Direct carrier multiplication due to inverse Auger scattering in CdSe quantum dots

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Direct carrier multiplication due to inverse Auger scattering in CdSe quantum dots

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Many optoelectronic devices could achieve much higher efficiencies if the excess energy of electrons excited well above the conduction band minimum could be used to promote other valence electrons across the gap rather than being lost to phonons. It would then be possible to obtain two electron–hole pairs from one. In bulk materials, this process is inherently inefficient due to the constraint of simultaneous energy and momentum conservation. We calculated the rate of these processes, and of selected competing ones, in CdSe colloidal dots, using our semi-empirical nonlocal pseudopotential approach. We find much higher carrier multiplication rates than in conventional bulk materials for electron excess energies just above the energy gap E_g. We also find that in a neutral dot, the only effective competing mechanism is Auger cooling, whose decay rates can be comparable to those calculated for the carrier multiplication process. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1690104]

Conventional single-absorber solar cells have a maximum thermodynamic efficiency of about 30%,[1] the major limiting factor being that most of the energy of incident photons in excess of the bandgap energy $\Delta = h\nu - E_g$ is wasted in thermal excitation of the lattice. It has long been hoped[2–6] that one would be able to increase the maximum attainable thermodynamic conversion efficiency up to 66% by utilizing this excess energy to generate additional electron–hole (e–h) pairs via ''direct carrier multiplication'' (DCM), also known in bulk semiconductor physics as ''impact ionization.''[3–12] In this process, which is the inverse of Auger recombination,[13] a highly excited carrier decays to its ground state and excites a valence electron across the bandgap (process 1, Fig. 1), thus producing two e–h pairs from one. In order to be competitive, the DCM process must be faster than phonon scattering, direct radiative recombination, and Auger cooling [a process whereby the hot electron relaxes to its ground state and the excess energy is transferred via Coulomb scattering to the hole, which is excited deep into the valence band (process 2 in Fig. 1)].

In *bulk* materials, the prospect of achieving efficient DCM for photon excess energy $\Delta \sim E_g$ seems unlikely,[3–12] as both (wave-vector) momentum and energy of the four particles involved need to be conserved. These constraints lead to large threshold energies $E_{th} = E_g + \delta E$,[7] with δE varying from ~0.1 to ~1 eV,[8–10] depending on the material. In *quantum dots*, however, the absence of the momentum conservation constraint opens the possibility of attaining $E_{th} = E_g$.[2] Furthermore, the close proximity of (confined) electron and hole wave functions, that in dots has been shown[13] to enhance all Auger rates, is also expected to enhance DCM rates. However, due to the lack of accurate wave functions for these systems (as discussed in Refs. 14–16 for the **k·p** approximation), the latter have never been calculated for dots; therefore, it is not known if DCM can compete with alternative decay channels.

In this work, we apply our semi-empirical nonlocal pseudopotential method[17] to investigate the dependence on the incident photon energy of the DCM rates and of the rates of selected competing processes in CdSe dots. For electron excess energies just a few meV above the energy gap E_g, we find that: (i) the DCM rates are of the order of 10^{10} s^{-1}, whereas in the usual bulk materials, rates of this magnitude are obtained only for excess energies about 1 eV above E_g; (ii) the lifetime of the competing Auger cooling (AC) mechanism is of about the same order of magnitude as that of the DCM process. For higher excess energies, the presence of an energy gap within the hole manifold[18] slows DCM considerably compared to AC, which is unaffected by it, leading to inefficient DCM in an energy window of the size of such a gap. As in the case of Auger multi-exciton recombination rates,[13] the main contribution to the DCM rates is found to come from the dot *surface*.

We consider a wurtzite spherical dot $Cd_{232}Se_{235}$ of diameter $d = 29.3$ Å, whose surface is saturated by ligand potentials.[19] The single-particle energies and wave functions

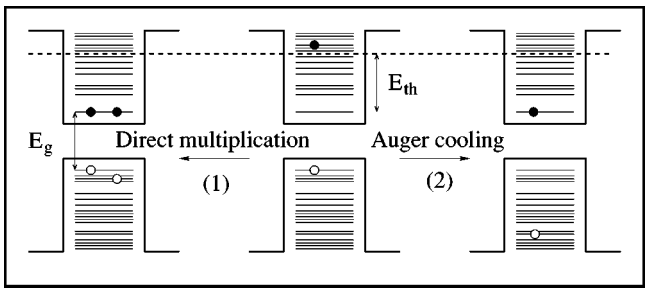

FIG. 1. Schematics of the main hot electron relaxation pathways: DCM (1) and AC (2).

