Comparison of organic-inorganic p-i-n and p-n heterostructures as potential solar cell designs for use in difficult weather conditions

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Abstract. This paper investigates the possibility of increasing the spectral sensitivity of an organic-inorganic p-i-n-heterostructure solar cell as compared to a p-n-structure solar cell. Both p-i-n and p-n structures are fabricated from gallium arsenide (GaAs) and copper phthalocyanine (CuPc) using the same technology. In fabricating the p-n-structure, CuPc is deposited in a thinner layer and is fully doped with oxygen; in fabricating the p-i-n-structure, CuPc is deposited in a thicker layer and only its upper part is doped. The main properties of both heterostructures are investigated. The shift in spectral absorption maximum towards the shorter wavelength portion of the spectrum is found to increase the spectral sensitivity and efficiency of the p-i-n-heterostructure n-GaAs/(i-CuPc)/p-CuPc compared to the p-n-heterostructure n-GaAs/p-CuPc. The discussed technology can be used to optimize the solar cell performance under the low temperature and cloud cover conditions.

1. Introduction
Solar energy is at present the most important green energy source in the world. However, the climatic conditions of central and northern Russia prevent its widespread implementation as solar cells lose their efficiency in cold and cloudy weather. Cloud cover reduces the intensity of the solar radiation that reaches the Earth’s surface and also changes the radiation's spectral properties.

During practically any type of cloud cover, light in the violet part of the spectrum is transmitted the most while light in the near-infrared part of the spectrum is transmitted the least. For instance, with stratocumulus clouds present, violet light is transmitted two-to-three times more than visible light of longer wavelengths or near infrared light. In cirrus clouds conditions, the total solar radiation is down 20-30%. Interestingly, the amount of violet and blue light that reaches the surface is even higher under cirrus clouds than in clear sky conditions – possibly due to multiple light refractions from snow – while there is 80% less near-infrared light transmitted compared to clear sky conditions [1].

This a problem because the most efficient solar cells available have their absorption maxima in the longer wavelength part of the visible spectrum and in the near-infrared region, whereas currently available multi-junction solar cells, which do absorb light in wider ranges of wavelengths, are not efficient under solar radiation of low intensity [2-3]. There hence is a need for a solar cell that can work under low intensity light conditions and is efficient when exposed to wavelengths of light in the violet to blue range [4-5].

At present, p-n-heterostructures with organic and inorganic semiconductors are widely used around the world. These heterostructures have relatively low light absorption efficiency in the 400-500
nanometer wavelength range due to the spectral properties of their comprising materials. The overall
efficiency of these heterostructures in cold and cloudy climates is thus limited, which makes finding a
way to improve the heterostructure’s sensitivity to the shorter wavelength region of the spectrum
important for central and northern Russia and locations with similar climates. The additional challenge
is that the improvement in sensitivity must come without significant cost increases, overly complex
manufacturing process, or a cell’s lifespan reduction [6-7].

One possible solution to this challenge are p-i-n-heterostructures with organic and inorganic
semiconductors. The introduction of the i-region into the structure allows for an absorption shift
towards the shorter wavelength region of the spectrum, which significantly increases the
heterostructure’s sensitivity to solar radiation wavelengths in the violet and blue region of the visible
spectrum.

Previously, mostly inorganic semiconductors were used to create p-i-n-structures [8-9]. Although
photodetectors made from inorganic semiconductors have higher energy conversion efficiency, they
do not have a wide absorption spectrum. In terms of a cell’s manufacturing process, making thin (less
than 10 nm) films from inorganic semiconductors presents an additional difficulty.

Organic-inorganic p-i-n-heterostructures present an opportunity for new research and development
in the field of optoelectronic materials and devices due to their utilization of the optical properties of
organic molecules on the one hand and high mobility and durability of inorganic materials on the other
hand.

In this work, we fabricate and compare organic/inorganic p-n junction heterostructure with
organic/inorganic p-i-n junction heterostructure. Both heterostructures are made from the same
materials and using the same technology for better comparison and ultimately in order to create a solar
cell with desirable properties [10].

2. Materials and methods
For the fabrication of the solar cell, gallium arsenide (GaAs) was chosen as our inorganic
 semiconductor and copper phthalocyanine (CuPc) was chosen as our organic semiconductor. Our
choice of copper phthalocyanine for our organic-on-inorganic p-i-n heterostructure can be explained
by its optical, electric and photoelectric properties, thermal and chemical stability, and its ability to
sublimate in vacuum yielding thin films. The gallium arsenide has high electron mobility and
durability; furthermore, its sensitivity range allows for an improved spectral sensitivity of the resulting
p-i-n-heterostructure, which in turn improves electrical and photoelectrical characteristics of the solar
cell and improves its efficiency.

