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Computational modeling of quantum-confined impact ionization in Si nanocrystals embedded in SiO_2

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Abstract

Injected carriers from the contacts to delocalized bulk states of the oxide matrix via Fowler–Nordheim tunneling can give rise to quantum-confined impact ionization (QCII) of the nanocrystal (NC) valence electrons. This process is responsible for the creation of confined excitons in NCs, which is a key luminescence mechanism. For a realistic modeling of QCII in Si NCs, a number of tools are combined: ensemble Monte Carlo (EMC) charge transport, ab initio modeling for oxide matrix, pseudopotential NC electronic states together with the closed-form analytical expression for the Coulomb matrix element of the QCII. To characterize the transport properties of the embedding amorphous SiO_2, ab initio band structure and density of states of the α-quartz phase of SiO_2 are employed. The confined states of the Si NC are obtained by solving the atomistic pseudopotential Hamiltonian. With these ingredients, realistic modeling of the QCII process involving a SiO_2 bulk state hot carrier and the NC valence electrons is provided.

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Keywords: Quantum confined impact ionization; Ensamble Monte Carlo; High field transport; Si nanocrystals

1. Introduction

Due to its indirect band gap, bulk Si is a very inefficient emitter, even at liquid He temperatures. Within the last decade, several approaches were developed towards improving the efficiency of light emission from Si-based structures. In spirit, all were based on the lifting of the lattice periodicity that introduces an uncertainty in the *k*-space and therefore altering the indirect nature of this material. Some examples are: SiGe or Si–SiO_2 superlattices [1,2] or Si nanocrystal (NC) assemblies [3]. Recently, blue electroluminescence (EL) from Si-implanted SiO_2 layers and violet EL from Ge-implanted SiO_2 layers were observed. An important process responsible for EL occurring in quantum dots and NCs is the quantum-confined impact ionization (QCII). A carrier initially at a high energy in the continuum states of the bulk structure when able to excite a valence band electron of a NC across its band gap creates an electron–hole pair (cf. Fig. 1). This process is responsible for the introduction of confined excitons in silicon NC LEDs, which is a key luminescence mechanism. In contrast to its crucial role, QCII has not been given the attention it deserves.

To model the QCII process, we start by characterizing the hot electron transport in oxides within the ensemble Monte Carlo framework. Density of states and band structure of common crystal phases of the SiO_2 used in our Monte Carlo transport calculation are obtained by using the ABINIT code [4], which is based on the density functional *ab initio* methodology. Next, we derive an analytical expression for the QCII probability in NCs that can become an instrumental result in assessing EL in the presence of other competing scattering mechanisms. The effect of QCII on bulk transport quantities is also discussed.

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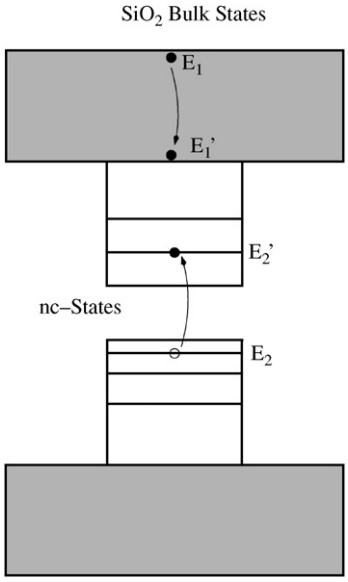

Fig. 1. Quantum-confined impact ionization in NCs.

2. Theoretical details

First-principles band structure and density of states (DOS) for SiO_2 were calculated within the density functional theory, using the pseudopotential method employing the local density approximation as implemented in the ABINIT code [4] in excellent agreement with the available results [5,6]. We demonstrate the utility and the validity of our *ab initio* DOS results by studying the high-field carrier transport in bulk SiO_2 up to fields of 10 MV/cm using the ensemble Monte Carlo technique which is currently the most reliable choice for studying hot carrier phenomena free from major simplifications [7,8]. We include the acoustic, polar and non-polar optical phonon scatterings. The corresponding scattering rates are intimately related with the band structure and the DOS of SiO_2 for which we use those of the α-quartz phase due to its strong resemblance of the amorphous SiO_2 in terms of both the short-range order and the total DOS [9]. Aiming for very high fields around 10 MV/cm, we also include the impact ionization process within the bulk SiO_2 medium; the relevant parameters were taken from the work of Arnold et al. [10].

