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Low Cost Solar Cells Based on Cuprous Oxide

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1. Introduction

The worldwide quest for clean and renewable energy sources has encouraged large research activities and developments in the field of solar cells. In recent years, considerable attention has been devoted to the development of low cost energy converting devices. One of the most interesting products of photoelectric researches is the semiconductor cuprous oxide cell. As a solar cell material, cuprous oxide - Cu$_2$O, has the advantages of low cost and great availability. The potential for Cu$_2$O using in semiconducting devices has been recognized since, at least, 1920. Interest in Cu$_2$O revived during the mid seventies in the photovoltaic community (Olsen et al., 1982). Several primary characteristics of Cu$_2$O make it potential material for use in thin film solar cells: its non-toxic nature, a theoretical solar efficiency of about 9-11%, an abundance of copper and the simple and inexpensive process for semiconductor layer formation. Therefore, it is one of the most inexpensive and available semiconductor materials for solar cells. In addition to everything else, cuprous oxide has a band gap of 2.0 eV which is within the acceptable range for solar energy conversion, because all semiconductors with band gap between 1 eV and 2 eV are favorable material for photovoltaic cells (Rai, 1988).

A variety of techniques exist for preparing Cu$_2$O films on copper or other conducting substrates such as thermal, anodic and chemical oxidation and reactive sputtering. Particularly attractive, however, is the electrodeposition method because of its economy and simplicity for deposition either on metal substrates or on transparent conducting glass slides coated with highly conducting semiconductors, such as indium tin oxide (ITO), SnO$_2$, In$_2$O$_3$ etc. This offers the possibility of making back wall or front wall cells as well. We have to note that electrochemical preparation of cuprous oxide (Cu$_2$O) thin films has reached considerable attention during the last years.

Electrodeposition method of Cu$_2$O was first developed by Stareck (Stareck, 1937). It has been described by Rakhshani (Jayanetti & Dharmadasa, 1996, Mukhopadhyay et al., 1992, Rakhshani et al., 1996, Rakhshani et al., 1996). In this work, a method of simple processes of electrolysis has been applied.

Electrochemical deposition technique is an simple, versatile and convenient method for producing large area devices. Low temperature growth and the possibility to control film thickness, morphology and composition by readily adjusting the electrical parameters, as well as the composition of the electrolytic solution, make it more attractive. At present,
electrodeposition of binary semiconductors, especially thin films of the family of wide-band gap II-IV semiconductors (as is ZnO), from aqueous solutions is employed in the preparation of solar cells. A photovoltaic device composed of a p-type semiconducting cuprous (I) oxide (Cu$_2$O) and n-type zinc oxide (ZnO) has attracted increasing attention as a future thin film solar cell, due to a theoretical conversion efficiency of around 18% and an absorption coefficient higher than that of a Si single crystal (Izaki et al. 2007)

Therefore, thin films of cuprous oxide (Cu$_2$O) have been made using electrochemical deposition technique. Cuprous oxide was electrodeposited on copper substrates and onto conducting glass coated with tin oxide (SnO$_2$), indium tin oxide (ITO) and zinc oxide (ZnO). Optimal conditions for high quality of the films were requested and determined. The qualitative structure of electrodeposited thin films was studied by x-ray diffraction (XRD) analysis. Their surface morphology was analyzed with scanning electronic microscope (SEM). The optical band gap values $E_g$ were determined. To complete the systems Cu/Cu$_2$O, SnO$_2$/Cu$_2$O, ITO/Cu$_2$O and ZnO/Cu$_2$O as solar cells an electrode of graphite or silver paste was painted on the rear of the Cu$_2$O. Also a thin layer of nickel was vacuum evaporated on the oxide layer. The parameters of the solar cells, such as the open circuit voltage ($V_{oc}$), the short circuit current ($I_{sc}$), the fill factor ($FF$), the diode quality factor ($n$), serial ($R_s$) and shunt resistant ($R_{sh}$) and efficiency ($\eta$) were determined. The barrier height ($V_b$) was determined from capacity-voltage characteristics.

Generally is accepted that the efficiency of the cells cannot be much improved. (Minami et al., 2004). But we succeeded to improve the stability of the cells, using thin layer of ZnO, making heterojunctions Cu$_2$O based cells.

