CHARACTERIZATION OF Cu₂O THIN FILMS USED IN SOLAR CELLS BY FLUORESCENCE AND FTIR SPECTROSCOPY

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Abstract: In this work Cu₂O thin films from a ZnO/Cu₂O solar cell, were prepared by magnetron sputtering and characterized by Fourier-transform infrared spectroscopy (FTIR) and spectrofluorometry analysis. FTIR spectrum shows peaks of CuO at the interface of the quartz substrate from oxidation. Fluorescence spectroscopy of the sample annealed at 900°C showed one narrow peak at 380 nm in the emission band. OPAL2 software was used to model the optical characteristics of the Cu₂O films and the ZnO/Cu₂O 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 (Cu₂O) [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 Cu₂O 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$_2$O 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$_2$O thin films were deposited on 10 × 10 × 0.5 mm$^3$ quartz substrates by reactive DC magnetron sputtering (Semicore Triaxis) at 400 °C 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$_2$O thin films were annealed at 900 °C for 3 min in rapid thermal annealing (RTA). In addition, annealed at 900°C Cu$_2$O thin films were post growth annealed at 550°C 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$_2$O thin film samples that were prepared and analyzed in this work [23,24].

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Cu$_2$O thin film preparation conditions</th>
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<tbody>
<tr>
<td>Sample 1</td>
<td>Cu$_2$O thin film of 200 nm thickness deposited on quartz substrate at 400°C</td>
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<tr>
<td>Sample 2</td>
<td>Cu$_2$O thin film of 500 nm thickness deposited on quartz substrate at 400°C, and annealed at 900°C</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Cu$_2$O thin film of 200 nm thickness deposited on quartz substrate at 400°C, and annealed at 900°C</td>
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</table>

Photoluminescence excitation and emission of the Cu$_2$O 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$_2$O films were determined from
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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$_2$O with peaks at 615 cm$^{-1}$ for Sample 1, and 614 cm$^{-1}$ for Sample 2. Thus, a small amount of Cu$_2$O 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$_2$O 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$_2$O thin film – Sample 1, 200 nm on quartz substrate°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$_2$O 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.
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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$_2$O samples were simulated using OPAL2 software.

Figure 5a presents the optical transmittance spectra for a 500 nm thick as-grown and annealed Cu$_2$O 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$_2$O 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$_2$O 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$_2$O thin films deposited on quartz.](image)

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$_2$O films with negligible contribution of the CuO phase.

For the metal oxide simulation (ZnO/Cu$_2$O), an 80 nm thick front Al:ZnO (AZO) layer, a 2 μm thick Cu$_2$O 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$_2$O subcell of a c-Si tandem cell [1, 2] are shown in Figure 6.

The complex refractive indices for the AZO and Cu$_2$O 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$_2$O thin film [2].

The calculated curves from Figure 6 suggest that photons are absorbed in the top ZnO/Cu$_2$O 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$_2$O subcell is about 10 % in the wavelength range from 300 – 1100 nm, suggesting that there are opportunities to enhance the optical characteristics.

![Figure 6](image)

**Fig. 6.** Percentage reflectance, absorptance and transmittance as a function of wavelength for the ZnO/Cu$_2$O subcell [2].

4. Conclusions

FTIR spectra for Cu$_2$O 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$_2$O with peaks at 615 cm$^{-1}$ for Sample 1, and 614 cm$^{-1}$ for Sample 2.

Thus, a small amount of Cu$_2$O 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 obtained via spectrofluorometry are in very good agreement with the literature[24].

The optical characteristics of the AZO/Cu$_2$O subcell were analyzed and the simulated results allow for a detailed knowledge of the implementation of Cu$_2$O as an absorber layer in tandem solar cells.

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