Our modeling for QCII is an extension of the approach by Kehrer et al. [11] who have dealt with the high-field impurity breakdown in n-GaAs. We assume the impacting carrier to be an electron; however, all the formulation can be reiterated by starting with an impacting high-energy hole in SiO_2. Above the mobility edge that is well satisfied for an energetic electron in SiO_2 the bulk SiO_2 wave function will be of the Bloch form

$$\psi_b = \frac{1}{\sqrt{V}} u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{1}$$

whereas for the NC wave function we use a simple hydrogenic form [11],

$$\psi_n = \frac{\alpha_v^{3/2}}{\sqrt{\pi}} u_v(\mathbf{r}) e^{-\alpha|\mathbf{r}|}, \tag{2}$$

Some remarks will be in order, regarding the choice of these wave functions. Even though the embedding medium is usually an *amorphous* oxide, for high-field transport purposes well above the mobility edge, one can safely use crystalline states (i.e., Bloch functions) [9,10]. On the other hand, the use of hydrogenic wave function, which is well suited for the impurity problem was preferred solely due to its analytical convenience. The latter can be relaxed in case a closed-form expression is not aimed for.

Furthermore, we are neglecting the exchange interaction between the impacting electron and the valence NC electron due to huge energy difference between them [12]. The scattering matrix element that is due to the Coulomb interaction between the two electrons is given by

$$M = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\alpha_c^{3/2}}{\sqrt{\pi}} u_c^*(\mathbf{r}_1) e^{-\alpha_c|\mathbf{r}_1|} \frac{1}{\sqrt{V}} u_{k'}^*(\mathbf{r}_2) e^{i\mathbf{k}'\cdot\mathbf{r}_2} \times \frac{e^2}{4\pi\varepsilon\varepsilon_0} \frac{e^{-\lambda|\mathbf{r}_1-\mathbf{r}_2|}}{|\mathbf{r}_1-\mathbf{r}_2|} \frac{1}{\sqrt{V}} u_k(\mathbf{r}_2) e^{i\mathbf{k}\cdot\mathbf{r}_2} \frac{\alpha_v^{3/2}}{\sqrt{\pi}} u_v(\mathbf{r}_1) e^{-\alpha_v|\mathbf{r}_1|},$$

yielding

$$|M|^2 = \left[\frac{64e^4\alpha_c^3\alpha_v^3\alpha^2}{(\varepsilon\varepsilon_0 V)^2}\right] |F_{cv}|^2 |F_{k'k}|^2 \times \frac{1}{[|\mathbf{k}-\mathbf{k}'|^2+\lambda^2]^2} \frac{1}{[|\mathbf{k}-\mathbf{k}'|^2+\alpha^2]^4}, \tag{3}$$

where

$$F_{cv} = \int_{\text{cell}} u_c^*(\mathbf{r}_1) u_v(\mathbf{r}_1) d^3\mathbf{r}_1,$$

$$F_{k'k} = \int_{\text{cell}} u_{k'}^*(\mathbf{r}_2) u_k(\mathbf{r}_2) d^3\mathbf{r}_2,$$

and $\alpha = \alpha_c + \alpha_v$. By using Fermi's golden rule, we can write

$$P(k) = \sum_{\text{NC}} \sum_{k'} \frac{2\pi}{\hbar} |M|^2 \delta\left[\frac{\hbar^2k^2}{2m_k} - E_v - E_c - E_g - \frac{\hbar^2k'^2}{2m_{k'}}\right] f_{\text{NC}}, \tag{4}$$

where E_g is that bandgap of the NC which is absorbed into the value of E_c. Here E_v is taken as positive hole energy. Taking $A = ((m_{k'}k^2)/m_k) - ((2m_{k'}E_v)/\hbar^2) - ((2m_{k'}E_c)/\hbar^2) - ((2m_{k'}E_g)/\hbar^2)$ and assuming

$$\sum_{\text{NC}} f_{\text{NC}} = N_{\text{NC}} = n_{\text{NC}} V, \tag{5}$$

where n_{NC} is the density per unit volume and in terms of the NC filling ration n_{NC} is

$$n_{\text{NC}} = \frac{f}{V_{\text{NC}}}, \tag{6}$$

$$P(k) = \sum_{k'} \frac{4\pi m_{k'}}{\hbar^3} |M|^2 \delta[A^2 - k'^2] n_{\mathrm{NC}} V. \quad (7)$$