2. Structural, morphological and optical properties of electrodeposited films of cuprous oxide

2.1 Experimental

2.1.1 Preparation of the films

A very simple apparatus was used for electrodeposition. It is consisted of a thermostat, a glass with solution, two electrodes (cathode and anode) and a standard electrical circuit for electrolysis. The deposition solution contained 64 g/l anhydrous cupric sulphate (CuSO$_4$), 200 ml/l lactic acid (C$_3$H$_6$O$_3$) and about 125 g/l sodium hydroxide (NaOH), (Rakhshani et al.1987, Rakhshani & Varghese, 1987). Cupric sulphate was dissolved first in distilled water giving it a light blue color. Then lactic acid was added. Finally, a sodium hydroxide solution was added, changing the color of the solution to dark blue with pH = 9. A copper clad for printed circuit board, with dimension 50 $\mu$m, 2.5 $\times$ 7 cm$^2$, was used as the anode. Copper clad and conducting glass slides coated with ITO and SnO$_2$ were used as a cathode. Experience shows that impurities (such as dirt, finger prints, etc.) on the starting surface material have a significant impact on the quality of the cuprous oxide. Therefore, mechanical and chemical cleaning of the electrodes, prior to the cell preparation, is essential. Copper boards were polished with fine emery paper. After that, they were washed by liquid detergent and distilled water. The ITO substrates were washed by liquid detergent and rinsed with distilled water. The SnO$_2$ substrates were soaked in chromsulphatic acid for a few hours and rinsed with distilled water. Before using all of them were dried. Thin films of Cu$_2$O were electrodeposited by cathodic reduction of an alkaline cupric lactate solution at 60° C. The deposition was carried out in the constant current density regime. The deposition parameters, as current density, voltage between the electrodes and deposition
time were changed. The Cu$_2$O films were obtained under following conditions: 1) current density $j = 1.26$ mA/cm$^2$, voltage between the electrodes $V = 0.3 - 0.38$ V and deposition time $t = 55$ min. Close to the value of current density, deposition time and Faraday’s law, the Cu$_2$O oxide layer thickness was estimated to be about 5 $\mu$m. The potentiostatic mode was used for deposition the Cu$_2$O films on glass coated with SnO$_2$ prepared by spray pyrolysis method of 0.1 M water solution of SnCl$_2$ complexes by NH$_4$F. The applied potential difference between anode and cathode was constant. It was found that suitable value is $V = 0.5$ to 0.6 V. The deposition current density at the beginning was dependent on the surface resistance of the cathode. For a fixed value of the potential, the current decreased with increasing film thickness. The film thickness was dependent on deposition current density $j$. For current density of about 1 mA/cm$^2$ at the beginning and deposition time of about 2 h, the film thickness was 5-6 $\mu$m approximately. The thickness of deposited film was determined using a weighting method, as $d = m/\rho s$, where $m$ is the mass and $s$ is the surface of the film. A density $\rho$, of 5.9 g/cm$^3$ was used.

The deposition of Cu$_2$O on a commercial glass coated with ITO was carried out under constant current density. The ITO/Cu$_2$O films was obtained under the following conditions: current density $j = 0.57$ mA/cm$^2$, voltage between the electrodes $V = 1.1 - 1.05$ V and deposition time $t = 135$ min. The Cu$_2$O oxide layer thickness was estimated to be about 5 $\mu$m. All deposited films had reddish to reddish-gray color.

### 2.1.2 Structural properties

The structure of the films was studied by X-ray diffraction, using CuK$\alpha$ radiation with a wavelength of 0.154 nm. The Bragg angle of $2\theta$ was varied between 20$^0$ and 50$^0$. The XRD spectrums of the films samples, deposited on copper, glass coated by SnO$_2$ and glass coated by ITO are shown in Fig.1, Fig.2 and Fig.3 respectively. It was found that all films are polycrystalline and chemically pure Cu$_2$O with no traces of CuO. XRD peaks corresponded to Cu$_2$O and the substrate material. The XRD spectrums indicate a strong Cu$_2$O peak with (200) preferential orientation.