P-i-n-heterostructure p-CuPc/i-CuPc/n-GaAs was produced through vacuum evaporation using the
following process [10]:

Prior to the deposition of the bottom electrode, the n-GaAs layer was etched for 30 seconds in
H2O2: NH4OH: H2O solution (1:1:3) and subsequently washed with distilled water preheated to 70-
80°C and then dried in alcohol vapors. Ohmic electrode layer – made of silver – was deposited on the
prepared n-GaAs substrate layer in vacuum (of about 10⁻³ Pa) keeping the substrate temperature at
473°C. A film of CuPc (thickness: d=d1+d2= 46.5nm; i-layer thickness: d2=20-25nm) was deposited on the
other side of the n-GaAs substrate layer by vacuum sublimation keeping the substrate temperature
constant at 313°C. The evaporation of the organic semiconductor layer occurred at the speed of 0.1-
0.2 nm/s. After deposition, the CuPc layer was doped by purified medical O2 for approximately 18.5
min to form a p-region. The concentration of the doping impurities was adjusted throughout the
doping process according to the known oxygen diffusion coefficient at the temperature of 313°C and
the partial pressure of 0.1 Pa. The resulting film thickness was determined using the Beer–Lambert
law. An Ag film was deposited on the top electrode by thermal evaporation (transmittance coefficient
of silver t = 10-15%; resistance R = 10 Ohm/cm²). The structure of the resulting p-i-n-heterostructure
is shown on the figure 1.
Figure 1. Structure of the p-i-n-heterostructure p-CuPc/i-CuPc/n-GaAs (on the left) and p-n-heterostructure p-CuPc/n-GaAs (on the right): silver bottom electrode; monocrystalline n-GaAs substrate layer doped with donor impurities (d_n); conducting region (i-CuPc) (d_i); p-CuPc layer doped by oxygen (d_p); top semitransparent Ag electrode.

We similarly fabricated a p-n-heterostructure p-CuPc/n-GaAs (figure 1, right) by vacuum evaporation method as described above except for the CuPc layer, deposited by vacuum sublimation, which was 20-25 nm thick and fully doped by oxygen. The conductivity of CuPc ranged from $10^{-14}$ to $10^{-7}$ Ohm/m.

The spectral properties’ measurements of the p-i-n-heterostructure and p-n-heterostructure were conducted using the single-beam spectrophotometer СФ-26. The changes in photoelectrical properties of both structures were measured according to the standard procedures using voltmeters В7-26 and В7-27, a micro ammeter М-Ф192, and a voltage supply П4108.

3. Results and Discussion

As can be seen on figure 2, upon illumination of the p-i-n-heterostructure on the side of the p-region, the illumination reaches the i-region with minor losses, where it is absorbed simultaneously generating charge carriers. Having undergone multiple vacuum sublimations, CuPc is a rather pure semiconductor (purification up to $10^{-4}$%). We can hence rule out ionization of the impurities and conclude that the ionization observed is due to the protostructure’s proper photoeffect.

Figure 2. Energy band diagram of the p-i-n-heterostructure n-GaAs/i-CuPc/p-CuPc (a) at thermodynamic equilibrium and (b) upon illumination on the side of the p-region.

The generation of photo charge carriers in the i-layer leads to the imbalance of concentration equilibrium, which in turn leads to holes moving towards the p-region and electrons moving towards the i-region. Since the i-layer has a strong and virtually uniform electric field ($E > 10^6$ V/m), the
charge carriers’ movement occurs due to drift. The drift length of holes is $\mu \tau E = 20$ nm when $\mu = 2.25 \times 10^{-14}$ m$^2$/V.s, which is commensurate with the absorption region dimensions (the i-region). The presence of the i-region ensures that the light is absorbed in this region and that the solar cell on the whole is efficient. The role of the p-i junction is in establishing maximal separation of the generated electrons and holes as it constitutes a potential barrier that keeps the holes in the p-region and electrons in the i-region. Such separation creates a change in the potential difference between the p-region and the i-region, which constitutes a photovoltaic effect.

In the external circuit this effect manifests in the following ways: if a small voltage (suppositionally $V = 0$) is applied, the photoelement generates its own photoelectric effect; if there are considerable external biases, the movement of the charge carriers leads to IL photocurrent generation in addition to the already present dark current $I_t$, which flows through the p-i-n heterostructure in the absence of – or in very low – incoming illumination.

The addition of the photocurrent to the dark current occurs in an algebraic manner. It is noticeable since the photoelement’s own current is small (when in reverse bias). Uninterrupted illumination and the subsequent presence of surplus photogenerated or injected charge carriers lead to a state best described by quasi Fermi levels. Excess concentration of $\delta n$ and $\delta p$ charge carriers generated by light in the i-region significantly exceeds their concentration at thermodynamic equilibrium $n_0$ and $p_0$. We are hence dealing with volume charge recombination, the speed of which can be calculated with the following formula:

$$ U = \frac{\delta n \delta p}{\delta n \tau_p + \delta p \tau_n} $$ (1)

The main properties of the fabricated p-i-n-heterostructure $\text{p-CuPc/i-CuPc/n-GaAs}$ and p-n-heterostructure $\text{p-CuPc/n-GaAs}$ can be seen in table 1.

