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Solar energy conversion in Mg-Zn_3P_2 junctions*

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Semitransparent Mg-Zn_3P_2 junctions have been investigated as solar energy converters. The junctions were fabricated on large grain polycrystalline undoped and Cd-doped Zn_3P_2 wafers. The junctions were characterized by using current-voltage, capacitance-voltage and photovoltaic spectra measurement. The highest solar energy conversion efficiency ($\eta \approx 2.5\%$) was obtained for devices made of doped wafers, although junctions made of the undoped ones indicated two times higher open-circuit voltage.

1. Introduction

Zinc phosphide (Zn_3P_2) fulfils the essential requirements of a semiconductor for low-cost, high-efficiency terrestrial photovoltaic solar energy converter [1]. It has a steep absorption edge near 1.5 eV close to the optimum value of energy gap required for solar cells at air·mass (AM1) condition [2]. Both of its constituent elements are cheap and abundant and the electron diffusion length in *p*-type Zn_3P_2 is relatively long (10 μm, [3]). This has led to intensive investigation of Schottky barriers on Zn_3P_2 particularly the Mg-Zn_3P_2 junction [4–6]. So far, the best achieved conversion efficiency is equal to about 5% for Mg-Zn_3P_2 devices obtained on polycrystalline materials [6].

From various metals which are working as an active contact to Zn_3P_2 and give a distinct photovoltaic signal, we have found Mg the most useful material for the Zn_3P_2-based Schottky barrier solar cells. The aim of this paper is to present the experimental results of the semitransparent Mg-Zn_3P_2 contacts for solar energy conversion.

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2. Experimental details

Zn_3P_2 was synthesized by a direct reaction of stoichiometric quantity of high purity zinc and red phosphorous. The synthesis was going on in an evacuated ampoule. The reaction was proceeded within 600–1100 K temperature range. Two-three sublimation processes were used to purify the obtained material. Next, large grain polycrystalline samples were produced by a physical vapour transport. Details are described elsewhere [7]. A part of material was doped by cadmium during the growth. The doping was in the range of 10^{18} cm^{-3}. Undoped Zn_3P_2 samples have resistivity in the range of 10^2–10^3 Ω cm, whereas the resistivity of the Cd-doped ones is 10 Ω cm approximately. All the used wafers were polycrystalline with the grains of 5 mm in diameter for undoped, and 1–3 mm in diameter for doped samples. $4 \times 8 \times 0.5$ mm wafers were cut out and mechanically polished with Al_2O_3 powder of decreasing grain size (1, 0.3, 0.05 μm). Mirror-smooth surface was obtained in this way. After polishing, the samples were degreased ultrasonically in trichloroethylene, acetone and methanol solution. Semitransparent contacts were obtained by vacuum (10^{-6} Torr) evaporation of Mg. The deposition was made through a metal mask which delineated circular diodes 1 mm in diameter. The devices were prepared without any antireflection coating. Back ohmic contacts to the samples were obtained by Au evaporation. Finally, the devices were annealed at 100°C for 1 h.

The devices were characterized by room-temperature measurements of the *I–U* and *C–U* characteristics. *C–U* measurements were performed at frequency 1 MHz by bridge method. The *I–U* dependences were measured in the dark and under illumination (100 $\mathrm{mW/cm^2}$) with EH tungsten lamp. Spectral measurements of photovoltage response were performed using the experimental arrangement with the Zeiss SPM–2 monochromator and lock-in system [8]. The arrangement used allows us to obtain directly the ratio of the investigated contact photoresponse to that of the reference detector (Zeiss Vth–1 thermocouple) with the constant spectral sensitivity in a wide wavelength range.

3. Results and discussion

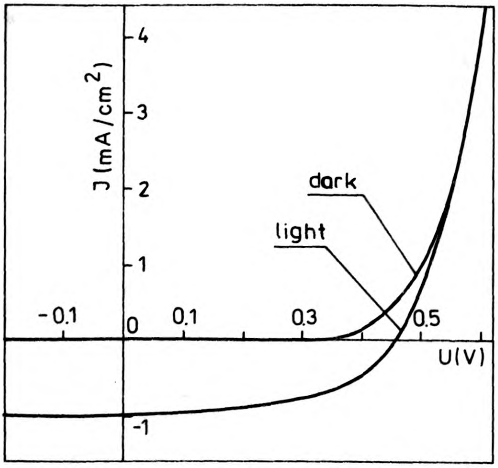
3.1. Characteristics of devices

The devices obtained on both the undoped and doped substrates exhibit a Schottky-like diode behaviour. The log *I–U* dependences shown in Figs. 1 and 2 can be approximated by the relation

$$J = J_0 \exp\left((U - J \cdot A \cdot R_s)/nkT\right) \tag{1}$$

where A is the contact area, J_0 is the zero-bias saturation current density, n — the ideality factor, and R_s — the series resistance.

The devices obtained on undoped substrates have a very high series resistance in the range of 1500–2000 Ω; whereas the devices obtained on doped substrates have much less series resistance (in the range of 10–40 Ω).



