UDC 621.315

Yu. F. VAKSMAN, I. A. IVANCHENKO, L. M. BUDIJANSKAJA
Odessa I. I. Mechnikov National University, Dvoryanska str., Odessa, 2, 65026

PROPERTIES AND CHARACTERISTICS OF PHOTOCELLS WITH HETEROJUNCTION STRUCTURE p-(Cu_2O)-n-(CdS) ON A THIN SUBSTRATE

Techniques to manufacture and to research the properties of film photocells (PhC) presented on the basis of p-(Cu_2O)-n-(CdS) heterojunction, produced on thin polyamide film by thermal vacuum evaporation. The obtained samples of PhC have shown the different types of voltage-current characteristic from clearly defined nonlinear up to almost linear. The maximum efficiency of PhC is equal to 2...3 %. Spectral dependence of short-circuit currents PhC which shape has shown the presence of two maximums corresponding to the contribution to photoe. m. f. as from layer of CdS near to 500—530 nm, and layer Cu_2O from 600 up to 800 nm, is investigated. The low weight of the separate PhC, equal to 20 mg, compensates insufficient magnitude of efficiency and makes it perspective for the further research and improvement of parameters.

One of the main advantages of film photocells (PhC), consisting in supply of the high output power per unit weight, is implemented only in case of their creation on thin dielectric or metal substrate. The dielectric substrate is more light, more elastic and cheaper metal. However, the dielectric substrate yields to metal one in thermal stability which is necessary to condense evaporated semiconductor substances on substrate heated to significant temperatures.

The purpose of this work is to develop a technique to manufacture and to research PhC properties with p-(Cu_2O)-n-(CdS) structure on thin (40 μm) polyamide film. These elements were created by vacuum deposition of cooper layers with consequent oxidation up to cooper monoxide and cadmium sulphide on substrate heated up to ~ 300 °C. Heterojunction, on which the photovoltaic effect takes place at illumination between semiconductor layers of p-(Cu_2O) and n-(CdS), creates. This combination represents the particular interest from the point of view to create heterojunction for room temperature and to realize the links between semiconductors with various crystal lattice.

Microscopic studies for a surface of polyamide film have shown, that it was smooth enough, but had imperfections as scratches. The size of scratches indicates, that at condensation of substances on substrate surface they are capable to become crystallization centers which generate inhomogeneous deposition of a material and worsening of films quality.

Temperature coefficients of expansion for polyamide film and the substances condensed on it do not coincide. The insignificant strain of substrate after the end of deposition process, therefore, occurs. This creates the definite difficulties during PhC manufacture, their research and application. However, in most cases, this factor is rather difficult to be eliminated because of limitedness to select a material for film-substrate.

PhC developed design (Fig. 1) allows to create the samples with working area of 1,3 cm^2. The process sequence is the following. When vacuum of ~10^{-5} mm Hg is reached, copper layer 2 with thickness of 500... 700 nm was deposited on substrate 1 cleaned and heated up to 200... 300°C. Layers of such thickness were sufficient to oxidize cooper along surface up to cuprous monoxide and had a good adhesion to substrate. The layer thickness in the indicated limits was supported by the definite weight for completely evaporated copper sample of M-27 Brand. The distance from evaporator up to the center of substrate was 6 cm.

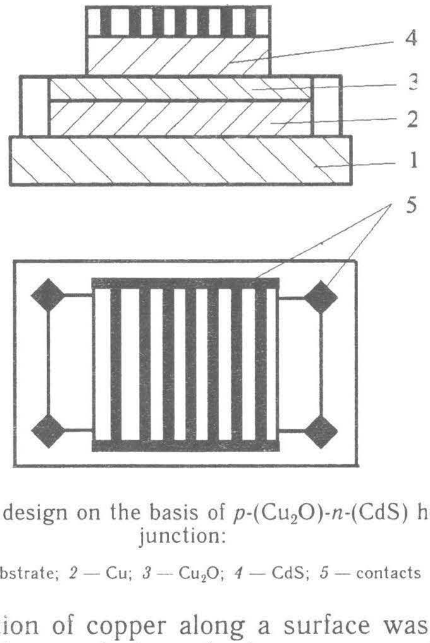

Fig. 1. PhE design on the basis of p-(Cu_2O)-n-(CdS) heterojunction:

1 — substrate; *2* — Cu; *3* — Cu_2O; *4* — CdS; *5* — contacts

Oxidation of copper along a surface was carried out at normal atmospheric pressure and the temperature of 180—230 °C. For 10 minutes the layer 3 of Cu_2O was created of crimson color and with thickness 200—400 nm of polycrystalline fine textured structures with crystallites ~ 1 mm by size.

After repeated pump-down up to working vacuum during 30—45 min the layer 4 of CdS was deposited with thickness of 1—3 mm at substrate temperature 250—300 °C.

CdS sample with weight of 300—500 mg evaporated from the graphitic crusible with length of 7 cm, heated up by current flowing through it. The thickness of walls along the crusible length was selected to provide a positive temperature gradient in the direction from a bottom of crusible to the outlet from it. It reduced the probability for ejection of particles which was not evaporated.

