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# Enhancement of electronic and charge transport properties of NiPc by potassium-tetrasulpho group

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ABSTRACT

We report significant enhancement in the electronic properties of nickel phthalocyanine (NiPc) by attaching a potassium-tetrasulpho functional group to synthesize its water soluble derivative nickel (II)4,4′,4″,4‴potassium-tetrasulphophthalocyanine ($K_4NiTSPc$). To study the potential of this organic compound for electronics applications, Au/K4NiTSPc/Ag diodes have been fabricated and their electronic parameters have been calculated. The mobility and conductivity of the device have been found to be $1.5\times10^{-4}\ cm^2\ V^{-2}\ S^{-1}$ and $2.5\times10^{-4}\ \Omega^{-1}\ cm^{-1}$. The $K_4NiTSPc$ has shown much better electronic properties as compared to NiPc reported in the literature, which makes it a promising candidate for its potential use in electronics applications.



## 1. Introduction

Researchers in the field of electronics have been focused to address the issues of high production cost, complex fabrication techniques and performance of the organic devices [1–3]. To overcome these problems a large number of solution processable organic semiconductors have proven viable materials for the fabrication of electronic devices [4,5]. By employing these materials, electronic devices can be fabricated by simple and cost effective fabrication techniques which include spin coating, printing, etc. Among the organic compounds, metallophthalocyanines (MPcs) and their soluble derivatives have acquired great importance due to their thermal and chemical stability [6]. Thin films of these compounds can be deposited by thermal evaporation without dissociation [7–9]. Previous investigations on phthalocyanines performed by our research group have shown that there is a need to improve the electrical properties in order to make the phthalocyanines suitable for practical application [7,10–12]. Most of the phthalocyanines compounds have shown high ideality factor, greater barrier height and large series resistance. For instance, the electrical properties of NiPc (without any functional group attached at the periphery) in surface-type Schottky diodes have been studied by Shah et al. [7,10,11] and various electrical parameters of metal/NiPc junctions from current–voltage (*I–V*), capacitance–voltage (*C–V*) and capacitance–frequency (*C–F*) characteristics have been determined. These studies have shown high ideality factor, greater barrier height and large series resistance. On the other hand low mobility and conductivity and small rectification ratio in these NiPc based diodes have also been observed. Very recently, Ahmad et al. [13] have investigated the NiPc derivative, Nickel (II) phthalocyaninetetrasulfonic acid tetrasodium salt (NiTSPc), for sensors application which indicate enhancement of the electrical properties of NiPc by attaching tetrasulfonic functional group. Keeping in view these facts, in this study, a derivative of NiPc, Nickel (II) 4, 4′, 4″, 4‴potassium-tetrasulphophthalocyanine ($K_4NiPTS$), has been synthesized by attaching a potassium-tetrasulpho functional group to NiPc. The $K_4NiTSPc$ is employed to fabricate surface-type Au/$K_4NiTSPc$/Ag Schottky diodes to determine its electronic properties. The current–voltage (*I–V*) characteristics of the device have been investigated in air at room temperature. The electronic parameters such as rectification ratio, mobility and conductivity have been significantly improved.

## 2. Experimental

To synthesize Nickel (II) 4,4′,4″,4‴ potassium-tetrasulphophthalocyanine ($K_4NiTSPc$), all reagents and solvents were purchased from Sigma Aldrich and used as received. $K_4NiTSPc$ was synthesized by a modification of the method of Webar and Busch [14]. The ammonium salt of 4-sulphophthalic acid was reacted

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with urea and $NiCl_2$ in nitrobenzene as solvent at 180 °C. After cooling, dilution with water and addition of KOH to make the sample alkaline, the solution was filtered to remove inorganic and low molecular mass impurities. The product was isolated by vacuum evaporation. Molecular structure of nickel (II) 4, 4′,4′′,4′′′ potassium-tetrasulphophthalocyanine ($K_4NiTSPc$) is shown in Fig. 1.

