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Synthesis of Ni(II) porphyrazine peripherally octa-substituted with the 4-*tert*-butylbenzylthio moiety and electronic properties of the Al/Ni(II)Pz/p-Si Schottky barrier diode

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ABSTRACT

Magnesium porphyrazinate substituted with eight 4-*tert*-butylphenylthio-groups on the peripheral positions has been synthesized by cyclotetramerization of 1,2-bis(4-*tert*-butylphenylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid, and further reaction of this product with nickel(II) acetate led to the metal porphyrazinate (M = Ni). These new compounds have been characterized by elemental analysis, together with FT-IR, ¹H NMR and UV–Vis spectral data. The electronic properties of a spin coated film of NiPz have been studied by fabricating metal-insulator-semiconductor (MIS) capacitors. Current-voltage (*I–V*) and capacitance-voltage (*C–V*) measurements were carried out. It was observed that the Al/NiPz/p-Si structure exhibits rectifying behavior with a barrier height value of 0.89 eV and with an ideality factor value of 1.81. It was seen that this value of the obtained barrier height is remarkably higher than those given for metal/Si semiconductor contacts in the literature. The Lien, So and Nicolet method, combined with conventional forward *I–V*, was used to extract the series resistance value and it was found to be 26 k Ω . High frequency *C–V* measurements were used to determine the mobile oxide charge in the NiPz layer and this was found to be 1.6×10^{11} cm⁻².

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1. Introduction

Porphyrazine macrocycles afford a skillful platform to build up detailed molecular superstructures and this property, coupled with a full and well-improved synthetic chemistry, has surpassed the synthesis of different catalytically essential metallo porphyrazines and original model compounds of various functions [1-3]. In contrast to the structural similarity between phthalocyanines and porphyrazines, the latter have been relatively less studied compared to the phthalocyanines [4–6]. The diffuse nature of porphyrazines π electronic structure would help us understand there are longrange interactions between different parts of the molecule. The presence of soft S donor atoms play an important role in affecting the solid-state interactions, and an extensive series of derivatives with physical and chemical properties comparable to those of phthalocyanines have been reported [7-9]. Derivatization of porphyrazines has generally been accomplished by the addition of various substituents to the peripheral positions. These substituents enhance the solubility of the products (e.g., tert-butyl) and provide additional functionalities for interaction with alkali or transition metal ions, mesophase formation, etc. [10–12]. Nickel porphyrazine (NiPz), compared with other metal-centered tetrapyrroles, e.g., metal phthalocyanines (Pc), offers new ways to induce, modify and to control molecular properties and has a high metal/ligand stability [4,13,14].

Schottky barrier diodes (SBDs) play a crucial role in modern semiconductor technology as the basis of a large number of electronic devices such as field-effect transistors (FETs), solar cells and photodetectors [15,16]. Recently there has been extensive investigation of organic materials for their use in SB diodes to improve the fundamental SB diode parameters such as the Schottky barrier height $\Phi_{\rm B}$ and the ideality factor *n*. A SB diode with the desired electronic properties can be obtained by means of the choice of a suitable interlayer. With that regard, phthalocyanines, porphyrins and porphyrazines have been considered to be one of the most stable organic semiconductors for various electronic and optoelectronic applications. Considerable attention has been given in recent years to the fabrication and characterization of SB diodes using some phthalocyanine compounds [17]. Although porphyrazines are of interest because of their potential applications, such as molecular electronics [18], sensors [19-21], organic solar cells



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[22], photodynamic therapy [23] and organic field effect transistors [24,25], unlike some phthalocyanine compounds, the electronic and interface properties of porphyrazines have not been widely studied. Furthermore, although there are a lot of works on heterojunctions with phthalocyanines and some other organic compounds, as yet there are no reports on porphyrazine plus a p-Si type junction.

The purpose of the present work is to synthesize nickel(II) inserted peripherally *tert*-butylbenzylthio substituted porphyrazine (NiPz) and to investigate the electronic properties of the Al/NiPz/p-Si SB diode by the insertion of the NiPz organic layer between the Si semiconductor and Al metal.

