Electric Properties of Organic-on-Inorganic n-Si/VOPc Heterojunction

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Abstract

In the current study vanadyl-phthalocyanine (VOPc) thin films were deposited by vacuum evaporation on n-Si substrate resulting in an organic-on-inorganic (n-Si/VOPc) heterojunctions. Ag films were deposited as electrodes. Thicknesses of the VOPc films were in the range of 100-300 nm. The dark I-V characteristics exhibited rectification behavior. The rectification ratio (RR) decreased from 4 to 0.4 as the thickness of the VOPc film decreased. The dark I-V characteristics were simulated by modified Schokley equation and space-charge limited currents (SCLC) approach. Investigations were carried out to study the effect of VOPc films thickness on reverse saturation current , diode quality factor and mobility of charge carriers.

Introduction

The low material and fabrication cost of organic semiconductors have resulted in extensive interest for their potential applications in semiconductor devices [1-4]. In order to improve device characteristics, heterojunction structures have been studied for various applications. Phthalocyanines [5, 6] are one of the well-studied organic photosensitive semiconductors [7-10]. They have high absorption coefficient in wide spectra, usually in the range of 200 nm-1000 nm, and high photo-electromagnetic sensitivity at low intensities of radiation. The deposition of phthalocyanines thin films by vacuum sublimation is easy. Their purification is simple and economical as the sublimation occurs at relatively low temperatures (400 – 600) ^{o}C.

Using copper phthalocyanine (CuPc) [9-11, 12, 13] and nickel phthalocyanine (NiPc) [5, 6, 8-10] a number of organic-inorganic semiconductors heterojunctions have been fabricated and investigated. Organic semiconductor vanadyl phthalocyanine (VOPc) has been used for fabrication of field-effect transistors [14] due to its high mobility (~1 cm^2/V s). It is also suitable for application in active matrix liquid crystal displays and organic logic circuits [15]. Ultrathin films of vanadyl phthalocyanine have been grown on hydrogen-terminated Si (111) surfaces by molecular beam epitaxy. It is found that epitaxial growth does not occur on the surface terminated with a mixture of polyhydride [16]. It means that important factors for the epitaxial growth of VOPc are homogeneity and microscopic flatness of the substrate surface. Polycrystalline VOPc films in phase II as p-type semiconductor have been fabricated on an indium-tin-oxide substrate [17]. The thickness of VOPc films was approximately 200-300 nm. Al/VOPc/ITO cells showed photovoltaic response: maximum was around 550 nm. It was found that VOPC act as p-type semiconductor and a photovoltage is generated mainly at the Al/VOPc interface. It would be reasonable to fabricate devices of VOPc films with lower thickness than reported in [17] and investigate its effect on the electrical properties. In the current study VOPc thin films were deposited by vacuum evaporation on n-Si substrates and the electric properties of the n-Si/VOPc sandwich type heterojunctions were studied.

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Experimental

VOPc was obtained from Sigma-Aldrich. Fig.1 shows the molecular structure of the vanadyl-phthalocyanine molecule [14] used as a p-type organic semiconductors. Energy gap of VOPc is equal to 2 eV [18]. Phthalocyanine gets doped unintentionally with O_2 in the film deposition process.

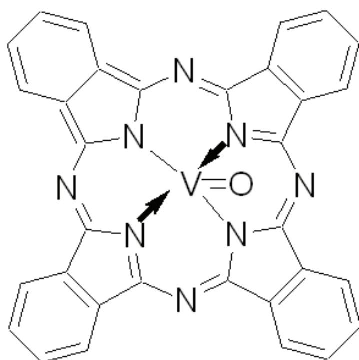

Fig. 1. Molecular structure of VOPc.

Concentration of donors (phosphorus) in n-Si was equal to $10^{16} cm^{-3}$. The Si wafers plane use was (100) which were etched by the following method: they were dipped into HF: HNO3: CH3COOH (1:6:1) solution for 10 seconds. Subsequently, the wafers were washed first with distilled water and then with ethyl alcohol. Finally plasma cleaning was done at P= $6x10^{-2}$ mbar, I= 0.4 A and for t= 10 min.