A solution (1 wt%) of the $K_4NiTSPc$ was prepared in distill water at room temperature. With a little shaking, a homogeneous solution was obtained. To determine the electronic properties of $K_4NiTSPc$, the surface-type Au/$K_4NiTSPc$/Ag Schottky diodes were fabricated. First, the substrates were cleaned for 10 min using distill water in the ultrasonic cleaner and after drying, the substrate was plasma cleaned for 5 min followed by the thermal deposition of Au and Ag electrodes using a shadow mask. During thermal deposition the chamber pressure was $5.5\times10^{-5}$ mbar while the deposition rate was kept at 0.1 nm/s. The thickness of the electrodes was 100 nm and the gap between the electrodes was 50 μm. The length of the gap was 3 mm. Afterwards the ~100 nm thin films of $K_4NiTSPc$ were deposited by drop casting. The fabricated devices were left at room temperature for 24 h to let the moisture evaporate. Cross-sectional view of the fabricated Au/$K_4NiTSPc$/Ag surface type Schottky diode is shown in Fig. 2. The current–voltage (*I–V*) characteristics of the diodes were measured at room temperature using Keithley 236 Source Measurement Unit.

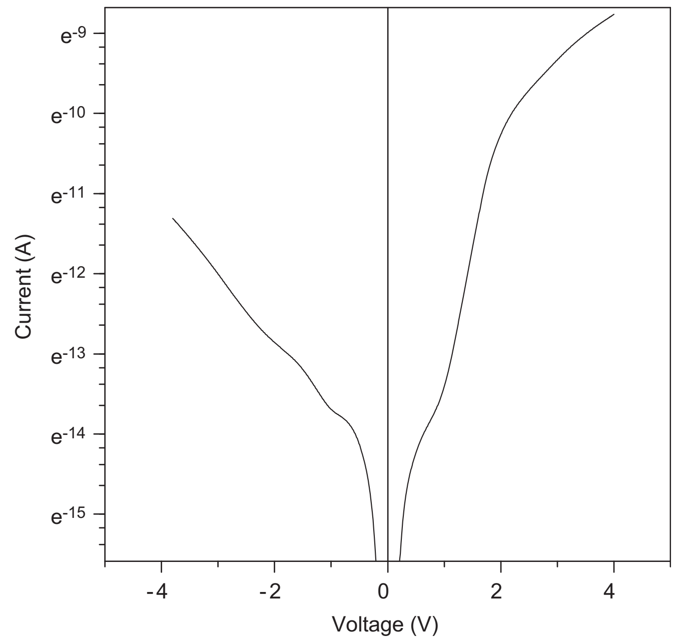


**Fig. 3.** Current–Voltage (*I–V*) characteristics of a surface type Au/$K_4NiTSPc$/Ag device.

## 3. Results and discussion

The forward bias and reverse bias *I–V* characteristics for the Au/$K_4NiTSPc$/Ag are shown in Fig. 3. The forward bias corresponds to the positive potential to the Au with respect to Ag. The samples display nonlinear, asymmetric and rectification behavior, which indicates the formation of the depletion regions at interfaces. The rectification ratio (RR) is determined as the ratio of the forward current to the reverse current at a certain applied voltage ($I_F/I_R$). The rectification ratio depending on the applied voltage reflects increased charge injection into the $K_4NiTSPc$. The value of rectification ratio is found as 19.8 at ± 1.4 V. This behavior is due to the fact that a space charge layer is formed at the interface. The I-V characteristics of the samples show an exponential increase in current due to decrease in the depletion layer width at the interface. Calculated values of ideality factor, barrier height and series resistance are given in Table 1. The thermionic emission theory is taken into consideration for the extraction of these diode parameters. According to the thermionic emission theory the current in Schottky barrier diodes can be given by [15]:

