

More Efficient Nanostructured Material for Noncontact Body Temperature Measurement

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Abstract – Existing methods of human body temperature measurement are briefly analyzed. The opportunities of different type of medical thermometers are described. The advantages of the latest infrared skin thermometers and of new thermal imaging systems are evidenced. The thermoelectric power factor which determines the sensitivity of infrared detectors is modeled in highly conducting nanostructured organic crystals. The optimal parameters that ensure the highest value of the power factor at room temperature are evaluated. It is shown that in existing crystals of tetrathiotetracene-iodide after the optimization of carriers' concentration it is possible to obtain higher values of power factor than in the best known inorganic materials. It is proposed to use these crystals as more efficient material for sensitive elements of thermoelectric sensors in infrared skin thermometry.

Index Terms – infrared skin thermometer, nanostructured organic crystals, thermoelectric power factor, thermoelectric infrared sensor.

I. INTRODUCTION

From the point of view of daily uses temperature is connected with the quality of thermal energy contained in different objects and it serves to express quantitatively the common notions of hot and cold. The simplest way to sense this is to touch the given object and to decide, if it is warm, hot or cold. But quantitatively, temperature is measured with thermometers. The notion of temperature is defined for objects that are in thermal equilibrium, or for the parts of them that are in local thermal equilibrium, i.e. in such state in which no further changes occur. These objects or their parts must contain a big number of constituent atoms or molecules. If there is no heat transfer between two objects (for example, the object and the thermometer), both objects have the same temperature. There are different temperature scales. Most of countries use the Celsius scale ($^{\circ}\text{C}$) for temperature measurements with 0°C for freezing point of distilled water and 100°C for boiling one at the sea level. Celsius scale has the same value of 1 degree as the Kelvin scale (K) used by scientists, but fixes its null point at $0^{\circ}\text{C} = 273.15\text{K}$, the freezing point of water. A few countries, including the United States, use also the Fahrenheit scale for different purposes. It is a historical scale on which water freezes at 32°F and boils at 212°F .

In the science, the statistical thermodynamics gives a formal definition of temperature [1, 2]. Temperature is a measure of statistically average kinetic energy of the particles forming a material object. This definition includes the notion of number of particle degrees of freedom. A simple particle (an atom or a molecule as material point) has three degree of freedom. To average kinetic energy of a simple particle it corresponds $(3/2)k_0T$ ($1/2$ for each degree of freedom), were T is the temperature, and k_0 is the Boltzmann constant

Thus, temperature is related to the motion of the particles that constitute the sample. But also it means that the sample contains a big number of particles.

The human body temperature is a very important parameter which determines into a large measure the state of man health. Therefore it is necessary to have good methods and adequate devices for quick and reliable measurement of temperature. Since the temperature scale has been established and the notion of normal body temperature was introduced a variety of methods and devices for temperature measurement have been applied. During a long time the thermometers with mercury into a glass tube were the most used. Although such thermometers are simple in use, they are dangerous for the environment, because the glass can break, the mercury can spill, but it is known that the mercury vapors are poisonous. Therefore later the mercury was replaced by other not poisonous liquids. Nevertheless, the glass can break and it is not conveniently.

Unfortunately, until now an ideal method and an ideal thermometer are not yet found, although body temperature measurement is very important not only for correct diagnosis, but also for further investigation and treatment of patients. In pediatrics the rectal measurement is still considered as the most precise, although it has several disadvantages as discomfort, emotional distress, requirement of significant time for measurement, possibility of complications connected with perforation or introduction of infections [3]. As a result of these disadvantages and of recommendations of UK National Institute of Health and Clinical Excellence (NICE) general guide [4] some medical institutions have abandoned rectal measurements.