Evaporation was carried out at crusible temperature in work area 650—750°C. The distance from crusible outlet up to substrate center is the same, as at evaporation of copper — 6 cm. The film structure CdS is polycrystalline with crystallite sizes of 0,5—1,5 μm and orientation of *c*-axis is mainly perpendicular to substrate planes. Masks of the corresponding form from sheet nickel set the configuration of deposited layers. Contacts 5 to layers of cooper monoxide and cadmium sulphide were produces by soldering of flexible leads by Wood alloy or indium produced.

The problem to joint PhC in the batteries is supposed to be solved by introduction of additional operation work to apply aluminium connective line.

During improvement of a technique to manufacture PhC samples with different types of volt—ampere characteristics (VCC) — from clearly nonlinear (rectification ratio 10^2—10^3 at 1 V forward bias) up to almost linear were obtained. Correlation between magnitudes of photoelectromotive force (pe. m. f.), generated PhC at illumination, and the rectification ratio calculated from current-voltage diagrams was not possible to determine it. The maximum efficiency, equal to 2—3%, was observed for samples with slightly marked nonlinearity of VCC.

Typical load VCC of PhC, measured at illumination equivalent to solar one, is shown in Fig. 2. Maximum power, equal to 3,5 mW/cm^2, is generated in PhC, working in the regime marked out by point *a* where efficiency reaches value of 3,5%, and the filling factor of VCC is equal to 0,24. The triangular form of a loading curve is explained by the fact that VCC is influenced by sequential R_s and shunting R_{sh} resistances PhC of the considerable in value and reach units and tens of Ohms, correspondingly. For samples with significant diode properties in most cases the quadrant of proper generation was absent, and photosensitivity was manifested as the change in inclination of direct and return branches of VCC.

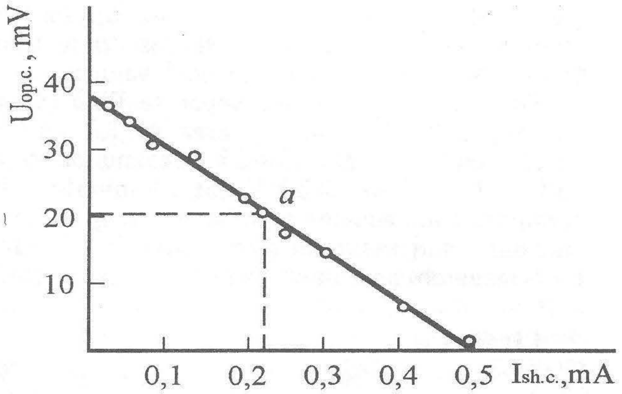

Fig. 2. Load VCC of PhC with p-(Cu_2O)-n-(CdS) heterojunction

The qualitative explanation of such behaviour (low sensitivity at small electrical bias and its raise with increase of reverse-bias voltage) can be given comparing the manufactured samples and surface-barrier photo diodes with the high-ohmic base, described in [1].

From expression for current of photodiode

$$j = -\frac{qB}{1+\frac{s}{V}} + \frac{qVp_s \cdot \left[\frac{qU}{kK} - 1\right]}{1+\frac{V}{s}},$$

where q — elementary charge, B — light flux, $V = \mu E$ — drift speed, p_s — equilibrium value of concentration at boundary, s — effective speed of surface recombination, it is seen, that, at small shifts, the relation s/V in the first member of expression, taking into account a photocurrent, can exceed a unit and then the photocurrent will be low. The increase of reverse-bias potential results in raise of V, the relation s/V decreases also and photocurrent increases.

For the investigated samples a surface is p-(Cu_2O)-n-(CdS) heterojunction, and high-ohmic base is cooper monoxide layer if it has slightly larger, than usual, thickness and increased resistivity that corresponds to features of manufacturing methods for such samples. The change of VCC inclination at illumination also testifies to presence of high resistance in series which considerably worsening the photovoltaic sensitivity of samples.

The thickness of cooper monoxide layer for samples with slightly nonlinear VCC was lower, than for samples with significant nonlinearity. It is possible, that this promotes to emerge the sections of direct contact of copper with cadmium sulphide, which shunt heterojunction and reduce rectification ratio.

It is known, that the padding resistor renders smaller influence on the shape of the quadrant of its proper generation, than sequential, especially at high level of illumination. It results in the fact that the samples with nonlinear VCC work worse as PhC.

VCC of photocells, having noticeable photoe. m. f., are described by the known equation [2]:

$$I = I_{pf} - I_s\left\{\exp\left[\frac{q(U-IR_s)}{MkT}\right] - 1\right\} + \frac{U - IR_s}{R_{sh}},$$

where I_{pf} — photocurrent, I_s — saturation current, M — empirical coefficient.

Direct VCC depends exponentially on voltage and temperatures. The form of the quadrant of its proper generation was more likely triangular, than square, i. e. was far from ideal for the above-mentioned causes. It is obvious, that the decrease of sequential resistance and the decrease of shunting sections would allow to increase efficiency of PhC up to the values exceeding the reached 3%, but the technological difficulties to obtain a layer of cooper monoxide being thin and uniform in thickness are not yet overcome.