Thin films of VOPc were thermally sublimed onto the n-type silicon substrates at 400-450 ^{o}C and at ~10^{-4} Pa in an Edwards AUTO 306 vacuum coater having a diffusion pumping system. The deposition rate of VOPc films was 6 nm/min. The substrate's temperature in this process was held at ~40 ^{o}C. The thickness of the films was obtained using an Edwards FTM5 film thickness monitor. Thicknesses of the VOPc films were in the range of 100-300 nm. The thickness of Ag films were 250 nm from front and back side respectively. Annealing of the samples was done at 150 ^{o}C for 2 hrs. The investigations [6] showed that usually phthalocyanines form ohmic contacts with Ag and Schottky-type junction with Al [9, 11, 19]. Fig. 2 shows a cross-sectional view of the fabricated Ag/n-Si/VOPc/Ag sample. Effective surface area of the samples was equal to 40 mm^2 ($4x10\ mm^2$). A filament lamp was used as a source of light. The measurements of voltage, current and capacitance were conducted at room temperature by using conventional meters.

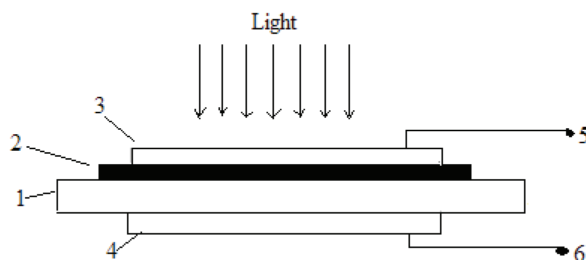

Fig. 2. Cross sectional view of Ag/n-Si/VOPc/Ag sample: 1- n-type silicon substrate, 2-VOPc film, 3 and 4 – Ag films, 5 and 6 – terminals.

Results and Discussion

Fig. 3 shows dark I-V curves of the n-Si/VOPc heterojunction sample at room temperature. The I-V curves show rectification behaviour. A positive potential was applied to VOPc with respect to n-Si. The thickness of VOPc films was equal to 300 nm.

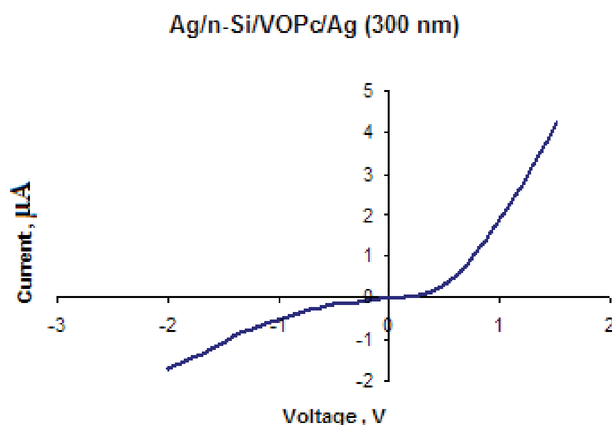

Fig. 3. Dark I-V curve of the n-Si/VOPc heterojunction at room temperature, thickness of VOPc film was equal to 300 nm.

The rectification ratio (RR) defined as a ratio of forward to reverse bias currents at fixed voltage (±1V) was equal to 4. Fig. 4 shows the dark I-V curves of the n-Si/VOPc heterojunction sample with VOPc films thickness of 100 nm.

It was found that RR of the n-Si/VOPc junctions strongly depends on the thickness of VOPc films (Fig.5). The RR of the heterojunction increases monotonously up to 4 with increase in VOPc films thickness.

The I-V characteristics of n-Si/VOPc heterojunction samples may be explained on the basis of thermoionic emission process described earlier [20,

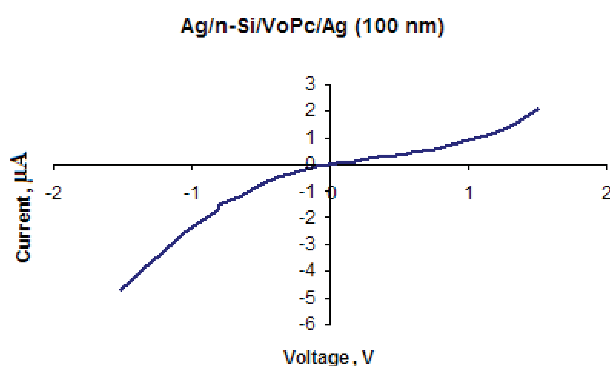

Fig. 4. Dark I-V curve of the n-Si/VOPc heterojunction at room temperature, thickness of VOPc film was equal to 100 nm.

