

Atomic and electronic structure of grain boundaries in crystalline organic semiconductors

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Abstract

Grain boundaries in organic crystalline semiconductors play an important role in charge carrier transport. We have developed a model for atomic and electronic structure calculations of grain boundaries in naphthalene polycrystals. Atomic structure was obtained by the Monte Carlo algorithm, while electronic structure was obtained by the charge patching method. The results for two naphthalene polycrystals are presented and discussed. They show the existence of trap states produced by grain boundaries.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Organic crystalline semiconductors are very promising materials for electronic and optoelectronic devices, such as transistors, light emitting diodes and solar cells [1]. Organic electronic devices have low processing costs; however, they still exhibit low carrier mobility and small efficiency. Real organic semiconductors are polycrystals and therefore contain many contact interfaces (grain boundaries) between monocrystals with different crystalline orientations. It is generally believed that grain boundaries introduce trap states that are bottlenecks for charge carrier transport [2]. However, there is very little understanding of the nature of these states, the degree of their localization and their energies.

In this paper, we present a methodology for the investigation of the role of grain boundaries in polycrystalline organic semiconductors. The methodology was applied to study the nature of the electronic states introduced by the grain boundaries in naphthalene polycrystals. The atomic structure of the material near the contact between two grains is obtained as a result of energy minimization by the Monte Carlo (MC) algorithm. Electronic states near the grain boundaries are calculated using the charge patching method (CPM) and the folded spectrum method. The results obtained for the electronic states and the degree of localization of the wave

functions of the highest occupied states will be presented and the consequences of the results for the device applications will be discussed.

2. Description of the model

A methodology for the calculation of the atomic and electronic structure of grain boundaries in naphthalene polycrystals is described schematically in figure 1. The initial atomic structure, which is the input parameter for the MC algorithm, comprises two coupled monocrystals with unit cells rotated for the given angle. The interaction between molecules is modelled using transferable potentials for phase equilibria [3, 4]. In each step of the MC algorithm, one randomly chosen molecule is translated and rotated. This change is accepted or rejected according to the Metropolis algorithm: if the energy of the new configuration of molecules is lower than the energy of the old, change is accepted; otherwise, it is accepted with a probability equal to the Boltzmann weight of the difference of the new and the old energy. The simulation is performed until the system reaches thermal equilibrium, which is evidenced by a saturation in the graph of the dependence of energy on the timestep. This configuration has a minimal energy and presets the final atomic structure of the grain boundaries in naphthalene. At

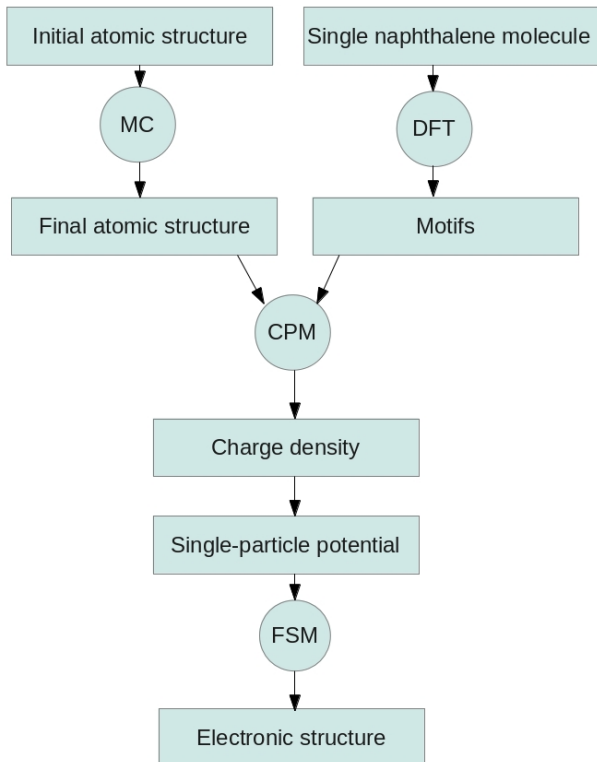


Figure 1. Schematic representation of the algorithm for atomic and electronic structure calculation.

the beginning, the temperature of the system is set to room temperature (300 K). The temperature is slowly decreased during the execution of the MC algorithm and the final temperature is 0 K. In this way, localization induced by dynamic disorder in the atomic structure is excluded.