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used in the calculation of the decay rates are computed with the semi-empirical nonlocal pseudopotential method described in Refs. 17 and 20, solved within a plane-wave basis, including spin–orbit effects. Electron and hole levels are labeled with increasing and, respectively, decreasing energy as e_i and h_j, with $i,j=1,2,...$, where $e_1=e_{\mathrm{cbm}}$ and $h_1=h_{\mathrm{vbm}}$ (CBM is the conduction band minimum and VBM is the valence band maximum). The threshold energy E_{th} is defined as the energy below which no DCM can take place. We label the electron states above it as $e_{\mathrm{th}+i}$, where $i=1,2,...$ increases with energy.

The DCM rate for the process $e_{(\mathrm{th}+i)}+h_1\rightarrow 2e_1+h_1+h_n$ is obtained under the standard time-dependent perturbation theory[13,21] as

$$R_{\mathrm{DCM}}(E_i)=\frac{\Gamma}{\hbar}\sum_n \frac{|M_{i,f_n}|^2}{(E_{f_n}-E_i)^2+(\Gamma/2)^2}, \tag{1}$$

where $E_i-E_{f_n}=\epsilon_{e_{\mathrm{th}+i}}-E_g-(\epsilon_{h_1}-\epsilon_{h_n})$, and $\epsilon_{e_{\mathrm{th}+i}}$ is measured from the CBM energy ϵ_{e_1}. Here, $M_{i,f_n}=M_d-M_e$,[21] where the direct part M_d is given by[13,21]

$$M_d(j,k,l,m)=\sum_{\sigma,\sigma'}\int\int \phi_j^*(\mathbf{r},\sigma)\phi_k^*(\mathbf{r}',\sigma)\frac{e^2}{\bar{\epsilon}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}\times\phi_l(\mathbf{r},\sigma)\phi_m(\mathbf{r}',\sigma')d^3r d^3r', \tag{2}$$

and the *exchange* matrix element M_e is obtained from Eq. (2), by exchanging the indices j and k. The AC rate for the decay $e_i+h_1\rightarrow e_1+h_n$ is given by[13]

$$R_{\mathrm{AC}}(E_i)=\frac{1}{\tau_{\mathrm{AC}}(E_i)}=\frac{\Gamma}{\hbar}\sum_{n,\alpha}\frac{|M_d(h_1,e_i,h_n,e_{1,\alpha})|^2}{(E_{f_n}-E_i)^2+(\Gamma/2)^2}, \tag{3}$$

where the sum runs over the spin $\alpha=\uparrow,\downarrow$ of the ground state electron as well. We use the dielectric screening function of Ref. 13, which enables us to separate surface and volume contributions to the integrals in Eq. (1). For $T\neq 0$, we take a Boltzmann average over the initial states as photogenerated carriers thermalize (i.e., form thermal distributions described by Boltzmann statistics) in less than 100 fs.[22]

When an e–h pair is photogenerated in a neutral dot (Fig. 1) the possible mechanisms competing with DCM are: (i) phonon scattering, (ii) direct radiative recombination, and (iii) Auger cooling. We do not calculate phonon scattering rates. Their determination is difficult even in the bulk where most of the times the ratio between phonon and impact ionization rates is treated as a fitting parameter,[7–9,11] and is adjusted to reproduce impact ionization experimental results. As there are no experimental data available as yet for DCM in dots, there is no easy way to estimate phonon scattering rates in these systems. We calculated the energy spacings $\epsilon_{e_{\mathrm{th}+i}}-\epsilon_{e_{\mathrm{th}-j}}$ between states $\{e_{\mathrm{th}+i}\}$ above and $\{e_{\mathrm{th}-j}\}$ below DCM threshold, and found that none matched $\hbar\omega_{\mathrm{LO}}$, the mismatches ranging from 10% ($\sim$2.6 meV) for $e_{\mathrm{th}+3}$, to $\sim$50% ($\sim$13 meV) for $e_{\mathrm{th}+1}$. Li *et al.*[23] calculated that in GaAs dots, due to anharmonic coupling of the confined LO phonon to the bulk acoustic phonons, the phonon-assisted electron relaxation rate can be higher than 10^{10} s^{-1} in a wide detuning range of tens of meV around the LO phonon energy. In CdSe dots, the detuning range for LO phonon-assisted electron decay is found experimentally[24] to be very narrow ($<$2 meV) at room temperature. It follows that the mechanism proposed by Li *et al.* does not apply to the system considered here, therefore, the decay rates between states $\{e_{\mathrm{th}+i}\}$ and $\{e_{\mathrm{th}-j}\}$ are expected to be small. As for (ii), we find that, due to the small overlap between the wave functions of the highly excited electron (localized mostly on the dot surface) and the ground state hole (localized mostly in the dot core), the highest direct radiative recombination rates are on the order of 10^6 s^{-1} (i.e., about two orders of magnitude smaller than those relative to the lowest excitonic allowed transitions), and are therefore much smaller than those of both AC and DCM.

