Modeling of conductive states in polymer nanocomposites with disordered GaAs nanowire array

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Abstract. We provide numerical Monte Carlo modeling of conductive properties of polymer nanocomposites, comprised by doping a polymer matrix with carbon nanotubes and III-IV GaAs nanowires. We apply the basic Su-Schrieffer-Heeger model, which is considered universal for every component of such ternary systems, and in a general case with required parameters. Such modeling of conductive characteristics is motivated by requirements of optimization of geometry and structure of novel photovoltaic devices.

1. Introduction

Among a great variety of photovoltaic applications polymer nanocomposites become more widely used [1-10], for example, in sensors, solar cells, organic light-emitting diodes (OLEDs), and other photovoltaic devices. To enhance efficiency of photovoltaic (PV) devices or control their electrical properties, conductive polymers may be doped with semiconductive nanowires (NWs) [7], for instance with III-V GaAs NWs, which have an optimum bandgap and demonstrate the best values of quantum yield in PV applications [4].

We study an abstract scheme of a feasible device with so-called “free standing” GaAs NWs in the bulk polymer composite, for example, polypropylene/single wall carbon nanotubes (PP/SWCNT). GaAs NWs may be polytypic, NWs are assumed to grow with the MBE method along the <111> crystal direction and have zinc blende (ZB) phase. After mechanical removal from Si substrate and subsequent coating with polymer, they tilt from vertical growth direction and become disordered inside PV polymer film. Typical length of NWs is 300 – 700 nm, diameter 10 – 50 nm and surface density 10/µm² [8]. Typical diameter of SWCNTs is 1 nm.

Addition of NWs to polymer matrix may lead to a decrease of conductivity because of shortening of percolation length and other factors. In literature, there are extensive data on percolation threshold depending on the type of nanofillers and their concentration. To estimate possible competing effect of both types of fillers (carbon allotropes and semiconductive NWs) and to determine the capabilities and electrical characteristics of such configurations, we have to take into account a number of their parameters, in frames of theoretical concepts and models such as dimers and effective medium for polymer composites [11, 12], as well perturbative theory with the tight-binding Hamiltonians for NW’s energy states [1, 6-16].

In this paper, we apply the typical tight-binding 3D lattice Ising-like models for the energy of PP/NW/SWCNT system, combining the Gaussian Disordered Model (GDM) [6] for NW interactions
with the polymer matrix, with effective masses of effective/homogeneous media [1,11,12], and the Su-Schrieffer-Heeger (SSH) model describing electronic properties of polymers and carbon allotropes separately ([20–23] and references therein).

2. The lattice model

We constrain the total Hamiltonian of the system with parts for conductive acceptor interactive states with the fermionic Hamiltonian for NWs, interactions of their electrons (holes) and hopping parameters of the composite $H = H_{NW} + H_{comp} + H_{hoppNW}$. For simplicity we assume that NWs and SWCNTs are non-interacting.

In frames of the $k \cdot p$ theory for GaAs the one-band Hamiltonian of the NW’s ZB phase is formulated in [14, 15]. In this case, it has only one parameter ($\Delta_0$) with effective media, compatible with [1]; the energies of conductive states are calculated depending on NW diameters from 10 to 30 nm in [15] and references therein, using the Hamiltonians of the band model.

The Su-Schrieffer-Heeger (SSH) model employed here [20–22] for simplest polymers and CNTs is based on the Schrödinger equation for the only conductive state of the $\pi$-electron of the carbon bond. We calculate the SSH Hamiltonian in the form [22]

$$H_{SSH} = \sum_i \frac{1}{2} M_i \dot{r}_i^2 + \sum_{ij} \frac{K}{2} b_{ij}^0 b_{ij}^0 - \frac{4 \sqrt{\gamma} \alpha}{\pi} \frac{d}{dK} - \sum_i \alpha \left[ \varepsilon_0 - \sqrt{\gamma} \alpha (b_{ij}^0 - b_{ij}^0) (C_i^+ C_j + C_j^+ C_i) - \varepsilon \sum C_i^+ C_i \right],$$

where $M_i$ and $r_i$ are the mass and position vector of the $i$th atomic site, $b_{ij} = |r_i - r_j|$ is the bond length between atomic sites; $b_{ij}^0$ is a dummy variable, $K$ is the spring constant, $t_0$ is the reference hopping integral, $\alpha$ is the linear electron-phonon coupling constant between sites $i$ and $j$, $C_i^+$ and $C_i$ are creation and annihilation operators for the $\pi$-electron at site $i$ respectively [22].

The lattice parameters such as the elementary cell of polymer and nanofiller SWCNT and hopping integrals are taken from literature. The first sum in (1), expressed as kinetic energy of electrons, plays the primary role in conductivity [24].

3. Numerical results and discussions

We performed Monte Carlo (MC) simulations for (1) with the Metropolis algorithm on spin variables, using normalized parameters, Plank constant $\hbar$, electron mass $m_e$, Boltzmann constant $k_B = 1$, $\beta = 1/T$ denotes inverse temperature, $T$ is absolute temperature referred to a certain energy coefficient. For simplicity, we used a small sc lattice, $98^3$. Accuracy of the MC algorithm is 0.001%.

The calculations for (1) is carried out for concentrations of CNTs of 1, 2 and 3 wt% and NWs of 0.5 wt% (a typical percolation threshold for polymer/CNT composites is expected at 2 wt%).

Fig. 1 shows some results, based on energy dependencies on conductivity and temperature [24]. The upper curves denoting the total energy correspond to polymer/CNT/NW system, and lower horizontal curves are calculated from potential energy only, which may be associated with polymer/CNT system separately.
Here we omit the theoretical considerations concerning detailed calculations of band NW’s Hamiltonians or random matrix and percolation phenomena [25-27]. The values of lattice constants, bandgaps, electron levels etc. are taken from extensive literature data.

4. Conclusion

We illustrate numerically, using the abstract model, that for ternary nanocomposite systems polymer/CNT/NW with possible different conductive properties of its components, that the versions of the SSH model are applicable. The semiconductor NW’s contribution into conductive characteristics of the composite may compete with those of carbon allotropes depending on type of carbon nanofillers, their size and concentration and percolation behavior of both fillers.

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