### 2.1.3 Morphological properties

The surface morphology of the films was studied by a scanning electron microscope JEOL model JSM 35 CF. Fig.4, Fig.5 and Fig.6 show the scanning electron micrographs of Cu$_2$O films deposited on copper, glass coated by SnO$_2$ and glass coated by ITO respectively. The photographs indicate a polycrystalline structure. The grains are very similar to each other in size and in shape. They are about 1 $\mu$m and less in size for the film deposited on copper, 1-2 $\mu$m for the film deposited on SnO$_2$ and about 1 $\mu$m for the film deposited on ITO.

### 2.1.4 Optical band-gap energy determination

The optical band-gap is an essential parameter for semiconductor material, especially in photovoltaic conversion. In this work it was determined using the transmittance spectrums of the films. The optical transmission spectrums were recording on Hewlett-Packard (model 8452 A) spectrophotometer in the spectral range 350-800 nm wavelength. Thin layers of a transparent Cu$_2$O were preparing for the optical transmission spectrums recording. The optical transmission spectrums of about 1.5 $\mu$m thick Cu$_2$O film deposited on glass coated with SnO$_2$ is presented in Fig.7. There are two curves, one (1) recorded before annealing and the other one (2) after annealing of the film for 3h at 130°C.
Fig. 1. X-ray diffraction spectrum of a Cu$_2$O film deposited on copper

Fig. 2. X-ray diffraction spectrum of a Cu$_2$O film deposited on SnO$_2$

Fig. 3. X-ray diffraction spectrum of a Cu$_2$O film deposited on ITO
Fig. 4. Micrograph obtained from a scanning electron microscope of Cu$_2$O deposited on copper

Fig. 5. Micrograph obtained from a scanning electron microscope of Cu$_2$O deposited on SnO

Fig. 6. Micrograph obtained from a scanning electron microscope of Cu$_2$O deposited on ITO
We can see that there is no difference in the spectrums. The absorption boundary is unchangeable. That means that the band gap energy is unchangeable with or without annealing. The little difference comes from different points recording, because the thickness of the film is not uniform. The transmittance spectrum of about 0.9 μm thick Cu₂O film, deposited on ITO, is presented in Fig. 8. 

For determination of the optical band gap energy $E_g$, the method based on the relation

$$\alpha h\nu = A(h\nu - E_g)^{n/2},$$

(1)

has been used, where $n$ is a number that depends on the nature of the transition. In this case its value was found to be 1 (which corresponds to direct band to band transition) because that value of $n$ yields the best linear graph of $(\alpha h\nu)^2$ versus $h\nu$. The values of the absorption coefficient $\alpha$ were calculated from the equation

![Fig. 7. Optical transmission spectrum of a 1.5 μm thick Cu₂O/SnO₂ film](image1)

![Fig. 8. Optical transmission spectrum of a 0.9 μm thick Cu₂O/ITO film](image2)
\[ \alpha = \frac{A}{d}, \]  

(2)

where \( d \) is the film's thickness determined using weighing method, and \( A \) is the absorbance determined from the values of transmittance, \( T(\%) \), using the equation

\[ A = \ln \frac{100}{T(\%)}. \]  

(3)

The values of the optical absorption coefficient \( \alpha \) in dependence on wavelength are shown in Fig. 9 for \( \text{Cu}_2\text{O}/\text{SnO}_2 \) film and Fig. 10 for \( \text{Cu}_2\text{O}/\text{ITO} \) film.

![Fig. 9. Coefficient \( \alpha \) vs wavelength \( \lambda \) for \( \text{Cu}_2\text{O}/\text{SnO}_2 \) film](image)

![Fig. 10. Coefficient \( \alpha \) vs wavelength \( \lambda \) for \( \text{Cu}_2\text{O}/\text{ITO} \) film](image)
Fig. 11 and Fig. 12 show \((ahv)^2\) versus \(hv\) dependence for the \(Cu_2O/SnO_2\) film and \(Cu_2O/ITO\) film corresponding. The intersection of the straight line with the \(hv\) axis determines the optical band gap energy \(E_g\). It was found to be 2.33 eV for \(Cu_2O/SnO_2\) film and 2.38 eV for \(Cu_2O/ITO\). They are higher than the value of 2 eV given in the literature and obtained for \(Cu_2O\) polycrystals. These values are in good agreement with band gaps.