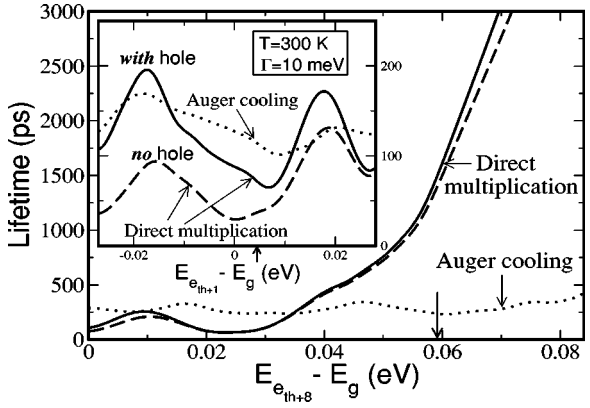

FIG. 2. DCM and AC lifetimes [at room temperature and for $\Gamma=10$ meV (see Ref. 26)] for an electron with energy a few meV above E_{th} ($e_{\mathrm{th}+1}$, inset) and a few tens of meV above it ($e_{\mathrm{th}+8}$, mainframe), as a function of $\epsilon_{e_{\mathrm{th}+i}}-E_g$. The arrows on the energy axes mark the excess energy $\epsilon_{e_{\mathrm{th}+i}}-E_g$ calculated for a spherical dot with $R=14.63$ Å.

We investigate *electron*-initiated DCM processes with impacting electron energies $\epsilon_{e_{\mathrm{th}+i}}$ just above threshold [i.e., $\epsilon_{e_{\mathrm{th}+i}}=E_{\mathrm{th}}+\delta\epsilon_i$ (with $\delta\epsilon_i=4$ to 60 meV)], where the hole occupies its ground state h_1. This configuration can either be generated directly by the absorption of photons with energies $h\nu_i=2E_g+\delta\epsilon_i$, if all excess energy $h\nu_i-E_g=E_g+\delta\epsilon_i$ is given to the electron (a typical scenario, for example, in $Si_{0.32}Ge_{0.68}$ for $h\nu=2E_g$[11,12]), or it can be the result of a higher energy excitation where the excess energy $h\nu_i-E_g$ is distributed between the electron and the hole. However, as the hole relaxation to the top of the valence band is typically much faster than our calculated DCM lifetimes, we can safely assume it to occupy its ground state in our ''initial'' DCM configuration. As in an actual dot ensemble, there are many factors that might affect the relative position of $\epsilon_{e_{\mathrm{th}+i}}$ and E_{th} (shape and size distribution, surface effects, external charges near the dot, etc.), we calculate DCM and AC lifetimes as a function of $\epsilon_{e_{\mathrm{th}+i}}-E_g$ (i.e., $h\nu-2E_g$, or the excess energy measured from E_g). This is shown in Fig. 2 for two energy levels above threshold, where, for illustrative purposes, we show a larger energy variation than expected from realistic effects (the arrows on the energy axis mark the value of $\epsilon_{e_{\mathrm{th}+i}}-E_g$ calculated for a spherical dot with $d=29.3$ Å). We then take an average over an energy range corresponding to a variation of 5% of the dot size (as determined by the variation of the ground state energy E_{e_1} for the same size variation[25]), as shown in Fig. 3 for the first eight

