\text{e}}^{\text{min}} + |E_{\text{h}}^{\text{min}}|),$$

(2)

where $E_{\text{gap}} = 1.12$ eV, $E_{\text{e}}^{\text{min}} = E_{\text{gap}}$ and $|E_{\text{h}}^{\text{min}}| = 3$ eV for silicon, the mean energies of electrons and holes, respectively, after all electrons and holes have made all possible secondary ionizations.

The minimum energies $E_{\text{e}}^{\text{min}}$ and $E_{\text{h}}^{\text{min}}$ for (2) are obtained by an analysis of the static band structure, as explained in section 2.2. The resulting values of the EEG for different materials are shown in table 1. We also show the results for the minimum energies for impact ionization and Coster–Kronig transitions, respectively, that were obtained from the band structures taken from [43].

Experiments focusing on the PCE are usually performed in timescales where electron-hole recombination plays a crucial role (i.e. picoseconds or longer). Therefore, a direct comparison of such experiments with the pure EEG is impossible. However, due to recombination, the electron density in the conduction band decreases and leads to a higher experimental value of the PCE, which can be assumed to be an upper limit for the EEG. The calculated EEG can be compared with experiments that had suppressed electron–hole recombination. The results for Si can be found in [34] and are shown in figure 6. For SiO$_2$, electron–hole recombination is not a process of primary importance [54]. Therefore, we can expect good coincidence between the experimental long-time value [36] and our calculation. For the two other materials shown in table 1, we can only compare our results for the pure EEG with the upper limit of the PCE for...
Table 1. For different materials, the band gap energy $E_{\text{gap}}$, the minimal kinetic energy of an electron needed for impact ionization $E_{\text{e}}^\text{min}$, the minimal energy of a hole for a Coster–Kronig transition $|E_{\text{h}}^\text{min}|$ and the predicted EEG calculated with (2) are presented in comparison with experimental values of EEG with damped electron–hole recombination [34] and the upper limit obtained in long-time measurements for the PCE [36].

| Material | $E_{\text{gap}}$ | $E_{\text{e}}^\text{min}$ | $|E_{\text{h}}^\text{min}|$ | EEG | Exp. | PCE |
|----------|------------------|----------------------|------------------------|-----|------|-----|
| Si       | 1.15             | 1.2                  | 3                      | 2.62| 2.6 $^a$ | 3.63 |
| SiO$_2$  | 8.9              | 13.5                 | 12.5$^b$              | 17  | 18$^c$ | 18            |
| C        | 4.65             | 4.8                  | 10.25                  | 9.85| –    | 13.1          |
| Ge       | 0.85             | 1.55                 | 1.8                    | 2.1 | –    | 2.96          |

$^a$ For a detailed comparison, see figure 7.
$^b$ Note that, for SiO$_2$, the width of the valence band is smaller than the band gap; therefore, holes cannot make a Coster–Kronig transition, and the mean energy of holes, which is half of the valence band width, is presented here and used in (1).
$^c$ Assumed equal to PCE, see text.

longer times [36]. New experiments with femtosecond lasers (FLASH) are needed to confirm our predictions.

3.3. Dependence of EEG on fluence

In figure 7, we show a detailed comparison of the calculated EEG of silicon, which depends on photon energy and fluence, with experimental values and earlier models. The figure contains the experimental data obtained by Tuzzolino [34] (red circles), several results of different theoretical calculations taken from previous studies by Brigida et al [33] (violet diamonds), Alig [39] (green crosses), Scholze et al [38] (blue upward-pointing triangles) and Fraser et al [40] (orange downward-pointing triangles). The results of the present calculations are shown with lines for different fluences. As can be clearly seen in this figure, all previous models yield values around the commonly assumed electron–hole PCE in Si, 3.63 eV (i.e. the direct band gap, as discussed above), which is the result of long-timescale experiments [35]–[40]. These values differ from the experiments with damped recombination [34] by a factor of two or more, while our simulation compares very well with the experimental data (figure 7).

We found almost no influence of the laser intensity on the EEG in the case of photon energies of several tens of eV. The EEG remains at $E_{\text{EEG}} \sim 2.6$ eV in the VUV photon energy region for fluences ranging three orders of magnitude around our chosen fluence, from 0.02 to 20 mJ cm$^{-2}$.

However, for higher energies around the L-shell edge of Si, the number of absorbed photons is very high in comparison to lower energies. The Auger decay of holes in the L-shell has characteristic times typically around 10 fs (for light elements [53]). Therefore, L-shell photoionization leads to only a short delay in high-energy electron production, which occurs in two steps. First, the photon is absorbed by the L-shell, leaving a hole behind. This hole is then filled by an electron from the valence band, which excites a second electron from the valence band into the conduction band or the continuum at a high energy equal to the difference...
between the L-shell ionization potential and the energy of the electron in the valence band. However, another effect plays a much bigger role here. As can be seen in figure 2, the probability of photoabsorption by L-shell electrons is almost two orders of magnitude higher than the photoabsorption by valence electrons. This fact is reflected in a sudden jump in the attenuation length as soon as the photon energy reaches the L-edge. Additionally, highly energetic electrons created after L-shell Auger decays then produce impact ionizations of secondary electrons. Finally, the electron density becomes so high that, even for a fluence of 2 J cm$^{-2}$, Pauli’s principle has to be taken into account. For high densities of excited electrons, the electron loses a large portion of its energy after a few impact ionizations and ends up in low-energy states. According to Pauli’s principle, electrons fill the lower states of the conduction band, and later generations of electrons cannot also be in the lowest energy states. As a result, the mean electronic energy increases and, according to (1), the EEG increases. Thus, for very high electron densities\(^3\), the EEG will deviate, demonstrating the limits of the validity of (2).