2. Experimental

2.1. Reagents, instruments and measurements

[Octakis(4-*tert*-butylbenzylthio)porphyrazinato]Mg(II) (1) (MgP z) and [2,3,7,8,12,13,17,18-octakis(4-*tert*-butylbenzylthio)²¹H,²³H porphyrazine] (2) (H₂Pz) were prepared according to the previously reported procedures and characterized by comparing their spectral data to those reported earlier [26]. The Mg(II) complex and the metal free porphyrazine (H₂Pz) were stable at room temperature, non-hygroscopic, insoluble in water, but soluble many common organic solvents. *Reagents:* Chemicals employed were of the highest grade available. Unless specified otherwise, reagent grade reactants and solvents were used as received from the chemical suppliers.

The FT-IR spectra were recorded in the 4000–400 cm⁻¹ range on a Perkin Elmer Spectrum One spectrometer using KBr pellets. The electronic spectra and absorbance measurements were recorded on an Agile 8453 UV–Vis spectroscopy system. Proton NMR spectra were recorded on Brucker 250 MHz and 500 MHz Varian Inova spectrometers. Elemental analyses were recorded on Thermo Flashea 1112 series equipment.

2.2. Synthesis of {2,3,7,8,12,13,17,18-octakis[4-tert-butylbenzylthio] porphyrazinato}Ni(II) (**3**)

To a solution of anhydrous Ni(CH₃COO)₂ (173 mg, 0.094 mmol) in 10 ml of absolute ethanol was added a solution of **2** (80 mg, 0.046 mmol) in 10 ml of THF, and the resulting mixture was refluxed under Ar for about 18 h. The precipitate that formed, composed of the crude product and the excess metal salt, was filtered then washed with hot THF. After evaporation of the solvent, the remaining product was treated with hot water to remove the unreacted metal salt, washed with methanol and dried. The pure dark blue porphyrazine was obtained. The product was very soluble in chloroform, THF and dichloromethane.

Yield: 71 mg (84%). FT-IR (KBr) v_{max} (cm⁻¹): 3028 (H–Ar), 2956 C–(CH₃)₃, 1636, 1513, 1461, 1263, 1191, 1105, 1018, 834. ¹H NMR (CDCl₃) (δ , ppm): 7.34–7.27 (d, m, 4H, Ar–H), 4.59 (m, s, 2H, CH₂–S), 1.33 (s, 9H, (CH₃)–C). *Anal.* Calc. for C₁₀₄H₁₂₀NiN₈S₈: C, 69.50; H, 6.73; N, 6.23; Ni, 3.27; S, 14.27. Found: C, 68.35; H, 6.57; N, 5.84; S, 12.73%.

2.3. MIS diode fabrication

For the MIS diode fabrication, p-type single crystal silicon (100) with resistivity in the $8-10 \Omega$ cm range was used. Prior to the deposition, the silicon substrates were cleaned by ultrasonic treatment in acetone, propanol and water for 10 min each, and subsequently etched in diluted HF solution, to remove the native SiO₂ layer. An Ohmic back contact was established by the thermal evaporation of 200 nm high purity (99.999%) Al followed by annealing

at 400 °C for 20 min in ambient nitrogen. The film of the Pz compound was prepared by the spin coating method. The elipsometric technique was used to measure the thickness of the NiPz film and it was found to be 110 nm. After the film deposition process, the substrate was immediately placed in a vacuum system for the processes. Al metal contacts were formed on a NiPz layer by vacuum thermal evaporation of Al at pressure of approximately 3.0×10^{-6} mbar using an Edwards Auto 500 thermal evaporator system. The current–voltage (*I–V*) measurements were performed using a KEITHLEY 6517A electrometer and data of current–voltage measurements were recorded on a PC using a GPIB data transfer card. The capacitance–voltage (*C–V*) measurements on the prepared Schottky diodes were also carried out using an Agilent 4284A LCR meter. All the measurements were performed under 10^{-3} mbar.

3. Results and discussions

3.1. Synthesis and characterization

The starting point of this new nickel(II) porphyrazine structure with eight (4-*tert*-butylbenzylthio) groups bound to the periphery is 1,2-bis-(4-*tert*-butylbenzylthio) maleonitrile (TBBTMnt), which was synthesized as a solid product in relatively high yield according a previous report (Scheme 1) [26]. The presence of electron donating S-groups is expected to shift the absorption range of the porphyrazine Q-band to higher wavelength and the *tert*-butyl groups are expected to enhance the solubility [4,13,14,27].

