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STRUCTURAL AND ELECTRICAL ANALYSIS OF CU_2O LAYERS FOR SOLAR CELL APPLICATION

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Abstract: In this work the structural and electrical properties of the Cu_2O layer of a metal oxide solar cell were investigated. Cu_2O films were synthesized by reactive direct current magnetron sputtering on quartz substrates and characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM) and Hall effect measurements. The grain size and surface roughness have important implications for the optical and electrical performance of the Cu_2O layer. The SEM analysis revealed an increase in grain size in the sample treated with rapid thermal annealing at 900 ºC. AFM analysis shows that the high thermal annealing increases the surface roughness by a factor of 10. The electrical properties of the Cu_2O film are enhanced after annealing at 900 °C.

1. Introduction

Research on silicon-based tandem heterojunction solar cells (STHSC) with metal oxides is valuable towards the development of high performance solar cells. The semiconducting metal oxides in the ZnO/Cu_2O heterojunction have a great perspective in research due to their convenient characteristics. Cu_2O is abundant, non-toxic and has a low production cost. High optical absorptance in the UV and visual wavelength range combined with a theoretical conversion efficiency close to 20% makes Cu_2O a promising candidate to use in a tandem heterojunction solar cell design. The current state of the art efficiency on a ZnO/Cu_2O heterojunction solar cell is reported at 8% with the potential to attain 14%, which implies that there is room for improvement and further research in order to optimize metal oxide implementation in tandem solar cells. Scanning-probe methods can provide valuable information on the structure of the material implemented in the solar cell design. Atomic force microscopy and scanning electron microscopy represent essential tools for the characterization and optimization of active and passive layers [1,2, 29-32]. Beside layer topography, AFM can probe electrical properties such as

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the localized photocurrents, variation in conductivity and contact potential. In principle, the force between the nano-scaled probe and the sample is maintained via an electronic feedback when scanning and that signal is characterizing the surface topography with an accuracy under 1 nm. If required, further material parameters can be analyzed via electrical operation modes, being elaborated more sophisticated theoretical models at atomic or subatomic level. [3, 4, 23-27]. Conductance mode requires a conductive tip in perpetual contact with the sample material and the electrical current between the tip and sample together with the movement of the cantilever that holds the tip, can be used as measurement signals. In contact potential mode, the tip becomes a Kelvin probe that measures the local surface potential difference between the tip and sample with an atom level resolution, which depends on surface and dopant charge and polarization effects or work function (metallic substrate). SEM can quickly and easily study the morphology of the layer material at 2D high resolution, due to backscattered and secondary electrons collected from the sample surface. Furthermore, Auger electrons, X-ray Fluorescence photons and other signals can be collected from the sample material with valuable use in material science. Crystallinity, nano-crystallinity, uniformity and even defect localization can be observed with SEM implementation.

The objective of this work is to analyze the Cu_2O absorber layer material of a ZnO/Cu_2O heterojunction solar cell [5-12, 28] used in a c-Si based tandem design, utilizing SEM and AFM methods. Mapping the topography using SEM and AFM can be correlated with electrical parameters towards further device optimization [13-21], since the optical and electrical properties of the solar cells are in correlation with the surface characteristics.

2. Experimental details

The Cu_2O thin film samples 1×1 cm^2 with thickness of approximately 500 nm were deposited on $10 \times 10 \times 0.5$ mm^3 quartz substrates using a DC/RF direct current/radio frequency magnetron sputtering Semicore Triaxis system. The procedure on quartz substrate cleaning used a Piranha solution, sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2), deionized water for rinsing and a nitrogen flow for drying. The deposition was done via reactive sputtering from a 99.999% Cu target in an atmosphere of Ar/O_2 of 6/39 sccm (cm^3/min) with the substrate at 400 ^{o}C and using 100 W of fixed power. The pre-sputtering time was 10 min to avoid any contamination. The as-grown films were annealed at 900^{o}C for 3 min in rapid thermal annealing (RTA) and after that post growth annealed at 550 ^{o}C for 2 hours in oxygen partial pressure with 2E-5 Torr. Table 1 presents the two different sputter-deposited Cu_2O thin film samples that were prepared and analyzed in this work. 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.

Hall effect measurements at room temperature were performed using a LakeShore 7604 system with the van-der Pauw configuration, in order to determine the carrier mobility, resistivity, and carrier concentration of the Cu_2O thin films. Layer morphology was investigated with a Quanta Inspect F 50 scanning electron microscope and an Innova Atomic Force Microscope.

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

Sample name	**Copper oxide thin films characteristics**
Sample 1	Copper oxide thin film of 500 nm thickness deposited on quartz substrate at 400^{o}C
Sample 2	Copper oxide thin film of 500 nm thickness deposited on quartz substrate at 400 ^{o}C, and annealed at 900^{o}C (3 min) and 550^{o}C (2 hours)

3. Results

3.1. Scanning electron microscopy

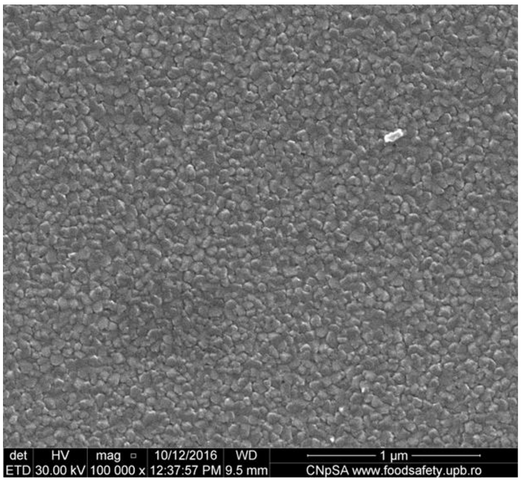

Fig. 1. SEM image of 200 nm *Sample 1* 100000×; 1 μm scale bar.