Atomic structure is the first input parameter for the electronic structure calculations. The second input parameters are charge density motifs obtained by density functional theory (DFT) calculation of a single naphthalene molecule. A motif is a description of the environment of an atom [5]. Two equal atoms can have different motifs if they have different neighbouring atoms. There are five motifs in the naphthalene molecule: $C_3-C_3C_2C_2$, $C_2-C_3C_2H$, $C_2-C_2C_2H$, $H-C_2-C_2C_2$ and $H-C_2-C_3C_2$, where CX is a carbon atom connected to X other carbon atoms. With the motifs and the atomic structure at hand, one can directly construct the charge density using CPM, avoiding the need for demanding self-consistent solving of DFT equations. CPM provides a similar accuracy to DFT but with a much smaller computational cost that allows us to calculate the electronic states for systems made up of several thousand atoms, which is not feasible using DFT. Charge density gives the single-particle potential. Finally, the Schrödinger equation can be solved using the folded spectrum method [6], which gives the electronic structure (wave functions and energy levels) around the desired energy, which is the top of the valence band in our case.

3. Results and discussion

In this section, the results obtained from electronic structure calculation for two naphthalene polycrystals will be

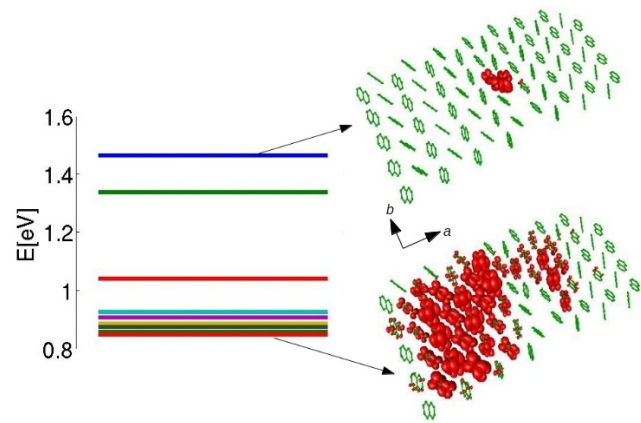


Figure 2. Energies of the ten highest occupied states (left) and wave functions of the first (right above) and tenth (right below) highest occupied state in the naphthalene polycrystal composed of two monocrystals with an angle of 5° between them.

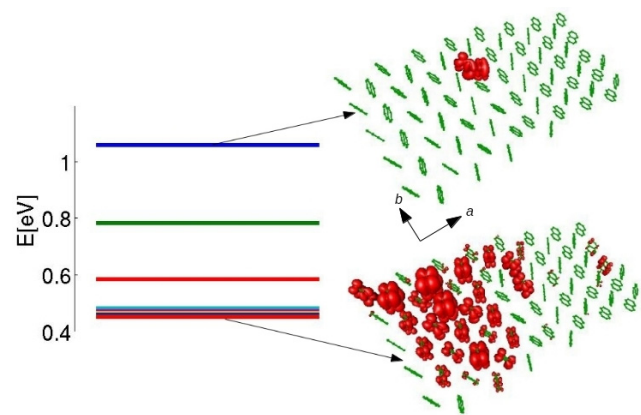


Figure 3. Energies of the ten highest occupied states (left) and wave functions of the first (right above) and tenth (right below) highest occupied state in the naphthalene polycrystal composed of two monocrystals with an angle of 10° between them.

presented. The number of molecules in the simulated system is 1000. For the electronic calculations only one layer of polycrystals was considered, which is sufficient to describe all electronic properties of the material. The contact surface is perpendicular to the a direction [7] of the unit cell of the naphthalene crystal. Results are presented in figures 2 (the angle between monocrystals is 5°) and 3 (the angle between monocrystals is 10°). On the left side of the figures, energies of the ten highest occupied states are sketched. On the right side, atomic structure and the wave functions for the highest (first) and the lowest (tenth) calculated states are illustrated.

We can see that the atomic structure of the monocrystal grains stays unchanged if the distance from the grain boundary is greater than half of the dimension of the unit cell in the a direction. Only molecules located on the grain boundary have slightly changed their orientations from the orientations in the monocrystal.

Looking into the energy states of both polycrystals, we can see that there exist three states in which the energies are notably higher than the energies of the other states. The highest states are about 0.6 eV above the valence band. For comparison, the energy gap in the naphthalene monocrystal is about 2.8 eV. These states are localized on the two

molecules belonging to different monocrystals and are located on the interface between monocrystals. The distance between these two molecules is less than the distance between two neighbouring molecules in the monocrystal. On the other hand, the lowest calculated states are completely delocalized, as in the monocrystal.

4. Conclusions

In this paper, we have explained our methodology for the atomic and electronic calculations of the grain boundaries in naphthalene polycrystals. Results have shown that grain boundaries have an impact on the atomic structure of the polycrystal only in the nearest environment (half of the unit cell) of the boundaries. On the other hand, they produce electronic states whose energies are significantly higher than the energies of the delocalized states that belong to the valence band. The wave functions of these states are located just on the grain boundaries. These states are trap states for the charge carriers and could be one of the reasons for the low mobility and small efficiency of this material.

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