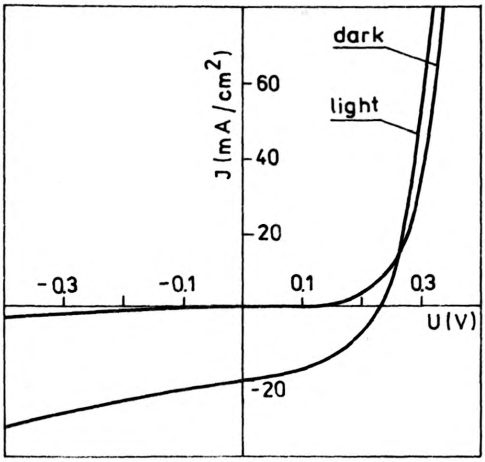


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Fig. 1. *I–U* light and dark characteristic for undoped devices

Fig. 2. *I–U* characteristic for doped devices

For devices based on doped substrates the ideality factor n reached the value from 1.3 to 2. There also were some devices with $n > 2$. As it was shown in [5], such a high value of n results from the existence, on Zn_3P_2 surface, of thin (a few Å) interface with states density about 10^{13} eV^{-1} cm^{-2}.

The C^{-2} vs. U dependences were linear over wide voltage range – see Fig. 3. The barrier height obtained from careful C^{-2} vs. U and I vs. U dependence analysis was equal to 0.6 eV for the best devices.

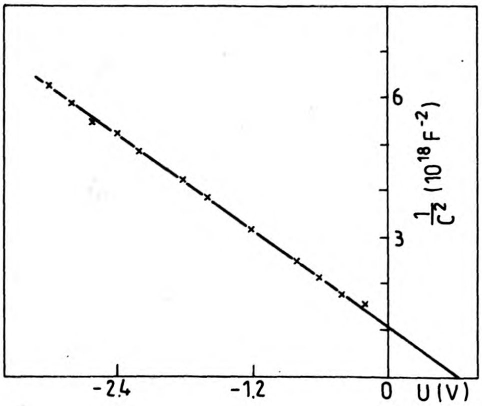

Fig. 3. Capacitance-voltage dependence for the doped junction

For the devices made on the undoped substrates the value of n was about 1.8 and the zero bias saturation current density was 1.6×10^{-8} A/cm^2. Because of nonlinear behaviour of C^{-2} vs. U characteristics for these devices the reliable value of barrier height ϕ_B from capacitance measurements could not be determined. The ϕ_B value was evaluated from density of saturation current as equal to 0.7–0.8 eV. The $\phi_B = 0.8$ eV was obtained as for ideal Schottky barrier (without any interface) and $\phi_B = 0.7$ eV was obtained assuming the existence of the interfacial states as in the case of the doped devices.

3.2. Photoelectric properties

Typical dark and light *I–U* characteristics for devices on undoped Zn_3P_2 are presented in Fig. 1. In order to avoid the influence of series resistance on *I–U* characteristics, the investigations were carried out under both the low current and illumination intensity (10 mW/cm^2). In this case the open circuit voltage was about $V_{oc} \approx 0.45$ V, short-circuit current density $J_{sc} \approx 1$ mA/cm^2, and fill factor $FF \approx 0.6$ results in the conversion efficiency about 2.5%. We found for undoped substrate that under higher illumination intensity, the series resistance strongly restricted the solar cell parameter. Under 100 mW/cm^2 illumination the fill factor was reduced to 0.3 and conversion efficiency was also drastically reduced to the value less than 1%.

As mentioned above, we also produced devices on Cd-doped Zn_3P_2 (in order to avoid the series resistance problem, among others) the resistivity of which was $\simeq 20$ Ω cm. Typical light and dark *I–U* characteristics for such devices are presented in Fig. 2. For this device we found that the typical values of solar cell parameters under 100 mW/cm^2 were: $V_{oc} \simeq 0.25$ V, $J_{sc} \simeq 20$ mA/cm^2, $FF \simeq 0.45$. The total energy conversion efficiency for the device reached the value of $\eta \approx 2.5\%$.

Comparing the above results, we found that the value of open-circuit voltage for devices obtained on Cd-doped substrates was lower by factor of 2 than for the devices obtained on the undoped substrates.

Other results of *I–U* measurements of Cd-doped devices in an occurrence of the shift of *I–U* curve for illuminated device towards low voltage and its crossing with the dark current curve at the low voltage region were observed. This shift may be the main reason of reduction of V_{oc} value. Similar effect was also observed in [9], where ITO–Zn_3P_2 solar cells were produced on substrate with comparable resistivity (1 Ω cm). This shift could arise due to a variety of reasons, including alteration of barrier height and charge trapping condition under the optical illumination.

The typical dependence of the photovoltaic (PV) signal of the produced Mg-Zn_3P_2 devices is presented in Fig. 4. Intensive PV effect was observed in the wavelength range of 0.4–0.9 μm. PV plot of Mg-Zn_3P_2 contact is shown on the background of a solar spectrum under the outer space AM0 and terrestrial AM1 conditions. The optimal fit of both location and shape of the photoresponse plot is visible. The PV maximum is noticed within energy range of 1.9–2.2 eV.

