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# Strain sensors based on twin and uniform crystals of TCNQ Ion-radical salts

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An investigation was made on the properties of organic semiconductor resistance strain sensors, fabricated on the basis of quasi-one dimensional ion-radical salts of tetracyanoquinodimethane (TCNQ) crystals, namely, three phenyl methyl phosphonium ($Ph_3Me(TCNQ)_2$) and 2N methyl-methyl tiuronium ($2CH_3MT(TCNQ)_2$). It was observed that, the sensitivity of resistance strain sensors, based on twinned crystals, grown by chemical process is significantly large up to 4000-6000, as compared to uniform crystals. Elastic steel beams were employed to measure the sensitivity of these sensors

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*Keywords*: Strain sensor, Piezoresistive material, Phenyl methyl phosphonium-tetracyanoquinodimethane, 2N methyl-methyl tiuronium

## 1. Introduction

Piezoresistive or tensity resistive effect, as the change of the resistance of metal due to applied mechanical load, was discovered by Lord Kelvin in 1856. The same effect in semiconductors Si and Ge, however was observed by Smith in 1954. This discovery laid the base of electromechanical sensor technologies, which have widespread applications, like tensile image detection, structural health monitoring, cardiovascular pressure measurement etc. In semiconductors, the piezoresistive effect is mostly in the form of a change of their intrinsic properties like change in resistivity due to the change of concentration of charge carriers. Strain sensitivity (S) is defined as [1]:

$$S= \frac{dR}{d\varepsilon}=\frac{d\rho}{\rho\varepsilon}+(1+2\nu) \qquad (1)$$

where dR is the change of initial resistance R, $\varepsilon$ is strain and $\nu$ is Poisson's ratio. The Poisson's ratio is determined by the following expression [2]:

$$\nu=-\frac{\varepsilon_t}{\varepsilon_a} \qquad (2)$$

where $\varepsilon_t$ and $\varepsilon_a$ are transverse and axial strains, respectively.

In metals, the piezoresisitive effect is observed only due to the change of the geometry of the sample, resulting from applied mechanical stress [4,5]. The piezoresistive effect in semiconductor materials is much greater than the geometrical effect in metals. In semiconductors, resistance changes not only due to change of geometry of the sample but also due to change of their stress dependent resistivity. The sensitive resistance strain gauges can be fabricated on the basis of semiconductor materials [3]. The piezoresistive effect in silicon is used in strain sensors, pressure sensors and acceleration sensors as well [6-9]. Piezoresistors can also be fabricated by using different semiconductor materials. Semiconductor-piezoresistors have high value of sensitivity, such as silicon based piezoresistors have sensitivity around 200 [10].

The piezoresistive based electromechanical transducers are more popular than the temperature, electrical and magnetic transducers [11-13]. Therefore, it is reasonable to discover new piezoresistive materials and fabricate devices for further development to meet the demands of future technology. Taking into account that organic semiconductor based sensors, are relatively cheaper and their sensitivity is comparable with that of inorganic sensors; a number of investigations have made in this area [14,15].

The piezoresistive properties of a number of press-tablets of tetracyanoquinodimethane (TCNQ) ion-radical salts as Li(TCNQ), Na(TCNQ), K(TCNQ), $Cs_2(TCNQ)_3$, $Qn(TCNQ)_2$ (Qn is quinolinium) and $Cs_2(TCNQ)_3$, $TEA(TCNQ)_2$ (TEA is three ethyl ammonium) crystals were investigated [16]. It was found that relative resistance-strain relationships were linear and with the increase of the value of pressure (from 3 kbar to 12 kbar), that was used at sample fabrication, the strain sensitivity was increased up to 20-50 for $Cs_2(TCNQ)_3$ and up to 100-120 for $TEA(TCNQ)_2$.

In Ref. [17], first pressure transducers fabricated on the basis of quasi-one-dimensional TCNQ ion-radical salt strain sensors have been described. As an active material for the strain sensors, the pressed tablets of the ion-radical salts of TCNQ with diquinolinium and phenantrolinium were used. The strain sensitivity of these sensors was in the range of 150-300.

