Photoconductive properties of organic–inorganic Ag/p-CuPc/n-GaAs/Ag cell

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Abstract: A thin film of copper phthalocyanine (CuPc), a p-type semiconductor, was deposited by thermal evaporation in vacuum on an n-type gallium arsenide (GaAs) single-crystal semiconductor substrate. Then semi-transparent Ag thin film was deposited onto the CuPc film also by thermal evaporation to fabricate the Ag/p-CuPc/n-GaAs/Ag cell. Photoconduction of the cell was measured in photoresistive and photodiode modes of operation. It was observed that with an increase in illumination, the photoresistance decreased in reverse bias while it increased in forward bias. The photocurrent was increased in reverse bias operation. In forward bias operation with an increase in illumination, the photocurrent showed a different behavior depending on the voltage applied.

Key words: organic–inorganic; thin film; photoconductive cell; copper phthalocyanine; gallium arsenide
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1. Introduction

As is well known[1−4], the low cost materials and cheaper fabrication technology of organic semiconductor devices are attracting extensive interest because of the potential applications of these devices as organic sensors, light emitting diodes and organic solar cells. The photo-electric cells based on organic–inorganic structures are very promising due to their ease of fabrication and better performance[5]. A hybrid organic–inorganic CdSe/poly (3-methyl-thiophene) junction that exhibits photovoltaic behavior was studied by Chartier *et al.*[6], and copper phthalocyanine and perylentetracarboxylic di-anhydride silicon cells were investigated by Mohammad *et al.*[7]. The hetero-structure devices, such as Au/p-MgPc/n-Si[8] and Au/ZnPc/Si[9], showed rectification properties in dark and photo-induced voltage in illumination. Inorganic semiconductors have been studied well and similarly some of the organic ones also. Therefore it may be easy to find an optimal combination of two kinds of semiconductor materials in order to improve the characteristics of the cell. In particular, it may be beneficial to fabricate photoelectric sensors for which, unlike solar cells, the power conversion efficiency does not play a vital role, but more important parameters are spectral sensitivity, linearity of input-output parameters characteristics, effect of temperature, humidity, etc.

Copper phthalocyanine (CuPc) is one of the well-studied organic photosensitive semiconductors[10, 11]. It has a high absorption coefficient in a wide spectrum (200–1000 nm) and a high photo-electromagnetic sensitivity at low intensities of radiation. The purification of CuPc by a sublimation process is technologically simple and economical because it requires a relatively low temperature (400–600 ℃). Thin films of CuPc are also deposited by vacuum sublimation. The recrystallization of CuPc is attained from organic solutions at room temperature.

The gallium arsenide (GaAs), having an energy gap of 1.4 eV, is a photosensitive inorganic semiconductor that has been widely used in electronic devices, including lasers and solar cells. Organic-on-inorganic structures of CuPc and GaAs were fabricated and the preliminary results of investigations were reported in Ref. [10]. The characteristics of organic-on-inorganic Ag/p-CuPc/n-GaAs/Ag sensors were evaluated at room temperature in the photovoltaic mode of operation. The tungsten filament lamp was used as a source of illumination in these experiments. Photo-voltage spectra illustrated that the cell is sensitive in the large spectral range of 200–1000 nm from the UV to visible and IR spectrum[10]. The study of the electric and photoelectric properties of organic cells in the integral mode of operation may provide some important information about the junction properties of the cell. Results of the investigation of temperature dependent I–V characteristics of organic–inorganic heterojunction diodes were reported earlier[12]. The frequency response of the Ag/p-CuPc/n-GaAs/Ag sensor was investigated in the temperature range of 23 to 74 ℃[12], and the voltage–current characteristics and photoelectric response were also studied in a wide temperature range of 82 to 350 K[13]. It was observed that the sensor's parameters, such as rectification ratio, threshold voltage, junction's shunt and series resistances, open-circuit voltage and short-circuit current, were temperature dependent. By using the experimental data on voltage–current characteristics and absorbance of the CuPc films, the energy-band diagram of the p-CuPc/n-GaAs heterojunction was developed. The differential responsivity of the Ag/p-CuPc/n-GaAs/Ag sensor was investigated[14] by scanning the sensor's surface with a light beam probe. It was found that in the differential mode of operation, the sensor's output voltage and current depend on the position of the light beam probe. This paper presents an investigation of photoconduction of the Ag/p-CuPc/n-GaAs/Ag cell that was measured in the photoresistive and photodiode modes of

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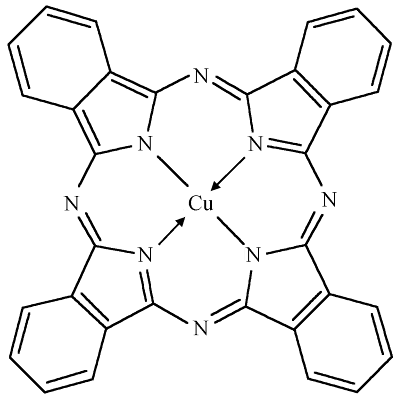

Fig. 1. Molecular structure of CuPc.

operations.