Fig. 11. Graphical determination of the optical band gap energy for \(Cu_2O/SnO_2\) film

Fig. 12. Graphical determination of the optical band gap energy for \(Cu_2O/ITO\) film

(x - before annealing; · - after annealing)
determined from the spectral characteristics of the cells made with electrodeposited Cu$_2$O films. The value of the energy band gap of Cu$_2$O/ITO is little higher than the value of Cu$_2$O/SnO$_2$ film. The reason is maybe different size of the grains. Fig.11 shows that there is no different in optical band gap energy determined from the curve plotted before annealing and from the curve plotted after annealing. Also, Fig.11 and Fig.12 show that there is no shape absorption boundary in the small energy range of the photons. Probably defects and structural irregularities are present in the films. The optical band-gap of the films was determined using the transmittance spectrums. It was found to be 2.33 eV for Cu$_2$O/SnO$_2$ film and 2.38 eV for Cu$_2$O/ITO.

3. Preparation of the Cu$_2$O Schottky barrier solar cells

Cu$_2$O Schottky barrier solar cells can be fabricated in two configurations, the so called back wall and front wall structures. By vacuum evaporating a thin layer of nickel on the Cu$_2$O film, photovoltaic cells have been completed as back wall type cells (Fig.13), or by depositing carbon or silver paste on the rear of the Cu$_2$O layers, photovoltaic cells have been completed as front wall type cells (Fig.14). Nickel, carbon or silver paste are utilized to form ohmic contacts with cuprous oxide films. From the energy band diagram (Fig.15) we can see that the Cu$_2$O work function $\Phi_s = \chi + 1.7$ eV, ($\chi$ is the electron affinity of Cu$_2$O) (Olsen et al.,1982, Papadimitriou et al.,1990). That means that Cu$_2$O will make ohmic contact with metals characterized with work function higher than 4.9 eV, as are Ni, C. Gold and silver essentially form ohmic contacts. A carbon or silver back contact was chosen because of simplicity and economy of the cell preparation. The rectifying junction exists at the interface between the cooper and Cu$_2$O layers in the case of back wall cells. In the case of front wall cells the rectifying junction exists at the interface between the SnO$_2$ (ITO) and Cu$_2$O layers.

Fig. 13. Profile and face of Cu/Cu$_2$O back wall cell structure
The evaporation of nickel has been made with Balzers apparatus under about 5.33 x 10^{-3} Pa pressure. The optical transmission of the nickel layer was 50\% for 550nm wavelength. The total cell active area is 1.0 cm². Antireflectance coating or any special collection grids have not been deposited.

The current-voltage characteristics of the best ITO/Cu₂O/C, Ni/Cu₂O/Cu and SnO₂/Cu₂O/C solar cells have been recorded in darkness and under 100 mW/cm² illumination, point by point. The light intensity was measured by Solar Meter Mod.776 of Dodge Products. The measurement was carried out using an artificial light source with additional glass filter, 10 mm thick to avoid heating of the cells. I-V characteristics, Fig.16, Fig.17 and Fig.18, were recorded first with periodically illumination of the source (curve •) to avoid the heating of the cell. After that I-V characteristics were recorded with continually illumination (curve ×). It is noted that the open circuit voltage \( V_{oc} \) and the short circuit current density \( I_{sc} \) decrease with increase in temperature. \( V_{oc} \) drops because of increase reverse current saturation with temperature because minority carriers increase with increase in temperature. \( I_{sc} \) decrease because of increase the recombination of the charges.
It should be stressed that this cells showed photovoltaic properties after heat treatment of the films for 3 hrs at 130 °C in a furnace. This possibly results in a decrease of sheet resistance value of the Cu$_2$O films, which was not measured, or in transformation the Cu$_2$O semiconductor from n to p type after heat treatment. Before heating $V_{oc}$ and $I_{sc}$ were about zero or negative. The serial resistance $R_s$ and shunt resistance $R_{sh}$ for all types of the cells were evaluated from I-V characteristics.

| Cell type       | $R_{so}$ | $R_s$ | $R_{sh}$ |
|-----------------|----------|------|---------|
| ITO/Cu$_2$O/C   | 10       | 1,02 | 76      |
| Ni/Cu$_2$O/Cu   | 20       | 8,3  | 40      |
| SnO$_2$/Cu$_2$O/C | 14      | 3,3  | 25      |

