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ANALYSIS OF CHEMICAL AND PHASE COMPOSITION
OF COPPER OXIDE PREPARED BY DIRECT CURRENT SPUTTERING
FOR PHOTOVOLTAIC APPLICATIONS

Paulina Sawicka-Chudy¹, Marek Wielgosz², Andrzej Wal³, Bogumil Cieniek², Grzegorz Wisz⁴,
Łukasz Głów⁴, Marian Cholewa⁴, Joanna Sawicka⁴

Abstract
This paper presents the application of X-ray fluorescence and X-ray diffraction methods for the study of copper oxide structures as an absorber layer in thin-film solar cells. The layers of copper oxide were applied by direct current magnetron sputtering. Quantitative and qualitative analysis of oxide layers were performed using XRF (X-ray fluorescence). The studies showed a high copper content in both samples, amounting to 98% and 96%, as well as trace amounts of other elements (nickel, lead). The XRD (X-ray diffraction) study showed Cu₂O and Cu₄O phases, amorphism ranging from 24% to 44%, and crystallinity from 55% to 75%. Crystallites of 30 nm were also determined. The aim of the study was to determine the chemical and phase composition of the layers obtained and to determine the degree of their contamination depending on the parameters of the manufacturing technology in terms of their application in photovoltaics. One of the samples showed an advantage both in terms of material and structural composition.

Keywords: XRF, XRD, copper oxide, photovoltaics

Introduction
Copper (II) oxide, (CuO), and copper (I) oxide, (Cu₄O), are materials with semiconductor properties, which are characterized by a p-type semiconductor, with a simple energy interruption (about 1.4 eV for CuO and about 2.2 eV for Cu₄O). Differences in the gap value result from the construction of the crystalline structure (Korkmaz et al. 2016, p. 142; Serin et al. 2005, p. 398). Scientists use many techniques to produce a copper oxides. These include the PLD (Pulse laser deposition) method (Chen et al. 2009, p. 927), magnetron atomization (Sawicka-Chudy et al. 2018, p. 715), or chemical methods (Markworth et al. 2001, p. 2408). The authors decided to verify the parameters of the Cu₂O obtained by DC magnetron sputtering in order to improve the efficiency of the heterojunction based on copper oxide as an absorber in the structure of thin-film solar cells. The aim of the study was to determine the chemical and phase composition of the layers obtained and to determine the degree of their contamination depending on the parameters of the manufacturing technology in terms of their application in photovoltaics.

Sample preparation and test methodology

Series Cu₂O thin film was deposited by DC magnetron sputtering using a modular PREVAC platform. N-type Si (100) wafers and glass slides were used as the substrate materials with dimensions of 5x4 and 6x5 mm, respectively. CuO layers were deposited in an Ar (99.9999%) and O₂ (99.999%) mixed atmosphere in different process parameters from a Cu target. The chamber was cleaned thermally before the experiment and the base pressure of the

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vacuum system was $1 \cdot 10^{-3}$ Pa. They were selected on the basis of earlier studies and numerical simulations (Sawicka-Chudy et al. 2018, p. 715; Sawicka-Chudy 2017, p. 71).

The authors present representative layers (P1, P2) from the series. The process parameters are shown in Table 1.

**Table 1. Process parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P1</th>
<th>P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>The distance between the source and substrate [mm]</td>
<td>38</td>
<td>58</td>
</tr>
<tr>
<td>Pressure process [Pa]</td>
<td>1.73</td>
<td>2.5</td>
</tr>
<tr>
<td>Power [W]</td>
<td>~80</td>
<td>~70</td>
</tr>
<tr>
<td>Time [min]</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Oxygen flow rates [cm$^3$/s]</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Argon flow rates [cm$^3$/s]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Substrate temperature [K]</td>
<td>473.15</td>
<td>473.15</td>
</tr>
</tbody>
</table>

In order to determine the chemical composition of the layers, the XRF method was applied. The measurements were made with a Thermo spectrometer type ARL QUANT’X EDXRF Analyzer. To determine the phase composition, the XRD method was applied using a D8 Advance diffractometer with CuKα radiation ($\alpha$ mean = 1.54178 Å) at a constant X-ray tube current of 40kV and 40mA. Peak dilatation and Scherrer’s formula were used to determine the average size of crystallites of compounds.

For the determination of elements, the modelless method was implemented in Uni-Quant ED software. The software records the spectra obtained for different radiation energies and, on the basis of the model, determines the elemental composition that best matches the results obtained. The range of elements detected by the spectrometer starts with fluorine and ends with uranium. In the next stage of the work, the structures of the analyzed oxide layers were examined using X-ray diffraction. The XRD measurement was carried out in coupled theta/2theta mode. The ICDD PDF-2 2012 database was used for Phase Matching.

