

EFFICIENT ELECTRONIC ENERGY TRANSFER FROM A SEMICONDUCTOR QUANTUM WELL TO AN ORGANIC MATERIAL

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We predict an efficient electronic energy transfer from the two-dimensional Wannier-Mott excitons confined in a semiconductor quantum well to the optically active organic molecules of the nearby medium (substrate and/or overlayer). The energy transfer mechanism is of the Förster type and, at semiconductor-organic distances of several nanometers, can easily be as fast as 100 ps, which is about an order of magnitude shorter than the average exciton lifetime in an isolated quantum well. In such conditions, the Wannier-Mott exciton luminescence is quenched and the organic luminescence is efficiently turned on. Our calculations, combining a microscopic quantum mechanical exciton model with a macroscopic electrodynamic description of the organic medium, take into account the dielectric constant discontinuities and can be applied to any organic-inorganic multilayer structure.

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A large effort has recently been devoted to the study of organic light emitting diodes [1] and lasers [2]. Förster-like energy transfer between different dye molecules in solid solutions has already been used to achieve light amplification in optically pumped organic thin films [3]. However, optically active organic materials have poor transport properties compared to inorganic semiconductors and the efficient electrical pumping of such devices is a challenging problem. Prompted by the rapid advances of epitaxial growth techniques for crystalline molecular materials (even on inorganic substrates), we consider here a novel hybrid configuration in which both inorganic semiconductors and organic materials are present: the basic idea is to pump the optically active organic molecules via electronic energy transfer from the two-dimensional Wannier-Mott excitons of a semiconductor quantum well. Hopefully, in this hybrid system, it would be possible to capitalize on the efficient electrical pumping of the inorganic semiconductor material.

In organic-inorganic heterostructures, in fact, it is possible to take advantage of the complementary functional properties of both types of material. This has been shown to be the case, for instance, in the coherent hybrid Wannier-Mott/Frenkel excitons at a covalent-semiconductor/molecular-solid interface [4]: such novel excitations share both the large radius of a Wannier-Mott exciton and the large oscillator strength of a Frenkel exciton, and consequently exhibit large optical nonlinearities [5]. The focus of the present paper is on the basic physics governing the incoherent resonant electronic energy transfer from the semiconductor quantum well to the organic material. Our model calculations, employing realistic material parameters, show that such energy transfer can

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be fast enough to efficiently quench the Wannier–Mott exciton luminescence and pump the organic molecule light emission.

The configuration we consider consists of a semiconductor quantum well of width L_w sandwiched between two semiconductor barriers of width L_b , the whole semiconductor structure embedded in bulk-like organic material (for the sake of simplicity, we choose a symmetric configuration and consider the organic material to be isotropic). The background dielectric constant ϵ_b of the semiconductor material is taken to be real, whereas the organic material dielectric constant $\tilde{\epsilon}$ has both a real and an imaginary part in the frequency region of interest. In fact, we are interested in an organic material having a broad band in the optical range overlapping the two-dimensional Wannier–Mott exciton sharp resonance energy ($\hbar\omega$). The Förster like energy transfer mechanism due to the dipole-dipole interaction can be calculated simply from the Joule losses [6] in the organic material. These are proportional to the imaginary part of $\tilde{\epsilon}$ and are produced by the penetration of the electric field generated by the semiconductor exciton polarization (explicitly taken into account as a source term in the macroscopic electrostatic equations). Neglecting retardation is a valid approximation as the typical exciton center of mass in-plane wavevector k is much larger than the wavevector of the corresponding resonant light ($k \gg \sqrt{\epsilon_b} \omega/c$). We also assume to be in the linear regime in which excitons can be described in the bosonic approximation.

We indicate with z the growth direction ($z = 0$ corresponding to the center of the quantum well) and with x the direction of the in-plane exciton wavevector. We adopt a microscopic quantum mechanical model of a quantum well Wannier–Mott exciton, where the polarization can be taken to vanish for $|z| > L_w/2$ and, inside the well, to be given by

$$\mathbf{P}(x, z) = \frac{d \hat{x}}{a_B \sqrt{S}} \frac{2}{L_w} \cos^2\left(\frac{\pi z}{L_w}\right) \exp(ikx), \quad (1)$$

where a_B is the exciton Bohr radius, S is the in-plane normalization area, d is the interband transition dipole moment, \hat{x} is a unit vector and the polarization chosen is that of the L -mode [4]. An analogous calculation can be carried out for the Z -mode. The corresponding electric field $\mathbf{E}(x, z) = -\nabla\Phi(x, z)$ can be obtained from the solution of the Poisson equation