Table 1. Serial and shunt resistance

The values are given in Table 1. $R_{so}$ is evaluated from the dark characteristics (curve $\Delta$) as $dV/dI$ for higher values of forward applied voltage. $R_{sh}$ is evaluated as $dV/dI$ from the dark characteristics in reverse direction for lower values of the applied voltage (Olsen & Bohara, 1975). $R_s$ is evaluated from the light I-V characteristics and it decreases with illumination. That means that $R_s$ is photoresponse. The high series resistance $R_s$ and low shunt resistance $R_{sh}$ are one of the reasons for poor performance of the cell.

Several cell parameters were evaluated from the $I$-$V$ characteristics. Table 2 contains the optimal current and voltage values ($I_m$ and $V_m$), the open circuit voltage ($V_{oc}$), the short circuit current ($I_{sc}$) and evaluated values of the fill factor $FF$ ($FF = \frac{I_mV_m}{I_{sc}V_{oc}}$), the efficiency $\eta$ ($\eta = FF \frac{I_{sc}V_{oc}}{P_m}$) and diode factor $n$.

| Cell type       | $I_m$ | $V_m$ | $I_{sc}$ | $V_{oc}$ | $FF$ % | $\eta$ 10-2 % | $n$ |
|-----------------|-------|------|----------|---------|-------|-------------|-----|
| ITO/Cu$_2$O/C   | 130   | 180  | 245      | 340     | 28    | 2,34        | 2,23|
| Ni/Cu$_2$O/Cu   | 28    | 120  | 50       | 270     | 24    | 0,70        | 2,06|
| SnO$_2$/Cu$_2$O/C | 46    | 90   | 74       | 225     | 25    | 0,41        | 2,20|

Table 2. Cell parameters

The diode factor was evaluated from the logarithmic plot of the dependence of $I_{sc}$ versus $V_{oc}$ which were measured for different illumination. The diode factor defined as

$$n = \frac{q}{kT} \frac{\Delta V_{oc}}{\Delta \ln I_{sc}}$$

is about 2 for all type of the cells.

The performances of the cells depend on the starting surface material, the type of the junction, post deposition treatment and the ohmic contact material. From the I-V characteristics, we can see that the cells are with poor performances, low fill factor FF and
very low efficiency. The high Rs and low Rsh (which is very far from ideally solar cell) are one of the reasons for poor performances. Because of high series resistance Rs, the values of the short circuit current density are very low. By depositing gold instead of nickel or graphite paste, the performance may be improved by decreasing of Rs.

Fig. 16. I-V characteristics for ITO/Cu2O/C solar cell ○-periodically illumination (100 mW/cm²); ×-continually illumination (100 mW/cm²); ∆-dark characteristic

Fig. 17. I-V characteristics for Ni/Cu2O/Cu solar cell ○-periodically illumination (100 mW/cm²); ×-continually illumination (100 mW/cm²); ∆-dark characteristic
Fig. 18. I-V characteristics for SnO₂/Cu₂O/C solar cell o-periodically illumination (100 mW/cm²); x-continually illumination(100 mW/cm²); Δ-dark characteristic

5. Potential barrier height determination of the cells

Capacitance as a function of reverse bias voltage at room temperature of Ni/Cu₂O/Cu, SnO₂/Cu₂O/graphite and ITO/Cu₂O/graphite solar cells was measured by RCL bridge on alternating current (HP type) with built source with 1000 Hz frequency. Results for 1/C² versus reverse bias voltage for all these types of cells are shown in Fig 19, Fig 20 and Fig 21, before annealing (○), immediately after annealing (●) and after three months of annealing (×). The dependence is straight line. The intercepts of the straight line with x-axis correspond to the barrier height $V_b$. Cu/Cu₂O cell showed photovoltaic effect without post deposition heat treatment and their photovoltaic properties are almost unchangeable in time (fig.19). In contrast to this cell, the ITO/Cu₂O (fig.20) and SnO₂/Cu₂O (fig.21) cells no showed photovoltaic properties and no potential barrier was found to exist (Georgieva & Ristov, 2002). Before annealing, the open circuit voltage $V_{oc}$ and the short circuit current $I_{sc}$ were about zero. After annealing of the films for 3 h at 130°C, the devices exhibited good PV properties and the potential barrier excised. But this situation was not stationary. That is another essential factor in the properties of these cells indicating the possibility of chemical changes in ITO/Cu₂O and SnO₂/Cu₂O junction (Papadimitriou et al., 1981).