The characteristics of the pressure sensors based on TCNQ salts with dimethyldipiridilium and methyltiuronium were described by Abashev et al [18]. These sensors were sensitive to strain and showed low sensitivity to the temperature changes. The strain sensors having composite of polymer of ion radical salt of TCNQ and trimethyl tiuronium TCNQ salt, as an active material, have also been fabricated [19]. The membrane of these sensors was fabricated from the polymer. On the basis of such a strain sensor, the pressure sensor was fabricated that was installed in the probe and was used for the measurement of the pressure in the patient's stomach. Conductivity of the composite was 5 S/m, the strain sensitivity of the sensor was 10 and temperature resistance coefficient was less than 0.1% $(^{o}C)^{-1}$. This composite showed good stability. Diameter of the sensor was 4 mm, the sensitivity was 2 mm of water column. In this work, unlike to the above mentioned reference papers, we have investigated the properties of organic semiconductor resistance strain sensors based on the crystals of complexes of tetracyanoquinodimethane (TCNQ) with three phenyl methyl phosphonium ($Ph_3Me(TCNQ)_2$) and 2N methyl-methyl tiuronium ($2CH_3MT(TCNQ)_2$), because of their potential for applications in the fields of microelectronics, medicines, surgery etc.

## 2. Experimental

Commercially available TCNQ (Fig. 1) was used for the crystal growth of $Ph_3MeP(TCNQ)_3$ and $2CH_3MT(TCNQ)_2$. Crystals were grown in the saturated solution prepared in acetonitrile by R. M. Vlasova (Ioffe Physical Technical Institute, St-Peterburg, Russia) and G. G. Abashev (State University, Perm, Russia). Visually, two kinds of the crystals: twinned and uniform of sizes of 5 x 1.6 x 0.5 mm$^3$ and 3x1.2 x 0.4 mm$^3$, respectively were selected.

Fig. 2 and Fig. 3 show molecular structure of $Ph_3MeP$ and projection of the $Ph_3MeP(TCNQ)_3$ structure on the (100) plane and the orientation of the crystal. The mechanical stresses, for the creation of uniaxial tension and compression, were applied in the [010] crystal direction that was coincided with the direction of the length of $Ph_3MeP(TCNQ)_3$ crystals. Fig. 4 shows the molecular structures of $2CH_3MT$ crystal.

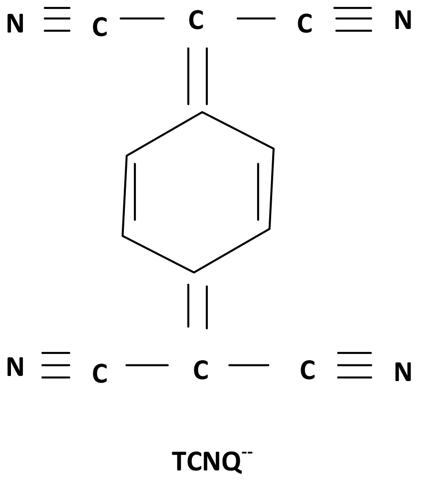


*Fig.1. Molecular structure of tetracyanoquinodi-methane (TCNQ).*

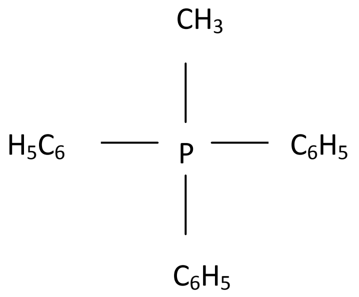


*Fig.2. Molecular structure of $Ph_3MeP$.*

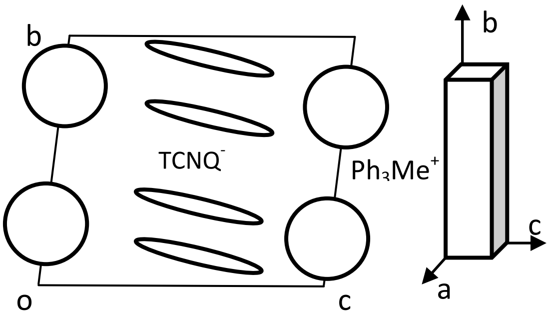


*Fig.3. Projection of the $Ph_3MeP(TCNQ)_3$ crystal structure on the (100) plane and the orientation of the crystal.*

For the investigation of the tensity resistive effect and calibration of these sensors, a lever system for the creation of uniaxial tension–a mechanism for the creation of pressure with needles and devices with bending elastic beams are used [20-22]. This process of testing tensity resistive effect on organic semiconductor thin and fragile crystals films is the most acceptable one. The devices with bending elastic beam and with elastic membrane have been described elsewhere [23,24].

