Singlet oxygen generation mechanism in the presence of excited nanoporous silicon

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Abstract. A theoretical analysis of the mechanism of generation of singlet oxygen in the presence of photoexcited nanoporous silicon is presented. It is shown that the generation of singlet oxygen is based on nonradiative energy transfer from nanoporous silicon to an oxygen molecule by the exchange mechanism. An analytical expression is obtained and a numerical estimation of the probability of energy transfer from nanoporous silicon to an oxygen molecule is given. It is shown that its numerical value on the order of $10^3 - 10^4 \text{s}^{-1}$ is in good agreement with experiment.

1. Introduction
Recent studies have shown the promise of nanoporous silicon (np-Si) for micro- and optoelectronics [1] as well as for biology and medicine [2,3]. As it was shown in a number of works [2,4,5], generation of singlet oxygen is possible in the presence of excited nanoporous silicon. This was shown both by direct measurement of luminescence [4], and indirectly, on the basis of the biological effect of singlet oxygen [5]. Therefore, clarifying the exact mechanism of this process is an important task. In [4-6], an assumption was made on the role of the exchange interaction in this process. In work [6], a mechanism is proposed for generating singlet oxygen due to the simultaneous tunneling of an electron and a hole with or without the participation of phonons. This mechanism is similar in essence to the tandem mechanism of energy transfer, considered in [7]. Nevertheless, this mechanism is not considered in this paper, because in our opinion it is less effective than the exchange interaction without charge transfer. In addition, although the appearance of a dipole mechanism of energy transfer due to violation of the spin selection rules during spin-orbit interaction in silicon and oxygen, nevertheless this effect is negligibly small due to the weakness of the spin-orbit interaction in oxygen. According to the quantum chemical calculations [8] and experiments, oxygen has a triplet form in the ground state, ie, the total spin of the oxygen molecule is $S = 1$. Oxygen allows for the existence of two long-lived singlet forms with energies of 0.98 eV and 1.63 eV above the ground state. The lifetime of an electron at the second excited level with an energy of 1.63 eV is of the order of 7 seconds, however, its lifetime in the first excited state with an energy of 0.98 eV is extremely large (~ 72 min for a free oxygen molecule). The last metastable form is singlet oxygen and is chemically active. It is well known that the size-quantization effect leads to an increase in the effective width of the forbidden band of the semiconductor. This leads to the possibility of resonant energy transfer from nanoporous silicon to the oxygen molecule. The purpose of this paper is a theoretical study of the process of energy transfer from excited nanoporous silicon to an oxygen molecule.
2. Theory

To calculate the probability of energy transfer in quantum mechanics, the perturbation theory method is usually used [9]. In the case of strong interaction, the density matrix method [10] is used. Nanoporous silicon can be represented by a simple quantum well model for electrons and holes. Its depth is determined by the work function of the electron from silicon. In this case, quantization exists only in one direction, in others there is free motion. The scheme of the process of energy transfer and energy levels of silicon and molecular oxygen is shown in Fig. 1, 2, 3. To calculate the energy transfer matrix element, it is necessary to know the wave functions of the initial and final states of the system. Since excited states are considered in the oxygen molecule, it is impossible to take them into account correctly without taking the configuration interaction into account [8]. Usually for the simplest systems, such as molecular oxygen, there is a small set of configurations to correctly estimate the energy and wave function of the electrons. Molecular orbitals (MO) can be represented as a linear combination of atomic orbitals (AO), centered on the nucleus A and nucleus B of the oxygen molecule (see Fig. 2). To compose AO, Slater orbitals are used, and it is assumed that the outer 2p electrons move in the Coulomb field with an effective charge $Z^* = 4.55$. For them, $n^* = 2$, therefore the general form of the wave functions of the molecular orbitals takes the following form (see also Fig. 2):

$$
\Psi_{\mu}(r) = C_{\mu}(r) \left( \frac{1}{\sqrt{\pi}} \sum_{n} \sin \theta \exp(\pm i \phi) \left( \exp(-\alpha r^2) \left( + \right) \exp(-\beta r^2) \right) \right)
$$