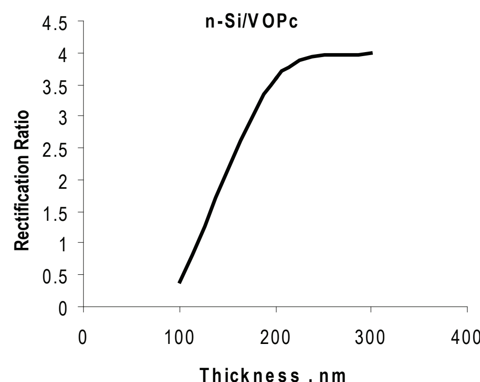

Fig. 5. Dependences of the rectification ratio on the thickness of VOPc films for the n-Si/VOPc heterojunction samples.

21]. For analysis of the dark I-V curves the modified Schockley equation may be used [21]:

$$I = I_o\left[Exp\{q(V - R_s)/nkT\} - 1\right] + (V - R_s)/R_{sh} \quad (1)$$

where R_s and R_{sh} are the device series and shunt resistances, and I and V are the terminal current and voltage, n is the diode quality factor, k is Boltzmann constant, T is absolute temperature, and Io is the reverse saturation current given in ref. [22]:

$$I_o = A \times T^2 Exp(-E_w/kT) \quad (2)$$

where A* is the Richardson constant and Ew is the effective barrier height.

Examination of *I-V* characteristics in Fig. 3 shows that the diode junction resistance, $R_j = \frac{\delta V}{\delta I}$, can easily be determined from the given plot. The R_{sh} obtained in the reverse bias from maximum junction resistance was equal to 3.5 MΩ and 1.1 MΩ, whereas Rs found at forward bias as minimum junction resistance was equal to 206 kΩ and 325 kΩ for the 300nm and 100 nm thick films respectively. The experimental ln(I)-V relationships for 300nm thick film is shown in (Fig.6). From the intersection of the curve (at V=0 V) it was found that I_o in Eq.1 is equal to 0.02 µA. Using Eq.1 the quality factors n for the curve in Fig.3 was found as 6, at 1 V.

The simulated data obtained by use of Eq.1 showed good agreement with the experimental results presented in Fig.3. The I-V characteristics of n-Si/VOPc heterojunctions with VOPc films thickness of 100 nm was studied using the same approach and reverse saturation current of 0.05 µm and a quality factor of 21 values were obtained . From the obtained data it was observed that n-Si/VOPc heterojunction with lower thickness of the VOPc film shows large deviations in R_s, R_{sh}, I_o and n values as compared with thicker sample films. Usually for thin film heterojunctions R_s is generally small [21], but in the case of n-Si/VOPc heterojunction it was the reverse. The reason of this will be discussed later in this report.

Fig.7. shows lnI-lnV characteristics of the n-Si/VOPc heterojunction at room temperature with thickness of VOPc film of 300 nm.

The forward bias current (I) is non-linear and its dependence on the voltage V is given by [23] :

$$I = c\,V^B \quad (3)$$

where c is the proportionality factor and B is the non-linearity coefficient that may be determined from the following expression [23] :

$$B = (\ln I_2 - \ln I_1) / (\ln V_2 - \ln V_1) \quad (4)$$

where I_1 and I_2 are currents measured at voltages V_1 and V_2 respectively . It was found that B depends on voltage (Fig.7) and varies from 0.8 to 2.4.

To explain the electrical behavior and the charge transport mechanism in organic semiconductors the trapping model with a space-charge-limited current (SCLC) was used [24]. Traps at locations arise mostly due to defects in structure and impurities. An exponential distribution of traps in the energy band diagram mostly is assumed [24]. For the trapping model of SCLC, Lambert theory is used [25]:

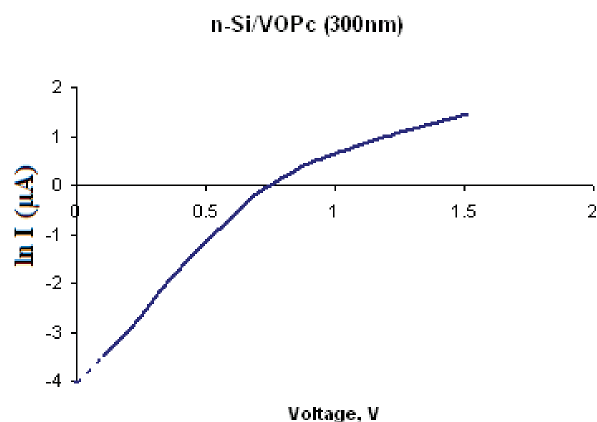

Fig. 6. The *lnI-V* curve of the n-Si/VOPc heterojunction at room temperature, thickness of VOPc film was equal to 300 nm.