### 4. Conclusions

In conclusion, the transient dynamics of ionization and redistribution of free electrons in semiconductors (silicon, in our case) during ultrashort VUV laser pulse irradiation were simulated with a Monte-Carlo method. The method was extended in order to take into account the band structure of the material and Pauli’s principle. The number and energy distributions of free electrons as a function of time from 0 to 25 f (laser pulse duration) were obtained and analysed in detail.

It was demonstrated that the band structure significantly influences the excitation of electrons. An essential part of the total energy provided by the laser pulse was accumulated in holes (∼65%). We demonstrated that the total number of excited electrons is determined by a statistical process that depends on the mean kinetic energies of electrons and holes, respectively. The recently introduced EEG [15], a concept accounting for the statistical nature of electron ionization, is capable of estimating the number of free electrons that are excited in irradiated semiconductors.

A simple formula to estimate this value at femtosecond timescales was proposed, based on the analysis of the electronic band structure of the material. The method of such an analysis was described, leading to a simple application of the proposed concept. The limits of validity of the concept are discussed while accounting for the timescales, photon energies and fluences of the laser pulse. The values of the EEP obtained for different materials compare well with the available experimental data.

The effects of L-shell ionization, as compared to ionization of the valence band, were considered. It was shown that, in addition to a short delay in high-energy electron production, the L-shell ionization produces another effect: the total number of absorbed photons and, in turn, the total number of excited electrons strongly increase relative to lower photon energies because the photoabsorption sharply increases when photon energy reaches the ionization potential of

\(^3\) We must note that, in the regime of such high-electron densities, when Pauli’s principle begins to play a role, one of the assumptions of our model is no longer satisfied: the interaction among free electrons becomes non-negligible. However, for the purposes of the present work, the effect of thermalization by the redistribution of energy among free electrons is not important and will not significantly change the outcome of the calculations and the conclusions drawn.

New Journal of Physics 12 (2010) 073037 (http://www.njp.org/)
the L-shell. Pauli’s principle comes into play, especially for high fluences, restricting secondary ionizations.

We encourage the creation of experiments with FLASH in the XUV regime around L-shell ionization energies to confirm our predictions and observe the effects discussed in the present work. Experiments on different materials would also be valuable for comparison.

Acknowledgments

The authors thank K Sokolowski-Tinten (Universität Duisburg-Essen, Germany) for bringing his interest to this topic and for essential comments. D Ivanov and O Osmani (Technische Universität Kaiserslautern, Germany) are acknowledged for fruitful discussions. The research was supported by German grants BMBF FSP 301 FLASH and the Emmy Noether programme of the Deutsche Forschungsgemeinschaft, grant RE 1141/11-1.

