Electrical properties of TCNQ/V_2O_5 heterojunction

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In this study the electrical properties of tetracyanoquinodimethane (TCNQ) and vanadium pentoxide (V_2O_5) structured composite were evaluated. The composite was formed by drop deposition of TCNQ film from solution in benzol on preliminary deposited V_2O_5 layer from its suspension in distilled water on Cu substrate. The sandwich Cu/V_2O_5/TCNQ/Ga and the surface Cu/V_2O_5/TCNQ/Cu type samples were fabricated. Resistance-temperature relationships and voltage-current characteristics of the composite samples were measured by using conventional digital voltmeter and ammeter at the temperature interval of 24 ^oC – 102 ^oC with an error of ± 0.5 %. It is observed that the DC electrical conductivity, non-linearity of voltage-current characteristics of the samples and activation energy for the surface type samples are temperature dependent. The surface type samples show quasi-linear resistance-temperature relationship, the temperature coefficient of resistance is sufficiently large and at 24 ^oC is equal to – 2.4 / ^oC and non-linearity coefficient of V-I characteristics is low (1.4), whereas the sandwich type samples exhibit non-linear resistance-temperature relationship, higher non-linearity coefficient (2.3) of V-I characteristics, lower temperature coefficient of resistance (-2.1 / ^oC). Sandwich type samples show small rectification behaviour, rectification ratio unlike to conventional semiconductors increases with temperature.

(Received September 24, 2007; accepted March 12, 2008)

Keywords: Organic semiconductor, Low molecular material, Tetracyanoquinodimethane, Vanadium pentoxide, Composite

1. Introduction

In recent years there has been considerable interest in the investigation of organic-inorganic structures: complexes and composites through novel synthesis and self-assembly techniques [1,2]. The organic semiconductors may be found suitable for applications in many fields of electronics dependent upon their electrical conductivity [3,4] and very often they determine the characteristics of the devices. For example, the efficiency of organic solar cells is generally limited due to the low conductivity of photosensitive materials [5,6]. It is known that the structure and properties of organic semiconductors highly depend upon their processing technology [3,4]. Generally, the organic materials have large molecular weight, strong intermolecular and weak Van der Walls intermolecular bonding. The poly-N-epoxypropyl-carbazole films grown from solution during rapid stirring [1,7] showed higher conductivity than that of the reference samples. In [8] the electrical conductivity of films composed of two photosensitive organic semiconductors poly-N-epoxipropylcarbazole and copper phthalocyanine deposited from solution at different gravity conditions from 1 g to 1107 g, was investigated. And 1.5-fold increase in the conductivity and 2-fold decrease of activation energy with increased acceleration were reported. Deposition of copper phthalocyanine organic thin films in high gravity by physical vapor transport was studied in [9]. It was shown that the optical absorption increased with increasing acceleration during film growth. Moreover, the absorption peaks were shifted to lower wavelength values as the acceleration was increased. X-ray diffraction indicated that the centrifugal force caused a strain in the films.

It is generally understood that the fabrication process of organic semiconductor devices is simple, inexpensive and the area may be promising especially for different kinds of sensors. The electric properties of some organic films deposited at high gravity were explained by space-charge limited currents (SCLC) [10]. Poly-N-epoxipropylcarbazole-copper phthalocyanine films showed highly non-linear voltage-current characteristics. For practical utilization of semiconductor organic thin films it would be important to investigate their electrical properties with different metals (as electrodes) in order to identify whether they form ohmic or Schottky contacts in different junctions or composites. Tetracyanoquino-dimethane (TCNQ) as a strong acceptor of electrons forms charge-transfer complexes and ion-radical salts with a number of organic materials that have potential applications in electronic engineering, for different kinds of sensors [11].

Vanadium pentoxide (V_2O_5) is a well investigated material [12,13] and at present its composites with polymers, as poly(ethylene oxide)/ V_2O_5 intercalative nanocomposites [2], and complexes with inorganic oxides as $(V_2O_5)_{1-x}$-$(MoO_3)_x$ [14] were investigated. These materials, in principle, can posses electrical, optical, and mechanical properties which may not be achieved with each component separately and are interesting for various scientific and technological applications.

