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CHARACTERIZATION OF Cu_2O THIN FILMS USED IN SOLAR CELLS BY FLUORESCENCE AND FTIR SPECTROSCOPY

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Abstract: *In this work Cu_2O thin films from a ZnO/Cu_2O solar cell, were prepared by magnetron sputtering and characterized by Fourier-transform infrared spectroscopy (FTIR) and spectroflorometry analysis. FTIR spectrum shows peaks of CuO at the interface of the quartz substrate from oxidation. Fluorescence spectroscopy of the sample annealed at 900^0C showed one narrow peak at 380 nm in the emission band. OPAL2 software was used to model the optical characteristics of the Cu_2O films and the ZnO/Cu_2O heterojunction, respectively optical band gap, reflectance, transmittance and absorptance.*

1. Introduction

The evolution of thin film solar cells have led to the development of new solar cell types, such as tandem solar cells based on crystalline silicon that yield higher conversion efficiencies in comparison to the single-junction implementation. Such improvements were necessary to keep the competitiveness versus conventional energy sources [1]. A promising material for thin film solar cell application is cuprous oxide (Cu_2O) [2-5]. This semiconducting metal oxide has a high optical absorption, is non-toxic, and has low production cost [6-8]. The theoretical limit of the conversion efficiency for a solar cell based on Cu_2O is close to 20% under one sun illumination [9-11].

Recent progress in spectroscopy methods allows characterization of thin films used in advanced solar cells. Important parameters, such as complex refractive indices of the thin films, can be derived from spectroscopic ellipsometry measurements and implemented in the simulation models of the solar cells [1, 22, 26].

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Two of the most efficient spectroscopy techniques for thin films characterization are Fluorescence spectroscopy, also known as spectrofluorometry, and Fourier-transform infrared spectroscopy (FTIR) [12-15]. Fluorescence spectroscopy is a type of electromagnetic spectroscopy that analyzes fluorescence from a sample. It involves using a beam of ultraviolet light that excites the electrons in molecules of certain compounds and causes them to emit visible light. On the other hand, Fourier-transform infrared spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas [16, 17]. A FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range, with a very large scale of applications in atomic and subatomic physics [18-21].

The objective of this work is to analyze the optical properties of the Cu_2O layer material within a metal oxide solar cell used in a c-Si tandem design using fluorescence, FTIR spectroscopy methods as well as numerical modeling of optical characteristics [10,25].

2. Materials and Experimental Setup

Cu_2O thin films were deposited on 10 × 10 × 0.5 mm^3 quartz substrates by reactive DC magnetron sputtering (Semicore Triaxis) at 400 ºC deposition temperature in O_2/Ar atmosphere. The pre-sputtering time was 10 min to avoid any contamination. The power was fixed at 100 W. As deposited Cu_2O thin films were annealed at 900 ºC for 3 min in rapid thermal annealing (RTA). In addition, annealed at 900ºC Cu_2O thin films were post growth annealed at 550ºC 2 hr in oxygen partial pressure (2E-5 Torr) to tune the electrical and optical properties of thin films [1, 11-13]. Table 1 presents the different sputter-deposited Cu_2O thin film samples that were prepared and analyzed in this work [23,24].

Table 1. Sample name and corresponding preparation conditions for the sputter deposited Cu_2O thin films

Sample name	Cu_2O thin film preparation conditions
Sample 1	Cu_2O thin film of 200 nm thickness deposited on quartz substrate at 400^{o}C
Sample 2	Cu_2O thin film of 500 nm thickness deposited on quartz substrate at 400^{o}C, and annealed at 900^{o}C
Sample 3	Cu_2O thin film of 200 nm thickness deposited on quartz substrate at 400^{o}C, and annealed at 900^{o}C

Photoluminescence excitation and emission of the Cu_2O thin films were investigated by the Nanolog 3 spectrofluorometer, Horiba Jobin-Yvon. For the FTIR spectroscopy measurements, a Perkin Elmer Spectrum 100 FT-IR Spectrometer was used, in the wave number range 2000 cm^{-1} to 400 cm^{-1}. The optical transmission properties of the Cu_2O films were determined from ultraviolet–visible spectrophotometer measurements (Shimadzu SolidSpe-3700 DUV) in the wavelength range from 290 to 1500 nm. The thin film thickness and complex refractive index were determined by spectroscopic ellipsometry, using an UVISEL ellipsometer from HORIBA Jobin Yvon in the wavelength range from 190 to 2100 nm.

