Heterojunction solar cell with 2% efficiency based on a Cu_2O substrate

Alberto Mittiga,[a] Enrico Salza, Francesca Sarto, Mario Tucci, and Rajaraman Vasanthi
Casaccia Research Center, ENEA, via Anguillarese 301, 00060, Rome, Italy

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We report on the fabrication of heterojunction solar cells made by deposition of transparent conducting oxide (TCO) films on Cu_2O substrates. The TCO films have been grown by ion beam sputtering on good quality Cu_2O sheets prepared by oxidizing copper at a high temperature. The best solar cell has reached an open-circuit voltage of 0.595 V, a short-circuit current density of 6.78 mA/cm^2, a fill factor of 50%, and a conversion efficiency of 2% under simulated AM1.5G illumination, which is the highest efficiency value reported for this kind of heterojunction devices. These devices represent a good starting point for the development of very low cost solar cells. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2194315]

In the literature there are many reports on solar cells based on cuprous oxide (Cu_2O) as active layer[1–7] because this semiconductor shows many interesting characteristics useful for solar cells production such as low cost, nontoxicity, good mobilities, fairly high minority carrier diffusion length, and direct energy gap. Although the theoretical limit of the energy conversion efficiency of a Cu_2O solar cell is about 20% (just considering radiative recombination), the highest efficiency obtained up to now on this substrate is 1.76%.[1,8] This is due to a very limited amount of work devoted to this semiconductor. The optimization of Cu_2O solar cells is slowed down by the lack of clear understanding of the electronic and thermodynamical properties of its intrinsic point defects and by the difficulties in the doping processes. Cu_2O is spontaneously a *p*-type semiconductor since it contains negatively charged copper vacancies and probably interstitial oxygen.[9] A large number of elements were tested as doping impurities. Up to now none demonstrated *n*-type conductivity and a possible explanation for this negative result is based on the self-compensation mechanism[10] or the low solubility of the doping impurities tried so far.[11] Instead some elements such as N,[12] Cl,[1] and Si (Ref. 13) promoted an increment in *p*-type conductivity, but the doping technology is still far to be well assessed for all of them; also the physical mechanism leading to *p*-type doping is not clearly understood except for the case of N.

In the absence of any mean to make a *p-n* homojunction, the devices with the highest photovoltaic efficiencies were metal-Cu_2O Schottky solar cells. Nevertheless it is generally accepted that their efficiency cannot be much improved[14] and also their stability is not assessed.[3] A better device could be a transparent conducting oxide (TCO)/Cu_2O heterojunction solar cell and many experiments have been performed using TCO based on ZnO, In_2O_3, SnO_2, and CdO. Up to now the highest efficiency reported for an heterojunction solar cell is 1.52%, obtained on a 0.0314 cm^2 ZnO/Cu_2O heterojunction.[4] To improve this result we have exploited both the copper oxidation process to obtain better substrates and the TCO deposition technology.

We have prepared Cu_2O substrates by oxidizing 100 μm thick 99.999% purity copper sheets in a tube furnace in a N_2/O_2 gas mixture flux. Of course Cu_2O properties strongly depend on the details of the oxidation process. In particular, a substrate having large grains, high mobility, and low resistivity is preferable. To this aim our oxidation process is composed of two main steps. The former is a 60 min long high temperature ($T>1100$ °C) annealing at 0.27 Torr O_2 partial pressure. Without extracting the sample from the furnace, this step is followed by a lower temperature annealing stage (800 °C) at 0.01 Torr O_2 partial pressure. The former step is needed to obtain grains with dimensions of the order of 1 mm^2, the latter to get partial equilibration of the sample to a lower defect density. The final room temperature mobility is about 100 cm^2/V^{-1} s. For substrates slowly cooled to room temperature we have found a resistivity greater than 22000 Ω cm. To reduce this value we have tried to dope the Cu_2O introducing impurities such as F, P, N, Cl, In, Mg, Si, and Na. A clear resistivity reduction has been reached only with Cl doping, but a strong reduction of the diffusion length occurs. Therefore we have adopted a different approach. We have terminated the oxidation process by a "quench" step extracting the sample from the furnace when it reaches 450 °C and quickly cooling it down to room temperature by dipping it into de-ionized water. The resultant resistivity is slightly above 1000 Ω cm. After a wet etching procedure for 50 s in a 1:1 solution $HNO_3(65\%)/H_2O$, to remove any trace of CuO from the surface, the heterojunctions are made depositing TCO films on the top face of the Cu_2O substrate. Two TCOs have been investigated: In_2O_3 doped with tin [indium tin oxide (ITO)] and ZnO. Both have been obtained by ion beam sputtering (IBS) at room temperature and their resistivities are about 10^{-3} and 4×10^{-3} Ω cm, respectively.

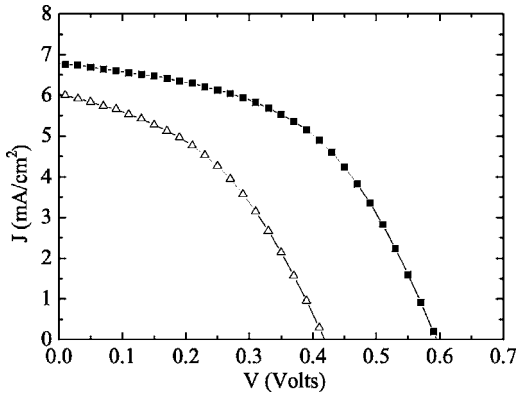

FIG. 1. *J-V* characteristics, under AM1.5G illumination, of the MgF_2/ITO/Cu_2O (open triangles) and MgF_2/ITO/ZnO/Cu_2O (squares) heterostructure solar cells.

