PHOTOELECTRIC CHARACTERISTICS OF HETEROJUNCTIONS FORMED ON THE BASIS OF INDIUM PHOSPHIDE

D.Sherban*, Tamara Potlog*, A.Simashkevich**, Eugenia Bobeico**

*Moldavian State University, Mateevich str. 60, MD-2009, Chisinau
Republic of Moldova
**Institute of Applied Physics, Academia str. 5, MD-2028, Chisinau
Republic of Moldova
Phone: (373.2) 577686; Fax: (373.2) 244248
E-mail: tpotlog@usm.md

ABSTRACT

The photoelectric properties of ITO/InP and ZnO/InP heterojunctions are analysed. Thin films of ITO and ZnO were deposited on glass and InP wafer substrates at the temperature of 450ºC by spray pyrolisys. ZnO thin films were also obtained by dipping the substrates into cold solution of Zn^{2+} complexes and then in the hot water for 2-3 s.

Investigation of short circuit current (I_{sc}) and open circuit voltage (U_{oc}) dependences for ZnO/InP heterostructures shows that U_{oc} for heterojunctions with ZnO film obtained both by spraying and by dipping tends to saturation with light intensity increasing, while I_{sc} depends linearly on illumination intensity.

At illumination of ZnO/InP heterojunctions with integral light 80 mW/cm^2 (AM1.5) at 300 K the value of the open circuit voltage reaches 0.66 V and the value of the short circuit current is 15.2 mA/cm^2. The conversion efficiency (η) of solar energy into the electric one is 3.8%. The range of spectral sensibility includes the wavelength between 0.52-0.98 µm. The photoelectric parameters of ZnO/InP structures are much less than the ones of ITO/InP heterojunctions (I_{sc}=28.6 mA/cm^2, U_{oc}=0.69 V, η=10.8%) deposited in the same technological conditions. This fact is conditioned by the high resistivity of ZnO thin films.

The range of spectral sensibility of ZnO/InP heterojunction made by dipping is homogenous in the range of 0.6-0.98 µm. For ITO/InP heterojunctions the photoresponse extends from 0.4 to 0.98 µm.

1. INTRODUCTION

The last years, the transparent conducting oxide thin films (ITO, SnO_2, ZnO etc.) were widely applied in photovoltaic conversion. The ITO/InP performance conversion of solar energy in the electric one at AM1 illumination condition with the following photoelectric parameters: open circuit voltage U_{oc}=0.707 V; short circuit current I_{sc}=30.8 mA/cm^2, fill factor *FF*=0.73 and conversion efficiency η=11.6 % were obtained [1].

The structures realised on the basis of indium phosphide with ZnO thin films are less studied. Zinc oxide is transparent in the field of wavelength of 0.4-2.0 µm and its electrooptic coefficients are changing and nonlinear depending on deposition conditions.

There are different methods for obtaining of these films. But the best optical properties were shown by the films deposited by spray pyrolysis and by dipping [2].

In this paper the photoelectric properties of ZnO/InP heterojunction (HJ) with ZnO film realised by different preparation methods are presented. These results are compared with the respective data obtained for ITO/InP heterojunctions.

2. SAMPLE PREPARATION

The investigated structures were obtained in a simple equipment [3] where ITO and ZnO layers have been deposited by spraying method on the glass and InP wafers surface.

ITO thin films were deposited by spraying alcoholic solution of indium chloride and tin chloride in different proportions in various gaseous environments: O_2, Ar or air atmosphere. The properties of the ITO films depend on the concentration of indium chloride and tin chloride in the solution, the substrate temperature, the spraying time and deposition speed. ITO films with maximum conductivity ($4.7{\cdot}10^3\ \Omega^{-1}cm^{-1}$) and maximum transmission coefficient in the visible range of the spectrum were realised from solutions containing 90% $InCl_3$ and 10% $SnCl_4$ and under following conditions: substrate temperature 450^0C, deposition rate 10 Å/min, spraying time 45 s. For the content of $InCl_3$ less than 90% the band gap remains constant equal to 3.44 eV.

ZnO thin films were deposited at temperature of 450°C by spraying alcoholic solution of zinc acetate and $ZnCl_2$ in gaseous environment of O_2 and Ar. Aluminum chloride was added in the solution of zinc acetate and $InCl_3$ into zinc chloride to decrease the resistivity of ZnO thin films so that the crystal lattice and photoelectric properties of the films didn't change essentially.