A model fit to the measured ellipsometry parameters was made using DeltaPsi ver. 2.6 software.

3. Results

3.1. Fourier-transform infrared spectroscopy

The FTIR transmission spectra for Sample 1 and Sample 2 are shown in Figure 1 and 2, respectively. The peaks of CuO noticed at 558 cm^{-1} for Sample 1, and 560 cm^{-1} for Sample 2 could be explained by the oxidation of Cu_2O with peaks at 615 cm^{-1} for Sample 1, and 614 cm^{-1} for Sample 2. Thus, a small amount of Cu_2O at the interface of the quartz substrate was transformed in CuO. There is no major difference between the recorded FTIR transmission spectra for the as-grown and annealed Cu_2O films deposited on quartz, which suggests that the film is stoichiometry-stable when heated to 900°C at a pressure of 0.1 Torr, i.e., the annealing process does not cause a transition to the more oxygen-rich phases.

Fig. 1. FTIR spectrum for as-grown Cu_2O thin film – Sample 1, 200 nm on quartz substrate°C.

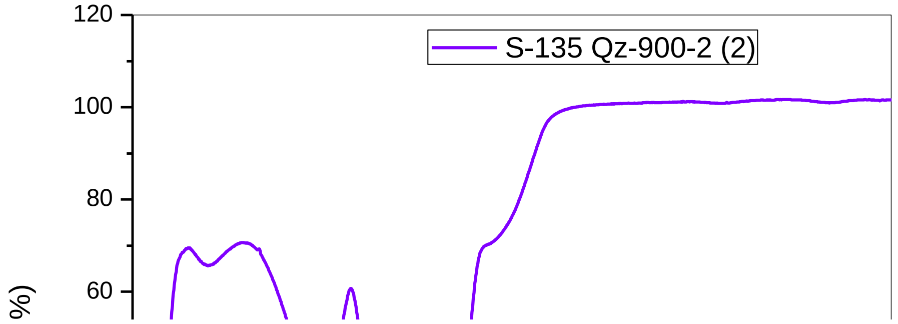

Fig. 2. FTIR spectrum for Cu_2O thin film – Sample 2, 500 nm on quartz substrate, annealed at 900°C.

3.2. Spectrofluorometry

Fluorescence spectroscopy is primarily concerned with electronic and vibrational states. In emission fluorescence measurement, the excitation wavelength is fixed and the detection wavelength varies, while in fluorescence excitation measurement the detection wavelength is fixed and the excitation wavelength is varied across a region of interest.

Filters and monochromators may be used in fluorimeters.

As it is found in literature, Cu_2O in nanoparticle or nanocube structure can have a broad emission band between 350-600 nm (with maxima centered at about 410 nm, 450 nm and/or 490 nm) with 326 nm or with 360 nm excitation [14, 15, 28].

Figure 3 and 4 show the emission spectra for Sample 1 and 3, respectively. For Sample 1, the luminescent emission band extends between 380-540 nm with two maxima at ~ 417 and 437 nm.

A 399 nm filter was used to cut the excitation influence on emission spectrum for Sample 1.