$$\epsilon(z)\nabla^2\Phi(x, z) = 4\pi \nabla \cdot \mathbf{P}(x, z), \quad (2)$$

with the appropriate boundary conditions at $z = \pm L_w/2$ and at $z = \pm(L_w/2 + L_b)$, i.e., continuity of the tangential component of the electric field $\mathbf{E}(x, z)$ and of the normal component of the electric displacement $\mathbf{D}(x, z) = \epsilon(z)\mathbf{E}(x, z)$. Writing $\Phi(x, z) = \phi(z) \exp(ikx)$, we have that $\phi(z)$ satisfies

$$\frac{d^2\phi}{dz^2} - k^2\phi = \frac{4\pi}{\epsilon_b} ik \frac{d}{a_B \sqrt{S}} \frac{2}{L_w} \cos^2\left(\frac{\pi z}{L_w}\right), \quad (3)$$

for $|z| < L_w/2$, and otherwise

$$\frac{d^2\phi}{dz^2} - k^2\phi = 0, \quad (4)$$

with the boundary conditions that $\phi(z)$ and $\epsilon(z) d\phi(z)/dz$ be continuous at the four interfaces. The corresponding solution in the organic material (from now on $k > 0$ and

$z > L_w/2 + L_b$) is given by

$$\phi(z) = -i \frac{2q^3}{k(k^2 + q^2)} \frac{d}{a_B \sqrt{S}} \frac{(e^{kL_w/2} - e^{-kL_w/2})}{(\epsilon_b + \bar{\epsilon}) - (\epsilon_b - \bar{\epsilon}) e^{-2kL_b - kL_w}} \exp(-kz), \quad (5)$$

with $q = 2\pi/L_w$. Thus, the electric field penetrating in the organic material is given by

$$E_x(x, z) = -ik \exp(ikx) \phi(z), \quad E_z(x, z) = k \exp(ikx) \phi(z), \quad E_y = 0. \quad (6)$$

We observe that the macroscopic approach we follow is fully adequate as the electric field is slowly varying on the molecular scale. It is now a simple matter to calculate the Joule losses in the organic material, the time-averaged power per unit volume being [7]

$$w(z) = \frac{\omega}{4\pi} \text{Im}(\bar{\epsilon}) k^2 |\phi(z)|^2, \quad (7)$$

with $\phi(z)$ given by Eq.(5). Thus, the total power delivered to the organic material is

$$W = S \int_{L_w/2+L_b}^{+\infty} dz w(z) = \frac{S\omega}{8\pi k} \text{Im}(\bar{\epsilon}) k^2 |\phi(z = L_w/2 + L_b)|^2 \equiv \frac{\hbar\omega}{\tau}, \quad (8)$$

where we have introduced τ as the average time required by an exciton to transfer its energy to an organic molecule (considering also the organic material in $z < -L_w/2 - L_b$, τ would be half as short). We can observe that the previous expression for τ does not depend on the excitation density (as long as the linear regime applies). In fact, if the bosonic exciton state is N times populated the corresponding polarization scales as \sqrt{N} and the power w as N , just as the total excitation energy $N\hbar\omega$; indeed, N cancels from both sides of Eq.(8). Besides, the same expression can be derived from a fully microscopic approach considering the Förster dipole-dipole energy transfer and the appropriate averaging procedure.

We estimate the order of magnitude of τ from Eq.(8) and Eq.(5), employing parameters representative of II-VI semiconductor quantum wells [8] and optically active organic condensed media such as metallophthalocyanines [9] or fullerenes [10]. Taking $L_w \simeq 60 \text{ \AA}$, $L_b \simeq 40 \text{ \AA}$, $k \simeq 3 \cdot 10^6 \text{ cm}^{-1}$ (appropriate to a thermalized exciton distribution with $T \simeq 100 \text{ K}$), $d/a_B \simeq 0.1 e$, $\epsilon_b \simeq 5$, $\bar{\epsilon} \simeq 4 + i3$, we obtain for this typical case $\tau \simeq 50 \text{ ps}$. Considering that in an isolated quantum well the exciton lifetime (for such a thermalized distribution) is a few ns [8], the energy transfer mechanism here proposed turns out to be fast enough to efficiently transfer a large fraction of the semiconductor electronic excitation energy to the adjacent organic molecules that will eventually decay emitting visible light.

Finally, we wish to stress that our model calculations can be easily applied to any hybrid multilayer structure and could be generalized to the case in which the structure is embedded in a microcavity and to the case in which the two-dimensional excitons are localized (i.e., in-plane translational symmetry is broken) or the semiconductor is excited in the continuum (i.e., free electron hole pairs, rather than bound excitons, are present).

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