There is no spin summation as the Coulomb interaction preserves spin. Using Eqs. (3) and (5) we can write

$$P(k) = \frac{V}{(2\pi)^3} \int \mathrm{d}^3\mathbf{k}' \frac{4\pi m_{k'}}{\hbar^3} \left[\frac{64 e^4 \alpha_c^3 \alpha_v^3 \alpha^2}{(\varepsilon\varepsilon_0 V)^2}\right] |F_{cv}|^2 |F_{k'k}|^2 \times \frac{1}{[|\mathbf{k}-\mathbf{k}'|^2 + \lambda^2]^2} \frac{1}{[|\mathbf{k}-\mathbf{k}'|^2 + \alpha^2]^4} \delta[A^2 - k'^2] n_{\mathrm{NC}} V, \quad (8)$$

$$P(k) = -\frac{\pi C}{2k} \frac{1}{3(\alpha^2-\lambda^2)^5} \left[-\frac{9(\alpha^2-\lambda^2)}{(|A|-k)^2+\alpha^2} + \frac{9(\alpha^2-\lambda^2)}{(|A|+k)^2+\alpha^2} - \frac{3(\alpha^2-\lambda^2)^2}{((|A|-k)^2+\alpha^2)^2} + \frac{3(\alpha^2-\lambda^2)^2}{((|A|+k)^2+\alpha^2)^2} - \frac{(\alpha^2-\lambda^2)^3}{((|A|-k)^2+\alpha^2)^3} + \frac{(\alpha^2-\lambda^2)^3}{((|A|+k)^2+\alpha^2)^3} - \frac{3(\alpha^2-\lambda^2)}{((|A|-k)^2+\alpha^2)} + \frac{3(\alpha^2-\lambda^2)}{((|A|+k)^2+\alpha^2)} + 12 \ln\left\{\frac{[(|A|-k)^2+\alpha^2][(|A|+k)^2+\lambda^2]}{[(|A|+k)^2+\alpha^2][(|A|-k)^2+\lambda^2]}\right\}\right]. \quad (9)$$

where

$$C = \left[\frac{32 e^4 \alpha_c^3 \alpha_v^3 \alpha^2 m_{k'}}{\hbar^3 \pi^2 (\varepsilon\varepsilon_0)^2}\right] |F_{cv}|^2 |F_{k'k}|^2 n_{\mathrm{NC}}.$$

Here the screening parameter within Thomas–Fermi approximation is given in cgs units by

$$\lambda = \left[4(3/\pi)^{1/3} \frac{n_0^{1/3}}{a_0}\right]^{1/2}. \quad (10)$$

We should note that the direct adoption of the bulk screening model to the case of NCs discards the polarization charges on the NC surface which are supposed to cancel the screening effect within the oxide region [15].

The α parameter of the wave function shown in Eq. (2) is extracted by fitting it to the wave function obtained from a pseudopotential-based electronic structure calculation for Si NCs [13] both of which are illustrated in Fig. 2. The effect of the carrier density due to Thomas–Fermi screening length can be observed in Fig. 3. As seen in Eq. (9), NC density and QCII scattering probability are directly proportional as expected.

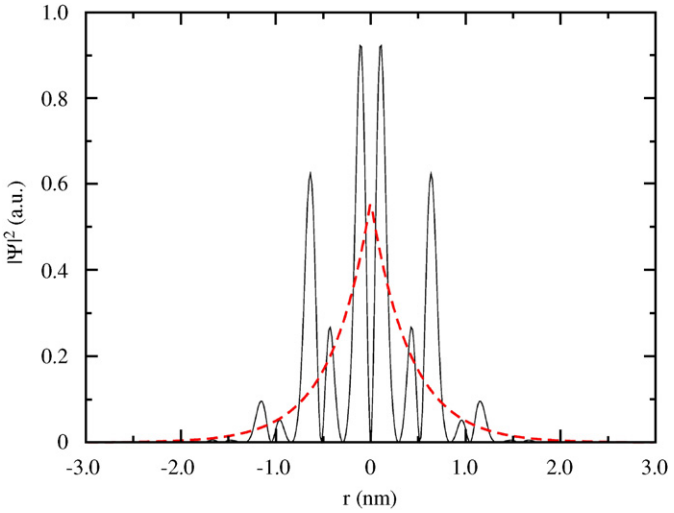

Fig. 2. Pseudopotential and the fitted hydrogenic wave functions.