Recently it was found that organic-inorganic devices based on interpenetrating networks, unlike to conventional semiconductor p-n junctions, show very high efficiency [15]. In this paper, the electrical properties of tetracyanoquinodimethane and vanadium pentoxide structured composite (heterojunction) were evaluated.

2. Experimental

In this work, commercially produced TCNQ ($C_{12}N_4H_4$) and vanadium pentoxide V_2O_5 were used. Fig. 1 shows a molecular structure of TCNQ. Molecular weight of TCNQ is equal to 204 amu.

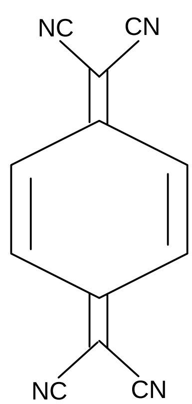


Fig. 1. Molecular structures of tetracyanoquinodi-methane (TCNQ).

The composite was formed at room temperature by drop deposition of TCNQ film from 5 wt.% solution in benzol on preliminary deposited V_2O_5 layer from its 5 wt.% suspension in distilled water on Cu substrate. The suspension was prepared at 100 ^oC by stirring of V_2O_5 powder in distilled water. The sandwich Cu/V_2O_5/TCNQ/Ga and the surface Cu/V_2O_5/TCNQ/Cu type samples were fabricated at room temperature (Fig. 2). The gap between copper electrodes and the width of the electrodes in the surface type samples were measured by optical microscope and were equal to 0.1 mm and 5 mm, respectively. The thickness of the V_2O_5 and TCNQ films estimated by SEM were equal to 50 μm and 100 μm, respectively. The diameter of the TCNQ film in the case of sandwich type samples was equal to 3 mm.

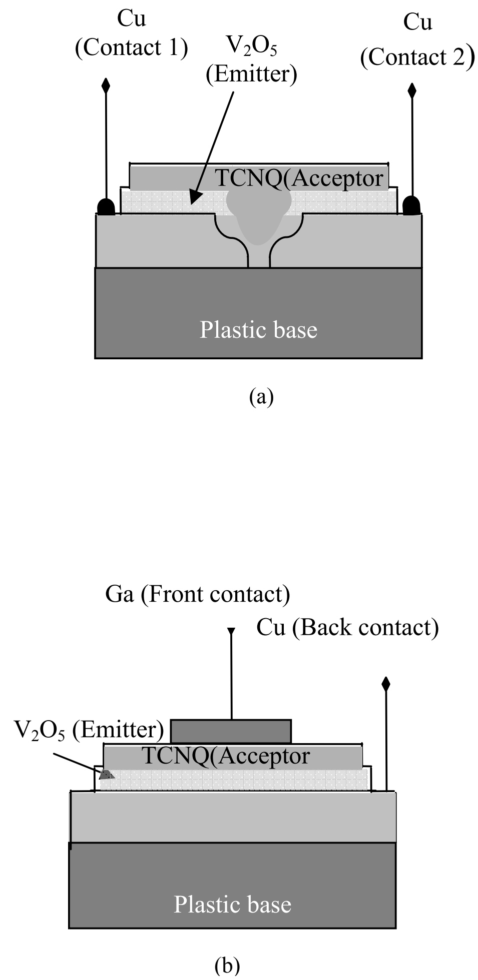


Fig. 2. Cross-sectional view of the surface Cu /V_2O_5 / TCNQ/ Cu (a) and sandwich types Cu / V_2O_5 /TCNQ/ Ga (b) samples.

Resistance-temperature relationships and voltage-current characteristics of the samples were measured by using conventional digital voltmeter and ammeter in the temperature interval 24 ^oC – 102 ^oC with an error of ± 0.5 %.

3. Results and discussion

Fig. 3 shows resistance-temperature relationship in the surface type Cu/V_2O_5/TCNQ/Cu sample.

It is seen that relationship is quasi-linear, resistance decreases with temperature and temperature coefficient of resistance at 24 ^oC is equal to -2.4% / ^oC.