References

[1] Amoruso S, Ausanio G, Bruzzese R, Vitiello M and Wang X 2005 Phys. Rev. B 71 033406
[2] Dachraoui H and Husinsky W 2006 Phys. Rev. Lett. 97 107601
[3] Crouch C H, Carey J E, Warrender J M, Aziz M, Mazur E and Genin F Y 2004 Appl. Phys. Lett. 84 1850
[4] Hommes V, Miclea M and Hergenroeder R 2006 Appl. Surf. Sci. 252 7449
[5] Manenkov A A and Prokhorov A M 1986 Usp. Fiz. Nauk 148 179
   Manenkov A A and Prokhorov A M 1986 Sov. Phys.—Usp. 29 104 (Engl. Transl.)
[6] Rethfeld B 2006 Phys. Rev. B 73 035101
[7] Ivanov D S and Zhigilei L V 2003 Phys. Rev. B 68 064114
[8] Stoian R, Rosenfeld A, Ashkenasi D, Hertel I V, Bulgakova N M and Campbell E E B 2002 Phys. Rev. Lett. 88 097603
[9] Vogel A, Noack J, Hüttman G and Paltauf G 2005 Appl. Phys. B 81 1015
[10] Rethfeld B 2004 Phys. Rev. Lett. 92 187401
[11] Povarnitsyn M E, Tima T E, Sentis M, Khishchenko K V and Levashov P R 2007 Phys. Rev. B 75 235414
[12] Sokolowski-Tinten K, Solis J, Bialkowski J, Siegel J, Afonso C N and von der Linde D 1998 Phys. Rev. Lett. 81 3679
[13] Sokolowski-Tinten K and von der Linde D 2000 Phys. Rev. B 61 2643
[14] Kaiser A, Rethfeld B, Vicanek M and Simon G 2000 Phys. Rev. B 61 11437
[15] Medvedev N and Rethfeld B 2009 Europhys. Lett. 88 55001
[16] Nagler B et al 2009 Nat. Phys. 5 693
[17] Sokolowski-Tinten K et al 2007 High Intensity XUV–FEL Interaction with Solids: First Experimental Results (Springer Series in Chemical Physics vol 88) (Heidelberg: Springer) p 737
[18] Hau-Riege S P et al 2007 Appl. Phys. Lett. 90 173128
[19] Zastrau U et al 2008 Phys. Rev. E 78 066406
[20] Chalupsy J et al 2007 Opt. Express 15 6036
[21] Rethfeld B, Kaiser A, Vicanek M and Simon G 2002 Phys. Rev. B 65 214303
[22] Lorazo P, Lewis L J and Meunier M 2006 Phys. Rev. B 73 134108
[23] Tobey R I, Prabhakaran D, Boothroyd A T and Cavalleri A 2008 Phys. Rev. Lett. 101 197404
[24] Couairon A, Sudrie L, Franco M, Prade B and Mysyrowicz A 2005 Phys. Rev. B 71 125435
[25] Kaganov M, Lifshitz I and Tanatarov L 1956 Zh. Eksp. Teor. Fiz. 31 232
   Kaganov M, Lifshitz I and Tanatarov L 1957 Sov. Phys.—JETP 4 173 (Engl. Transl.)
[26] Anisimov S, Kapeliovich B and Perelman T 1974 Zh. Eksp. Teor. Fiz. 66 776
   Anisimov S, Kapeliovich B and Perelman T 1974 Sov. Phys.—JETP 39 375 (Engl. Transl.)

New Journal of Physics 12 (2010) 073037 (http://www.njp.org/)
[27] Elsayed-Ali H E, Norris T B, Pessot M A and Mourou G A 1987 Phys. Rev. Lett. 58 1212
[28] Medvedev N and Rethfeld B 2009 Proc. SPIE 7361 73610E
[29] Eckstein W 1991 Computer Simulations of Ion–Solid Interactions (New York: Springer)
[30] Hernandez-Mangas J M, Arias J, Bailon L, Jaraiz M and Barbolla J 2002 J. Appl. Phys. 91 2
[31] Gervais B and Bouffard S 1994 Nucl. Instrum. Methods B 88 355
[32] Medvedev N A and Volkov A E 2008 AIP Conf. Proc. 999 238
[33] Brigida M et al 2004 Nucl. Instrum. Methods in Phys. Res. A 533 322
[34] Tuzzolino A J 1964 Phys. Rev. A 134 205
[35] Delerue C, Allan G and Lannoo M 1993 Phys. Rev. B 48 11024
[36] Alig R C, Bloom S and Struck C W 1980 Phys. Rev. B 22 5565
[37] Bartram R H and Lempicki A 1996 J. Lumin. 68 225
[38] Scholze F, Henneken H, Kuschnerus P, Rabus H, Richter M and Ulm G 2000 Nucl. Instrum. Methods Phys. Res. B 439 208
[39] Alig R C 1983 Phys. Rev. B 27 968
[40] Fraser G W, Abbey A F, Holland A, McCarthy K, Owens A and Wells A 1994 Nucl. Instrum. Methods Phys. Res. A 350 368
[41] Kauffman R L, Jamison K A, Gray T J and Richard P 1975 Phys. Rev. A 3 872
[42] Demarest J A and Watson R L 1978 Phys. Rev. A 17 1302
[43] Papaconstantopolous D A 1986 Handbook of the Band Structure of Elemental Solids (New York: Plenum)
[44] Ramos L E, Teles L K, Scolfaro L M R, Castineira J L P, Rosa A L and Leite J R 2001 Phys. Rev. B 63 165210
[45] Bearden J A and Burr A F 1967 Rev. Mod. Phys. 39 125
[46] Carron N J 2007 An Introduction to the Passage of Energetic Particles through Matter (New York and London: Taylor and Francis)
[47] Werner W S M 2001 Surf. Interface Anal. 31 141
[48] Seely J F and Harris E G 1973 Phys. Rev. A 7 1064
[49] Kane E O 1967 Phys. Rev. 159 624
[50] Gryziński M 1965 Phys. Rev. A 138 A305
Gryziński M 1965 Phys. Rev. A 138 A322
Gryziński M 1965 Phys. Rev. A 138 A336
[51] Bonitz M, Bornath Th, Kremp D, Schlanges M and Kraeft W D 1999 Contrib. Plasma Phys. 39 329
[52] Kremp D, Bornath Th, Bonitz M and Schlanges M 1999 Phys. Rev. E 60 4725
[53] Keski-Rahkonen O and Krause M O 1974 At. Data Nucl. Data Tables 14 139
[54] Murat M, Akkerman A and Barak J 2008 IEEE Trans. Nucl. Sci. 55 3046

New Journal of Physics 12 (2010) 073037 (http://www.njp.org/)