The cyclotetramerization process of the dinitrile derivative (TBBTMnt) by the template effect of magnesium butanolate in butanol resulted in the blue-green octakis(4-*tert*-butyl-benzyl-thio)porphyrazinato magnesium **1** in very good yield (Fig. 1). The metal-free derivative **2** was obtained in a reasonable yield of 30–40% by treatment of **1** with trifluoroacetic acid at room temperature for 8 h. The change of color from dark blue-green to purplish blue and the lowering of the solubility are apparent differences between the magnesium and metal-free products. Insertion of metal ions into **2** with nickel(II) acetate was performed in THF and ethanol at reflux temperature for 18 h and afforded derivative **3** in approximately quantitative yield (84%). The elemental analysis results closely follow the values calculated for **3**.

Spectroscopic investigations on the newly synthesized intermediates and porphyrazine are in accordance with the proposed structures. In the FT-IR spectrum of TBBTMnt, the stretching vibration of C \equiv N is observed at 2213 cm⁻¹, the *tert*-butyl peak around 2978 cm⁻¹, the S–CH₂ peak around 680 cm⁻¹ and the aromatic C– H peaks around 3028 cm⁻¹. These values comply with those reported in the literature for similar compounds and with the previous report for TBBTMnt [26,28]. The sharp C=N vibration around 2213 cm^{-1} disappeared after the formation of porphyrazine **1**. The N-H stretching vibration of the inner core of the metal-free porphyrazine **2** was observed around 3289 cm⁻¹ after demetallation of 1 [25,29,30]. The FT-IR spectrum of the NiPz (3) derivative showed a stretching vibration of the tert-butyl peak around $2863-2956 \text{ cm}^{-1}$ and aromatic C-H peaks around 3028 cm^{-1} , which are very similar with the literature (M = Cu, Co, Zn) as expected [4.26].

In the ¹H NMR spectra of **1**, **2** and **3**, chemical shifts corresponding to the *tert*-butyl protons came out at the expected values: a singlet at 1.3 ppm in the ligand TBBTMnt, 1.14 ppm in **1**, 1.17 ppm in **2** and 1.33 ppm in **3** [5,26,29,31,32].

To identify the structure of the porphyrazines (1–3), electronic spectra are especially useful. The electronic absorption spectra of the metallo-porphyrazines (1 and 3) exhibit a strong absorption between 648 and 674 nm which is due to a $\pi \rightarrow \pi^*$ transition and



Scheme 1. (i) Mg turnings, I₂, n-BuOH; (ii) CF₃CO₂H; (iii) EtOH-THF and Ni(OAc)₂.



Table 1UV-Vis data for the porphyrazines in dichloromethane.

Compound	Band λ , nm (log ε , dm ³ mol ⁻¹ cm ⁻¹)		
	В	Q	
1	380 (4.42)	678 (4.38)	
2	352 (3.97)	653 (3.75)	714 (3.88)
3	327 (3.84)	656 (4.13)	

obtained, it was observed that the compound did not show any

appreciable aggregation in the concentration range 10^{-3} – 10^{-6} M.

Fig. 1. Schematic representation of the porphyrazines.

is commonly referred to as the Q-band, by which the first intense bands of the porphyrazine core are dominated. A second intense and broad $\pi \rightarrow \pi^*$ transition in the near UV region in the range 327–380 nm, called the soret or B-band, is also a characteristic of these tetrapyrole derivatives [4,5,26]. The UV–Vis spectra of the porphyrazines (**1**, **2** and **3** as 4×10^{-5} M solutions in dichloromethane) prepared in the present work exhibited an intense single Qband absorption for the $\pi \rightarrow \pi^*$ transition around 648–674 nm and B-bands in the UV region around 326–346 nm (Fig. 2). The change of symmetry of the porphyrazine core from D_{4h} in the case of the metallo-species to D_{2h} in the metal-free derivative **2** is apparent, showing a split Q-band at 647 and 714 nm, as expected, for **2** (Table 1) [26,28–30]. The UV–Vis spectra were measured at different levels of concentration to assess whether or not compound **3** reveals any aggregation properties. In light of the results

$\begin{array}{c} 1.2 \\ 0.9 \\ 0.6 \\ 0.3 \\ 0.0 \\ 300 \\ 400 \\ 500 \\ 500 \\ 600 \\ 700 \\ 800 \end{array}$

Fig. 2. Electronic spectra of octakis(4-*tert*-butylbenzylthio) substituted porphyrazines **1**, **2**, and **3** as 4×10^{-5} M solutions in CH₂Cl₂.