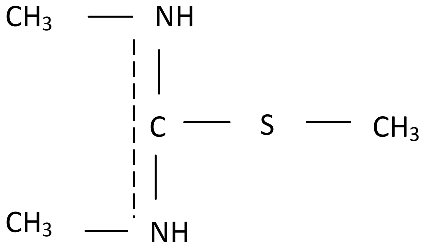
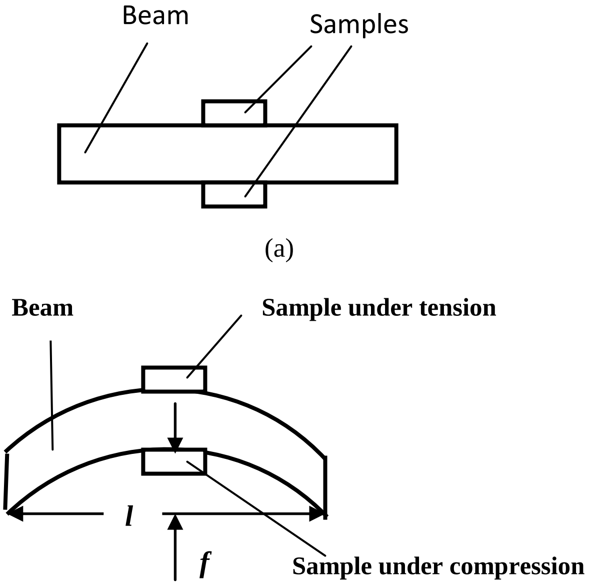


*Fig.4. Molecular structure of 2CH$_3$MT.*



(a)

(b)

*Fig.5. Simplified schematic diagram of the elastic beam of constant cross-section: (a) without load and (b) under load.*

For experiments, we have used the setup with beam of constant cross-section [25,26]. Fig. 5 shows a simplified schematic diagram of the elastic beam of constant cross-section with and without load. The concrete setup of this procedure has already been explained by Karimov [25]. The longitudinal deformation can be determined by using the expression [23,25]:

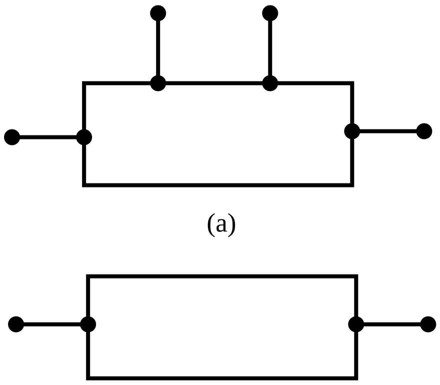
$$\varepsilon = \frac{4hf}{l^2} \tag{3}$$

where $l$ is the distance between two supports, $h$ is thickness of the beam and $f$ is bending of the beam.

The samples were bonded on the surface of the beam. The thickness of the samples was kept less than the thickness of the beam, at least of one order of magnitude. Ideally the beam should transmit the surface displacement to the strain sensor without any distortion [27]. The surface of the beam should be made smooth by sanding, but not polished [28].

For bonding the samples, the surface of the beam is cleaned by toluene and spirit. The thin film of the corresponding glue is deposited on the beam and the strip of the thin paper is then glued on the beam. Finally, the sample is pasted on the beam through the paper. The role of glue (adhesive) is very important; it should be strong, low-viscous and well-cured that forms a very thin elastic bond line [26]. In some cases, in order to provide better quality of the sample pasting, the sample is put in vacuum conditions or undergone to thermal treatment [28].

Fig. 6 shows four terminals (a) and two terminals (b) crystal strain sensors. The terminals were connected to the crystals by silver paste. Usually, if the sample's contact resistances are larger than the bulk resistance, the four terminals are used otherwise two terminals are preferred.

