Physics Letters A 381 (2017) 3441–3444

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

An analytical Seebeck coefficient model for disordered organic semiconductors

Xuewen Shi [a,b,c], Nianduan Lu [a,b,c], Guangwei Xu [a,b,c], Jinchen Cao [a,b,c], Zhiheng Han [a,b,c], Guanhua Yang [a,b,c], Ling Li [a,b,c], Ming Liu [a,b,c]

[a] Key Laboratory of Microelectronic Devices & Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing, 210009, China

ARTICLE INFO

Article history:
Received 22 March 2017
Received in revised form 23 August 2017
Accepted 5 September 2017
Available online 6 September 2017
Communicated by R. Wu

Keywords:
Seebeck coefficient
Organic semiconductor
Percolation theory

ABSTRACT

An analytical Seebeck coefficient model for disordered organic semiconductors based on hopping transport and percolation theory is proposed here. This model demonstrates the relationships between Seebeck coefficient and temperature, carrier concentration as well as disorder degree of materials. As compared with experimental data, the simulated results show a convincing coincidence with experimental results. Moreover, the effect from doping is addressed. The calculation results show that the Seebeck coefficient will decrease with increasing doping ratio, after passing a minimum value then a sharp increase of Seebeck coefficient appears.

1. Introduction

Recently, researchers have witnessed the rapid development of organic semiconductors, which provide a number of merits, for instance, lower cost, flexibility, easy to synthesis, capability of massive production, and less weight. These advantages are already presented in the form of the display, sensors and novel photovoltaic cells [1,2]. Another promising application of organic semiconductors is the thermoelectric devices owing to their intrinsically low thermal conductivity and potential low cost associated with ease of low temperature processing [3]. While some organic thermoelectric materials have been reported [4], the development of organic thermoelectric devices is still subjected to inadequate fundamental investigation involving the development of new materials and device architecture. One of the most important characteristics for all organic thermoelectric materials is energy conversion efficiency, which can be described as thermoelectric figure of merit $ZT = S^2\sigma T/k$, where S is Seebeck coefficient, σ denotes electrical conductivity, k is thermal conductivity and T is absolute temperature. It is apparent that increasing S can significantly enhance the figure of merit compared with other parameters. However, due to lacking of thorough understanding of the relationships between Seebeck coefficient and material parameters, such as degree of disorder, doping level and conductivity, it has taken researchers numerous efforts to choose appropriate materials in laboratory by altering a number of material parameters within a large range to fulfill practical applications.

In this paper, an analytical Seebeck coefficient model in disordered organic semiconductors was proposed. The model illustrates the relations between Seebeck coefficient and disorder degree of materials, carrier concentration as well as temperature via deducing basic current equation from Seebeck effect. The proposed model can successfully fit existing experimental results, which proves that it can be used to predict Seebeck coefficient for materials and helps researchers to synthesis specific materials. Furthermore, we also analyze the effect of doping on Seebeck coefficient.

2. Model theory

There is a direct energy conversion from heat to electricity in thermoelectric materials. When semiconductors are placed in a temperature gradient environment, the carriers (electrons or holes) can diffuse from heat side to cool side. At the same time, the accumulated carriers in cool side will induce an electric field which will counteract the diffusion. The current is therefore the superposition of diffusion current (from temperature gradient) and drift current (from electric field) as

$$J = \sigma \mathbf{E} + q\frac{d(D_n n)}{dx}, \tag{1}$$

E-mail addresses: lunianduan@ime.ac.cn (N. Lu), lingli@ime.ac.cn (L. Li).

http://dx.doi.org/10.1016/j.physleta.2017.09.006
0375-9601/

where σ is conductivity in semiconductors, D_n is diffusion coefficient, n is carrier concentration, q is elementary charge, and $\mathbf{E} = -\frac{1}{q}\frac{d\epsilon_F}{dx}$ with ϵ_F denoting Fermi level. Based on Einstein relation, $\frac{D_n}{\mu} = \frac{D_n}{(\frac{\sigma}{nq})} = \frac{k_B T}{q}$, where μ is the carrier mobility and k_B is the Boltzmann constant, equation (1) can be rewritten as

$$J = \sigma\left(-\frac{1}{q}\frac{d\epsilon_F}{dx} + \frac{1}{\sigma}\frac{k_B}{q}\frac{d(T\sigma)}{dT}\frac{dT}{dx}\right). \tag{2}$$

In an open circuit, $J = 0$ and one can infer from equation (2) that the Seebeck coefficient is [5]

$$S = \frac{1}{q}\frac{d\epsilon_F}{dT} = \frac{1}{\sigma}\frac{k_B}{q}\frac{d(T\sigma)}{dT}. \tag{3}$$

Generally, conduction mechanism in disordered organic semiconductors is hopping theory [6,7], although transport process can also be described by using band-like model in single crystal pentacene [8]. In this work we adopt the hopping mechanism. Since generalized Einstein relation and Fermi–Dirac distribution function have been used in the model, the materials discussed should be non-degenerate semiconductors [9].