2. Experimental

For the fabrication of a cell, CuPc (a p-type organic semiconductor) and GaAs (an n-type inorganic semiconductor) with a (100) crystal orientation and donor impurities of $N_D = 2 \times 10^{18}$ cm^{-3} were used. Figure 1 shows the molecular structure of the CuPc used as a p-type organic semiconductor[15, 16]. It is known that at least seven crystalline polymorph states of CuPc exist, which are α, β, γ, R, δ, ε, etc[16]. The n-type α-CuPc is metastable at a temperature of 165 ℃ and can be converted thermally or with solution to the β-form. Both α and β forms are the most frequently encountered states of CuPc. The fabricated CuPc films were in the β-form because thermal sublimation was used for film deposition. The structure that characterizes the β-form is a monoclinic crystal P$2_1/a$ with $a = 19.407$ Å, $b = 4.79$ Å, $c = 14.628$ Å and $\beta = 120.93$ Å[16]. It has a band gap of about 1.6 eV and conductivity of 5×10^{-13} $\Omega^{-1}\cdot$cm^{-1} at a temperature of 300 K[15, 17]. The molecular weight of the CuPc molecule is 576 a.m.u. and its sublimation temperature varies from 400 to 580 ℃ at a pressure of 10^{-4} Pa[7, 11].

The GaAs substrates were etched with a solution of 1 part H_2O_2, 1 part NH_4OH and 3 parts H_2O for 30 s. Etching of the substrates was followed by washing with distilled water at 70–80 ℃ and drying in spirit's vapor. The CuPc powder was purified twice by vacuum sublimation. Thin films of CuPc with a thickness of 20–40 nm were deposited on GaAs substrates also by sublimation at a temperature of 400–450 ℃ in vacuum of $\sim 10^{-4}$ Pa. During this process, the substrate temperature was held at $\sim$40 ℃. After deposition, the CuPc was doped by atmospheric O_2 for approximately 30 min.

On one side, a semitransparent Ag thin film having 6%–10 % transmittance of incident light was deposited on the CuPc film by vacuum evaporation while on the other side, i.e., on the GaAs substrate, another Ag thin film was deposited to form an ohmic electrode. A detailed experimental procedure was described in Ref. [13]. Earlier investigations showed that the Ag forms ohmic contacts with CuPc and GaAs[10]. Figure 2 shows cross-sectional and top views of the fabricated cell.

The active diameter of the cell, i.e. diameter of the CuPc film, was about 3 cm. To stabilize the parameters, the fabricated Ag/p-CuPc/n-GaAs/Ag cell was carried through an aging process. About 10–15 aging cycles (heating up to 100 ℃ and then cooling to 25 ℃) were carried out during 80–120 h under filament lamp illumination with light intensity of 50 mW/cm^2. In this process, the cells were short-circuited to make the aging as close to the extreme conditions as possible for their practical utilization.

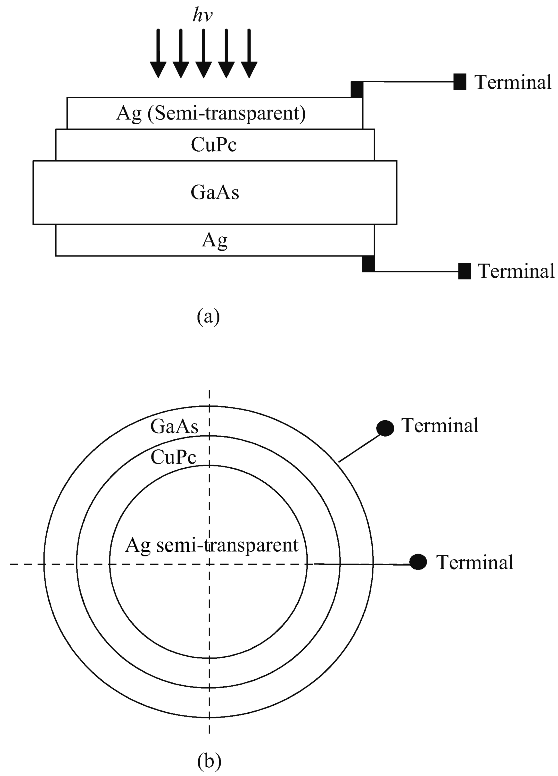

Fig. 2. Cross sectional view of organic–inorganic heterojunction sensor fabricated by using n-GaAs substrate and a thin p-CuPc film. (a) Side view. (b) Top view.