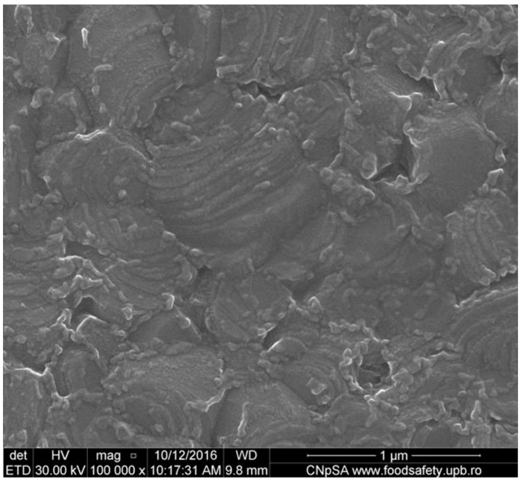

Fig. 2. SEM images of 200 nm *Sample 2*, 100000×; 1 μm scale bar.

SEM images of Sample 1 and Sample 2 are shown in Figure 1 and Figure 2, respectively. The SEM images show an increase in grain size as a consequence of annealing the Cu_2O thin films. The average grain size increases from about 60-70 nm for the as-grown film (Sample 1) to about 600-700 nm after annealing. In general, for thin-film optical applications it is desirable to have a columnar grain structure with a lateral grain size that is larger than the thickness of the thin film. The optical transmittance spectra for the Cu_2O films (data not shown) suggest that the transmittance properties are enhanced in the visible and near-infrared wavelength range after the annealing process. This is likely due to the larger grain size and a corresponding reduction of grain-boundary scattering, possibly together with a less strained film.

3.2. Atomic force microscopy

Atomic Force Microscopy (AFM) provides accurate, high-resolution imaging, with a resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The major difference between AFM and competing technologies such as optical microscopy and electron microscopy is that AFM does not use lenses or beam irradiation.

The root-mean square surface roughness (R_{RMS}) for each sample was extracted from the AFM images. R_{RMS} is defined as the standard deviation of the surface height profile (h_i) from the mean height ($\langle h \rangle$), given by (1).

$$R_{RMS} = \left[\frac{1}{N} \sum_{n-1}^{n} \left(h_i - \langle h \rangle \right)^2 \right]^{\frac{1}{2}} \tag{1}$$

AFM analysis allows quantitative information to be extracted on surface roughness. A systematic description of various analytical methods used for roughness characterization can be found in [21-23, 33]. We analysed Sample 1 and Sample 2 and the corresponding AFM - 3D images (10 µm × 10 µm) are presented in figures 3 and 4, respectively. The AFM analysis suggests that the R_{RMS} increases from 1.58 nm for the as-grown film (Sample 1) to 15.65 nm for the annealed film (Sample 2)

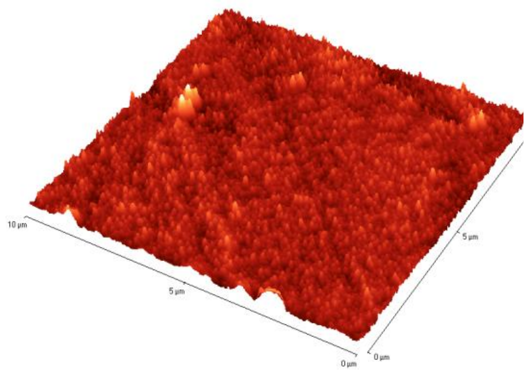

Fig. 3. AFM - 3D image, *Sample 1*, R_{RMS} = 1.58 nm.

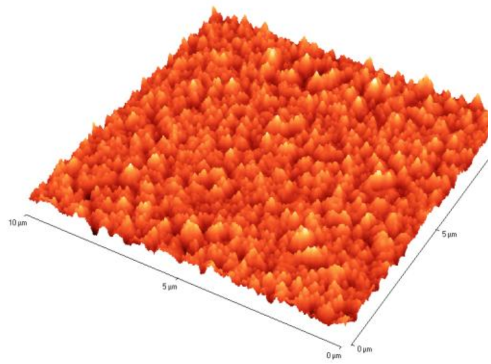

Fig. 4. AFM - 3D image, *Sample 2*, R_{RMS} = 15.65 nm.

3.3. Electrical properties

The majority carrier (hole) mobility, film resistivity, and majority carrier concentration for the as-grown (Sample 1) and annealed (Sample 2) Cu_2O film on quartz, derived from room temperature Hall effect measurements, are presented in Table 2. The data suggests that the electrical properties were enhanced after rapid thermal annealing at 900 ˚C.

Table 2. Majority carrier (hole) mobility, film resistivity, and majority carrier concentration for the as-grown (Sample 1) and annealed (Sample 2) Cu_2O films on quartz

Sample name	**Mobility (cm^2/V·s)**	**Resistivity (Ohm·cm)**	**Concentration (cm^{-3})**
Sample 1	14	193	2.3e15
Sample 2	49	218	5.0e14

3. Conclusions

SEM images revealed an increase in grain size when annealing the Cu_2O thin films at 900 ^oC. This results in enhanced transmittance properties in the visible and near-infrared wavelength range. AFM measurements allowed extracting quantitative information on the surface roughness (R_{RMS}) of the samples and it was observed that the surface roughness increased approximately 10 times for the sample that was subjected to an annealing process at 900 ^oC. Furthermore, Hall effect measurements show that the electrical properties of the Cu_2O film are improved after annealing at 900^oC.

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