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Phthalocyanine based Schottky photodiode as detector in the Vis – near IR range.

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The photodiode on the basis of Al/CuPh Schottky junction is considered. It was shown that on the contrary Si and Ge Schottky diodes the CuPc photodiodes manifest strong reverse current - bias voltage dependence. Given photodetectors can be used in the Vis -IR range from 0.3μm up to 1.2μm. The current responsivity of photodiode has been measured at 1.06μm wavelength to be 100μA/W. The possibility of the control of quantum efficiency by electric field will be also concerned.

Introduction.

For many applications nonorganic Schottky diodes are superior other detectors [1, 2]. They are relatively insensitive to surface contaminations and show a high stability in intense VUV radiation. Practically their current sensitivity doesn't depend on bias voltage. Here we investigate organic diode on the basis of Al/CuPc Schottky junction. Such structure manifests rectification properties and can serve as photodetector. We will discuss here some new details concerning with peculiarities of photodetector construction and underline the possibility to control the quantum efficiency of organic diodes by external electric field.

Experimental.

Cooper phthalocyanine (CuPc), from NIOPIK was used without further purification. Chemical structure of CuPc is shown in Fig. 1. We used standard glass covered with by ITO electrodes. CuPc in the form of powder was evaporated on ITO electrode at a deposition rate 1-2 nm/min at $5x10^{-5}$ Torr. The CuPc film deposited was *ca.* 400nm and thought to be an α-type polycrystalline solid [3]. The top metal electrode, *ca.* 20nm, was deposited on the CuPc film by vacuum evaporation of Al. Cooper wires were attached to both electrodes by indium solder alloy. Layout drawing of CuPc Schottky diode is shown in Fig. 2. Here the dielectric layer composed of ferroelectric

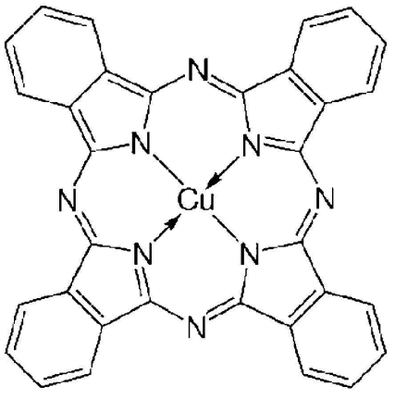

Fig. 1. Chemical structure of CuPc.

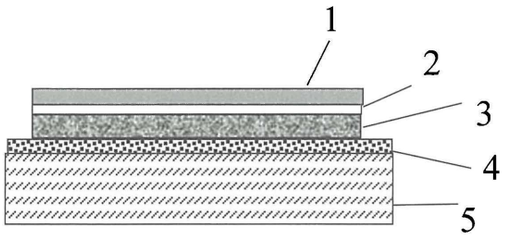

Fig. 2. Construction of Schottky photodiode. *1*.- Al electrode; *2*.-13 Lagmuir-Blodgett layers of random copolymer consisting of 70% vinilidene fluoride and 30% trifluoroethylene P(VDF-TrFE 70:30); *3*.- thin film of CuPc; *4*.– ITO electrode; *5*.– glass support.

copolymer plays special role. Then dielectric polymer layer is not present the electromigration Al into the bulk of CuPc film occurs. The screening of the Al film by thin polymer layer is sufficiently enough both to prevent migration of Al electrode and not to destroy the charge transport of the organic diode.

Current-voltage *I-V* curves were measured by using a TEC-18 power supply and electrometric amplifier U 5-11. Photocurrent was measured using both 100W tungsten lamp and YAG laser working in CW mode. The tungsten lamp was placed at a distance of one meter from the photodiode window. The light energy of one pulse of YAG was 0.25 mJ and pulse power 2.2W. As source of IR we used