Sublingual cavity and axillae measurements are more convenient than rectal ones, but are less precise. Relatively new alternative for body temperature measurements are tympanic and infrared skin thermometers. The first measures by the help of a special sensor the quantity of infrared heat produced by tympanic membrane. The measurements are also not sufficiently precise. The infrared skin thermometer is the latest developed method of body temperature

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measurement. It measures the quantity of infrared heat produced by temporal arteries. Only a few studies have been carried out on this subject. Harvard Medical School, USA has proven that Exergen Corporation's Infrared temporal artery thermometer is more accurate than infrared ear thermometry and more accurate than even rectal thermometers in responding to change in fever.

In the last time different thermal imaging systems that provide a thermographic image of human body temperatures (typically the face) at a distance obtain more and more applications. The IR-160R Automated Body Monitoring System has temperature measurement accuracy of 0.25 degrees C. An advantage of this noncontact temperature measurement is the exclusion of contamination spreading, that is possible by contact methods. A Japanese electronic firm NEC/Avios has launched in January 2011 a mirror with a system which measures the temperature distribution on the human face, determines the average temperature and on this base calculates the body temperature. But it is clear that in order to increase the effectiveness of these measurements it is necessary to have good infrared sensors.

The aim of this paper is to propose optimized parameters of a nanostructured organic material as more efficient sensitive element of thermoelectric detectors of infrared radiation for sensors of temperature measurements.

II. THERMOELECTRIC SENSORS OF INFRARED RADIATION

Thermoelectric detectors are largely used for the detection of infrared radiation in the long wave lengths diapason of spectrum where the photoelectric detectors are not sensitive, usually for wave lengths longer than 1.5 μm . In the same time, it needs to note that the Earth atmosphere has windows of transparency only in several intervals of infrared spectrum for wave lengths between 2,0 – 2,5 μm , 3,2 – 4,2 μm , 4,5 – 5,2 μm and 8,0 – 13,5 μm . In order to increase the detector sensitivity it is important to collect the infrared radiation from the possible larger spectral interval. Also, it is very necessary to have more efficient thermoelectric materials. Intensive investigations are made in this direction in many scientific laboratories.

The main parameter that determines the opportunity of a material to be used in detectors of infrared radiation is the thermoelectric power factor $P = \sigma S^2$, where σ is the electrical conductivity and S is the thermopower (Seebeck coefficient). New materials are needed with as higher as possible values of the thermoelectric power factor P . One would think that for this it is sufficiently to increase in the same material the electrical conductivity and the thermopower. But these requirements are contradictory. In ordinary materials the increase of σ leads to the decrease of S and vice versa. In order to overcome this situation it needs to search and investigate new materials with more complicated electronic and phonon spectra.

The best bulk thermoelectric material Bi_2Te_3 has values of thermoelectric power factor $P \sim 40 \mu\text{W}/\text{cm}\cdot\text{K}^2$ near room temperature. Recently, high values of power factor have been measured in low-dimensional quantum well superlattice structures [5]. For example, in [6] values of power factor of the order of 62-66 $\mu\text{W}/\text{cm}\cdot\text{K}^2$ were obtained in $n\text{-PbTe/PbEuTe}$ quantum wells which are almost 1.7 times higher than that measured in Bi_2Te_3 . Theoretically [7, 8] even higher values of the power factor are expected in the

material of such quantum wells. However, the technology to produce such structures is complicated and expensive.

In the last years organic materials attract more and more attention as materials with more diverse properties and less expensive. Already it exists a new generation of organic based electronic devices. It was also shown [9, 10] that among organic compounds it is possible to find materials which will have considerably increased thermoelectric power factor. Such materials unite together the advantages of low-dimensional quantum systems and of multi component materials with more diverse and complicated interactions.

Our latest investigations [11, 12] have shown that the quasi-one-dimensional nanostructured organic crystals of tetrathiotetracene-iodide can have very promising thermoelectric properties. In this paper we will model the power factor in dependence of crystal parameters in order to find those that ensure the highest value.