3.2. Electronic properties of Al/NiPz/p-Si

Current–voltage (*I–V*) and capacitance–voltage (*C–V*) measurements are two fundamental characterization technique for SB diodes. The forward bias *I–V* characteristic of the Al/Pz/p-Si structure at room temperature is given in Fig. 3. Although the reverse bias current exhibits a weak voltage dependence, the forward current of the diode increases exponentially with the applied voltage, which is the characteristic behavior of rectifying contacts. This plot also indicates that there is a deviation from linearity in the forward bias In *I* versus *V* graph for sufficiently large applied voltages. The observed *I–V* characteristics indicate that the Al/Pz/p-Si structure exhibits a rectifying behavior with a rectification ratio, which is the ratio of the forward current to the reverse current at a certain applied voltage, of 3.1×10^4 at ±1 V. In this case, it is reasonable to represent the dependence of the current *I* on the applied voltage *V*,



Fig. 3. The current-voltage characteristic of the Al/Pz/p-Si Schottky barrier diode.

according to thermionic emission of the SB diode model with a series resistance, by the well-known expression [33]:

$$I = I_0 \left(\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1 \right)$$
(1)

where

$$I_0 = AA^*T^2 \exp\left(-\frac{q\Phi_{\rm B}}{kT}\right) \tag{2}$$

and I_0 is the saturation current, R_s is the series resistance of the diode, V is the applied voltage, q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature in K, A is the area of diode, A^* is the effective Richardson constant for p-type Si ($A^* = 32 \text{ cm}^{-2} \text{ K}^{-2}$) [34], n is the ideality factor and Φ_B is the effective Schottky barrier height at zero bias. Solving Eq. (2) for Φ_B yields,

$$\Phi_{\rm B} = \frac{kT}{q} \ln \left(\frac{AA^*T^2}{l_0} \right) \tag{3}$$

In most cases, it is not easy to decide which type of carrier transport mechanisms is responsible for the observed conduction mechanism. However, the value of the ideality factor n can help in determining the possible conduction mechanism. For an ideal Schottky barrier diode n = 1, but in a real SB diode, the ideality factor has a value greater than unity for several reasons, such as image force lowering of the Schottky barrier at the interface, the presence of an interfacial thin native oxide layer and series resistance [33,35]. The ideality factor n is given by

$$n = \frac{q}{kT} \frac{dV}{d(\ln I)} \tag{4}$$

With the aid of Eqs. (3) and (4), the barrier height and ideality factor n of the diode were calculated from the intercept and slope of the linear region of the forward bias $\ln I-V$ characteristic, and they were found to be 1.81 and 0.89 eV, respectively.

To obtain the significance of this value of $\Phi_{\rm B}$, we compared our findings with conventional MS contacts such as Al/p-Si and Au/n-Si diodes. The current-voltage characteristics of p-Si/C junctions fabricated by pulsed laser deposition at different temperatures were investigated by Gupta et al. [36]. The values of various junction parameters, such as ideality factor, barrier height and series resistance, were determined from the forward bias I-V characteristics. The values of the barrier height were found to be 0.37 and 0.41 eV for junctions fabricated at room temperature and 200 °C, respectively. More recently, the current-voltage characteristics of Au/n-Si Schottky barrier diodes over the wide temperature range 70-310 K were investigated by Sharma [37]. Sharma observed a decreasing trend in barrier height (from 0.79 eV at 310 K to 0.27 V at 70 K) with the decrease in operating temperature. The $\Phi_{\rm B}$ value of 0.89 eV that we have obtained for the Al/NiPz/p-Si device is remarkably higher than that achieved with conventional MS contacts such as Al/p-Si and Au/n-Si diodes. The obtained results reveal that the Pz organic film controls the carrier transport of the diode at the contact interface and the conventional Al/p-Si diode can be designed to exhibit the desired properties by means of the choice of the organic molecule.

The obtained high value of the ideality factor and the deviation from the linearity in the forward bias current–voltage plot at sufficiently large voltages suggest the presence of an organic interlayer and series resistance. Several methods have been proposed to obtain series resistance in a Schottky barrier diode. The Lien, So and Nicolet method [38] was employed for an accurate evaluation of the series resistance (R_s) from the standard ln *I–V* plot. This method is based on an auxiliary function defined by

$$F(V,I) = \frac{V}{\alpha} - \frac{kT}{q} \ln\left(\frac{I}{AA^*T^2}\right)$$
(5)

where α is an arbitrary parameter greater than the ideality factor *n*. According to this method, plots of F(V, I) versus current show a minimum for $I_{\alpha} = \frac{kT}{qR_s}(\alpha - n)$. The plot of I_{α} versus α is a straight line whose slope leads to the value of the series resistance R_s . The plot of F(V, I) versus I for various values of α ranging from 2 to 3.2 is shown in Fig. 4.