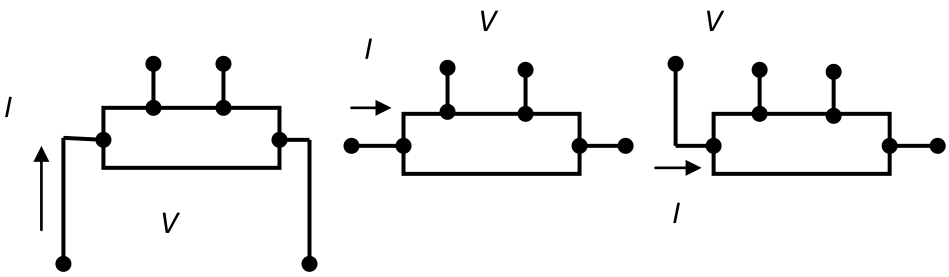


(a)

(b)

*Fig.6. Organic semiconductor crystal strain sensors: (a) four terminal and (b) two terminal samples.*

The apparent, bulk and contact resistances were measured with four terminals sensors. Fig. 7 shows a schematic diagram of an apparent resistance ($R_a$), bulk resistance ($R_b$) and contact resistance ($R_c$) (resistances measurements) as a function of measured corresponding voltages (V) and currents (I).



(a) (b) (c)

*Fig.7 Measurements of an apparent, bulk and contact resistances of the organic semiconductor crystals: (a) $R_a = V/I$, (b) $R_b = V/I$, (c) $R_c = V/I$.*

## 3. Results and discussions

Fig. 8 and Fig. 9 show relative bulk resistance (dR/R)-deformation (ε) relationships for the two twinned and one uniform $Ph_3MeP(TCNQ)_3$ crystal sensors, respectively at tension and compression. It is seen that the relationships for twinned crystal are non-linear and asymmetrical at tension and compression. The value of resistance strain sensitivity for twinned crystal is high: S is equal to 2000-4000 under tension and 500-1000 under compression (Table 1). However, such relationships for uniform crystal are almost linear as shown in Fig. 9. The resistance strain sensitivity for uniform crystal is equal to 100-140 under tension and 70-80 under compression (Table 1). The obtained results show that the strain sensitivity of the sensors based on twinned crystals is considerably higher than the sensitivity of the uniform crystal based sensors. Therefore, it would be reasonable to investigate the stability of these strain sensors based on twinned crystals. Fig. 10 shows relative bulk resistance–time relationship for the $Ph_3MeP(TCNQ)_3$ twinned crystal sensor. It is seen that if strain of these sensors is kept constant for about six hours the fractional change of their resistance practically remains constant, as well.

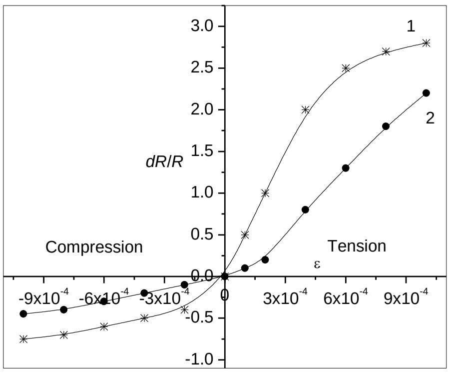


*Fig.8. Relative bulk resistance (dR/R)-deformation (ε) relationships for two twinned Ph3MeP(TCNQ)3 crystal sensors at tension and compression.*

Fig. 11 shows an apparent, bulk and contact resistances-strain relationships for $Ph_3MeP(TCNQ)_3$ crystal sensors. The sensitivity of these sensors due to bulk resistance is higher than that of the contact resistance. Anomalous high tensity resistive effect in twinned $Ph_3MeP(TCNQ)_3$ crystal sensors is due to the significant change of the conductivity of the interlock regions, under deformation.

Fig. 12 and Fig. 13 show apparent, bulk and contact relative resistance (dR/R)-deformation (ε) relationships for the twinned and uniform $2CH_3MT(TCNQ)_2$ crystal sensors, respectively at tension and compression. The reasons of higher strain sensitivity of the twinned $2CH_3MT(TCNQ)_2$ crystal sensors are seems the same as in $Ph_3MeP(TCNQ)_3$ crystal sensors: the presence of the structural defects are most likely responsible for this effect.