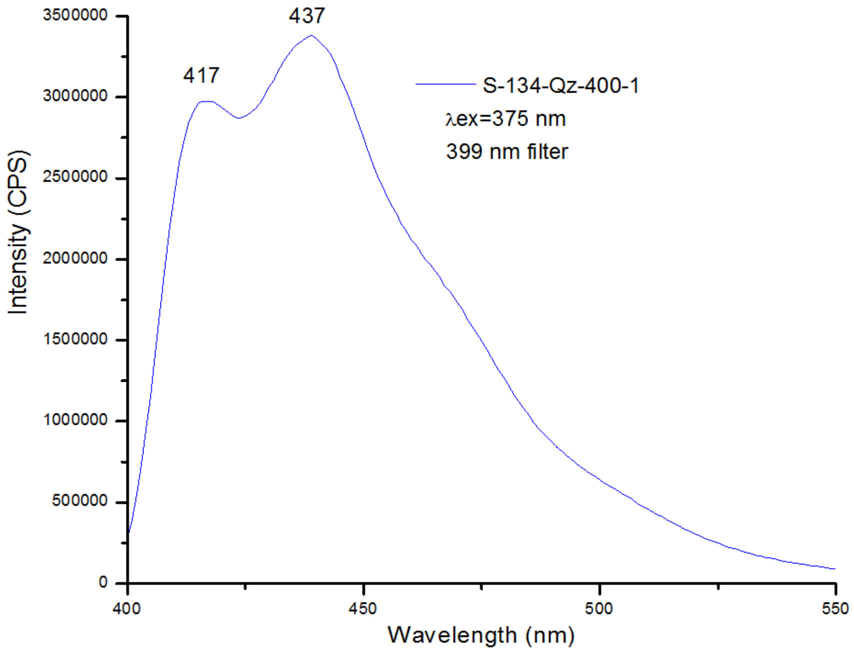

Fig. 3. Emission spectrum for Sample 1, with 375 nm excitation and 399 nm filter.

For Sample 3, only a narrow luminescent peak was registered at 380 nm, using a 326 nm excitation. A 370 nm filter was used to cut the excitation influence on emission spectrum for Sample 3.

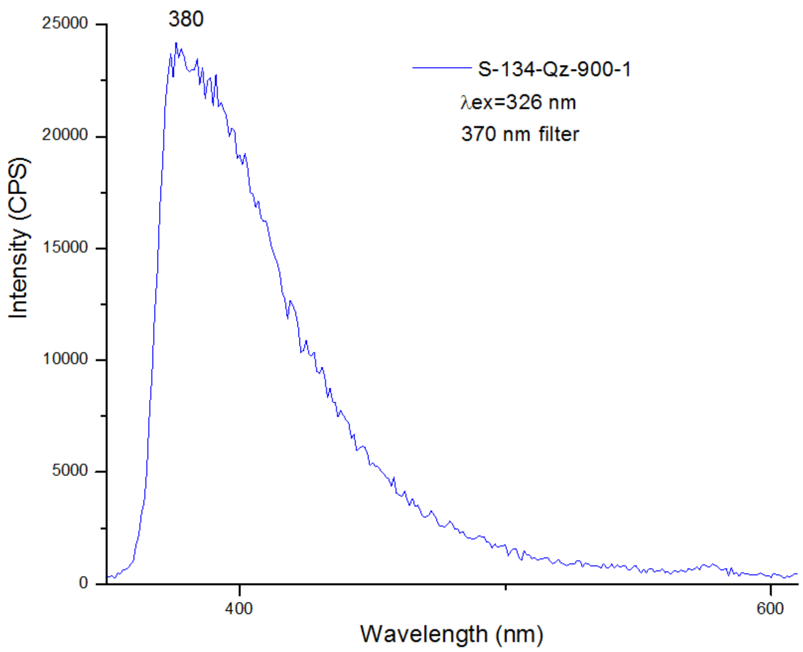

Fig. 4. Emission spectrum for Sample 3, with 326 nm excitation and 370 nm filter.

3.3. Optical analysis

The optical characteristics of the Cu_2O samples were simulated using OPAL2 software.

Figure 5a presents the optical transmittance spectra for a 500 nm thick as-grownand annealed Cu_2O thin films on quartz.

Based on the measured transmittance spectra, a Tauc plot analysis was performed in order to determine the optical band gap of the Cu_2O thin films [16, 17].