III. CRYSTAL MODEL

The quasi-one-dimensional organic crystals of tetrathiotetracene-iodide, TTT_2I_3 are formed of segregate chains or stacks of planar molecules of tetrathiotetracene TTT, and iodine. The distance between molecules along chains is two times smaller than between different chains. Therefore the overlapping of electronic wave functions of TTT molecules along chains is big, but between chains is negligibly. Only TTT chains are conductive because the iodine electronic wave functions are strongly localized. The conduction mechanism along chains is of band type, but between chains it is of hopping type. The latter gives small contribution and is neglected. The charge carriers are holes. The TTT_2I_3 crystals can be considered as nanostructured material, because the distance between conducting chains is of the order of one nanometer.

The parameters of TTT_2I_3 are: the mass of molecule $M = 6.5 \cdot 10^5 m_e$ (m_e is the mass of free electron), the lattice constants $a = 18.35 \text{ \AA}$, $b = 4.96 \text{ \AA}$, $c = 18.46 \text{ \AA}$ (the direction of chains is along b), the sound velocity along the chains $v_s = 1.5 \cdot 10^5 \text{ cm/s}$, the carriers concentration for ordinary stoichiometric crystals $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$. The electrical conductivity along the chains σ at room temperature varies in the crystals grown from solution between 800 and 1800 $\Omega^{-1}\text{cm}^{-1}$ [13], whereas for crystals grown from gas phase, which are purer and more perfect, it varies between 10^3 and $10^4 \Omega^{-1}\text{cm}^{-1}$ [14]. The electrical conductivity is very sensible to crystal impurities and defects. The thermopower S along stacks is less sensitive to crystal impurities and defects and at room temperature varies between 40 and 45 $\mu\text{V/K}$ for crystals grown from solution [13] and $S = (36 \pm 3) \mu\text{V/K}$ for those grown from gas phase.

In order to describe the thermoelectric properties of TTT_2I_3 crystals we will apply the model presented in [15]. The electronic states are described in the tight binding and nearest neighbor approximations. So as the conduction band width is not very large, the effective mass approximation is not applicable and the variation of electron and phonon quasi-momentums into the whole Brillouin zone is taken into account. The dispersion law for holes is taken in the usual for tight binding approximation cosinusoidal form, but for longitudinal acoustic phonons the exact one-dimensional expression is used.

The model takes into account simultaneously two electron-phonon interactions and also the scattering of carriers on impurities and defects. It is important, because under certain conditions between both electron-phonon interactions the interference can take place. The first interaction is similar to that of deformation potential, and the second is polaron similar, but the induced polarization is considered. Due to the interference, both electron-phonon interactions considerably compensate each other for a narrow strip of states in the conduction band. As a result, the relaxation time of carriers as a function of carrier energy takes the form of Lorentzian with rather pronounced maximum.

Such behavior of relaxation time will ensure simultaneously high values of electrical conductivity and increased values of the thermopower. This situation is favorable to expect a growth of the thermoelectric power factor P .

IV. MODELING OF THE THERMOELECTRIC POWER FACTOR

The linearized kinetic equation for no equilibrium holes distribution function has been deduced. Near room temperature the scattering of carriers on acoustical phonons can be considered elastic. In this case the kinetic equation is solved exactly and, replacing the phonon distribution function by its high- T limit, the following expression for the relaxation time is obtained

$$\tau(E) = \frac{\hbar M v_s^2 w^2 [E(\Delta - E)]^{1/2}}{2a^2 k_0 T w'^2 \gamma^2 [(E - E_0^{s,p})^2 + 4w^2 \gamma^{-2} D]}, \quad (1)$$

where w is the energy transfer of a carrier from a molecule to the nearest one along the chains, E is the carrier energy, $0 \leq E \leq \Delta$, Δ is the width of the conduction band, $\Delta = 4w$, w' is the derivative of the transfer energy w with respect to the intermolecular distance, k_0 is the Boltzmann constant, $\gamma = 2e^2 \alpha_0 / (a^5 |w'|)$ is the ratio of amplitudes of above mentioned electron-phonon interaction mechanisms, e is the carrier charge, α_0 is the average polarizability of molecule, $E_0 = 2w(\gamma \pm 1) / \gamma$ is the resonance energy which corresponds to the maximum of $\tau(E)$, when $0 \leq E_0 \leq \Delta$. The dimensionless parameter D in Eq. (1) describes the scattering of carriers on impurities. It is proportional to the linear concentration of impurity and may be made much less than unity, if the crystal purity is sufficiently high.