In twinned $2CH_3MT(TCNQ)_2$ crystals, the strain sensitivity is found in the range of 4000-6000 under tension and 500-1500 under compression. Whereas, in uniform crystals, the strain sensitivity is measured in the range of 20-30 under tension and 15-20 under compression.

The sensitivity of the resistance strain sensors can reach to very high value in uniform semiconductors, for example, PbS films [18], or in special states as frozen conductivity (FC) in the CdS films [19]. The frozen conductivity of semiconductors is a high conductive state that can be kept for a long time even after switching off the external excitation source. Table 1 shows data of the strain sensitivity of a number of sensors fabricated from inorganic and organic semiconductors. Thus sensitivity of the resistance strain sensors depends on the concentration of defects in semiconductors and state of the electronic system. As a little information is available in the literature about the resistance strain effect on organic semiconductor strain sensors, an effort was therefore, made to investigate the properties of these sensors based on quasi-one dimensional tetracyanoquinodimethane (TCNQ) ion-radical salts crystals.

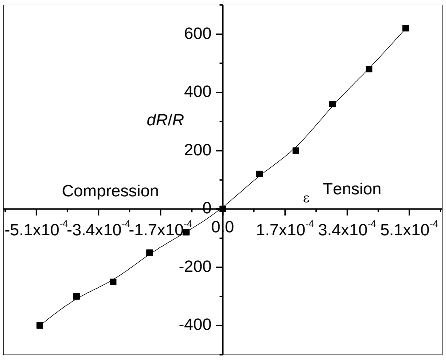


*Fig.9. Relative bulk resistance (dR/R)-deformation (ε) relationship for one of the uniform $Ph_3MeP(TCNQ)_3$ crystal sensor at tension and compression.*

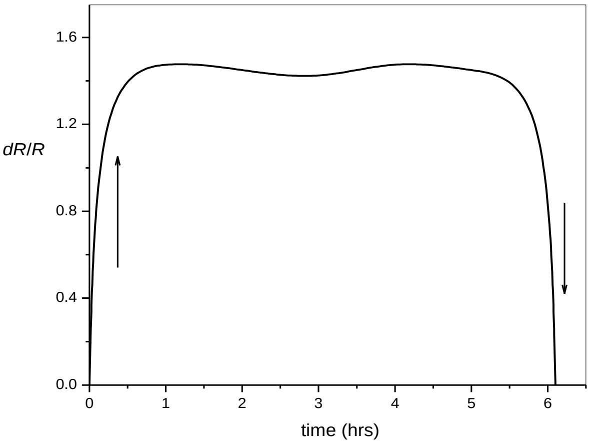


*Fig.10. Relative bulk resistance-time relationship for the twinned $Ph_3MeP(TCNQ)_3$ crystal sensors under deformation of tension ($\varepsilon = 3\times10^{-4}$) during of 6 hrs.*

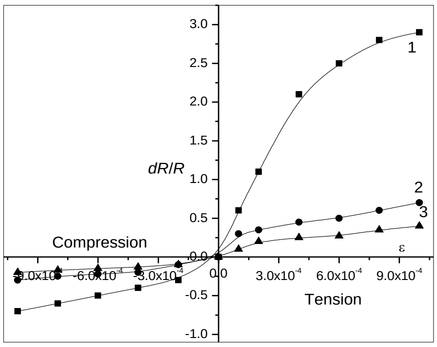


*Fig.11. An apparent (1), bulk (2) and contact (3) resistances-strain relationships for $Ph_3MeP(TCNQ)_3$ crystal sensors.*

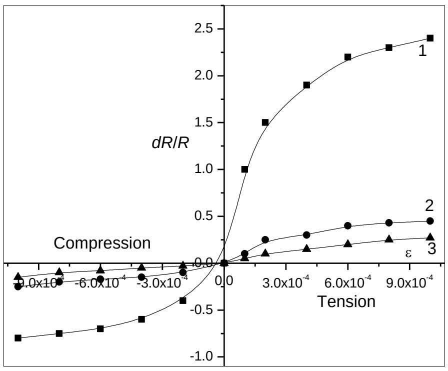


*Fig.12. An apparent (1), bulk (2) and contact (3) relative resistances (dR/R)-deformation (ε) relationships for twinned $2CH_3MT(TCNQ)_2$ crystal sensor under tension and compression.*