The Tauc plots are presented in Figure 5b, suggesting that the optical band gap is increased from E_g = 2.06 eV for the as-grown Cu_2O film) to E_g = 2.19 eV after annealing.

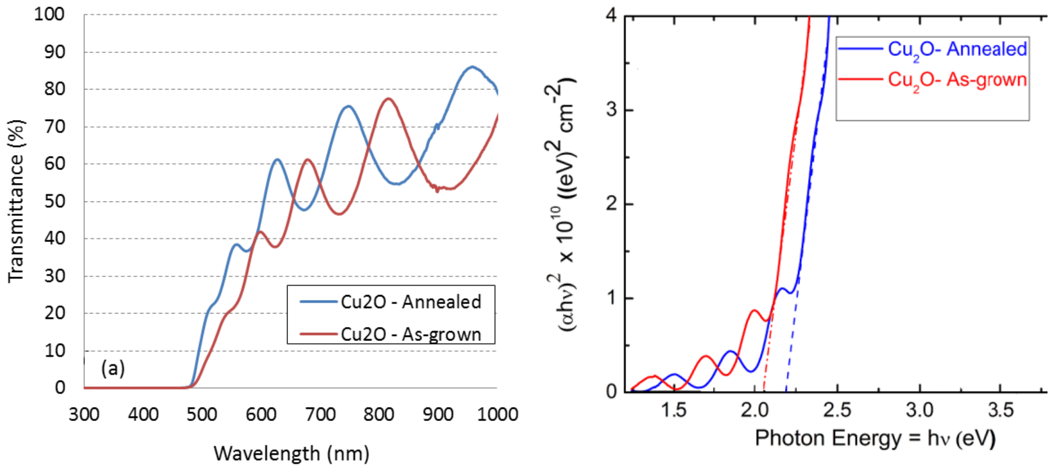

Fig. 5. (a) Optical transmittance spectra and (b) Tauc plot for the as-grown and annealed Cu_2O thin films deposited on quartz.

The widening of the optical band gap after annealing at 900°C might be due to partial elimination of defects states [16] and more phase-pure Cu_2O films with negligible contribution of the CuO phase.

For the metal oxide simulation (ZnO/Cu_2O), an 80 nm thick front Al:ZnO (AZO) layer, a 2 µm thick Cu_2O layer, and a 75 nm thick bottom AZO layer (transparent conductive oxide) were implemented in the model.

The calculated spectral reflectance, absorptance, and transmittance as a function of wavelength for the ZnO/Cu_2O subcell of a c-Si tandem cell [1, 2] are shown in Figure 6.

The complex refractive indices for the AZO and Cu_2O layers were obtained from spectrometric ellipsometry measurements and implemented in the optical analysis [1, 27].

The absorber layer thickness of 2 μm was chosen mainly due to experimental constraints, i.e. the experimentally feasible thickness range is typically a few micrometers as a result of the relatively low deposition rate for the sputtered Cu_2O thin film [2].

The calculated curves from Figure 6 suggest that photons are absorbed in the top ZnO/Cu_2O subcell in the wavelength range below ~600 nm and transmitted in the wavelength range above ~600 nm.

The average optical reflection for the ZnO/Cu_2O subcell is about 10 % in the wavelength range from 300 – 1100 nm, suggesting that there are opportunities to enhance the optical characteristics.