For higher energies a decrease of PV response due to recombination mechanism was observed. In the long-wavelength part of photoresponse the signal distinctly dropped at the energy close to the energy gap of Zn_3P_2. Below this energy the exponential-like decrease of photosignal was noticed. Transitions in this region could be connected with some density-of-states tails and/or impurity levels.

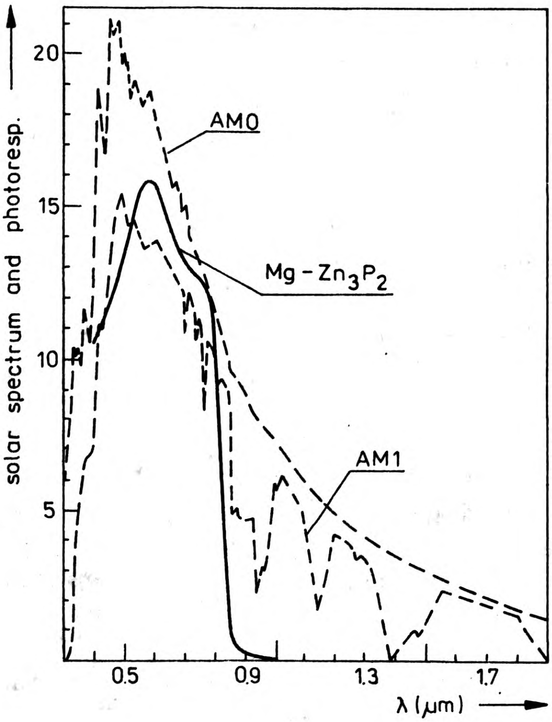

Fig. 4. Spectral dependence of the photovoltaic (U_{oc}) signal of semitransparent Mg-Zn$_3$P$_2$ junction on the background of solar spectra

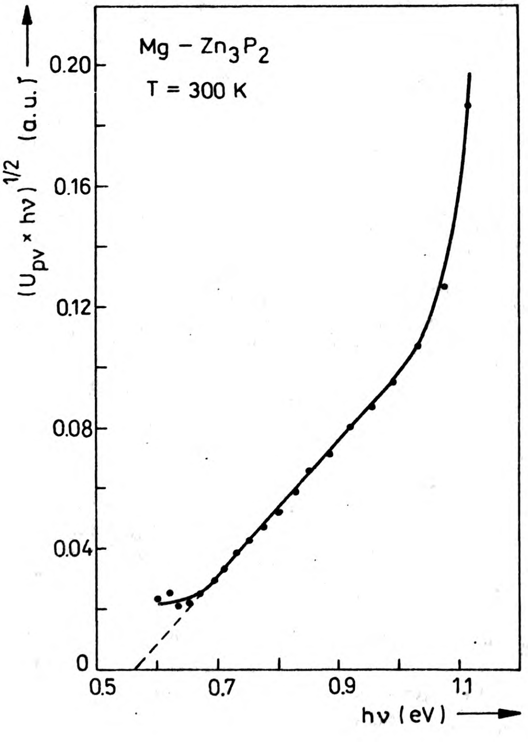

Fig. 5. Low energy part of the photovoltaic signal (U_{oc}) spectrum for the same junction. The axis units allow us to determine ϕ_B from rectilinear part of this dependence

By means of simple Fowler distribution theory [10] the barrier height was determined. According to this model the open-circuit photovoltage U_{PV} on the contact is proportional to the squared photon energy, i.e.

$$U_{PV} \cdot h\nu \sim (h\nu - \phi_B)^2 \tag{2}$$

where ϕ_B is barrier height.

Figure 5 presents an example of the barrier height determination. A typical value of ϕ_B for Mg-Zn_3P_2 junctions made on undoped substrates was equal to about 0.6 eV. This value is in a good correlation with the one obtained from the electrical method (see above). For the doped devices smaller ϕ_B values were obtained.

4. Conclusions

The up-to-date state of our solar energy conversion studies on Mg-Zn_3P_2 Schottky barriers was presented. The cells were fabricated on large grain polycrystalline undoped and Cd-doped substrates. The highest conversion efficiency (without any AR coating) $\eta = 2.5\%$ was obtained for devices fabricated on doped substrate, although the open-circuit voltage was about two times greater for junction made on undoped substrates ($V_{oc} \approx 0.45$).

It is evident that further decreasing of series resistance as well as AR coating will give the distinct improvement of conversion efficiency (see [11]).

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Преобразование солнечной энергии в диодах из Mg-Zn_3P_2

Исследовано преобразование солнечной энергии в диодах изготовленных из поликристаллических нелегированных и легированных Cd образцов. Для изучения свойств диодов измерено вольт-амперные, емкостные и спектральные характеристики. Большой КПД ($\eta \approx 2,5\%$) получено для диодов изготовленных из легированных образцов, но у диодов изготовленных из нелегированных образцов напряжение холостого хода было в два раза больше.