Another method of ZnO thin films obtaining is substrate dipping into cold solution of Zn^{2+} complexes and then in the hot water for 2-3 s. The solution of Zn^{2+} complexes is prepared as follows:

NH_4OH was poured in the solution of 0.5 M $ZnCl_2$ or 0.5 M $ZnSO_4$ so that a white sediment of $Zn(OH)_2$ was obtained. Then a bidistilled water is added in the obtained sediment to obtain 0.1M solution of Zn^{2+} complexes.

ZnO thin films are obtained by Zn^{2+} complex decomposition in hot water (95-100°C). At the beginning, the glass or InP substrates, with the carrier concentration $\sim10^{16}cm^{-3}$ and resistivity ~0.4-0.6 Ohm·cm, are dipped in the solution of Zn^{2+} complexes, and then, they are washed in the hot water. After 24-25 dippings the interference pattern appears, firstly, the yellow colour, which is changing in the red, violet, green etc. ones with increasing the number of dippings. The obtained films have high resistivity $\sim10^7$Ohm·cm. 0.1 M $SnCl_2$ was added in the solution of Zn^{2+} to decrease the film resistance. This value decreases with two orders reaching $\sim10^5$Ohm·cm. Afterwards, ZnO films are subjected to thermal treatment in the air at various temperatures. It was established that the optimal temperature of the this treatment is 380-400° C (Figure 1). The resistivity decreases till 10^3Ohm·cm after the thermal treatment. The film thickness varies depending on the number of dippings in the range of 0.17 µm and 0.4 µm.

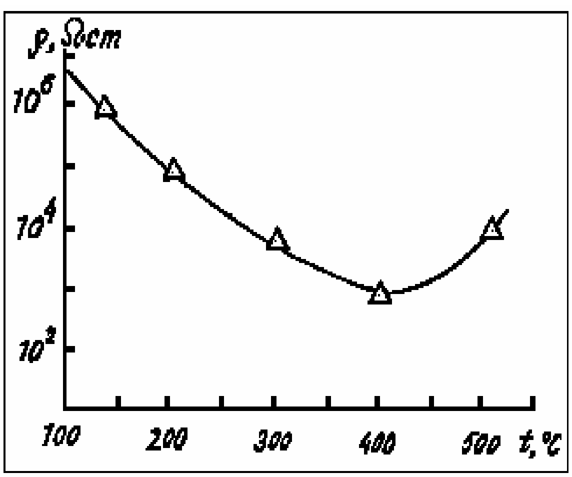

Fig. 1. The dependence of the ZnO thin films resistivity on the thermal treating temperature.

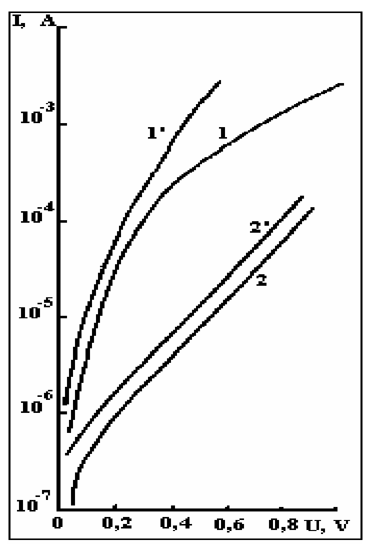

Fig. 2. Dependences of ln I_d=f(U_d) (curves 1, 1′- dipping method) and ln I_{sc}=f(U_{oc}) (curves 2, 2′- spraying method) of ZnO/InP heterostructures.

The crystalline structure of ZnO films deposited on glass was identified by X-ray diffraction method. The analysis of X-ray diffraction pattern shows that ZnO thin film has crystalline structure and prevalent orientation in the perpendicular direction to C substrate axis regardless of used deposition techniques.

The band gap values determined from the transparency spectra of ZnO films obtained by spraying and dipping were 3.44 eV and 3.20 eV, respectively.

On the basis of obtained films the ZnO/pInP and ITO/pInP heterojunctions were obtained. As an ohmic contact for pInP the Ag+25%Zn alloy deposited by vacuum thermal evaporation and then treated at 450°C temperature in a hydrogen flux for 5 min was used. The contact on ZnO frontal layer of structure is applied by vacuum thermal evaporation of a Cr/Au grid through a special masc.