The resistance, current and voltage were measured by FLUKE 87 multimeters. The open-circuit voltage of multimeter was equal to 2.77 V, whereas at the measurement of the resistance of the cell in reverse and forward biases the output voltage was equal to –0.44 V and 0.18 V, respectively. The filament lamp was used as a light source. The measurements were conducted at room temperature. The experimental setup was verified by a commercially available photo-diode.

3. Results and discussion

Figure 3 shows the dependence of reverse (R_R) and forward (R_F) bias resistances of the Ag/p-CuPc/n-GaAs/Ag cell on illumination. It can be seen that R_R decreases 3.24 times and R_F increases 1.07 times with an increase in illumination (G) from "0" (dark condition) to 525 fc. The resistance–illumination relationships are linear and the rate of change of resistance with illumination ($\Delta R_R/G = 0.058$ kΩ/fc) in the reverse bias is very large.

Figures 4(a) and 4(b) show current–voltage characteristics of the Ag/p-CuPc/n-GaAs/Ag cell at different values of illumination and applied voltage. Figure 4(a) is typical of photodiodes that show that the reverse bias current increases with the illumination due to the generation of electron–hole pairs

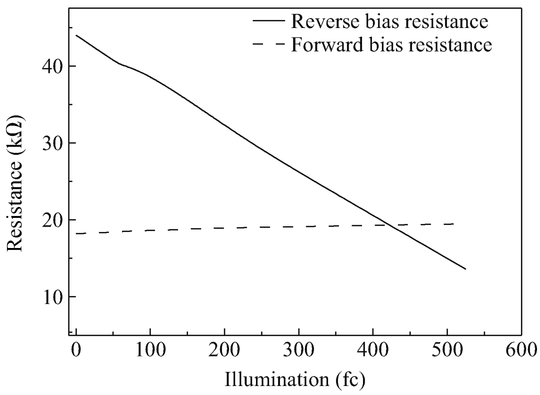

Fig. 3. Dependence of reverse (R_R) and forward (R_F) bias resistances of the Ag/p-CuPc/n-GaAs/Ag cell on illumination.

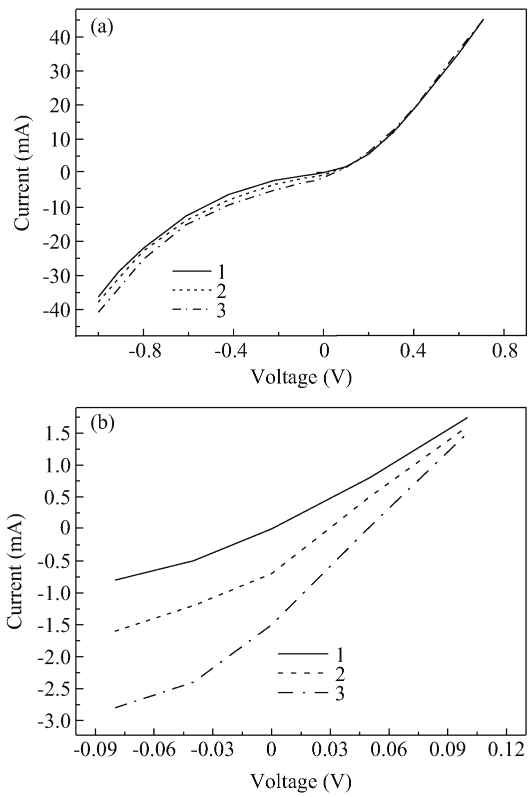

Fig. 4. Current–voltage characteristics of the Ag/p-CuPc/n-GaAs/Ag cell at different illuminations (1: dark, 2: 90 fc, 3: 595 fc) and at different values of applied voltages (a, b).

