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Zinc Oxide/Cuprous(I) Oxide-Based Solar Cells Prepared by Electrodeposition

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The aim of this research was to fabricate zinc oxide/cuprous(I) oxide-based heterojunction solar cells with the use of electrodeposition methods, and further to investigate their structures and photovoltaic properties. The ZnO and Cu_2O were used as n- and p-type semiconductors, respectively, to fabricate photovoltaic devices based on Ag/ZnO/Cu_2O/Cu(100) heterojunction structures. The crystallite sizes of ZnO and Cu_2O were determined to be 25.4(3) nm and 69.8(6) nm, respectively. It was pointed out that efficiencies of the solar cells can be gradually adjusted, using different thicknesses of Cu_2O layers, to achieve values as high as 2.7%. The standard diode model and high device performance provide new insights into the issue, outlining guidelines for high-performance solar cells and suggesting that a metal-n-type semiconductor–p-type semiconductor nanostructure-crystal layered, sandwiched-type architecture is a promising platform to boost the efficiency.

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1. Introduction

The solar cells based on copper oxide and zinc oxide are a promising alternative to conventional silicon cells because of the relatively low cost of production and theoretical efficiency of ≈16% [1–9]. This paper focuses on the characteristics of the ZnO layer — n-type, and Cu_2O/CuO — p-type semiconductors prepared by using a method of electrodeposition, which allows to create transparent semiconductor layers with good optoelectronic properties [4]. Cuprous(I) oxide (Cu_2O) semiconductors are promising elements of a whole functional-oxide solar cell material because of their photoelectronic properties — band-gap energy of 2.1 eV, environmental friendly properties such as non-toxicity and low material cost [1, 2].

One of the primary motivations of this research is the change of solar cell architecture. In other words, one can change the device architecture to the inverted structure in which a hole-blocking layer (such a zinc oxide, ZnO) is inserted between a silver electrode and an active layer of Cu_2O. It was proven that an optimization of thickness of Cu_2O layer could increase the efficiency of ZnO/Cu_2O-based heterojunction solar cells. In order to improve efficiency, dependence between structural medication and photovoltaic properties were investigated.

2. Materials and methods

The Cu_2O and ZnO layers were deposited layer-by-layer one on crystalline Cu(100) base with a 5 mm thickness by applying a method of electrodeposition. Platinum wire was used as a counter electrode in each process.

The Cu_2O layer was obtained from electrolyte-solution of copper(II) sulfate ($CuSO_4$, 0.4 mol/L, Wako 97.5%), L-lactic acid (3 mol/L, Wako) and distilled water. The electrolyte pH was adjusted to 12.5 by adding NaOH. During the deposition the solution temperature was kept at 65 °C and the current density at 1.5 mA/cm^2. The process time was set to: 20, 40, 60, 80, and 100 min. The estimated thicknesses of the Cu_2O layers were calculated from the value of current density, deposition time and the Faraday law and confirmed by cross-section SEM investigation. The obtained values were: 1, 2, 3, 4, and 5 µm, respectively, for each deposition time.

The ZnO layers were galvanostatically electrodeposited from 0.025 M aqueous solution of Zn(NO_3) at the temperature of 75 °C on the Cu_2O substrates. The current density of electrodeposition was set at 3 mA/cm^2 and the electrodeposition time was set to 50 min. The thickness of the ZnO layers was determined to be 250 nm. Because of the constant deposition time, the thickness of the ZnO layer was unmodifiable in all samples. The top electrodes of silver paste (TAAB, S 270) were printed on the rear of ZnO. The ZnO/Cu_2O solar cells prepared in the present study were investigated by a structural analysis, spectroscopic and photovoltaic measurements.

All the crystalline components in the Ag/ZnO/Cu_2O/Cu(100) solar cells were investigated by X-ray diffraction (XRD) and grazing incidence X-ray diffraction (GIXD) on an Empyrean PANalytical powder diffractometer, using Cu K_α radiation.

The spectroscopic studies were carried out in the vacuum system with the use of PHI 660/5700 spectrometer. All the measurements were taken at room temperature.

The current–voltage characteristics were carried out by 2400 Series Source Meter, Keithley Instruments. The source of the simulated light was a 75 W 4000 K xenon lamp equipped with a sunlight filter to adjust the emission spectrum of the lamp to the 1000 W/m^2. The solar cells were covered with a metal aperture to define an active area of 0.01 cm^2.

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3. Results and discussion

First, the structure of the deposited layers were investigated. For this purpose the layers were deposited separately on cuprous substrates. Only after structural investigation samples were fabricated as functional devices to study optoelectronic properties. XPS measurements were performed on Cu(100) substrate in order to reveal possible contaminations and to determine Cu baseline positions for further references. The examination of the spectra did not reveal the existence of contaminations.