The values of barrier height $V_b$ and the open circuit voltage $V_{oc}$ upon illumination by an artificial white light source of 100 mW/cm² for all types of cells are presented in table 3. Also in this table are given their values after aging for 3 months (★). Only Cu/Cu₂O cell has stationary values of $V_b$ and $V_{oc}$. The values of barrier height $V_b$ are great then the values of open circuit voltage $V_{oc}$. The great $V_b$ gives the great $V_{oc}$ in consent with the photovoltaic theory.
Evaluation of the barrier height, before annealing (○); after annealing (●); after 3 months of annealing (▲).

Fig. 19. $1/C^2$ vs applied voltage of Cu/Cu$_2$O cell.

Evaluation of the barrier height, before annealing (○); after annealing (●); after 3 months of annealing (▲).

Fig. 20. $1/C^2$ vs applied voltage of ITO/Cu$_2$O cell.
Table 3. Values of barrier height $V_b$ and open circuit voltage $V_{oc}$ for all types of cells after annealing and after aging for 3 months (*).

| Cell type       | Cu/Cu$_2$O | ITO/Cu$_2$O | SnO$_2$/Cu$_2$O |
|-----------------|------------|-------------|-----------------|
| $V_b$ (mV)      |            | 378         | 330             | 180             |
| $V_{oc}$ (mV)   | 310        | 249         | 118             |
| $V_b^*$ (mV)    | 370        | 150         | 60              |
| $V_{oc}^*$ (mV) | 310        | 105         | 30              |

Evaluation of the barrier height, before annealing (●); after annealing (○); after 3 months of annealing (×).

Fig. 21. $1/C^2$ vs applied voltage of SnO$_2$/Cu$_2$O cell.

6. ZnO/Cu$_2$O heterojunction solar cells

Until now, we have made Schottky barrier solar cells. As we could not improve their efficiency and their stability, we decided to make heterojunction p-n solar cells based on a p-type Cu$_2$O thin films. We selected ZnO as an n-type semiconductor. ZnO is a transparent oxide that is widely used in many different applications, including thin film solar cells. The p-n junction was fabricated by potentiostatic deposition of the ZnO layer onto SnO$_2$ conducting glass with a sheet resistance of 14 $\Omega$ and potentiostatic deposition of Cu$_2$O onto ZnO, Fig. 22.

6.1 Electrochemical depositing of ZnO

ZnO/Cu$_2$O heterojunction solar cells were made by consecutive cathodic electrodeposition of ZnO and Cu$_2$O onto tin oxide covered glass substrates. Zinc oxide (ZnO) was cathodically deposited on a conductive glass substrate covered with SnO$_2$ as cathode by a potentiostatic method (Dalchiele et al., 2001, Izaki et al., 1998, Ng-Cheng-Chin et al., 1998). Conducting glass slides coated with SnO$_2$ films are commercial samples. The electrolysis takes place in a
simple aqueous 0,1M zinc nitrate [Zn(NO$_3$)$_2$] solution with pH about 6, maintained at 70°C temperature. The cathodic process possibly can be described by the following reaction equations (Izaki & Omi, 1992):

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^{-}
\]

\[
\text{NO}_3^{-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2 + 2\text{OH}^{-}
\]

\[
\text{Zn}^{2+} + 2\text{OH}^{-} \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\] (5)

ZnO films were electrochemically grown at constant potential of 0.8 V between the anode and cathode. For a fixed value of the potential, a current density decreased with increasing the film thickness. The deposition time was varying from 10 min to 30 min. Deposited films were rinsed thoroughly in distilled water and allowed to dry in air at room temperature. The anode was zinc of 99.99% purity.