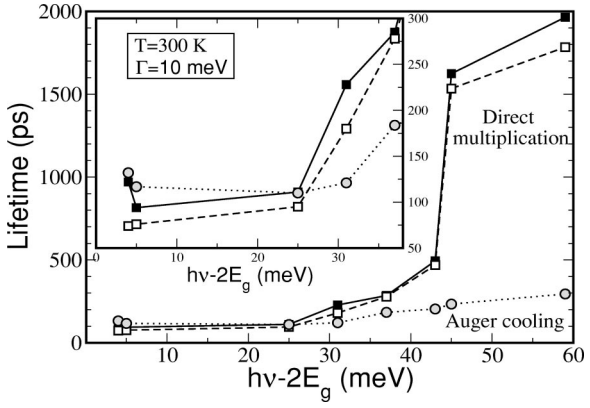

FIG. 3. DCM lifetimes with (filled squares and solid line) and without (empty squares and dashed line) a hole present, compared to AC lifetimes (filled circles and solid line), for different (initial) impacting electron levels $e_{\mathrm{th}+1}$, as a function of the photon excess energy $h\nu-2E_g$ at room temperature. Inset: detail of the curve crossings in the low-energy region of the graph.

energy levels above threshold. The AC lifetimes are obtained by summing over 30 deep hole final states $\{h_n\}$, whose energy is centered around $\epsilon_{h_1}-E_g$.

Bulk versus dot. We find (insets in Figs. 2 and 3) that the DCM rate in dots is already on the order of 10^{10} s^{-1} for energies just a few meV above $E_{\mathrm{th}}=E_g$, whereas in conventional bulk materials (GaAs, $In_{0.53}Ga_{0.47}As$, $Si_{0.5}Ge_{0.5}$, for example), it only reaches values of that order of magnitude for energies $\sim$1 eV above E_g.[9,10] This represents a great performance improvement.

Neutral versus charged dot. For excess energies just above threshold (insets of Figs. 2 and 3), the DCM lifetime calculated in the presence of a hole is about a factor of two larger than that computed without it, both on average and at the arrow. The presence of a (photogenerated) hole in the ground state, in fact, reduces the number of final states available to the e–h pair created via DCM, thereby increasing the lifetime, compared to the configuration with no hole. The presence of a hole in h_1 has a much smaller effect on the DCM lifetime for excess energies a few tens of meV above threshold, ($e_{\mathrm{th}+8}$, Fig. 2 mainframe), as in this case the energy of the impacting electron is much larger than the energy of the transition $h_1\rightarrow e_1$, and the final state closest in energy to $\epsilon_{e_{\mathrm{th}+i}}$ corresponds to higher transitions ($h_{3,4}\rightarrow e_1$).

Surface versus volume contributions. We find that for all excitation energies, the surface contribution to the DCM rate is about an order of magnitude larger than the volume contribution, similarly to what was found for Auger multiexciton recombination lifetimes.[13]

DCM *versus* AC *and role of the valence gap*. For excess energies $\sim E_{\mathrm{th}}$ (inset of Fig. 2), the DCM process is faster than AC, both on average (122 ps compared to 132 for AC), and at the arrow, where the DCM lifetime with hole is about 2/3 of τ_{AC}, yielding a DCM efficiency of 61%. When the electron is photogenerated with a higher excess energy (level $e_{\mathrm{th}+8}$, Fig. 2), however, AC will prevent efficient DCM. This is due to the presence of a large energy gap, which is found[18] within the hole manifold of spherical dots between the states h_4 and h_5. For a CdSe dot with $d=29.3$ Å, this gap is about 130 meV wide and located $\sim$50 meV below the VBM. In this energy range, there are therefore no energy-conserving transitions $h_n\rightarrow e_j$ available to the DCM process. Such a peculiar situation does not exist, however, for deep hole states (the ones involved in the AC process), therefore the AC lifetime is almost constant for all energies. As a consequence, τ_{DCM} becomes more than one order of magnitude larger than τ_{AC} for energies above the $h_4\rightarrow e_1$ transition but below the $h_5\rightarrow e_1$ transition (Fig. 3). It follows that a natural way to enhance the DCM process relative to AC would be the introduction of a fast hole-trapping species whereby the hole is removed from the dot core and trapped at its surface, leading to a suppression of the Auger cooling mechanism. Exciting high electron levels at DCM threshold could then represent an efficient alternative to VBM/CBM pumping to achieve population inversion, a crucial step towards lasing, in colloidal quantum dots.

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