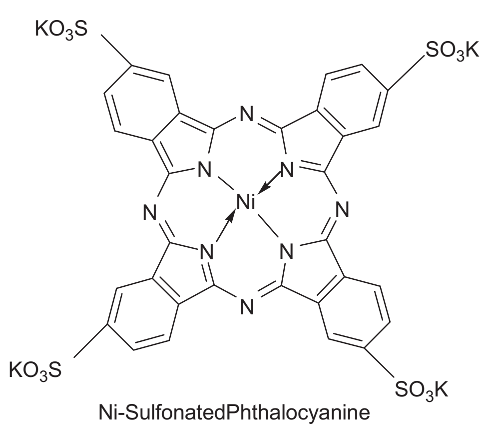


**Fig. 1.** Molecular structure of nickel (II) 4,4′,4′′,4′′′ potassium-tetrasulphophthalocyanine ($K_4NiTSPc$).

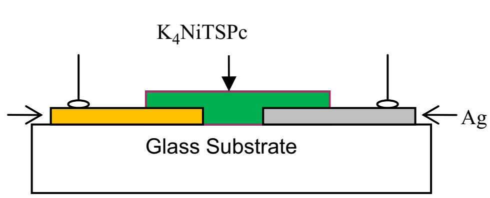


**Fig. 2.** Cross-sectional view of the Au/$K_4NiTSPc$/Ag diode.

$$I=I_o\left[\exp\left(\frac{q(V-IR_s)}{nkT}\right)-1\right] \tag{1}$$

where

$$I_o=AA^*T^2\exp\left(\frac{-q\phi_b}{kT}\right) \tag{2}$$

$I_o$ is the saturation current, $V$ is the applied voltage, $R_s$ is the series resistance, $A^*$ is the effective Richardson constant equal to $10^{-2}$ A cm$^{-2}$ K$^{-2}$ for organic material [16], $A$ is the effective diode area ($3\times10^{-5}$ mm$^2$ in this case), $T$ is the temperature (300 K in this case), $k$ is the Boltzmann constant and $\phi_b$ is the barrier height. The reverse saturation current $I_{o,}$ determined from the semi-log *I–V* curve of Fig. 3, is equal to $2.59\times10^{-8}$ A. Using the value of reverse saturation current $I_o$, the effective barrier height of the junction $\phi_b$, which is the contact potential barrier that exists at the interface of the metal and semiconductor, has been calculated using Eq. (2). Its value is found as 0.72 eV.

The quality of a diode is measured by the ideality or quality factor '*n*' using the *I–V* characteristics. The value of *n* is unity for an ideal diode [15] but it deviates from the ideal value and usually it is observed greater than unity. The value of the ideality factor for the diode was calculated from the slope of the linear region of the forward bias semi-logarithmic current–voltage characteristics. The value of *n* has been determined from the linear region of the *I–V* curves (Fig. 3) using the following relation [17]:

$$n=\frac{q}{kT}\frac{dV}{d(\ln I)} \tag{3}$$

**Table 1**
Comparison of the electronic parameters of the $Au/K_4NiTSPc/Ag$ and Au/NiPc/Ag junction diodes.

| | Ideality factor | Rectification ratio (RR) | Barrier height (eV) | Mobility ($cm^2 V^{-1} S^{-1}$) | Conductivity ($\Omega^{-1} cm^{-1}$) | Rs |
|---|---|---|---|---|---|---|
| **$Au/K_4NiTSPc/Ag$ [present work]** | 11 | 19.8 at $\pm$1.4 V | 0.72 | $1.5\times10^{-4}$ | $2.5\times10^{-4}$ | 47 KΩ |
| **Au/NiPc/Ag** [11] | 70 | 3 at $\pm$14 V | 1.11 | $9.3\times10^{-9}$ | $3.42\times10^{-7}$ | 12 MΩ |