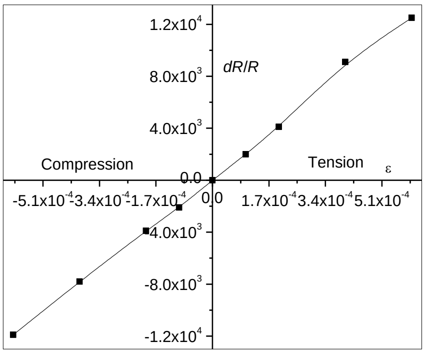


*Fig.13. Relative bulk resistances (dR/R)-deformation (ε) relationships for the uniform $2CH_3MT(TCNQ)_2$ crystal sensor under tension and compression*

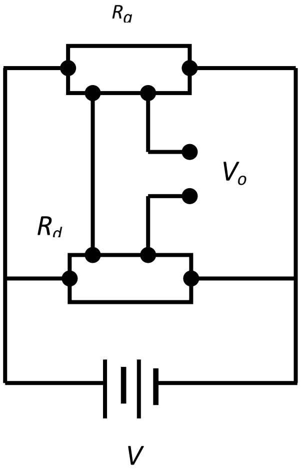


*Fig.14. The circuit for connections of the four terminal resistance strain sensors: $R_a$ and $R_d$ are active and dummy resistance strain sensors, $V_o$ is output voltage.*

*Table 1: Strain sensitivity of the sensors fabricated from inorganic and organic semiconductors*

| Sr. # | Semiconductor | Sensitivity of the sensor | Reference |
|---|---|---|---|
| 1 | PbTl (film) | 170 | [17] |
| 2 | BiTlSb (film) | 400-500 | [17] |
| 3 | PbS (film) | 300-3000 | [17] |
| 4 | CdS (film) | 1000 | [25] |
| 5 | CdS in condition of frozen conductivity | 105 | [25] |
| 6 | TCNQ ion-radical salts with diquinolinium and phenantrolinium (press-tablets) | 150-300 | [14] |
| 7 | Ph3MeP(TCNQ)2 crystals (twinned crystals) | 2000-4000 (tension)<br>500-1000 (compression) | [26] |
| 8 | Uniform crystals | 100-140 (tension)<br>70-80 (compression) | [26] |
| 9 | 2CH3MT(TCNQ)2 crystals (twinned crystals) | 4000-6000 (tension)<br>500-1500 (compression) | Present work |
| 10 | Uniform crystals | 20-30 (tension)<br>15-20 (compression) | Present work |

The organic semiconductor strain sensors based on crystals usually have four terminals. Therefore, a prominent circuit was developed for the connection of active and dummy four terminal sensors to measure the deformation. Fig. 14 shows the circuit for the investigation of properties of four terminals resistance strain sensors.

At same temperature and environment, active sensor ($R_a$) is found under strain, where as dummy sensor ($R_d$) lies in stress-free region. This circuit allows compensating the effect of temperature changes to the output voltage. If the rise in temperature is same for both sensors, the voltage drop at the sensors applied to output of the circuit should be equal and opposite in polarity to compensate the effect of temperature. If active strain sensor is loaded, i.e. under strain, the voltage drop across it is not compensated by the voltage of dummy sensor as it is in stress-free region.

## 4. Conclusions

The properties of organic semiconductor resistance strain sensors based on quasi-one dimensional crystals of ion-radical salts of tetracyanoquinodimethane (TCNQ) were investigated. It was observed that the sensitivity of the sensor due to bulk resistance is higher than that of the apparent and contact resistances. It was also found that $Ph_3Me(TCNQ)_2$ and $2CH_3MT(TCNQ)_2$ twinned crystals based bulk resistance strain sensors show very high sensitivity, up to 4000-6000, as compared to uniform crystals. It is considered that the reason of such a high resistance strain sensitivity of the twinned crystal sensors is most likely due to the presence of the structural defects. For the potential uses of these fabricated sensors, the connection of sensors with four terminals in the circuits to compensate the effect of temperature is presented.

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