Thin Solid Films 612 (2016) 327–330

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

A probabilistic model of the electron transport in films of nanocrystals arranged in a cubic lattice

Ilka Kriegel [a], Francesco Scotognella [b,c,*]

[a] Department of Nanochemistry, Istituto Italiano di Tecnologia (IIT), via Morego, 30, 16163 Genova, Italy
[b] Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
[c] Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Giovanni Pascoli, 70/3, 20133 Milan, Italy

ARTICLE INFO

Article history:
Received 19 January 2016
Received in revised form 9 June 2016
Accepted 10 June 2016
Available online 11 June 2016

Keywords:
Semiconductor nanocrystals
Nanocrystal films
Conductivity model

ABSTRACT

The fabrication of nanocrystal (NC) films, starting from colloidal dispersion, is a very attractive topic in condensed matter physics community. NC films can be employed for transistors, light emitting diodes, lasers, and solar cells. For this reason the understanding of the film conductivity is of major importance. In this paper we describe a probabilistic model that allows the prediction of the conductivity of NC films, in this case of a cubic lattice of Lead Selenide or Cadmium Selenide NCs. The model is based on the hopping probability between NCs. The results are compared to experimental data reported in literature.

1. Introduction

The interest on the electronic and optical properties of nanocrystal (NC) films is significantly increasing in the last years. NC films combine the easy processability of ink-based films with the outstanding physical properties of semiconductor nanocrystals [1]. The boundless chemical and physico-chemical effort to make NC films of different compounds ensuring charge mobility along them is testified by several works of many research groups [2–4]. In particular, PbSe NC thin films are promising for optoelectronics due to their low band gap [5–7].

However, charge carrier mobility among NCs is also very important in NC-polymer or NC-molecule hybrid films, which are employed in hybrid solar cells, as in Giansante et al. [8] and Mastria et al. [9].

The research group of Guyot-Sionnest presented an elegant description of a hopping model for the charge mobility in CdSe cubic superlattices [10]. Carbone, Carter, and Zimanyi describe a Monte Carlo simulation to study hole and electron mobility and electron conductivity in PbSe films [11]. Besides films based on semiconductor NCs, Ederth et al. presented a model for the optical and electronic properties of indium tin oxide nanoparticle films [12], where indium tin oxide nanoparticles show a plasmonic behaviour [13].

Here we describe a probabilistic model useful to predict the electron conductivity. We demonstrate the results on a NC film of PbSe and CdSe NCs. We studied the electron conductivity as a function of the size of the nanocrystals. The comparison between our model and the experimental results reported in literature show a good agreement. The beauty of the presented model is that the path of only one carrier is taken into account, while for other possibly present carriers a probability function has been implemented. This makes the approach attractive because of the low computational cost and can be implemented in scenarios in which charge carrier transfer, followed by transport, occurs is hybrid conducting NC films.

2. Outline of the model

We consider different cubic superlattices of PbSe and CdSe nanocrystals, in which the parameter that changes is the size of the NCs (diameter), ranging from 3 to 8 nm for PbSe and from 2.9 and 5.1 nm for CdSe, respectively. We take into account only the nearest neighbour hopping. To quantify the hopping rate between the site 1 and the site 2 (being 1 and 2 two nanocrystals of the film), we refer to the work reported by Carbone, Carter, and Zimanyi [11] and references therein. In particular, the hopping rate P is

$$P_{1\to 2} = exp\left(\frac{-\Delta E + el\vec{F}\cdot\hat{i}_{12}}{k_B T}\right) \quad (1)$$

if the exponent of P (with exponent we refer to $\frac{-\Delta E+el\vec{F}\cdot\hat{i}_{12}}{k_B T}$) is <0 (i.e. $\frac{-\Delta E+el\vec{F}\cdot\hat{i}_{12}}{k_B T}<0$) P will be a value in the range (0;1). If the exponent is positive, i.e. $\frac{-\Delta E+el\vec{F}\cdot\hat{i}_{12}}{k_B T}\geq 0$, P will be above 1, which means a probability of >100% and is therefore set equal to 1 (i.e. maximum

* Corresponding author at: Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy.
E-mail address: francesco.scotognella@polimi.it (F. Scotognella).

http://dx.doi.org/10.1016/j.tsf.2016.06.029
0040-6090/

hopping rate). In the Eq. (1) e is the electron charge, l is the hopping length, k_B is the Boltzmann constant, T the temperature. For PbSe the hopping length corresponds to the sum of the diameter of the PbSe NC, from 3 to 8 nm, and the ligand length, 0.44 nm as in Ref. [11]. For CdSe, the hopping length corresponds to the sum of the diameter, from 2.9 to 5.1 nm, and the ligand length, 0.2 nm [14]. In the model we used the same temperature of the experiments performed by Kang et al., i.e. 200 K for PbSe [15] and 300 K for CdSe [14]. The dot product is maximum when the hop direction is parallel to the electric field F.

ΔE refers to the difference in energy between the final level on NC 2 and the initial level on NC 1, $E_2 - E_1$. Following the calculations of An et al. [16] and the model of Carbone et al. [11], the energy of the initial site is

$$E_1 = E_{1,0} + (N_1 - 1)\left(\frac{X_C}{d}\right) \tag{2}$$

while the energy of the final site is

$$E_2 = E_{2,0} + N_2\left(\frac{X_C}{d}\right). \tag{3}$$

$E_{1,0}$ and $E_{2,0}$ are the lowest electron levels. We refer to Kang and Wise [17] and Carbone et al. [11] for PbSe, while we refer to Norris and Bawendi for CdSe [18]. X_C/d is the charging energy with X_C the charging parameter ($X_C = 827.26$ meV·nm as in Carbone et al. [11]) N_1 and N_2 are the number of electrons on the quantum dot site 1 and 2, respectively. Due to symmetry and spin degeneracy of the lowest electron level of PbSe, there can be eight electrons in a PbSe site [11,16]. A similar situation (eight electrons in a NC site) occurs in the case of CdSe NCs with a wurtzite crystalline structure [19]. In our model, based on the percolation path of a single electron, we quantified N_1 and N_2 in order to have a high probability to have $N_1 = 1$ and $N_2 = 0$, and a decreasing probability to have $N_1 > 1$ and $N_2 > 0$.