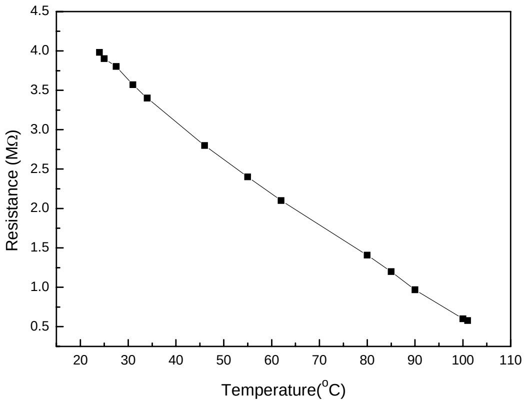


Fig. 3. Resistance–temperature relationship in the surface type Cu/V_2O_5/TCNQ/Cu sample.

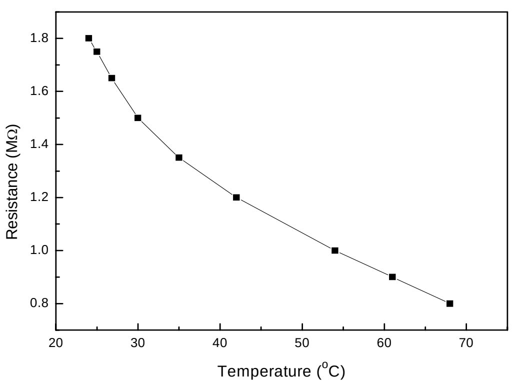


Fig. 4. Resistance-temperature relationship in the sandwich type Cu/V_2O_5/TCNQ/Ga sample.

Fig. 4 shows resistance-temperature relationship in the sandwich type Cu/V_2O_5/TCNQ/Ga sample: the relationship is non-linear, resistance decreases with temperature and temperature coefficient of resistance at 24 °C is equal to -2.1 %/ °C.

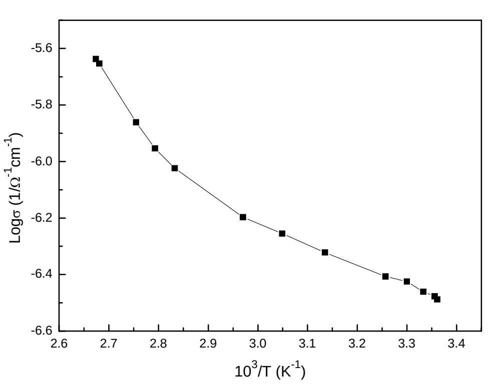


Fig. 5. Conductivity-temperature relationship for the surface type Cu/V_2O_5/TCNQ/Cu sample.

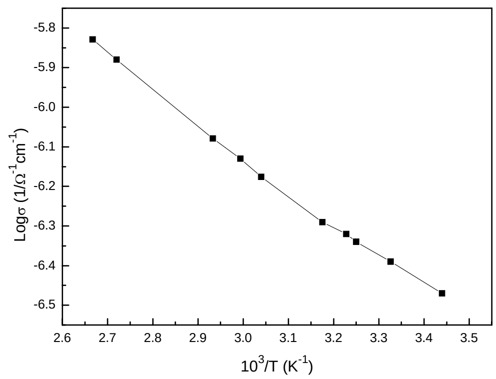


Fig. 6. Conductivity-temperature relationship for the sandwich type Cu/V_2O_5/TCNQ/Ga sample.

Figs. 5 and 6 show the conductivity-temperature relationships for the surface Cu/V_2O_5/TCNQ/Cu and sandwich Cu/V_2O_5/TCNQ/Ga type samples, respectively.

It is seen that conductivities decrease with temperature. The room temperature conductivities of the Cu/V_2O_5/TCNQ/Cu and Cu/V_2O_5/TCNQ/Ga samples were equal to 3.2×10^{-7} Ω^{-1} cm^{-1} and 3.7×10^{-7} Ω^{-1} cm^{-1}, respectively. Activation energy (*E*) of conductivity was determined from the following well-known expression for the conductivity of organic semiconductors as reported in [3, 4]:

$$\sigma = \sigma_o e^{-E/kT} \tag{1}$$

Where *k* is Boltzmann constant, *T* is absolute temperature and σ_o is pre-exponential factor. Room temperature activation energies for the Cu/V_2O_5/TCNQ/Cu and Cu/V_2O_5/TCNQ/Ga samples were equal to 0.19 eV and 0.17 eV, respectively.