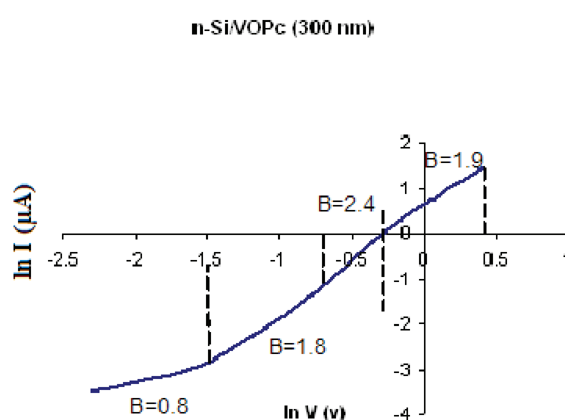

Fig. 7. The *lnI-lnV* curve of the n-Si/VOPc heterojunction at room temperature, thickness of VOPc film was equal to 300 nm.

$$J = 9\,\varepsilon\,\theta\,\mu\,V^2 / 8\,d^3 \qquad (5)$$

where J is the current density, ε , θ , μ and d are permittivity (= 4 for phthalocyanines [9,11]), trap factor , mobility and film's thickness respectively . Trap factor θ is defined as the ratio of free carrier density (p_o) to total carrier density:

$$\theta = p_o / (p_o + p_t) \qquad (6)$$

where p_t trapped carrier density, and may be calculated using:

$$\theta = J_1 / J_2 \qquad (7)$$

where J_1 and J_2 are current densities at the beginning and at the end of square law region if we take B=1.8 then we can find $\theta = 0.22$ (Figure 7). When majority of traps are filled a large increase in current takes place (Fig.7): region where B equal 2.4. With additional increase in voltage the square law (B=1.9) region is again observed in lnI-lnV characteristics. The same analysis was done for lnI-lnV relationship of the n-Si/VOPc heterojunction with 100 nm thick VOPc film. Mobility was found from Eq.5. It was observed that the ratio of mobilities for samples with VOPc thickness of 100 nm and 300 nm {μ(100)/ μ(300)} was equal to 0.5. It means the mobility of charge carriers was lower in case of thin compared to thick films.

As is known the surface structure differs from bulk of materials. Therefore between the surface and bulk a transitional structure may be considered: region at which the surface structure gets transformed into bulk structure. Usually at the interface of the semiconductor-semiconductor or metal-semiconductor the concentration of traps and recombination centers are large in comparison to the bulk of the semiconductor. Probably, due to decrease in the thickness of the VOPc film, the fraction of this transitional structure (disordered space) at the interface to the total volume of VOPc increases. As the properties of a material are closely linked to the structure, thus the observed effects on the VOPc films thickness on the investigated parameters and characteristics of the cell may be explained as due to the interface structure of the VOPc. Moreover at lower thickness of the semiconductor film the energy gap may increase [26] and probably the work function of the electrons too.

The low rectification ratio that was observed in the case of the samples with thinnest VOPc films may be due to tunneling effect that is observed in conventional as well as in tunnel or Zener diodes [22].

Conclusions

n-Si/VOPc heterojunctions were fabricated and investigated. It was found that electrical properties of the samples strongly depend on the thickness of VOPc films. By simulation of dark I-V characteristics using modified Shockley equation and space-charge-limited currents approach a number of the heterojunctions' parameters such as quality factor, series and shunt resistances and reverse saturation currents were determined .At lowest thickness of VOPc films the cells exhibited the lowest rectifi-

cation ratio and mobility of charge carriers , and highest series resistance and quality factor. We have assumed that the structure and energy band diagrams of the heterojunctions may include transitional structures from the interface to the bulk of VOPc.

Acknowledgments

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