Following Vissenberg and Matters, we assume the density of (localized) states (DOS) follows exponential form [10],

$$g(\epsilon) = \frac{N_t}{k_B T_0}\exp\left(\frac{\epsilon}{k_B T_0}\right) \quad (-\infty < \epsilon \le 0), \tag{4}$$

where N_t denotes the number of localized states per volume, ϵ is energy, and T_0 is parameter indicating the width of DOS. The proportion of localized states occupied by carriers can be written as [10]

$$\delta = \frac{1}{N_t}\int g(\epsilon) f(\epsilon, \epsilon_F) d(\epsilon)$$
$$\simeq \exp\left(\frac{\epsilon_F}{k_B T_0}\right)\Gamma\left(1 - \frac{T}{T_0}\right)\Gamma\left(1 + \frac{T}{T_0}\right). \tag{5}$$

In equation (5), it is assumed that carriers occupy the sites with energy far below 0. The probability that carriers hop between sites depends on distance among sites and energy distribution of localized states. By using percolation theory and variable-range hopping (VRH) mechanism, Vissenberg et al. had given the expression of conductivity [10]:

$$\sigma(\delta, T) = \sigma_0\left(\frac{\pi N_t \delta (\frac{T_0}{T})^3}{(2\alpha)^3 B_c \Gamma(1 - \frac{T}{T_0})\Gamma(1 + \frac{T}{T_0})}\right)^{\frac{T_0}{T}}, \tag{6}$$

where α is a parameter describing overlap of electronic wave function, B_c is constant denoting percolation criterion with the value of 2.8. Note that product of δ and N_t is carrier concentration, thus it can be replaced by symbol n in equation (6). Substituting equation (6) into equation (3), one can obtain the expression of S:

$$S = \frac{k_B}{q}\left\{1 - \frac{T_0}{T}\ln\left[\frac{nT_0^4 \sin(\frac{\pi T}{T_0})}{(2\alpha)^3 B_c T^4}\right] + \frac{1}{n\sin(\frac{\pi T}{T_0})}\left[n\pi\cos\left(\frac{\pi T}{T_0}\right) - \frac{4T_0}{T}n\sin\left(\frac{\pi T}{T_0}\right)\right]\right\}. \tag{7}$$

Approximation $\Gamma(1 - \frac{T}{T_0})\Gamma(1 + \frac{T}{T_0}) \simeq \frac{\pi T/T_0}{\sin(\pi T/T_0)}$ is used when calculating S. Finally, one can obtain the Seebeck coefficient, which is the function of temperature T, disorder parameter T_0, and carrier concentration n.

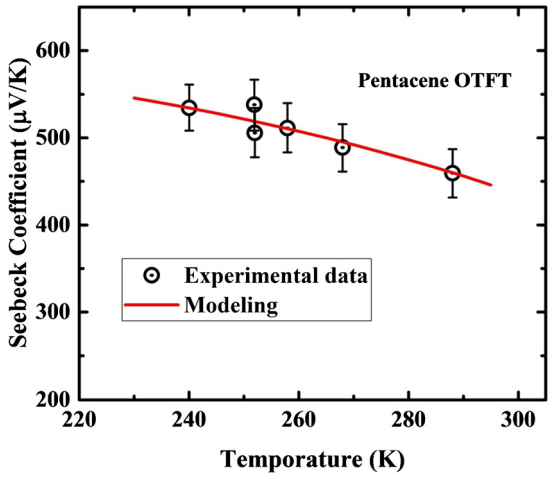

Fig. 1. Temperature dependence of Seebeck coefficient in organic semiconductors. Line represents theory model and symbols is experimental data from Ref. [8].

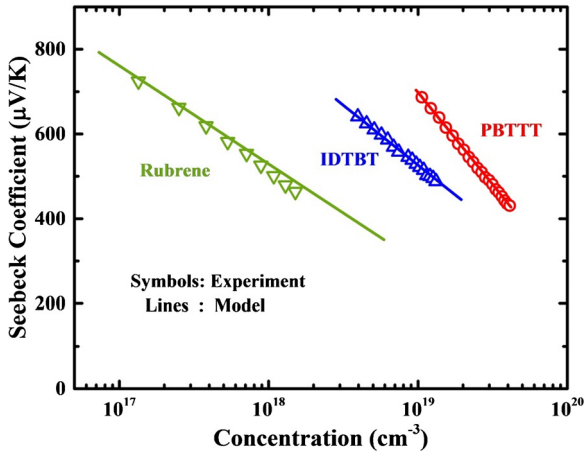

Fig. 2. Relation between carrier concentration and Seebeck coefficient. The Seebeck coefficients for different materials are measured in FET. Lines and symbols are theoretical and experimental results, respectively. Experimental results are from Ref. [9] and [10].

3. Results and discussion

Fig. 1 shows the comparison between the experimental data and theoretical calculation for temperature dependence of Seebeck coefficient. Symbols are experimental data from Adrian von Mühlenen [11], where Seebeck coefficient was measured in pentacene thin-film transistors and line is theoretical Seebeck coefficient calculated from equation (7). The fitting parameters are $\alpha = 8.4 \times 10^7$ cm^{-1}, $n = 1 \times 10^{21}$ cm^{-3}, $N_t = 10^{21}$ cm^{-3} and $T_0 = 440$ K. The positive Seebeck coefficient values suggest that the dominant carrier is hole in pentacene material. From Fig. 1, one can also see that S decreases slowly with increase of temperature. Physically, it has been pointed out, higher Seebeck coefficient are often associated with very high density of states near the Fermi level [12], if the carrier concentration is constant (corresponding to the gate voltage in Ref. [11]), that is Fermi level keeps constant, the higher temperature results in the lowering of the transport energy and decrease of the Seebeck coefficient [13].

The dependence of Seebeck coefficient on carrier concentration is illustrated in Fig. 2. Symbols are the measured Seebeck coefficients from organic FETs based on rubrene [14], poly(2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b)thiophene) (PBTTT) and indacenodithiophene-co-benzothiadiazole (IDTBT) [15] at room temperature, respectively. Lines are fitting results from equation (7). For