Fig. 7 shows dependences of activation energies on temperature: the relationships show that for the Cu/V_2O_5/TCNQ/Ga sample the activation energy is practically constant, whereas in the case of Cu/V_2O_5/TCNQ/Cu one it increases with temperature beyond a temperature that is equal to 70 °C.

In [14], it was found that electrical conductivity behaviour of $(V_2O_5)_{1-x}$-$(MoO_3)_x$ thin films obeys the $T^{-1/4}$ law and it was explained by the temperature dependence of individual transition rates, assisted by multiphonon interactions. Our experiments show that electrical conductivity of the V_2O_5 samples on the whole obeys $T^{-1/4}$ law whereas composite V_2O_5-TCNQ samples show visible deviations from that: it may be due to effect of TCNQ films.

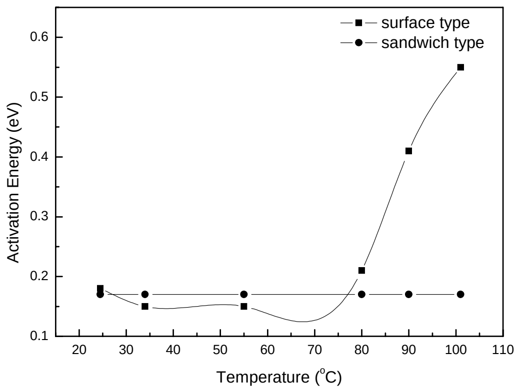


Fig. 7. Dependences of activation energies on temperature for the $Cu/V_2O_5/TCNQ/Cu$ and $Cu/V_2O_5/TCNQ/Ga$ samples.

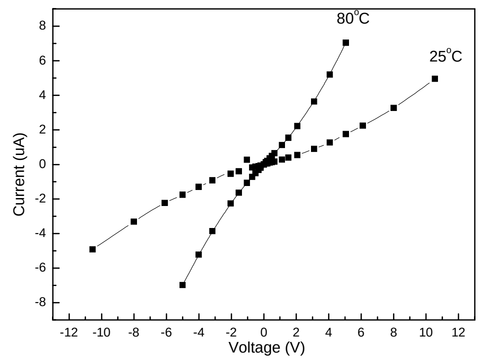


Fig. 8. Voltage-current relationships in the $Cu/V_2O_5/TCNQ/Cu$ sample at different temperatures.

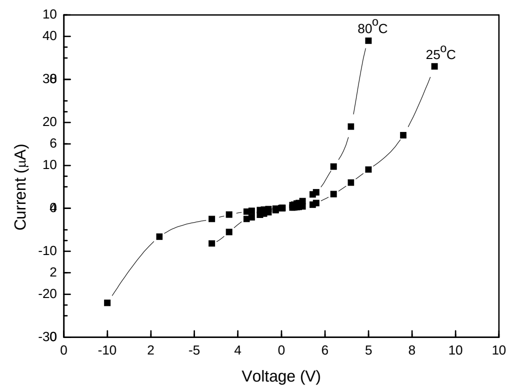


Fig. 9. Voltage-current relationships in the $Cu/V_2O_5/TCNQ/Ga$ sample at different temperatures.

Figs. 8 and 9 show voltage-current relationships in the $Cu/V_2O_5/TCNQ/Cu$ and $Cu/V_2O_5/TCNQ/Ga$ samples, respectively, at different temperatures. The characteristics are non-linear, symmetric in the case of $Cu/V_2O_5/TCNQ/Cu$ and non-linear, slightly asymmetric for $Cu/V_2O_5/TCNQ/Ga$. In the last case, rectification ratio as a ratio of currents at applied voltages (for example, V= ± 4 V) were equal to 2.4 and 2.3 at 25 °C and 80 °C, respectively. One of the reasons of low rectification ratio obtained in $Cu/V_2O_5/TCNQ/Ga$ samples may be the presence of surface states in heterojunction interface [16] that can make junction resistance less dependent on the polarity of the applied voltage.