**Results and discussion**

XRF analysis of layers

In the case of both samples, due to the low layer thickness (about 220 nm), a signal from the emission of silicon was also obtained. Examples of XRF spectra for both layers at 20 kV X-ray energy are shown in Fig. 1a-1b (for sample P1) and Fig. 1c-1d (for sample P2). The average results obtained from the whole measurement are collected in Table 2. On their basis, it can be concluded that the layer contains only a few traces of metals other than copper.
Figure 1a. Spectrum of elemental composition of the examined micro-area, layer on glass, sample P1

Figure 1b. Spectrum of elemental composition of the examined micro-area, layer on silicon, sample P1

Figure 1c. Spectrum of elemental composition of the examined micro-area, layer on glass, sample P2
Figure 1d. Spectrum of elemental composition of the micro-area under investigation, layer on silicon, sample P2

Table 2. Percentage analysis of the composition of copper oxide layers deposited on silicon

<table>
<thead>
<tr>
<th>Determined element</th>
<th>Content by quantitative analysis XRF [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P1</td>
</tr>
<tr>
<td>Cu</td>
<td>98.94</td>
</tr>
<tr>
<td>Ni</td>
<td>1.020</td>
</tr>
<tr>
<td>Pb</td>
<td>0.030</td>
</tr>
<tr>
<td>Pn</td>
<td>0.010</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
</tr>
</tbody>
</table>

A quantitative analysis study showed a high copper content in both samples, 98% and 96%, as well as trace amounts of other elements such as nickel and lead. Despite the fact that the samples were produced by the same method and only the parameters of the apparatus changed, the quantitative composition of the elements differs significantly.

**XRD analysis of layers**

Figures 2 and 3 show the XRD spectra obtained in the studies of copper oxides on the glass substrate (a), and the silicon substrate (b).
Figure 2. XRD spectra for Cu₂O samples deposited on glass

Figure 3. XRD spectra for Cu₄O samples deposited on silicon

As the XRD diffraction graphs show, the structures differed significantly, indicating the influence of the preparation method. On the basis of the position of the diffraction line, it was found that they originated from phases Cu₂O and Cu₄O. Several researchers also reported Cu₄O in their study (Yonglong 2014; Guan, Hashimoto, Kuo 1984). Table 3 shows the phases detected, grain size, and the crystallinity and amorphicity of the samples.

Table 3. Parameters obtained during the XRD test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal direction</th>
<th>Grain size</th>
<th>Crystalline</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (glass)</td>
<td>Cu₂O, Cu₄O</td>
<td>-</td>
<td>75.8%</td>
<td>24.2%</td>
</tr>
<tr>
<td>P1 (silicon)</td>
<td>Cu₂O</td>
<td>-</td>
<td>70.2%</td>
<td>29.8%</td>
</tr>
<tr>
<td>P2 (glass)</td>
<td>Cu₄O</td>
<td>31.8 nm</td>
<td>69.8%</td>
<td>30.2%</td>
</tr>
<tr>
<td>P2 (silicon)</td>
<td>Cu₄O</td>
<td>28.0 nm</td>
<td>55.7%</td>
<td>44.3%</td>
</tr>
</tbody>
</table>
For sample P1 it was not possible to measure the grain size, due to the combination of reflections from different phases. Higher crystallinity values were obtained on glass, but on silicon a more homogeneous layer was obtained. At the same time it can be stated that sample P1 in both measuring systems shows a higher content of crystalline structure in relation to amorphous structure, which is very important in the construction of solar cells.

**Conclusion**

The paper presents the results of investigations of two layers of copper oxide prepared by direct current magnetron sputtering. The chemical and phase composition of the obtained layers was analyzed in order to improve the efficiency of the heterojunction based on Cu$_2$O as an absorber layer. The measurement results of fluorescence spectra (quantitative analysis) give the main element as copper for P1 and P2 at 98% and 96% respectively. However, this analysis also showed traces of other elements. The XRD test showed the dominant phase of Cu$_2$O for P1 sample and its higher crystallinity for both types of substrates. Considering the sum of the results obtained, the advantage of the P1 sample in terms of both material composition and structure should be confirmed. For this reason, the important parameters of the magnetron application process for Cu$_2$O layers are high purity in the working chamber (lower pressure), and lower oxygen content. It also seems essential to choose the right distance between the material source and the layer to be deposited, which reduces the number of defects that occur.

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Bibliography


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