Thermal vacuum evaporation of thin Cu(I)Br films for photovoltaic application

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Abstract. In the present study, thermally evaporated thin copper (I) bromide films were investigated as a potential hole-transport material for hybrid perovskite solar cells in a standard configuration. The films were deposited on top of glass substrates; the measured transparency was 80 %. The structural and morphological analyses revealed a dense polycrystalline structure of $\gamma$-CuBr. The analysis of the surface chemical composition demonstrated that copper was in a Cu$^{1+}$ state and the films were stoichiometric. Electrical measurements were performed with deposited planar silver or copper electrodes. The layers were highly resistive; however, a current increasing with the time was observed when the samples were biased by a dc voltage of 20 V for two hours, which we speculate might be due to a possible new conduction mechanism.

1. Introduction
Copper halides are known for their mixed ionic-electronic conductivity of Cu$^+$ and holes, and have been widely studied for application in gas sensors [1, 2]. Originally, the electrical properties of these materials were thoroughly investigated in conjunction with their potential application as selective sensors for NH$_3$ gas [1]. CuBr is naturally a p-type semiconductor with hole concentration originating either from copper vacancies or oxygen impurities. More recent reports suggested that CuBr might be directly used in transparent heterojunction solar cells and a conversion efficiency of 2 % was achieved without optimization of the structure [3].

Organic-inorganic perovskite solar cells (PSC) have undergone a rapid development in recent years and have reached efficiencies up to 22 % [4]. In state-of-the-art perovskite solar cells, the planar (n-i-p) architecture is mainly used. It comprises a transparent conducting oxide (TCO), an n-type semiconductor as an electron-transport material (ETM), a CH$_3$NH$_3$PbI$_3$ perovskite active layer, a p-type semiconductor as a hole-transport material (HTM), and a metal as a back contact. For both types of architectures, planar (n-i-p), and inverted (p-i-n), organic compounds are used as HTM. For most of the efficient solar cells with a planar configuration, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) is dominantly used as the hole-transport material. However, its synthesis is complex and requires extensive purification [5], which results in a rather expensive material that compromises the commercialization of PSCs as a cost-competitive photovoltaic technology solution. In inverted p-i-n devices, PEDOT:PSS is used as HTM. It is hygroscopic and has acidic character, which leads to a degradation of the TCO and the perovskite

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active layer. Significant scientific effort has been focused on the search of suitable inorganic p-type semiconductors as a low-cost alternative HTM for PSCs. Devices using CuI in inverted cells were reported to have reached efficiencies as high as 16.8% [6]. CuBr is also a promising material for perovskite solar cells. It is an earth-abundant wide band-gap material (2.9 eV) with high transparency in the visible spectrum and can be used in inverted and in standard architecture devices. High-purity thin copper halide films are easily deposited by physical vapor deposition (PVD) techniques.

In this work we investigated the properties of thin CuBr films deposited by direct thermal evaporation from CuBr powder. Dense and uniform layers were achieved in the process of their optimization.

2. Experimental
The films studied were deposited by thermal vacuum evaporation of commercial CuBr powder on top of glass substrates. The film thickness was controlled by varying the amount of the material in the boat, while the other parameters were kept constant. The boats were covered during evaporation to eliminate the effects of thermal dissipation of the powder during glowing.

Planar silver or copper electrodes with a distance of 1.3 mm between them were deposited by RF magnetron sputtering on top of glass substrates followed by evaporation of CuBr layers on top covering the gap between the electrodes. The electrical characteristics were obtained using a Keithley 2400 SourceMeter.

Analysis of the structural properties of the films was carried out by X-ray diffraction experiments. The measurements were conducted on an XRD Brucker D8 advanced spectrometer using Cu Kα1 radiation in a θ-2θ configuration. The surface chemical composition was examined by X-ray photoelectron spectroscopy by a Kratos Axis Supra spectrometer. The radiation source was a non-monochromatic Al X-ray source. The pass energy was 160 eV for the survey scan and 2 eV for the high-resolution spectra. The positions of the lines were corrected for charging according to the position of the adventitious carbon at 285 eV. The optical properties were studied by a UV-Vis-NIR Shimadzu UV-3600 spectrophotometer.

3. Results and discussion

3.1. Structural properties, morphology, and chemical composition
At room temperature, cuprous bromide is known to crystallize in a zincblende lattice structure. Figure 1 presents XRD data for a typical thin CuBr film deposited by thermal evaporation. It is evident that the material is polycrystalline with preferential orientation along the (111) direction. The X-ray diffraction pattern indicates Bragg peaks for (111), (220), (311), and (331) reflections and is in agreement with the literature data for the γ-CuBr phase [3]. The average crystallite size was estimated by the Scherrer equation. For samples with various thicknesses, the crystallite size was between 98 ± 2 nm for the thinnest and 128 ± 3 nm for the thickest samples.