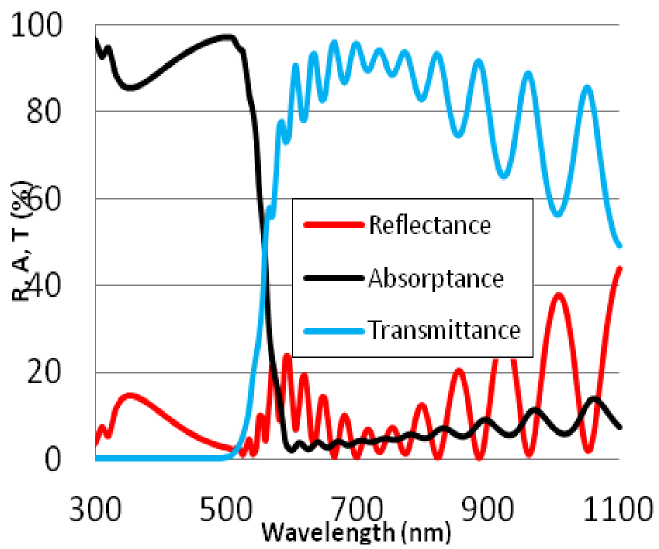

Fig. 6. Percentage reflectance, absorptance and transmittance as a function of wavelength for the ZnO/Cu_2O subcell [2].

4. Conclusions

FTIR spectra for Cu_2O thin films deposited on quartz show peaks of CuO noticed at 558 cm^{-1} for Sample 1, and 560 cm^{-1} for Sample 2 which could be explained by the oxidation of Cu_2O with peaks at 615 cm^{-1} for Sample 1, and 614 cm^{-1} for Sample 2.

Thus, a small amount of Cu_2O at the interface of the quartz substrate was transformed in CuO.

For copper oxide thin film of 200 nm thickness deposited on quartz substrate at 400 ºC the luminescent emission band extends between 380-540 nm with two maxima at ~ 417 and 437 nm, and the sample annealed at 900ºC presents one peak at 380 nm.

The experimental results obtainded via spectrofluorometry are in very good agreement with the literature[24].

The optical characteristics of the AZO/Cu_2O subcell were analyzed and the simulated results allow for a detailed knowledge of the implementation of Cu_2O as an absorber layer in tandem solar cells.

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REFERENCES

[1] Ø. Nordseth, R. Kumar, K. Bergum, L. Fara, S. E. Foss, H. Haug, F. Dragan, D. Craciunescu, P. Sterian, I. Chilibon, C. Vasiliu, L. Baschir, D. Savastru, E. Monakhov, B. G. Svensson. Optical Analysis of a ZnO/Cu2O Subcell in a Silicon-Based Tandem Heterojunction Solar Cell, Green and Sustainable Chemistry 7 (**2017**) 57-69.

[2] Ø. Nordseth, R. Kumar, K. Bergum, L. Fara, S. E. Foss, H. Haug, C. Dumitru, V. Muscurel, F. Dragan, D. Craciunescu, P. Sterian, I. Chilibon, C. Vasiliu, L. Baschir, D. Savastru, E. Monakhov, B. G. Svensson. Electro-Optical Modeling of a ZnO/Cu2O Subcell in a Silicon-Based Tandem Heterojunction Solar Cell. 33rd European Photovoltaic Solar Energy Conference and Exhibition, session 1CV.3.85, (**2017**) 172–177.

[3] Y. Takiguchi, S. Miyajima. Device simulation of cuprous oxide heterojunction solar cells, Jpn. J. Appl. Phys. 54 (**2015**) 112303.

[4] R. Mitroi, V. Ninulescu, L. Fara. Tandem solar cells based on Cu2O and c-Si subcells in parallel configuration: numerical simulation, International Journal of Photoenergy 2017 (**2017**) 7284367.

[5] R. Mitroi, V. Ninulescu, L. Fara. Perfomance optimization of solar cells based on heterojunctions with Cu2O: numerical analysis. Journal of Energy Engineering 143(4) (**2017**) 04017005.

[6] L. Fara, M. Yamaguchi. Advanced Solar Cell Materials, Technology, Modeling, and Simulation. IGI Global Publishing House, Hershey (2013).

[7] B. G. Svensson, S. J. Pearton, C. Jagadish. Oxide Semiconductors, Semiconductors and Semimetals. Elsevier & Academic Press, Amsterdam, 88 (**2013**)

[8] F. Drăgan, L. Fara, P. Sterian, D. Crăciunescu, C. Dumitru. Colored building integrated photovoltaic systems based on DSSC and metal oxides solar cells, Symposium “Energy and environment in contemporary context”, ROMEXPO, Bucharest (**2017**)

[9] Shockley, W. and Queisser, H.J. (**1961**) Detailed Balance Limit of Efficiency of PN Junction Solar Cells. Journal of Applied Physics, 32, 510-519.