Once the minimum point and corresponding value of the current (I_{α}) on each F(V, I) versus I plot was determined, we then plotted the I_{α} versus α graph using the obtained I_{α} value. Fig. 5 shows the $I_{\alpha}-\alpha$ plot of the Al/Pz/p-Si SB diode. From the slope of the $I_{\alpha}-\alpha$ plot, the value of the series resistance has been determined as 26 k Ω . The high series resistance behavior may be ascribed to the decrease in the increasing rate in current due to space charge injection into the Pz organic thin film. The observed high value of the series resistance indicates that the series resistance is a current-limiting factor for the studied SB diode.

Many types of oxide charges, such as fixed oxide charge, oxide trapped charge, mobile oxide charge and interface trapped charge, can influence the capacitance–voltage (C–V) characteristics of the SB diode. Therefore, the determination of the oxide charges, especially mobile oxide charges (Q_m), is important for information about the quality of the MIS type SB diodes. Here, high frequency C–V measurements were used to determine the mobile oxide charges. Fig. 6 shows the forward and reverse bias C–V characteristic of the Al/NiPz/p-Si structure measured at signal frequency of 2 MHz at room temperature. As can be seen from the C–V curve in Fig. 6, the capacitance towards high negative voltage increases and reaches the capacitance of the NiPz layer alone. The number of mobile oxide charges was determined by using the following relation,

$$Q_{\rm m} = \frac{C_{\rm OX} \Delta V_{\rm FB}}{qA} \tag{6}$$

where C_{OX} is the oxide capacitance, ΔV_{FB} is the flat band voltage shifts, q is the electronic charge and A is the area of the capacitor. In an ideal metal–insulator–semiconductor (MIS) capacitor (with no oxide charge), flat band capacitance occurs at zero applied voltage. However, most real oxides contain charges which give rise to non-ideal *C*–*V* curves; and thus the flat band voltage is shifted from zero, due to compensation for the charge in the oxide. The most commonly used method to determine the value of the flat band voltage, and which is used in this work, is the method based on



Fig. 4. Semi-logarithmic plot of F(V, I) vs. *I* for different values of α .



Fig. 5. I_{α} vs. α plot of the Al/NiPz/p-Si structure.



Fig. 6. High frequency C-V characteristic of the Al/NiPz/p-Si SB diode at room temperature.

the calculation of the flat band capacitance C_{FB}. In order to calculate the CFB value, the substrate doping density $N_{\rm D}$ has to be known. $N_{\rm D}$ was determined from the slope of the C^{-2} versus V plot [39] and was found to be 1.6×10^{14} cm⁻³. Fig. 6 depicts the C^{-2} –V plot from C-V data of the Al/NiPz/p-Si/device at 2 MHz. After calculating the $C_{\rm FB}$ value, the flat band voltage for the diode investigated was determined from the C-V characteristic of the diode under 2 MHz, and was found to be 0.45 V. By using this value of the flat band voltage in Eq. (6), the number of mobile oxide charges was calculated and was found to be 1.6×10^{11} charges/cm².

4. Conclusion

In conclusion, we have described the synthesis and spectral characterization of a new Ni(II) porphyrazine surrounded by eight tert-butylphenyl groups on the periphery. A distinctive property of these compounds is that they have good solubility in many common organic solvents. The presence of the bulky tert-butyl groups hinders aggregation at relatively higher concentrations (e.g., 10^{-3} M).

The Al/NiPz/p-Si structure has been fabricated and it is shown that this structure exhibits rectifying behavior with a rectification ratio of 3.1×10^4 at ± 1 V. The main SB diode parameters, such as the ideality factor, series resistance and barrier height, were obtained from the measured I-V data. It was observed that these values are remarkably higher than those given for metal/Si semiconductor contacts in the literature, that is, it has been shown that the NiPz interlayer produces an increase in the barrier height. The oxide charge calculations on this MIS capacitors showed that the combination of Al/NiPz/p-Si is a promising structure with low oxide charges suitable for MIS based devices.

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