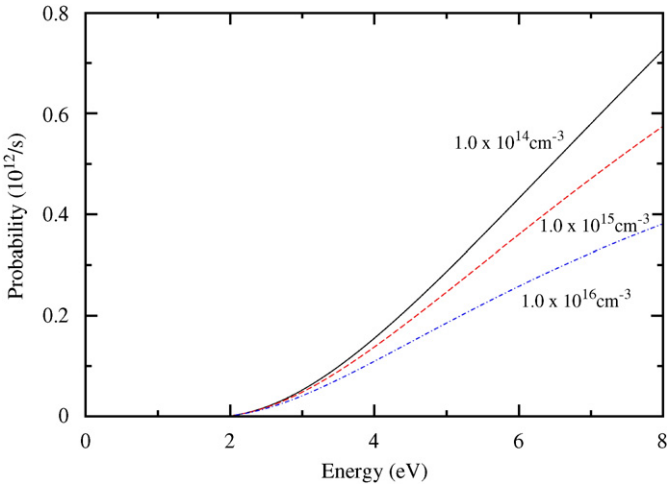

Fig. 3. QCII probability for carrier densities; 10^{14}, 10^{15}, and $10^{16}\,\mathrm{cm}^{-3}$.

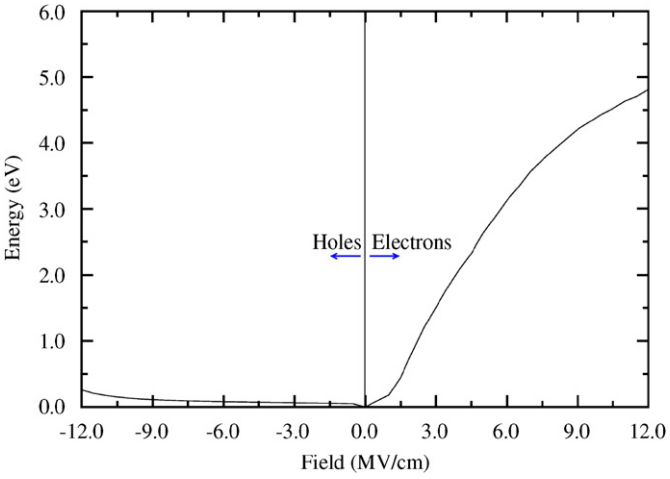

Fig. 4. SiO_2 field vs. energy profile for both electrons and holes.

3. Results

We simulate the high-field transport for both electrons and holes within SiO_2 and important observation is that the energy gained by the holes is well below 0.5 eV even for fields above 10 MV/cm due to excessive scattering, which is a consequence of the very large DOS close to the valence band edge (see Fig. 4). For Si NCs embedded in SiO_2 the EL peak is typically around 2 eV [14]. Based on our results, we can conclude that such an energy cannot be imparted by the bulk SiO_2 holes to the NC carriers through the QCII process. Other mechanisms such as direct tunneling from contacts to NCs may be responsible for the p-type EL.

Turning to electrons that can become indeed hot in SiO_2 matrix, we simulate the high-field transport with and without

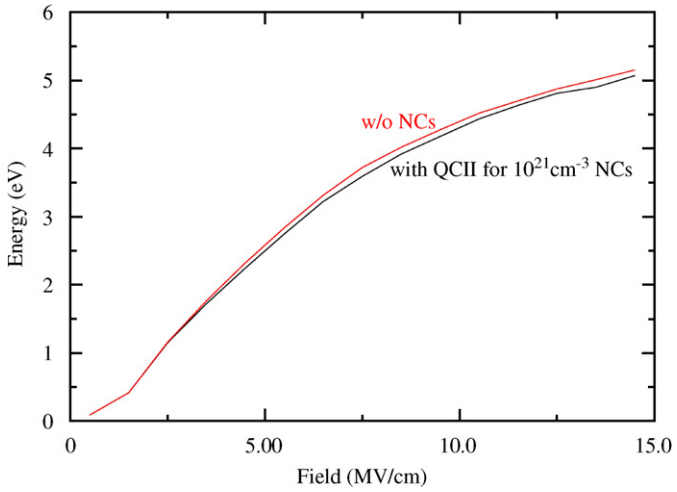

Fig. 5. SiO_2 field vs. energy profile with and without QCII.