Figure 1a shows the GI XRD patterns obtained at 1°, 2°, 3°, and 5° incidence angles of Ag/ZnO interfaces. Based on this results the conclusions are that there are not any processes such as diffusion, atoms exchange, or oxidation between Ag/ZnO and ZnO/ Cu_2O layers. It was found that Cu_2O layers are polycrystalline with no traces of CuO (Fig. 1b). The XRD patterns for Cu_2O were obtained from PDF2 00-001-1142 card. The crystallite size was estimated using the well-known Scherrer equation. The crystallite sizes of Ag, ZnO, and Cu_2O were determined to be 5.8(2), 25.4(3), and 69.8(6) nm, respectively. Figure 1c shows the backscatter Laue diffraction pattern from the front (100) face of the crystalline copper. The Laue diffraction pattern is very symmetric, with sets of diffraction spots arranged in the rings around the centre of the pattern. The core-level XPS spectrum for Cu $2p$ spectral lines measured from a surface of Cu(100) is shown in Fig. 1d. This spectrum consists of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ lines. The first unshifted part of the main lines refers to copper. The second shifted part depicts the Cu^+ ion of CuO bonds [10]. The O^{2-} ions are either from the Cu_2O interlayer or from oxidation of the metallic Cu due to the exposure to air in spite of the surface preparing methods.

In order to optimize the cell efficiency and its thickness it is necessary to determine the best thickness value of Cu_2O layer. For this purpose the optoelectronic properties — the current–voltage characteristics were carried out. The basic current mechanism could be described by diode equation. The diode equation shown in (1) describe the current–voltage characteristic of a solar cell under illumination and can be written as [7, 8]:

$$I(U) = I_0^{\text{eff}}[\exp(\frac{qU}{k_B T n^{\text{eff}}}) - 1] - I_{sc}, \qquad (1)$$

where $I(U)$ — the total current, U — voltage, I_{sc} — the short circuit current (photogenerated current), I_0^{eff} — the effective saturation current, q — the elementary charge, k_B — the Boltzmann constant, T — the absolute temperature, n^{eff} — the effective ideality factor. In this equation the influence of ohmic and recombination currents is included in I_0^{eff} and n^{eff} parameters.

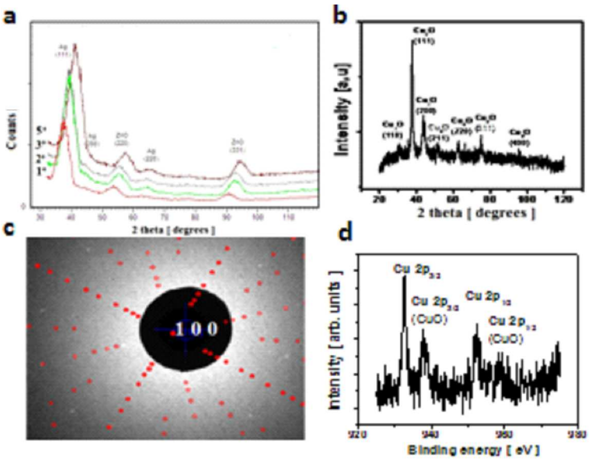

Fig. 1. (a) GI XRD at 1°, 2°, 3°, and 5° incidence angles of Ag/ZnO interface. (b) GI XRD at 1° incidence angle of Cu_2O layer. (c) Backscatter Laue diffraction pattern from the crystalline (100) copper substrates. (d) The XPS core level spectrum of Cu $2p$ registered from Cu(100) substrate for increase of the etching time of 60 s using the beam of Ar^+ ions of 500 eV energy.

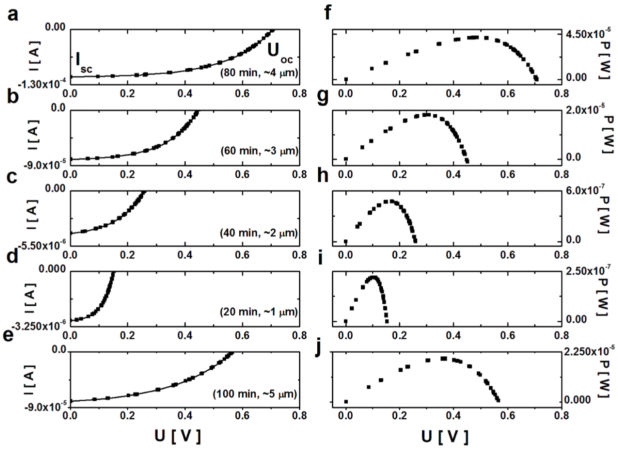

Fig. 2. Experimental (dots) and theoretical (solid lines) current–voltage characteristics of the Ag/ZnO/Cu_2O/Cu(100) solar cells as a function of electrodeposition times (a,b,c,d,e) and their power-voltage curves (f,g,h,i,j). (a)–(e) Current–voltage characteristics of Ag/ZnO/Cu_2O/Cu(100) and (f)–(j) power–voltage curve of Ag/ZnO/Cu2O/Cu(100) of Cu_2O thickness 4, 3, 2, 1, and 5 μm, respectively.