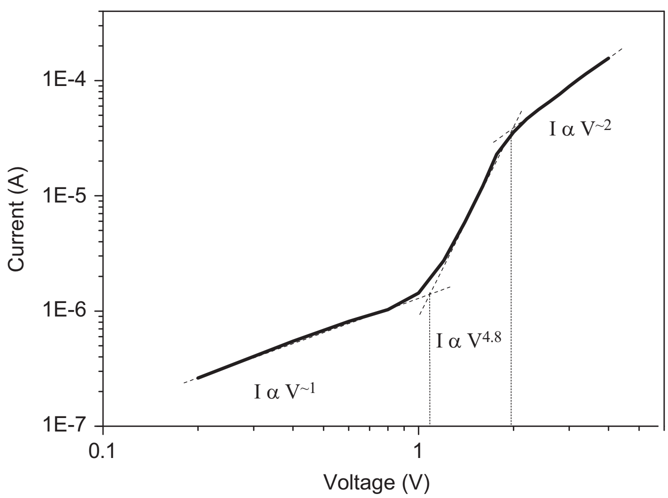


**Fig. 4.** Double logarithmic current voltage characteristics (log *I*–log *V*) of a surface type $Au/K_4NiTSPc/Ag$ diode.

High values of ideality factors can be attributed to the non-homogenous barrier. It may also be due to the other effects, such as non-homogeneous thickness of organic film and organic layer effect, etc. [18–20]. The effect of the bias voltage drop across the interface layer could also be one of the factors for such high values of $n$. According to [21], the greater values of $n$ can result from the analysis of $I$–$V$ data in regions where the organic bulk properties are dominant as compared to interfacial processes. Therefore, the large deviation of the ideality factor from unity suggests that the transport mechanisms of the device cannot be well modeled by the thermionic emission only as the value of '$n$' reaching 11. The higher values of ideality factor can also be attributed to secondary mechanisms and defects at the interface [15,21,22].

The $I$–$V$ characteristics of the $Au/K_4NiTSPc/Ag$ diode are depicted in a $\log I$–$\log V$ scale in Fig. 4. As it can be seen from the Fig. 4, three major regions have been found. At low voltages, from 0 to 1.0 V, the current increases linearly with an increase in the bias voltage. It can also be observed that for voltage between 1.0 and 2.0 V the current is directly proportional to the $V^{4.8}$. With further increase of bias voltage, the current shows $V^2$ dependence for the applied bias voltage. The transport through $K_4NiTSPc$ layer in the second and third regions with slope $\geq 2$, is like space-charge-limited-current (SCLC). The second region having a slope equal to 4.8 indicates space-charge-limited-current (SCLS) with exponential distribution of deep traps in the band gap of organic semiconductor ($K_4NiTSPc$) [23]. The third region has a slope of 2 which can be same to SCLC with all traps being filled. The presence of traps might be due to impurities and various defects in the chemical structure of organic thin film. By using the equation for traps filled region mentioned in [11], the values of free carrier mobility $\mu$ and conductivity for $Au/K_4NiTSPc/Ag$ junction diodes are found $1.5\times10^{-4}$ cm/(V s) and $2.5\times10^{-4}\,\Omega^{-1}\,cm^{-1}$, respectively.

## 4. Conclusion

In conclusion, the comparison of the electronic parameters of $Au/K_4NiTSPc/Ag$ Schottky diode and Au/NiPc/Ag shows that the electronic properties of nickel thalocyanine (NiPc) have been remarkably improved by attaching a potassium-tetrasulpho functional group to form a water soluble derivative Nickel (II) 4, 4′, 4″, 4‴ potassium-tetrasulphophthalocyanine (K4NiTSPc). The conductivity and mobility of the device have been increased by 3–5 orders of magnitude than the NiPc based devices previously reported. The work reported here, can be helpful for the fabrication of future organic electronic devices such as sensors, transistors and solar cells using solution processable metal phthalocyanines.

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