**Table 1. Main properties of p-i-n-heterostructure n-GaAs/(i-CuPc)/p-CuPc and p-n-heterostructure n-GaAs/p-CuPc.**

| Heterostructure type | Short-circuit current density, mA/m$^2$ | No-load voltage, V | Spectral sensitivity range, nm | Spectral sensitivity maximum, nm | Efficiency, % |
|----------------------|-----------------------------------------|-------------------|-------------------------------|-------------------------------|--------------|
| p-i-n-heterostructure | 48.8                                    | 0.34              | 200 - 1000                    | 420                           | 8.1          |
| p-CuPc/i-CuPc/n-GaAs |                                         |                   |                               |                               |              |
| p-n-heterostructure  | 80.4                                    | 0.62              | 200 - 1000                    | 720                           | 4.3          |
| p-CuPc/n-GaAs        |                                         |                   |                               |                               |              |

The observed results show that the introduction of the i-layer of the 20-25 nm thickness shifts the spectral sensitivity maximum from the red (720 nm) to the violet wavelength region (420 nm) of the visible spectrum. The p-i-n-structure’s improved photon absorption in the shorter wavelength region, which contains higher energy photons compared to the longer wavelength region, increases the cell’s efficiency by 2 times in comparison to the p-n-structure. The sensitivity (based on the photoelectric effect) of our fabricated p-i-n-heterostructure is $U_{xx}/P = 1 \times 10^4$ V/Watt, the illumination intensity is $E = 2.55$ W/m$^2$, and the solar cell fill factor is $FF = 33\%$.

The spectral properties of the p-i-n heterostructure $\text{p-CuPc/i-CuPc/n-GaAs}$ and p-n heterostructure $\text{p-CuPc/n-GaAs}$ can be seen on figure 3.

Table 2 shows the sensitivity data (based on the photoelectric effect) in the relevant for this study 400-500nm wavelength range of the p-i-n-heterostructure n-GaAs/(i-CuPc)/p-CuPc and p-n-heterostructure n-GaAs/p-CuPc.
Figure 3. The spectral properties of the p-i-n heterostructure p-CuPc/i-CuPc/n-GaAs and p-n heterostructure p-CuPc/n-GaAs.

Table 2. The sensitivity (based on the photoelectric effect) of the p-i-n heterostructure n-GaAs/(i-CuPc)/p-CuPc and p-n heterostructure n-GaAs/p-CuPc in the 400-500 nm wavelength range.

| λ, nm | 400 | 410 | 420 | 430 | 440 | 450 | 460 | 470 | 480 | 490 | 500 |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| (Uxx/P) · 10^{-4}, В/Бт | 62  | 80  | 100 | 93  | 90  | 88  | 70  | 70  | 60  | 50  | 45  |
| p-CuPc/i-CuPc/n-GaAs | | | | | | | | | | | |
| (Uxx/P) · 10^{-4}, В/Бт | 7   | 9   | 10  | 11  | 12  | 12  | 13  | 15  | 17  | 18  | 19  |
| p-CuPc/n-GaAs | | | | | | | | | | | |

Our data shows the following:

- The p-i-n heterostructure's sensitivity exceeds that of p-n heterostructure by 10 times at the wavelength of 420 nm.
- On average, the sensitivity to the most significant for this study violet wavelength range (400-450 nm) of the p-i-n structure is 8.4 times higher than of the p-n structure.
- To the second most important range for this study, the blue wavelength range (450-480 nm), the sensitivity of the p-i-n structure is 5.1 times higher than of the p-n structure.
- To the light blue region of the visible spectrum (480-500 nm), the sensitivity of the p-i-n structure is 2.9 times higher than of the p-n structure.

The data suggests the possibility of using p-i-n heterostructure n-GaAs/(i-CuPc)/p-CuPc in solar cells to make them more efficient in low temperature and cloud cover conditions than currently available traditional solar cells are.

4. Conclusion

The p-i-n heterostructure n-GaAs/(i-CuPc)/p-CuPc and p-n heterostructure n-GaAs/p-CuPc were fabricated and their properties studied. The addition of the undoped CuPc layer of the 20-25 nm thickness was found to shift the spectral sensitivity maximum from 720 nm for p-n structure to 420 nm for p-i-n structure. The p-i-n structure's sensitivity in the 400 to 500 nm range was also found to be 2 to 10 times increased compared to the structure without the i-layer. Subsequently, the efficiency of the p-i-n heterostructure n-GaAs/(i-CuPc)/p-CuPc increased as well: 8.1% in comparison to 4.3% observed for the p-n heterostructure n-GaAs/p-CuPc.

P-i-n heterostructure n-GaAs/(i-CuPc)/p-CuPc is a promising solar cell design as it proves to remain efficient under the conditions of low temperature and cloud cover. This technology can be effective not only for single junction cell studied in this paper, but also as part of the upper layers of multi-junction solar cells.
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