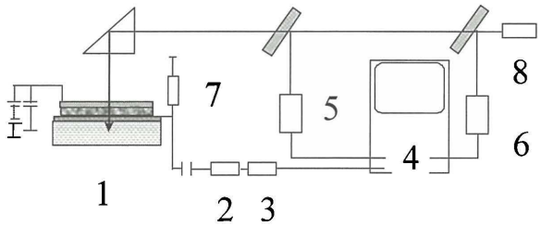

Fig. 3. Experimental set-up for the measurement of photovoltage. *1*-Schottky photodiode; *2*-amplifier; *3*-time-delay line; *4*-oscilloscope; *5*-photomultiplier to control the form of the laser pulse; *6*-photomultiplier for oscilloscope triggering; *7*-load resistor (100 kΩ), *8*-pulse YAG laser.

black body (globar) heated up to 1180°C. Photocurrent spectra were measured by ZMR-3 monochromator equipped with registration electronics. The set-up for the measurements of the characteristics of YAG laser pulse is shown in Fig. 3. Langmuir-Blodjett technique applied for preparation of polymer protective layer is described elsewhere [5]. All experiments were carried out at room temperature.

Results and discussion.

The dark current vs. electric field is shown in Fig. 4. The strong rectification of diode and monotonic increase of the reverse current vs. applied bias voltage are clearly seen there. The rectification takes place due to Schottky barrier. Barrier appears because working function of Al (4.2eV) essentially less than working function of CuPh (4.8 eV). The ommic contact occurs on the opposite boundary, ITO/CuPc. In this case the working function of Al is very close to working function of ITO(4.75eV) [6].

The linear increase of logarithm conductivity vs. $U^{1/2}$ confirms contribution from Frenkel-Poole emission as shown in Fig. 5 [8]. Fig. 6 presents reverse photocurrent under illumination of tungsten 100W lamp. The photovoltage across serial resistor (100kΩ) as function of bias is shown in Fig. 7. From data of Fig. 7 we calculated current responsivity as 100μA/W.

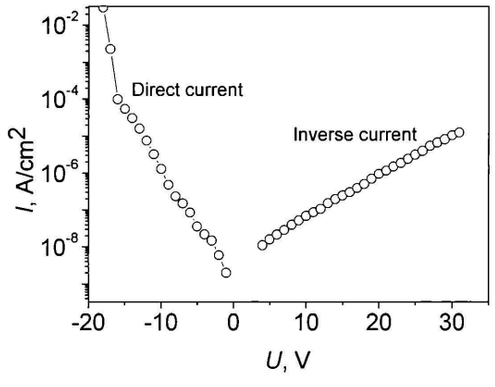

Fig. 4. Dark current density *I* vs. applied DC bias *U*.

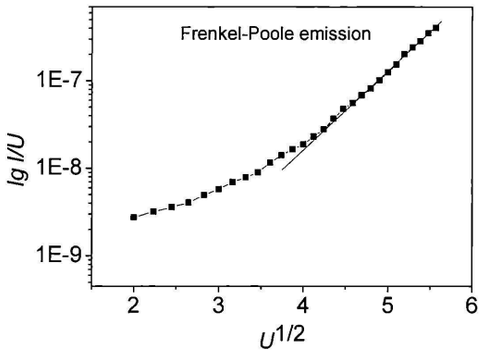

Fig.5. *lg(I/U)* vs. $U^{1/2}$, where I is dark current density in reverse direction (A/cm^2) and U – bias voltage (V).

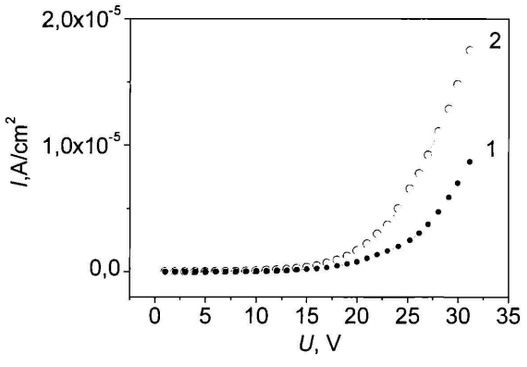

Fig. 6. Current density in reverse direction (+ in Al electrode): 1- in darkness; 2- under illumination of tungsten 100 W lamp.