The mean value of the conductivity of the film can be written as

$$\langle\sigma\rangle = C\frac{l_{tot}}{A_{tot}}P \tag{4}$$

being C a constant (in Siemens), l_{tot} is the length of the NC film, A_{tot} is the NC film cross section, $<P>$ is

$$\langle P\rangle = \frac{1}{N} \tag{5}$$

where $<N>$ is the mean value of the number of attempted steps to reach the final electrode. For each electron that starts from its percolation path (from the starting electrode to the final electrode, see Fig. 1), N is a natural positive number that increases whenever the hopping from a site to another site is successful or not (following Eq. (1)). To perform a statistical analysis of the percolation path, we do this simulation 500 times.

3. Results and discussion

The simulation takes into account the hopping of an electron which travels from the starting electrode (corresponding to $x = 0$) to the final electrode (corresponding to $x = 200$). In Fig. 1 we show a sketch of the "electron walk" along the cubic superlattice of a PbSe NC film (in the figure we truncated the plot to $x = 30$). We underline that in this simulation we only consider the hopping between nearest neighbours.

In Fig. 1 only the successful steps are depicted, underlining that the successful hopping probability follows the Eq. (1). In Fig. 2 we show the histogram (the calculation for a single electron has been reiterated 500 times) of the conductivity for a film of 8 nm large PbSe nanocrystals. In agreement with Eq. (4), we found the parameter C that relates

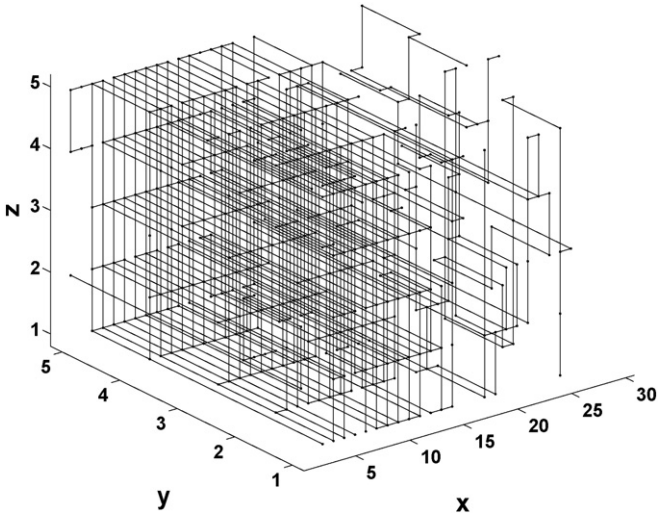

Fig. 1. Example of a percolation path of an electron in a PbSe NC film.

the $<P>$ with $<\sigma>$. For PbSe the parameter C has been found to be equal to 1.5×10^7 S.

We have studied the conductivity as a function of the diameter of the NCs, from 3 to 8 nm. In Fig. 3 we show the trend of the conductivity, with the standard deviation for each NC diameter. Each point corresponds to a distribution, as reported for 8 nm in Fig. 2, and for all the diameters the distribution is skewed.

To find out the agreement between our simulations and the experimental results, we show in Fig. 4 such comparison (the experimental data are taken from Kang et al. [15]). This comparison is dependent on the C parameter. However, the trend of the simulation is in good agreement with the experimental results.

We would like to underline that the simulation is quite efficient in terms of computational costs (taking also into account that 500 simulations is well above the convergence) and the only parameter is C.

To validate our model we perform a simulation for a similar NC thin film, but made of CdSe NCs (Fig. 5). We have simulated the conductivity (as in Eq. (4) with the parameter C equal to 250) then converted to electron mobility $\mu = ne\sigma$, where n is the carrier concentration (here we have used a value of 10×10^{17} cm^{-3} [20,21]) and e is the electron charge.

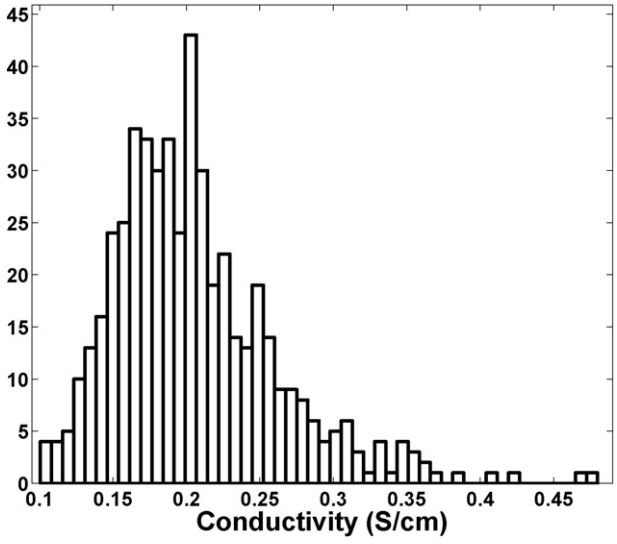

Fig. 2. Histogram of the conductivity of a PbSe nanocrystal film in which the nanocrystals have diameter of 8 nm.