Here $a_0$ is the Bohr radius of the electron, $C_{\mu}$ is the normalization constant. The wave functions of the states of the oxygen molecule for the ground state $3\Sigma_g^-$ (triplet):

$$
\Psi_{3\Sigma_g^-}(\xi_1, \xi_2) = F_{\mu}^{3\Sigma_g^-}(r_1, r_2) \cdot \chi_{3\Sigma_g^-}(1,2) = \frac{1}{\sqrt{2}} \cdot \left[ \pi_{\mu}^{-}(1) \pi_{\mu}^{-}(2) - \pi_{\mu}^{+}(1) \pi_{\mu}^{+}(2) \right] \cdot \chi_{3\Sigma_g^-}(1,2).
$$

where $\chi_{3\Sigma_g^-}(1,2)$ is one of the three symmetric spin functions with total spin (-1,0,1). For the second excited state $1\Sigma_g^+$ (singlet):

$$
\Psi_{1\Sigma_g^+}(\xi_1, \xi_2) = F_{\mu}^{1\Sigma_g^+}(r_1, r_2) \cdot \chi_{01\Sigma_g^+}(1,2) = \frac{1}{\sqrt{2}} \cdot \left[ \pi_{\mu}^{-}(1) \pi_{\mu}^{-}(2) + \pi_{\mu}^{+}(1) \pi_{\mu}^{+}(2) \right] \cdot \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \beta(1) \alpha(2) \right]
$$

The effect of excited configurations can be assumed to be small. The matrix element of energy transfer is represented by the expression:

$$
M_{if} = \int d^3 r_1 d^3 r_2 d^3 r_3 \psi_f^*(\xi_1, \xi_2, \xi_3) \tilde{V} \psi_i(\xi_1, \xi_2, \xi_3) d^3 r_1 d^3 r_2 d^3 r_3
$$

where

$$
\tilde{V} = \frac{1}{2} \times \sum_{\mu \nu} V^{\mu \nu}_{\mu \nu}
$$

with

$$
V^{\mu \nu}_{\mu \nu} = \frac{1}{\sqrt{2}} \left[ \pi_{\mu}^{-}(1) \pi_{\mu}^{-}(2) - \pi_{\mu}^{+}(1) \pi_{\mu}^{+}(2) \right] \cdot \chi_{3\Sigma_g^-}(1,2) \cdot \chi_{3\Sigma_g^-}(1,2).
$$
Here $\xi = (\mathbf{r}, \sigma)$ is the set of coordinate and spin variables. The interaction operator is taken to be the Coulomb interaction operator between all three electrons (an excited electron in silicon and two electrons per MO oxygen), namely $V = V_{12} + V_{23} + V_{13}$, where $V_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ is the Coulomb interaction operator.

The total wave function of the initial state (silicon and oxygen molecule), antisymmetric when replacing any two electrons has the form:

$$\Psi = T^U \cdot \Psi_0$$

The antisymmetric wave function of the final state has a similar form. The substitution of the electronic $\Psi_e^c(\mathbf{r}_1)$ and hole $\Psi_{h1}(\mathbf{r}_1)$ wave functions in (4) yields:

$$M_{if} = 2 \cdot (M_{\text{cou}} + \frac{M_{\text{cou}}}{2} - M_{\text{ex}})$$

According to the spin selection rules, the matrix element of the Coulomb interaction without taking into account the spin-orbit interaction is zero. The nonzero matrix element of the exchange interaction is:

**Figure 2.** Oxygen molecule and coordinate notation.
A simple estimation shows that the wave function in silicon has longer "tails" than the oxygen molecule, and therefore the structure of the wave functions in silicon is not important. It is important to calculate the overlap between the tail of the silicon wave functions and the function of oxygen. In the matrix element itself, the calculation procedure is similar, taking into account the fact that the Coulomb potential is expanded in multipoles and in the final expression all contributions are summed. For simplicity, we assume that all three matrix elements are equal in order of magnitude.