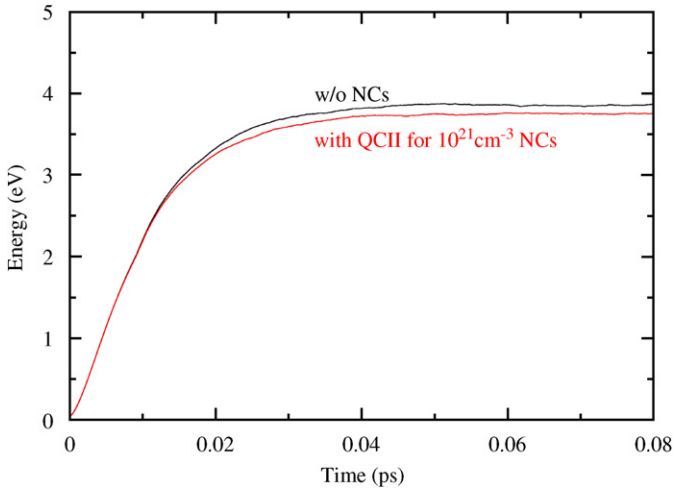

Fig. 6. Time evolution of the average energy of electrons with and without QCII.

QCII by setting the carrier and NC densities to 10^{15} and $10^{21}\,cm^{-3}$, respectively. It can be inferred from the average energy versus field behavior (see Fig. 5) that QCII does not have significant effect. In Figs. 6 and 7 we illustrate the temporal evolution of the average carrier energy and velocity with and without QCII at a fixed electric field value of 8 MV/cm; carrier and NC densities are again chosen as $10^{15}\,cm^{-3}$ and 10^{21}, respectively. It can be observed that steady state is attained for these hot electrons within about 30 fs. Furthermore, there is a no pronounced effect of QCII on the average velocity and energy profiles.

4. Conclusions

QCII is an important high-field process that can lead to luminescence. As our main contribution, we propose a closed-form expression of the QCII probability that is incorporated into the EMC high-field transport framework that involves other major scattering mechanisms. The scattering rates are computed using *ab initio* DOS for SiO_2 matrix. Our results for a range of parameters indicate that QCII has a marginal effect on the carrier average energy and velocity characteristics both in the transient and steady-state regimes. Finally, it needs to be mentioned that we consider a specific QCII process that yields an electron–hole pair within the NCs (cf. Fig. 1); there are other variants of this process (still to be named as QCII) which may have much more dramatic effect on the average carrier transport quantities such as bulk carrier multiplication leading to dielectric breakdown.

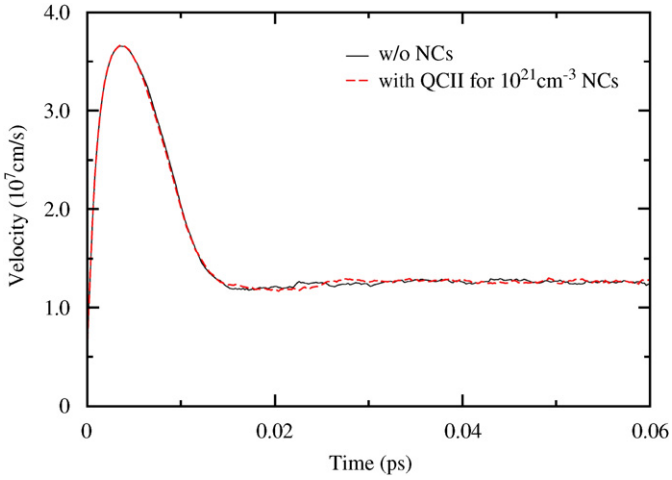

Fig. 7. Time evolution of the average velocity of electrons with and without QCII.

Acknowledgments

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