The SEM micrographs presented in figure 2 a) and b) reveal that the direct thermal evaporation results in the formation of homogeneous and dense films that follow a columnar growth. Figure 2 b) presents a cross-section of a 4-μm thick CuBr film grown in two separate runs with equal amount of material in the boat with the other parameters kept constant. Although no interface is clearly visible between the two CuBr layers grown one on top of the other, it can be seen that the columnar structure continues to grow with the same density following the growth direction.

XPS measurements were performed on some of the samples to study the chemical composition; a quantitative analysis of the surface concentrations

![Figure 1. A 0-2θ XRD scan of a CuBr film grown onto a glass substrate.](image-url)
estimated the ratio of copper to bromine to be 0.92. The position of the Cu2p photoelectron line and the CuLMM Auger line indicate that the copper is in Cu and Cu1+ states (figure 3 and figure 4, respectively). The Br3p line appears at 182.8 eV and the Br3d peak, at 69.3 eV, which are the proof for the CuBr compound. In addition, the Cu shake-up satellite feature which is characteristic for Cu(II)Br is not present at 934.7 eV. These results indicate that the evaporated layers are stoichiometric.

3.2. Optical properties
The optical properties of CuBr were studied by optical absorption spectroscopy at room temperature. The optical transmission of a relatively thick sample of a few micrometers is presented in figure 5. It shows high transparency up to the absorption edge. However, we observed changes in the absorption

![Figure 2](image1.png)

**Figure 2.** SEM a) surface image and b) cross-section of two layers deposited one on top of the other in two separate runs using the same amount of material in the boat.

![Figure 3](image2.png)

**Figure 3.** High-resolution spectrum of the Cu2p photoelectron line.

![Figure 4](image3.png)

**Figure 4.** High-resolution spectrum of the CuLMM Auger line.

![Figure 5](image4.png)

**Figure 5.** Optical transmission spectrum of a CuBr thin film.

![Figure 6](image5.png)

**Figure 6.** Tauc plot with the estimated optical band-gap. The inset shows the typical absorption spectrum of CuBr.
spectra with the time. When the samples were exposed to ambient environment, they started changing their color from transparent to whitish, which is an indicator of a possible chemical reaction with oxygen or water vapor. This would affect the stability of the solar cell, if the material were used as HTM. The optical band-gap was estimated using the Tauc plot to be 2.98 eV (figure 6). The absorption spectrum is plotted in the inset, showing the characteristic $Z_{12}$ and $Z_3$ excitons for CuBr.

3.3. Electrical properties

Two types of structures were used in order to examine the electrical properties of the as-deposited CuBr layers. Thin films were evaporated on top of Cu electrodes or on top of Ag electrodes and I-V scans were conducted in the interval from -4 V to +4 V. The CuBr layers were highly resistive and the measured resulting current was close to 5 nA at +4 V. In order to examine the layers for possible ionic conductivity, the samples were subjected to a 20-V applied voltage and the current was measured as a function of the time for two hours. The results are presented in figure 7. It can be seen that the current increases significantly with the time for both types of structures and exceeds 1.2 mA. Based on this observation, we speculate here that a new conduction mechanism has occurred. The electronic conductivity might have increased as a result of possible motion of copper ions, which might have doped the CuBr layer creating additional copper vacancies. Optical micrographs showed the onset of cathodic deposition to one side of the layer (figure 8). At the opposite electrode, no change was observed. At a larger magnification, the interface reveals the formation of a dendrite-like material (figure 9 and figure 10 for samples with Cu and Ag electrodes, respectively). These results agree with previous investigations [7], where similar experiments demonstrated that the dendrites are formed by metallic Cu, as the authors studied CuBr in a planar configuration with Au electrodes. They attributed

Figure 7. Evolution of current with time at 20 V applied dc potential.

Figure 8. Interface between CuBr and Ag electrode before (left) and after (right) applying 20 V.

Figure 9. Optical micrograph of the sample with Cu electrodes after exposure to 20 V.

Figure 10. Optical micrograph of the sample with Ag electrodes after exposure to 20 V.
this behavior to the process of electrolytic decomposition of a polar material subjected to a steady-state voltage exceeding the decomposition threshold. They observed such decomposition above a threshold of 5 V with electrode spacing of 0.25 mm. Our results confirm that ionic conductivity is present at high applied voltages even at room temperature. However, this effect would be negligible in the operating voltage range of a solar cell. Further investigations are needed to study the temperature dependence of the ionic conduction in the interval of the operating temperatures of solar cells under outdoor conditions.

4. Conclusions
Uniform stoichiometric thin Cu(I)Br films with a polycrystalline structure were successfully deposited by thermal vacuum evaporation and their properties were studied for a possible application in perovskite solar cells. The layers presented a transparency of 80 % but it was observed that the optical properties deteriorated after storage in ambient environment. This implies that if Cu(I)Br were used as HTM in perovskite solar cells, encapsulation would be required to prevent degradation of the device.

The electrical measurements showed that the samples had high resistivity; further investigations are needed in order to dope the material and achieve the desirable p-type conductivity and high hole concentration. An increase of the current with the time was observed when a 20-V bias was applied to the samples with copper or silver planar electrodes, which we attempted to relate to the properties of the evaporated CuBr film.

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