The deposition conditions of the thin films of Cu$_2$O have been described in 2.1.1. The deposition potential is pH sensitive. It suggests, also and it has already been reported that the Cu$_2$O layer was formed by the following reaction:

\[
2\text{Cu}^{2+} + 2\text{e}^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}
\] (6)

even this reaction does not explain the large pH dependence of deposition potential (Izaki et al. 2007, Wang & Tao, 2007). The present study was conducted, in a first instance, on undoped zinc oxide films and cuprous (I) oxide films. The structure of the films was studied by X-ray diffraction measurements using monochromatic Cu K$_\alpha$ radiation with a wavelength of 0,154 nm operated at 35 kV and 24 mA. Morphology and grain size was determined through micrographs on a JEOL JSM 6460 LV scanning electron microscope.

Figure 23 shows the X-ray diffraction patterns of ZnO film prepared at 0.8 V potential for 10 min. The Bragg angle of 20 was varied between 20° and 70°. It can be seen that the film has crystalline structure. XRD peaks corresponding to ZnO (signed as C) and the substrate material SnO$_2$ (signed as K) were determined with JCPDS patterns. The XRD spectrum indicates a strong ZnO peak with a (0002) or (1011) preferential orientation.

Figure 24 shows a scanning electron micrograph of undoped electrodeposited ZnO film. The photograph shows small rounded grains. It is difficult to determine the grain size from the micrograph. But using Scherrer’s equation ($D = \frac{0.9\lambda}{\beta\cos\theta}$), the apparent crystallite size of ZnO is about 20nm, which means that it is nanostructured film.
Thin films of ZnO grown by electrochemical deposition technique on SnO$_2$/glass substrate are optically transparent in a visible spectral region, extending to 300 nm wavelength. The transmission is relatively low (~50%) in the blue region (400–450 nm) Fig.25. The transmission maximum is about 60–70% through the red light region. Probably defects and structural irregularities are presented in the films, indicating low transmission.

Assuming an absorption coefficient $\alpha$ corresponding to a direct band to band transition and making a plot of $(\alpha h\nu)^2$ versus energy $h\nu$, the optical band gap energy $E_g$ was determined through a linear fit. It was found to be 3.4 eV, which corresponds to the documented room temperature value of 3.2 to 3.4 eV.
6.2 Some characteristic of the cells

To complete Cu$_2$O/ZnO/SnO$_2$ heterojunction as solar cell, thin layer of carbon paste or carbon spray was deposited on the rear of the Cu$_2$O. Front wall cells were formed. A carbon back contact was chosen because of simplicity and economy of the cell preparation and because the cells with carbon give high values of the short circuit current density despite the evaporated layer of nickel. The total cell active area was 1 cm$^2$. Antireflectance coating or any special collection grids have not been deposited. The best values of the open circuit voltage $V_{oc} = 330$ mV and the short circuit current density $I_{sc} = 400 \mu$m/cm$^2$ were obtained by depositing carbon paste and illumination of 100 mW/cm$^2$. The $V_{oc}$ increases as logarithmic function with solar radiation, ($V_{oc} = \frac{kT}{e} \ln \left( \frac{I_{sc}}{I_0} + 1 \right)$). The $I_{sc}$ increases linear with solar radiation, (Fig.26).

Our investigations show that the ZnO layer improves the stability of the cells. That results in a device with better performances despite of the Schottky barrier solar cells (Cu$_2$O/SnO$_2$). First, the cells show photovoltaic properties without annealing, because potential barrier was formed without annealing. The barrier fell for a few days which result in decreasing the open circuit voltage despite the values of $V_{oc}$ for just made cells. It decreases from 330 mV to 240 mV. But after that the values of $V_{oc}$ keep stabilized, because of stabilized barrier potential. It wasn’t case with Schotky barrier solar cells, because barrier potential height decreases with aging. In ZnO/Cu$_2$O cells, thermal equilibrium exists. The $V_{oc}$ decreases and $I_{sc}$ increases with increasing the temperature, that is characteristic for the real solar cell. It could be seen from the current-voltage ($I-V$) characteristic in incident light of 50mW/cm$^2$, Fig.27.