Non-linearity of voltage-current characteristics may be estimated by the following expression [17]:

$$I = cV^B \qquad (2)$$

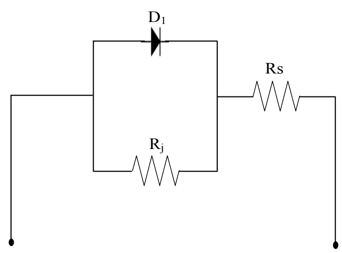
Where c is a proportional factor and B is a nonlinearity coefficient that may be determined from the following expression:

$$B = \frac{(\ln I_2 - \ln I_1)}{(\ln V_2 - \ln V_1)} \qquad (3)$$

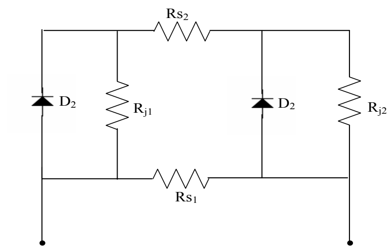
Where I_1 and I_2 are currents measured at voltages V_1 and V_2, respectively. The nonlinearity coefficient (B) at 25 °C and 80 °C was determined equal to 1.4 and 1.3 for the surface type $Cu/V_2O_5/TCNQ/Cu$ samples and equal to 2.3 and 2.7 for the sandwich type $Cu/V_2O_5/TCNQ/Ga$ samples, respectively. In the case of $Cu/V_2O_5/TCNQ/Ga$ sample non-linearity coefficient was estimated at forward bias, "+" applied to V_2O_5.

The nonlinearity of *I-V* characteristics observed experimentally may be caused by several reasons such as: (i) increase of conductance of the composite by current's heating (thermistor's effect), (ii) space-charge-limited currents (SCLC), (iii) effect of electric field etc. [3,4,16,17]. The latter case has a low probability because of the relatively low electric field applied to samples (around 10^3 V/cm). In the case of SCLC usual nonlinearity coefficients are greater (B = 2-3) [3,4] and increase with temperature, i.e. this may be a reason of non-linearity in $Cu/V_2O_5/TCNQ/Ga$ sample. In the case of $Cu/V_2O_5/TCNQ/Cu$ sample the situation may be more complicated, but in the first approximation we may assume that nonlinearity behaviour of voltage-current characteristics may be due to the "thermistor's" effect [17] as well, because the *B* decreases with temperature.

If we describe the $Cu/V_2O_5/TCNQ/Ga$ and $Cu/V_2O_5/TCNQ/Cu$ samples as the varistor, and thermistor respectively, the following equivalent circuits may be designed (Fig. 10).



(a)



(b)

Fig. 10. Equivalent circuits of theCu/V_2O_5/TCNQ /Ga (a) and Cu/V_2O_5/TCNQ/Cu (b) samples as the varistor, and thermistor, respectively.

Where R_J and R_S represent junction and series resistances of varistor, R_{J1} and R_{J2} represent V_2O_5-TCNQ and TCNQ-V_2O_5 junction resistances, R_{S1} and R_{S2} represent series resistances of the V_2O_5 and TCNQ layers. Diodes shown in the equivalent circuits represent electronic switches. All junction resistances in the equivalent circuit are considered as voltage and temperature dependent, whereas series resistances, are assumed to be only temperature dependent. As the rectification ratio in Cu/V_2O_5/TCNQ/Ga sample is small, we may assume that junction and series resistances may have comparable values.

4. Conclusion

The electrical properties of tetracyanoquinodimethane (TCNQ) and vanadium pentoxide (V_2O_5) structured composite (or heterojunction) were evaluated on the sandwich Cu/V_2O_5/TCNQ/Ga and the surface Cu/V_2O_5/TCNQ/Cu type samples. Resistance-temperature relationships, voltage-current characteristics of the composite samples were measured in the interval of 24 ^oC - 102 ^oC. It is observed that the DC electrical conductivity, activation energy (for the Cu/V_2O_5/TCNQ/Cu sample) and non-linearity of voltage-current characteristics of the samples are temperature dependent. On the bases of Cu/V_2O_5/TCNQ/Ga samples varistors may be fabricated with high non-linearity coefficient and low temperature coefficient of resistance and Cu/V_2O_5/TCNQ/Cu samples may be used in the fabrication of thermistors with linear resistance-temperature relationship and low non-linearity coefficient.

Acknowledgement

We are grateful to GIK Institute of Engineering Science and Technology for the support extended to this work.

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