3. PHOTOELECTRIC PROPERTIES OF ZnO/InP HETEROJUNCTION

The examination of current-voltage (I-V) characteristics in the dark and at illumination 80 mW/cm^2 with integral light shows that the illumination leads to parallel shifting of characteristic at illumination relative to the dark one. Independent of ZnO film deposition technique the IV curve of heterojunction ZnO/pInP and ITO/pInP at illumination is described by the following equation:

$$I = I_s\left(\exp\frac{eU}{nKT} - 1\right) - I_f \qquad (1),$$

where I_s is the saturation current, I_f is photocurrent, n is the diode factor, which indicates the mechanism of charge carrier transport through the potential barrier. The value of diffusion potential for ZnO/InP heterojunction with ZnO deposited by spraying and by dipping are 0.6V and 0.8V and the saturation currents are $2.0\cdot10^{-8}$A and $2.5\cdot10^{-6}$A, respectively. Analysing *lnI=f (U)* curves (Figure 2) we can conclude that the dependence of short circuit current (I_{sc}) and dark current (I_d) on voltage follows the same exponential law, but n determined from characteristics at illumination is less, e.g. *n=2,6*, as the one determined from the dark characteristics, e.g. *n=3,1*. This is determined, probably, by series resistance decreasing at heterojunction illumination.

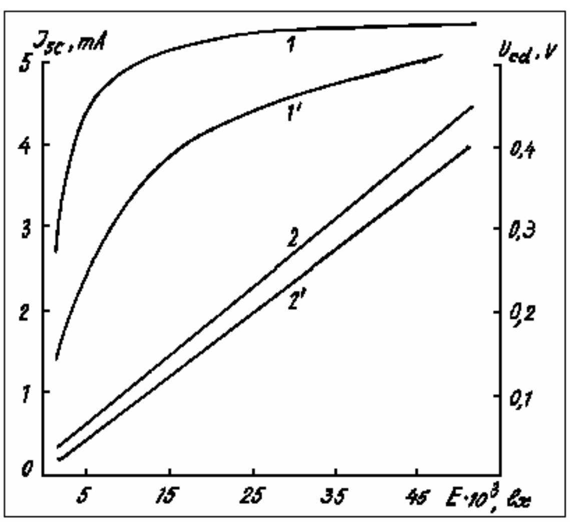

Fig. 3. Dependence of U_{oc} (curves 1, 1´- dipping method) and I_{sc} (curves 2, 2´- spraying method) on illumination intensity for ZnO/InP heterojunctions

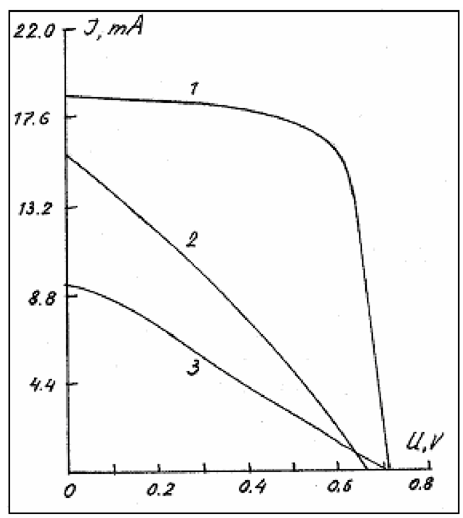

Fig. 4. The IV curves of ITO/pInP (136 mW/cm^2, curve 1) and ZnO/pInP (80 mW/cm^2, curve 2, 3) structures under illumination with integral light.

The investigation of short circuit current I_{sc} and open circuit voltage U_{oc} dependences on the illumination intensity for HJ ZnO/pInP shows that U_{oc} for heterostuctures with ZnO film obtained both by spraying and by dipping tends to saturation with light intensity increasing, while I_{sc} depends linearly on illumination intensity (Figure 3).

Indeed, the voltage becomes

$$U = U_{oc} = \frac{nkT}{e}\ln\left(\frac{I_{sc}}{I_s}+1\right) \quad (2),$$

when current intensity $I=0$ $(R=\infty)$.

It can be seen that at short circuit current condition $(R=0;\ U=0)$ the photocurrent value I_f results from the relation (1): $I(U=0)=I_{sc}=I_f$. Taking this in consideration and the fact that short circuit current depends linearly on illumination $I_{sc}=BE$, the relation for open circuit voltage can be written as follows:

$$U_{oc} = \frac{nkT}{e}\ln\frac{BE}{I_s} \quad (3).$$

The value of n coefficient determined from the dependence $U_{oc}=f(\ln E)$ is in a good agreement with the one determined from $\ln(I_{sc})=f(U_{oc})$.