[a]Electronic mail: alberto.mittiga@casaccia.enea.it

TABLE I. Photovoltaic parameters [V_{oc}, J_{sc}, fill factor (FF), and efficiency] under AM1.5G light and dark *J-V* parameters (n, J_0, R_s, and R_{sh}) obtained for the $MgF_2/ITO/Cu_2O$ and $MgF_2/ITO/ZnO/Cu_2O$ heterostructure solar cells.

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF %	Efficiency %	J_0 (A/cm^2)	n	R_s (Ω)	R_{sh} (Ω)
$MgF_2/ITO/Cu_2O$	419	6.04	42.3	1.07	2×10^{-6}	2.37	40	2094
$MgF_2/ITO/ZnO/Cu_2O$	595	6.78	50	2.01	4.8×10^{-7}	3.02	34	6880

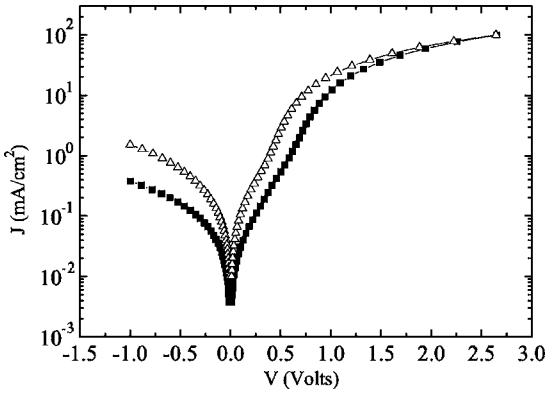

FIG. 2. *J-V* characteristic, in dark and room temperature condition, of the $MgF_2/ITO/Cu_2O$ (open triangles) and $MgF_2/ITO/ZnO/Cu_2O$ (squares) heterostructure solar cells.

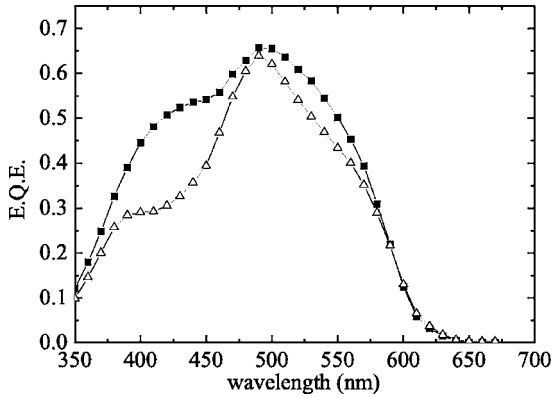

FIG. 3. External quantum efficiency of the $MgF_2/ITO/Cu_2O$ (open triangles) and $MgF_2/ITO/ZnO/Cu_2O$ (squares) heterostructure solar cells.

We have made two kinds of cells: the former is a simple heterojunction between the Cu_2O substrate and a 300 nm thick ITO layer while in the latter we have introduced a 50 nm thick ZnO layer between the ITO and the Cu_2O substrate. The area of the TCO contact is 0.5 cm^2. To improve the current extraction a copper grid having a shadowing factor of 11% is evaporated through a mask on the TCO and then the entire front contact of the sample is covered by an evaporated MgF_2 antireflection layer. Finally gold evaporation provides a good Ohmic contact on the back side of the Cu_2O sheet.

The solar cells have been characterized by measuring the current voltage (*I-V*), both in dark and under AM1.5G light conditions, and the external quantum efficiency (EQE). In Fig. 1 a comparison of light $I-V$ of samples with and without ZnO layer are reported. The photovoltaic parameters of the cells are summarized in Table I. In Fig. 2 the *I-V* of the two cells, measured at room temperature in dark condition, are shown and the calculated ideality factors (n), reverse saturation current densities (J_0), and series (R_s) and shunt resistances (R_{sh}) of the heterojunction are listed in Table I. The data obtained for the EQE of our cells, reported in Fig. 3, are consistent with the measured J_{sc} values. The effect of the interference fringes due to the TCO thickness is evident. It can be reduced using an appropriate antireflection coating. In the ITO/Cu_2O cell we have used a 142 nm thick MgF_2 layer while in the $ITO/ZnO/Cu_2O$ cell the MgF_2 thickness has been reduced to 80 nm with better results.

Since Cu_2O has an energy gap of 1.95 eV, it should be possible to obtain solar cells with high V_{oc} values, but low built-in potential, defects near the interface, and local shunts generally produce high J_0 and low R_{sh} values thus reducing the V_{oc}. Our data show that the introduction of the ZnO layer gives a clear improvement on J_0 and R_{sh} of the ITO/Cu_2O cell resulting in a device with higher V_{oc}. Probably the improvement is due to a higher built-in potential since the electron affinity of the ZnO is lower than that of the ITO. The dark and light *I-V* characteristics also show that, at the actual stage of our work, the cell performances are strongly limited by the series resistance which is mainly due to the high resistivity of the Cu_2O substrate.

Anyway, the efficiency of our best cell has the highest value ever reported for any Cu_2O based solar cell.

In conclusion we have shown that the use of good quality Cu_2O sheets and IBS room temperature TCO deposition can greatly improve the performances of TCO/Cu_2O solar cells. All the photovoltaic parameters seem to have wide room for improvement, confirming that Cu_2O is a trustworthy candidate for low cost solar cells realization.

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