Lux-ampere characteristic of PhC, shown in Fig. 3, is linear in a wide interval of illuminations E according to expression $I_{sh.c.} = kE$, where k — coefficient of proportionality. It is typical for gate PhC. The deviation from linearity at values of illumination intensity, higher than $12 \cdot 10^4$ Lux, is connected with the to influence of considerable R_s and R_{sh} which was registered also on light and loading VCC.

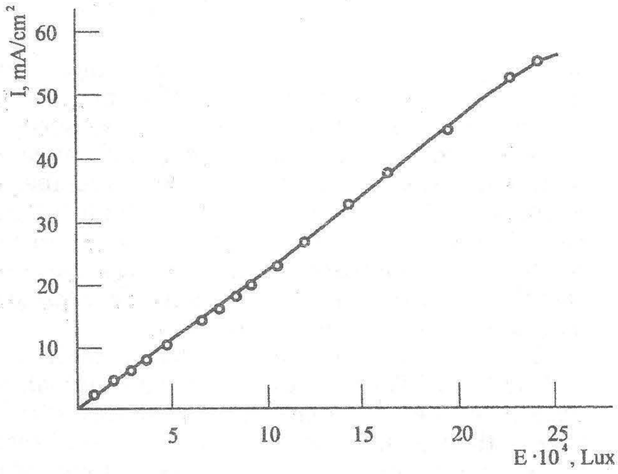

Fig. 3. Lux-ampere characteristic PhC on polyamide film

Measurement of spectral dependence for short-circuit currents PhC was carried out on double monochromator DMR-2 for visible and infrared radiation. The obtained spectra of sensitivity were brought in a common level of energy.

Heterojunction with structure p-(Cu_2O)-n-(CdS) has noticeable photovoltaic sensitivity in visible and short-range IR-area of a spectrum (Fig. 4).

Investigation of spectral PhC characteristics has shown presence of the maximums, adequate to the contribution in photoe. m. f. both as from cadmium sulphide layer near 500—530 nm, and cooper monoxide layer from 600 up to 800 nm. Relative magnitude of maximums testifies about a volume, that the space-charge region for cooper monoxide layer is distributed on the big depth, therefore, Cu_2O is PhC base. The threshold wavelength of the photoresponse or absorption edge in heterojunction define the height of optical barrier that is equal of approximately 0,3 eV.

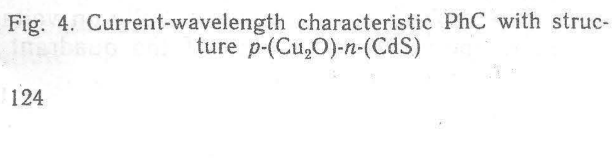

Fig. 4. Current-wavelength characteristic PhC with structure p-(Cu_2O)-n-(CdS)

The fact that the noticeable sensitivity of a sample is observed in short-range IR-area of spectrum up to 1200 nm, which cannot be connected with transitions of zone-zone type in cadmium sulphide and cooper monoxide, is directed.

The maximum of PhC sensitivity at wavelength of 800 nm can be caused by impurity excitation or zone-zone transitions in the triple composition such as $Cu_2(O_xS_{1-x})$ which bandgap width should beless, than for Cu_2O. It is assumed, that the triple composition is formed at deposition of cadmium sulphide on cooper monoxide heated up to 300 °C.

It is noted, that, during long-time illumination of samples by integral light, the value of short circuit current decreases approximately on 1/5 of original magnitude. This shows that the high defect density and surface states in heterojunction with which influence the similar phenomena frequently observed for PhC film are connected.

The conducted research has shown, that PhC film on the basis of p-(Cu_2O)-n-(CdS) heterojunction can be produced on thin polyamide film by method of thermal vacuum evaporation. Thus, there are the difficulties connected with the different temperature coefficient of expansion for film-substrate and depositing films of Cu and CdS.

The mechanism to originate photoe. m. f., is obviously analogous to the mechanism applied to the other PhC film, and will consist in separation of minority nonequilibrium current carriers in heterojunction. Coincidence of mathematical expression for current-voltage diagrams of the obtained PhC and the described ones in [2], and also the presence of two maximums on spectral characteristics of PhC, certifies this.

Rather low efficiency of PhC is explained by their polycrystalline structure, creation of the sections shunting heterojunction, and a high serial resistance of film layers. For our samples, these values was: R_s — from units up to tens Ohm, R_{sh} — from the 100-th shares up to units Ohm. They are far from the best values.

The low weight of the separate PhC (about 20 mg) with the working area of 1,3 cm^2 at short-circuit currents 15—25 mA and open-circuit voltage 0,25—0,30 V (at illumination by sunlight) compensates insufficient magnitude of efficiency and makes it perspective for the further research and improvement of parameters.

Literature

1. *Chopra K.*, *Das S.* Thin-film solar cells. — M.: World, 1996.

2. *Serdyuk V. V.* Physics of solar cells. — Odessa: Логос, 1994.