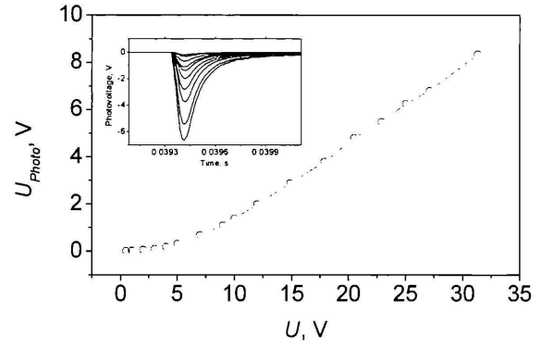

Fig. 7. Photovoltage U_{Photo} as function of the applied bias field U. **Insert.** Images of the oscilloscope pulses for different values of bias voltage. Photovoltage was exited by YAG lasers working in CW mode of duration τ=100μs and measured across serial resistor R_L=100kΩ.

In the literature increase of reverse current in Schottky diodes is explained by influence of the high electric fields on both intrinsic energy levels of semicoductor and Schottky barrier height [7].

The response of a photon detector is generally described by the quantum efficiency η*(E)* or by the current responsivity *s(E)*. The quantum efficiency of a semiconductor photodiode is the number of electron-hole pairs created by an incident photon of energy *E*, while the responsivity is the photocurrent per incident radiation power. Quantum efficiency and responsivity are related by (1)

$$s(E) = \eta\,(E)\, e/E \qquad (1),$$

where e is the elementary charge. For s(1.06μm) = 100μA/W we calculate η(1.06 μm)=1.16×10^{-4}. This result is twice as large as the record responsivity of the pyroelectric lead lanthanum titanate ($Pb_{0.9}La_{0.1}TiO_3$). To compare we demonstrate the detection of laser pulses both by Schottky diode and organic pyroelectric having large pyroelectric coefficient 5nC/cm^{2}K (Fig. 8). In this case Schottky diode operated in photogalvanic mode.

Photocurrent spectra for Schottky diode and organic pyroelectric are shown in Fig. 9. As source of IR we used black body (globar). These data

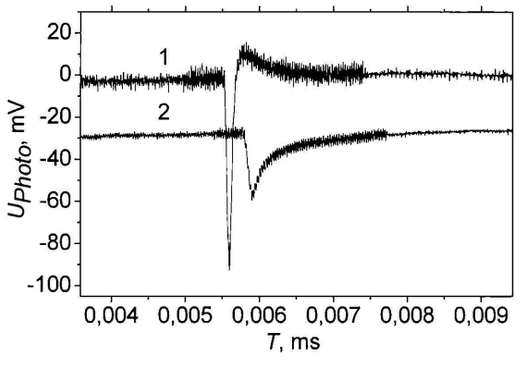

Fig. 8. Comparison of photonic and heat detectors. *1*-Pyroelectric effect in organic pyroelectric with pyroelectric coefficient γ=5nC/cm^{2}K; *2* –Photogalvanic effect in Al/CuPc Schottky diode.

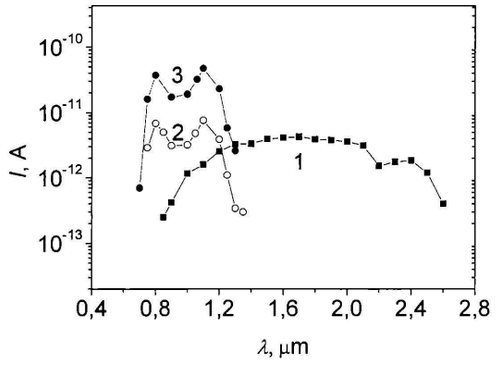

Fig. 9. Photocurrent vs. wavelength. *1* – spectrum of organic pyroelectric; *2*- spectrum of CuPc film in photovoltaic mode U=0; *3*-spectrum of CuPc under bias voltage of U=5V.

unambiguously confirm photonic character of response in CuPc.

Conclusions.

We propose new construction of organic Schottky diode by application of thin buffer layer of polymer film in between Al electrode and organic p-type semiconductor composed of CuPc. The polymer film protects anode preventing electro migration of Al into the bulk of the semiconductor. We found strong dependence of current responsivity vs. bias voltage. It means that one can control the quantum efficiency of photodiode by external electric field. In fact here we propose simple and cheap photodetector to measure energy and power of light emitting diodes and various types of lasers.

Acknowledgments.

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