Barrier potential height was determined for one device from capacitance measurement as a function of reverse bias voltage at room temperature. Capacitance dependence of reverse bias voltage at room temperature was measured by RCL bridge on alternating current (HP type) with bilt source with 1000 Hz frequency. Results for ($1/C^2$) versus voltage are shown in Figure 28. The Cu$_2$O/SnO$_2$ cells without the ZnO layer show a lower $V_{oc}$. The improvement in $V_{oc}$ could be due to the increase of the barrier height using ZnO layer as n-type semiconductor.
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Fig. 26. Dependence of the $V_{oc}$ and $I_{sc}$ vs. solar irradiation

The values of barrier height $V_b$ and the open circuit voltage $V_{oc}$ upon illumination of 100 mW/cm$^2$ for just made cell and the cell after few days are presented in Table 4. Also in this table are given their values after few days of depositing. The values of the barrier height are greater than the values of open circuit voltage $V_{oc}$. The greater $V_b$ gives the great $V_{oc}$, that correspond to the photovoltaic theory.

| Cu$_2$O/ZnO/SnO$_2$ cell | $V_b$(mV) | $V_{oc}$(mV) |
|--------------------------|-----------|-------------|
| just made                | 368       | 330         |
| after few days           | 276       | 240         |

Table 4. Values of barrier height $V_b$ and open circuit voltage $V_{oc}$ for just made cell and after few days.

Fig. 27. Volt-current characteristics of the Cu$_2$O/ZnO/SnO$_2$ solar cell upon 50mW/cm$^2$ Illumination
The values $V_{oc}=316$ mV, $I_{sc}=0.117$ mA/cm$^2$, fill factor $=0.277$, upon 50 mW/cm$^2$ illumination are compared with the values: $V_{oc}=190$ mV, $I_{sc}=2.08$ mA/cm$^2$, fill factor $=0.295$; upon 120 mW/cm$^2$ illumination (Katayama et al. 2004) made with electrochemical deposition technique. Maybe doping of the ZnO films with In, Ga and Al (Machado et al., 2005, Kemell et al., 2003) will decrease the resistivity and increase the electro conductivity of the films, consequently and the short circuit current density of the cells.

7. Conclusion

The performance of the Cu$_2$O Schottky barrier solar cells are found to be dependent on the starting surface material, the type of the junction, post deposition treatment and the ohmic contact material. Better solar cells have been made using an heterojunction between Cu$_2$O and n-type TCO of ZnO. It is a suitable partner since it has a fairly low work function. Our investigation shows that the ZnO layer improves the stability of the cells. That results in a device with better performances despite of the Schottky barrier solar cells (Cu$_2$O/SnO$_2$). First, the cells show photovoltaic properties without annealing, because potential barrier was formed without annealing. To improve the quality of the cells, consequently to improve the efficiency of the cells, it has to work on improving the quality of ZnO and Cu$_2$O films, because they have very high resistivity, a factor which limits the cells performances. Doping of the ZnO films with In, Ga and Al will decrease the resistivity of the deposited films and increase their electroconductivity. SEM micrographs show that same defects are present in the films which act as recombination centers. Behind the ohmic contact, maybe one of the reason for low photocurrent is just recombination of the carriers and decreasing of the hole concentration with the time. The transmittivity in a visible region have to increase. Also, it is necessary to improve the ohmic contact, consequently to increase the short circuit current density ($I_{sc}$). For further improvement of the performances of the cells maybe inserting of a buffer layer at the heterojunction between Cu$_2$O and ZnO films will improve the performance of the cells by eliminating the mismatch defects which act as recombination centers. Also it will be protection of reduction processes that maybe exists between ZnO and Cu$_2$O.
Even low efficiency it may be acceptable in countries where the other alternative energy sources are much more expensive.

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The first book of this four-volume edition is dedicated to one of the most promising areas of photovoltaics, which has already reached a large-scale production of the second-generation thin-film solar modules and has resulted in building the powerful solar plants in several countries around the world. Thin-film technologies using direct-gap semiconductors such as CIGS and CdTe offer the lowest manufacturing costs and are becoming more prevalent in the industry allowing to improve manufacturability of the production at significantly larger scales than for wafer or ribbon Si modules. It is only a matter of time before thin films like CIGS and CdTe will replace wafer-based silicon solar cells as the dominant photovoltaic technology. Photoelectric efficiency of thin-film solar modules is still far from the theoretical limit. The scientific and technological problems of increasing this key parameter of the solar cell are discussed in several chapters of this volume.

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