The photoelectric parameters of ZnO/InP heterojunctions were calculated from the load characteristic measured at illumination with integral light 80 mW/cm^2 (AM1.5) and temperature T=300 K (Figure 4). The open circuit voltage reaches the value 0.66 V, while I_{sc}=15.2 mA/cm^2 for ZnO/pInP heterojunctions with ZnO thin film deposited by solution spraying and 0.7V and I_{sc}=9.0 mA/cm^2, respectively, for the one with ZnO film deposited by dipping in solution. The fill factor values equal to 0.3 and 0.28, respectively, indicate high values of series resistance of these structures. The conversion efficiency η one makes up 3.8% for HJ obtained by spraying method and 2.2% for HJ obtained by dipping. The photoelectric parameters for ITO/pInP heterojunction are: U_{oc}=0.69 V; I_{sc}=28.6 mA/cm^2; FF=0.75; η=10.8%.

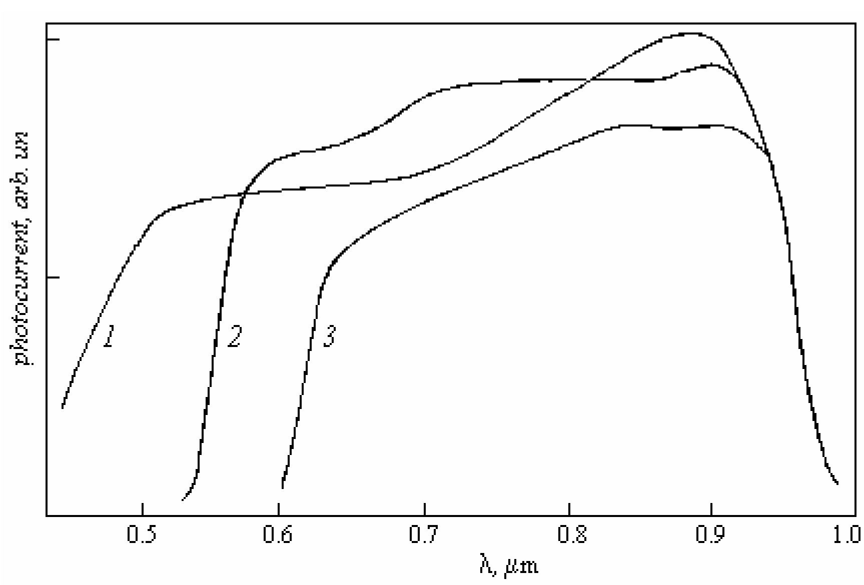

Fig.5. Spectral response of ZnO/InP HJ (curves 2,3) and of the ITO/InP HJ (curve 1).

The spectral response of the short circuit current for the ZnO/pInP and ITO/pInP cells illuminated through the wide band gap semiconductor (ZnO, ITO) is shown in Figure 5. The range of spectral sensibility of ZnO/pInP heterojunction is homogenous and includes the wavelengths between 0.52 and

0.98 μm (Figure 5, curve 2), for the heterostructure with ZnO thin film obtained by spraying method, and 0.6 and 0.98 μm (Figure 5, curve 3), for the one with ZnO thin film obtained by dipping method. In the case of ITO/InP heterojunction, the photoresponse extends from 0.4 to 0.98 μm (Figure 5, curve 1). Performed researches permit to establish that the photoelectric parameters of obtained structures depend on ZnO film deposition method as well as on temperature of thermal treatment.

CONCLUSIONS

The photoelectric parameters of investigated structures depend on the TCOs film obtaining method. The best results were established for ITO/pInP and ZnO/pInP structures where ITO and ZnO thin films were deposited by spraying alcoholic solution of indium chloride and tin chloride or zinc acetate mixed with aluminum chloride onto InP wafers at a substrate temperature of 450ºC in various gaseous environments.

The photoelectric parameters for ITO/pInP heterojunctions are: U_{oc}=0.69 V; I_{sc}=28.6 mA/cm^2; FF=0.75; η=10.8% and for ZnO/pInP: U_{oc}=0.66 V; I_{sc}=15.2 mA/cm^2; FF=0.30; η=3.8%.

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