We calculate the probability of energy transfer. Since in the initial and final states there is a continuous motion in the plane of the quantum well, in contrast to the case of a completely discrete spectrum, perturbation theory can be used to calculate the probability of energy transfer. To calculate the transfer rate, it is necessary to sum the probability of energy transfer across all the initial and final states. The generation rate of singlet oxygen has the following form:

$$G = \frac{2\pi}{\hbar} \int d\Gamma_i d\Gamma_f |M_{ex}|^2 f_c f_h \delta(E_i - E_f)$$

Since we normalize the wave functions in the box in the plane of free motion, the density of the initial states has the form (for the finite ones, similarly):

$$d\Gamma_i = \frac{L_z L_y q^2 d\Gamma_c}{(2\pi)^2}$$
The calculations yield that the total matrix element is proportional to $q_c q_h \cos(q_c - q_h)$, where $q_{eh}$ is the wave vector of the electron (hole) in the plane of the well. This means that, in the process of scattering, firstly, there is no conservation of the quasimomentum, and secondly, the matrix element is maximal for the momenta of the electron and hole co-directed with each other. Therefore, the missing impulse should be transferred to the oxygen molecule. The speed becomes:

$$G = \frac{2\pi}{\hbar} \int q_c dq_c dq_h dq_h |\tilde{M}_{ex}|^2 f_c f_h \delta(E_i - E_f)$$

Here $\tilde{M}_{ex}$ is the reduced matrix element equal to $\tilde{M}_{ex} = M_{ex} L_x L_y$. Using the delta function property and integrating over the corners, this expression can be calculated:

$$G = \frac{2\pi \hbar^2}{h^2 T} n_c n_h e^{-\frac{1}{2} \left( E_0 - \frac{\hbar^2 k_f^2}{2m_{xx}} \right)} X^3 \langle A \rangle_0^2 \frac{m_{xx} + m_{yy}}{24 m_{hh}^2}$$  (7)

Here, $\langle A \rangle_0 = \langle \tilde{M}_{ex} / (q_c q_h) \rangle$ is the value of the reduced matrix element averaged over the directions of the hole in silicon, and $X = \frac{2m_{hh}}{h^2} \left( E_0 - \frac{\hbar^2 k_f^2}{2m_{xx}} \right)$, where $E_0 = \Delta - E_g$ and $\Delta$ is the transition energy in the oxygen molecule. In this case, $m_{xx}$, $m_{yy}$, $m_x$, $m_{hh}$ are the effective masses of charge carriers in silicon, and $n_c$, $n_h$ are the two-dimensional carrier concentrations in the well.

According to expression (7), a numerical calculation was made for two-dimensional electron and hole concentrations in silicon of the order of $10^{13}$ cm$^{-2}$. In this case, the wall thickness of the porous silicon was adopted 1.2 nm. For such concentrations and such a wall thickness, in the case of an oxygen molecule adsorbed on the surface of porous silicon, $G \sim 10^4$ s$^{-1}$. This rate correlates well with the transfer time obtained from the experiment of 120 µs [4]. The total transfer rate rapidly decays with increasing distance between porous silicon and the oxygen molecule due to the exchange nature of the interaction of electrons and for the distance from the surface of nanoporous silicon to an oxygen molecule of 0.6 Å, the rate decreases by an order of magnitude.

The effectiveness of the transfer process depends on a number of conditions. First, the characteristic residence time of the oxygen molecule in the adsorbed state should exceed the transport time. Secondly, the lifetime of the oxygen molecule in the first excited state, as well as the lifetime of the exciton, are greater than the inverse transfer time. In this case, the electron in oxygen will pass to the second excited state, from which it relaxes to the first excited state. These conditions are realized in practice. The account of phonons and the mechanism considered in [7] are not considered here.

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