The parameter γ is not known in TTT_2I_3 crystals, because the molecule polarizability is not known. We will take $\gamma = 1.6$, that corresponds to $\alpha_0 = 42 \text{ \AA}^3$. For comparison, in anthracene $\alpha_0 = 25 \text{ \AA}^3$, but TTT molecule is bigger and α_0 must be greater too. The dependence of relaxation time on carrier energy is presented in Fig.1 for $\gamma = 1.6$ and different degrees of crystal purity ($D = 0.2, 0.1$ and 0.05). The dash-dotted line corresponds to the case, when only the first electron-phonon interaction mechanism is applied. It is seen that in this case the relaxation time is a very smooth function of energy with a small maximum of the order of 0.5×10^{-14} s. When both electron-phonon interactions are included, the relaxation time obtains a more pronounced maximum which grows with the decrease of D and becomes even sharp at $D = 0.05$ (solid line in Fig.1). This sharp maximum corresponds to the purest crystal and is more than 15 times higher than that of dash-dotted line. The maximums of relaxation times determine maximums of electrical conductivity as functions

of Fermi energy or carriers' concentration. And sharp dependence of relaxation time on energy ensures simultaneously increased values of the thermopower.

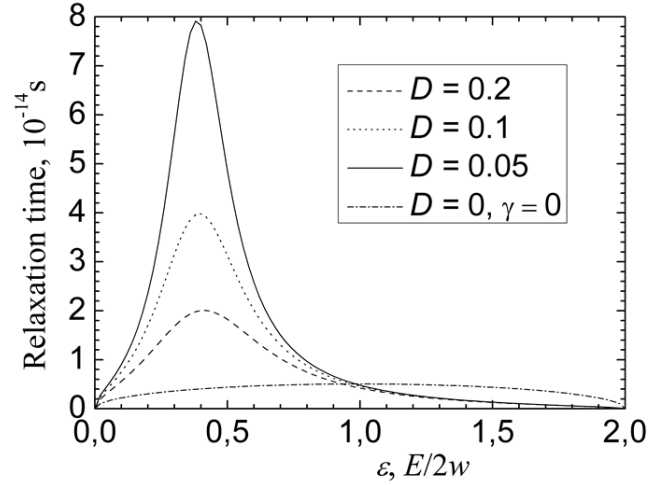


Fig. 1. Relaxation time as a function of energy in the conduction band. The dash-dotted line is for only first interaction, when $D = 0, \gamma = 0$.

The expression for the power factor P is presented through the transport integrals R_n as follows

$$P = R_1^2 / (e^2 T^2 R_0), \quad (2)$$

where

$$R_n = - \frac{2e^2 a z}{\pi \hbar^2 b c} \int_0^\Delta (E - E_F)^n [E(\Delta - E)]^{1/2} \tau(E) f_0' dE. \quad (3)$$

Here z is the number of chains through the transversal section of the unit cell, E_F is the Fermi energy, $f_0'(E)$ is the derivative of Fermi distribution function with respect to E . The integration in Eq. (3) is carried out on all energies in the conduction band, so as it is not too large.

The expression (2) has been calculated for TTT_2I_3 crystals in dependence of dimensionless Fermi energy $\varepsilon_F = E_F / 2w$ for $\gamma = 1.6$ and different values of parameter D , mentioned above. In ordinary TTT_2I_3 ε_F is a little less than 0.4 and $z = 4$.

In Fig. 2 the calculated dependences of P on ε_F at room temperature are presented. It is seen that the power factor P has also maximums which are rather large. These maximums are the result of competition between the increase of electrical conductivity and the decrease of thermopower. The lowest maximum is of the same order as in Bi_2Te_3 , the middle one is two times higher, and the last is almost four times higher.