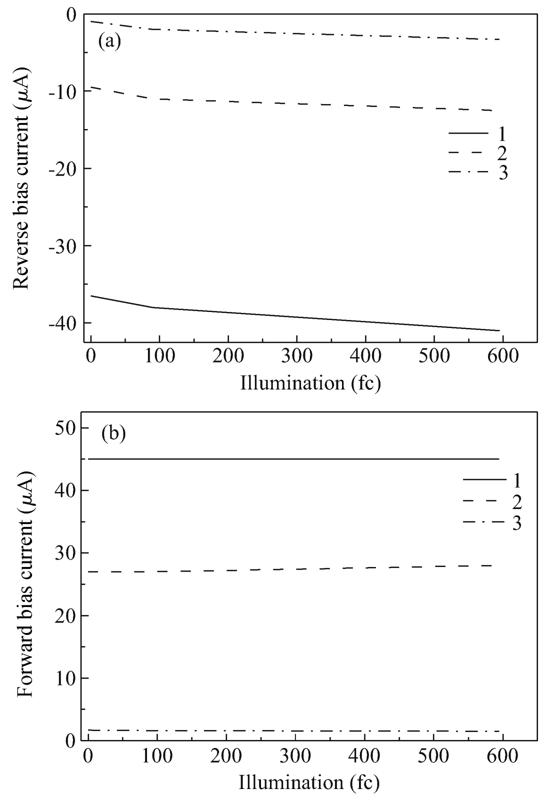

Fig. 5. Current–illumination relationships of the Ag/p-CuPc/n-GaAs/Ag cell at different applied voltages. In Fig. 5(a), 1, 2 and 3 represent –0.1, –0.5 and –1 V, respectively, and 1, 2 and 3 in Fig. 5(b) represent 0.7, 0.5 and 0.1 V, respectively.

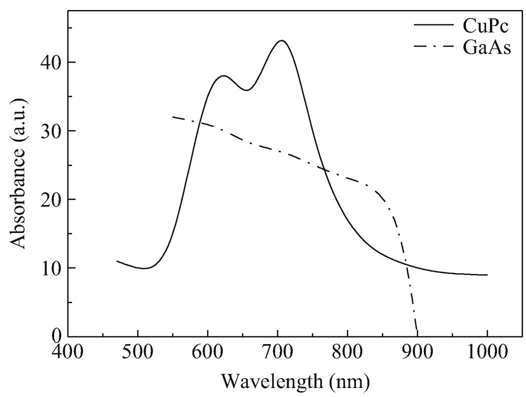

Fig. 6. Absorbance–wavelength relationships for CuPc and GaAs (in arbitrary units).

under the effect of light[18, 19] and the resistance of the cell decreases accordingly. Figure 4(b) shows that starting from the forward bias voltage of 0.035 V applied to the cell, the dark current value is above the value of the current under illumination that is responsible for the increase in resistance (Fig. 3) under illumination at forward bias voltage.

Figure 5 shows the current–illumination relationships of the Ag/p-CuPc/n-GaAs/Ag cell at different applied voltages. In Fig. 5(a), 1, 2 and 3 represent –0.1, –0.5 and –1 V, respectively, while in Fig. 5(b), 1, 2 and 3 correspond to 0.7, 0.5 and 0.1 V, respectively. It can be seen that the reverse bias current increases with illumination at any applied voltage. The forward bias current is constant, and the increase and decrease in current with illumination depends on the value of applied voltage. At the same time, both the reverse and forward bias currents increase with applied voltage. The properties of the Ag/p-CuPc/n-GaAs/Ag cell in principle follow the properties of the conventional photo-diodes[18, 20].

Figure 6 shows the absorbance-wavelength relationships for CuPc[13] and GaAs[19]. It can be seen that in the visible spectrum, both materials show good absorbance. At the same time in the IR spectrum, absorbance of CuPc is greater and covers a wider range of wavelength, whereas in the UV spectrum, the absorbance of the GaAs seems better. So the absorbance spectrum of the CuPc and GaAs are complementary, which makes the Ag/p-CuPc/n-GaAs/Ag cell sensitive in the UV, visible and IR spectra. The Ag/p-CuPc/n-GaAs/Ag cell can potentially be used in light meters, telemetry systems for data transmission and as a teaching aid in organic solid state electronics[21, 22].

4. Conclusion

The Ag/p-CuPc/n-GaAs/Ag cell was fabricated and its photoconduction properties in the photoresistive and photodiode modes of operation were investigated. It was observed that the photoresistance was decreased in reverse bias and increased in forward bias with an increase in illumination. The photocurrent increased in reverse bias and showed different behavior (it was constant, increased or decreased) in forward bias, depending on the applied voltage.

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