Figure 2 presents the results from current–voltage characteristic tests (a)–(e) and calculations of power obtained from this experimental data (f)–(j). The shape (tendency) of $U-I$ and $U-P$ curves is unchanged despite the change of Cu_2O layer thickness. The shapes of $U-I$ are exponential and the $U-P$ upset down parabolic-like. The influence of the Cu_2O interlayer thickness d is shown in form of shifts of the open-circuit voltage (U_{oc}) and P peaks in direction of larger values of U (see Fig. 2 and Table I). The values of solar cell parameters are also presented in Table I. It is very important to predict these characteristics to obtain maximum possible power.

The analysis of the data given in Table I shows that the values of electrical parameters depend on the thickness of Cu_2O layer. The efficiency of the solar cells varies between 0.04% and 1.71%. The maximum value was

TABLE I

The measured parameters of the present solar cells. aa — thickness of Cu_2O layer of $Ag/ZnO/Cu_2O/Cu(100)$ solar cells [µm], bb — open-circuit voltage U_{oc} [V], cc — short-circuit current density J_{sc} [A/m^2], dd — fill factor FF, ee — efficiency η [%]

aa	bb	cc	dd	ee
1	0.15	5.8	0.44	0.04
2	0.26	13.2	0.47	0.16
3	0.45	46.5	0.41	0.86
4	0.71	92.6	0.42	1.71
5	0.57	88.0	0.32	1.6

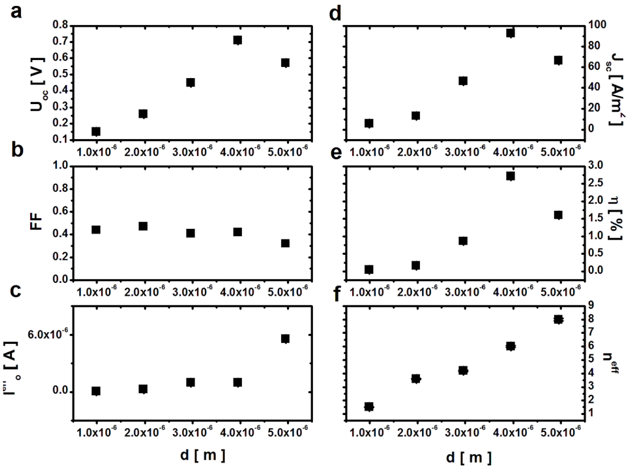

Fig. 3. The solar-cell parameters as a function of Cu_2O layer thickness d for $Ag/ZnO/Cu_2O$. (a) The open-circuit voltage U_{oc}. (b) The fill factor FF. (c) The effective saturation current I_0^{eff}. (d) The density of short circuit current J_{sc}. (e) The efficiency η. (f) The effective ideality factor n^{eff}.

obtained at thickness of 4 µm. Relative errors were smaller than 3%.

Figure 3a shows the fitted data based on Eq. (1). The results are in a good agreement with the experimental records. The mismatch between the analysis and the data from the current–voltage characteristics leads to different values of the effective solar parameters (Fig. 3b). On the basis of this model we were able to adjust the experimental data and get values of effective parameters (see Fig. 3c–f). Figure 3e and f shows the values of I_0^{eff} and n^{eff} obtained with Eq. (1). The results show behavior of the n^{eff} values in the range from 1.5 to 8. These values are approximately 3 times higher than obtained from tests.

4. Conclusions

It was shown that for a typical $Ag/ZnO/Cu_2O/CuO/Cu(100)$-based heterojunction solar cell with a 250 nm thick ZnO interlayer the optimal thickness value of Cu_2O interlayer is about 4 μm. The efficiency of such solar cells was found to be 1.71%. The results obtained from the diode model used in this study is in a good agreement with the experimental current–voltage data. The model allows to determine the values of the I_0^{eff} and n^{eff} parameters. All of the investigated values of solar cell parameters strongly depend on the thickness of Cu_2O interlayer.

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