But the maximums are placed at lower values of Fermi energy than those that correspond to ordinary crystals. At ε_F a little less than 0.4 the power factor is very small. In order to increase P it needs to diminish ε_F , or carriers' concentration. It is possible because the TTT_2I_3 crystals admit non stoichiometric composition. The iodine plays the role of acceptors. In order to diminish the carriers' concentration in needs to diminish the iodine concentration and to obtain a compound of the type $\text{TTT}_2\text{I}_{3-\delta}$, where δ is the deviation of stoichiometry.

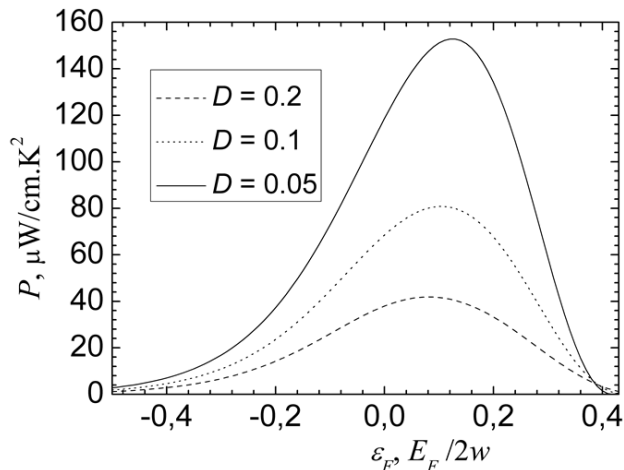


Fig.2. Power factor P as a function of dimensionless Fermi energy ε_F for $\gamma = 1.6$.

Thus, for $\varepsilon_F = 0.2$ (n is diminished by 1.6 times from $1.2 \times 10^{21} \text{ cm}^{-3}$ to $7.5 \times 10^{20} \text{ cm}^{-3}$) and $D = 0.05$ it follows $P = 134 \text{ } \mu\text{W/cm.K}^2$, a very good result.

For this carriers' concentration the electrical conductivity $\sigma = 9.3 \times 10^3 \text{ } \Omega^{-1}\text{cm}^{-1}$ and the thermopower $S = 120 \text{ } \mu\text{V/K}$. As it is seen from Fig.2, the maximum of P corresponds to $\varepsilon_F = 0.12$, when $P = 153 \text{ } \mu\text{W/cm.K}^2$. Even in less pure crystals for which $D = 0.1$, the maximum of P is still high, $\sim 80 \text{ } \mu\text{W/cm.K}^2$.

Surely, if the crystal purity will be still more increased, so that the parameter D will be less than 0.05, one can expect even higher values of the power factor than the highest in Fig.2. One may think that this will be possible.

V. CONCLUSIONS

The thermoelectric power factor P , which is the main physical parameter that determines the opportunity of a material to be used in sensitive elements of infrared radiation detectors, has been modeled in nanostructured quasi-one-dimensional organic crystals of tetrathio-tetracene-iodide, TTT_2I_3 , in dependence of crystal parameters. A more complete crystal model is used that take into account two electron-phonon interactions and the scattering of carriers on impurities. One interaction is similar to that of deformation potential and the second is of polaron type.

It is shown that, due to the interference of these electron-phonon interactions, the thermoelectric power factor P as a function of Fermi energy (or carriers' concentration) obtains maximums which depend on crystal purity. For ordinary crystals with stoichiometric concentration P is very small. But if the carriers' concentration is diminished by 1.6 times from $1.2 \times 10^{21} \text{ cm}^{-3}$ to $7.5 \times 10^{20} \text{ cm}^{-3}$, P is increased in the crystals with the highest degree of purity up to $134 \text{ } \mu\text{W/cm.K}^2$, a very good result.

For optimal parameters the maximal value of $P = 153 \text{ } \mu\text{W/cm.K}^2$ is predicted. It is expected that in crystals with higher degree of purity the thermoelectric power factor will achieve still greater values.

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