[10] F. Drăgan, A. Badea, L. Fara. Modeling and simulation of optical characteristics in a textured a-Si thin film solar cell using the transfer matrix method. Annals of Academy of Romanian Scientists, series on Science Information, vol 10, no 1, pp 15-24, **2017**.

[11] T. Minami, Y. Nishi, T. Miyata , “Efficiency enhancement using a $Zn_{1-x}Ge_x$ -O thin film as an n-type window layer in Cu_2O-based heterojunction solar cells”, in Appl. Phys. Express **9**, 052301, **2016**.

[12] Bergum, Kristin, Heine Nygard Riise, Sandeep Gorantla, Per Lindberg, Ingvild Julie Thue Jensen, Anette Gunnaes, Augustinas Galeckas, Spyros Diplas, Bengt Svensson, and Edouard Monakhov. "Improving carrier transport in Cu_2O thin films by rapid thermal annealing." Journal of Physics: Condensed Matter (**2018**).

[13] Svensson, B.G., Pearton, S.J. and Jagadish, C. (**2013**) Oxide Semiconductors, Semiconductors and Semimetals. Vol. 88, Elsevier & Academic Press, Amsterdam.

[14] Z Yang, C-KChiang and H-T Chang, Nanotechnology 19 (**2008**) 025604.

[15] Katelyn Ann Cohen, Thesis at Dickinson College Dickinson Scholar **2012**

[16] J. Gan, V. Venkatachalapathy, B. G. Svensson and E. V. Monakhov, “Influence of Target Power on Properties of CuxO Thin Films Prepared by Reactive Radio Frequency Magnetron Sputtering”. Thin Solid Films 594 (**2015**) 250-255.

[17] Y. Wang, P. Miska, D. Pilloud, D. Horwat, F. Mücklich and J. F. Pierson, “Transmittance enhancement and optical band gap widening of Cu2O thin films after air annealing”. J. Appl. Phys. 115 (**2014**) 073505.

[18] Popescu IM. Aplicaţii ale laserilor. Editura Tehnică; **1979**.

[19] Collaboration, LAGUNA-LBNO, et al.The LBNO long-baseline oscillation sensitivities with two conventional neutrino beams at different baselines. arXiv preprint arXiv:1412.0804. **2014** Dec 2.

[20] Dima, M., et al. Classical and quantum communications in grid computing. Optoelectronics and Advanced Materials, Rapid Communications. **2010** Nov 1;4(11):1840-3.

[21] Stefanescu, E., et al. Study on the fermion systems coupled by electric dipol interaction with the free electromagnetic field. In Advanced Laser Technologies 2004 **2005** Jun 7 (Vol. 5850, pp. 160-166). International Society for Optics and Photonics.

[22] POPESCU, D., et al. FDTD analysis of photonic crystals with square and hexagonal symmetry. Journal of Advanced Research in Physics. 2012 Jan 24;2(2).

[23] Popescu, II., et al. The Photon Wave Function and the Fresnel Formulas. Romanian Reports in Physics. **2010** Jan 1;62(2):360-8.

[24] Sterian PE. Fotonica. Printech; **2000**.

[25] Iordache, Dan-Alexandru, et al. Complex computer simulations, numerical artifacts, and numerical phenomena. International Journal of Computers Communications & Control. **2010** Dec 1;5(5):744-54.

[26] Fara, S., et al. New results in optical modelling of quantum well solar cells. International Journal of Photoenergy. 2012; **2012**.

[27] Iordache, D.A., et al. Charge coupled devices as particle detectors. Advances in High Energy Physics. 2013;2013.

[28] FAZACAŞ A, Sterian P. Propagation of the Raman soliton in optical fibers. Romanian Reports in Physics. **2013**; 65(4):1420-30.