Full length article

Sputter deposition of copper oxide films

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ARTICLE INFO

Keywords:
Direct current magnetron sputtering
Copper oxide
Energy per atom
Negative ion bombardment

ABSTRACT

Copper oxide thin films are grown by reactive magnetron sputter deposition. To define the parameter space to obtain CuO films, the influence of the oxygen partial pressure, the total pressure, and the discharge current was investigated on the phase formation. A clear change from pure copper, over cuprite (Cu$_2$O), and paramelaconite (Cu$_4$O$_3$) to tenorite (CuO) thin films with increasing oxygen partial pressure was observed using X-ray diffraction and Fourier transform infrared spectroscopy. The main driving force defining the phase composition is the oxygen partial pressure, while the influence of the total pressure, and the discharge current is minimal. A clear condition to obtain phase pure CuO films could be defined based on the measured discharge voltage. Both the domain size, and the Bragg peak position for pure CuO thin films can be correlated to the negative ion bombardment during film growth.

1. Introduction

Cuprite (Cu$_2$O), paramelaconite (Cu$_4$O$_3$), and tenorite (CuO) are the three main copper oxide phases which have been widely studied because of the low production cost, the abundant availability, and the non-toxic nature of copper. Copper oxide films are applied in a broad range of applications such as the synthesis of p-type semiconductors [1, 2], solar cells [3], photocatalysis [4], spintronic devices [5], and n-nanoe energetic materials which could be an interesting source of on-board energy to produce heat [6]. In this latter application, a multilayer stack of aluminum and tenorite films are deposited which can then serve as an energy source due to a exothermic (thermite) reaction between both materials. Among the various techniques that have been used to synthesize copper oxide films [7-17], reactive magnetron sputtering [18-30] is a promising method to achieve large area coatings and high deposition rates, a better control over the physical properties of films, or the ability to work at low temperature. Several groups have demonstrated that during magnetron sputter deposition, the synthesis of single cuprite, paramelaconite, and tenorite phases can be obtained. Typical strategies are based on varying the oxygen partial pressure [2, 19, 20, 22, 24-30], the oxygen flow rate [18, 22, 24, 25, 31-34], the sputtering pressure [32, 34, 35], the oxygen to sputtering gas ratio [36-42], or the argon gas pressure at constant oxygen partial pressure [3, 42]. Also the influence of some typical deposition parameters, such as the substrate temperature, substrate bias voltage [24, 38], and the sputtering power [18], have been investigated.

These studies reveal in general that there is a good control of the film stoichiometry, but the underlying reason is less clear. Indeed, it is surprising that despite the broad range of experimental conditions the same crystalline copper oxide phases are detected, and their presence is correlated to the oxygen content in the magnetron discharge. This indicates that the formation is purely driven by the discharge chemistry, and to a less extend by the process parameters such as total pressure and discharge current. However, the addition of a reactive gas to a magnetron discharge has a dramatic impact on the process parameters, and it is well known that the film stoichiometry, microstructure [43], and texture during reactive magnetron sputtering is the result of a complex interplay between different fundamental processes such as the chemical reactions during film growth, and the mobility of the deposited atoms. Hence, the influence of the total pressure and discharge current remains an open question. To tackle this interesting problem, we use in this paper the concept of energy per arriving atom (EPA). As demonstrated quantitatively by our research group, film properties are a strong function of adatom mobility which on its turn is defined by the EPA [44-46]. The EPA can be derived from energy flux and deposition rate measurements. This simple strategy allows to convert different deposition conditions into a single parameter which permits a fast way to compare several experiments. More specific, the phase composition of deposited copper oxide films during reactive DC magnetron sputtering is investigated at different discharge currents, argon and/or total pressures. The EPA is calculated for each deposition condition, and the phase formation is evaluated as a function of the oxygen fraction and the EPA. As mentioned above, we aim in this study to clearly define the parameter space to deposit high quality CuO thin films. Therefore, also
energy-resolved mass spectrometry was used to study the ejection of negative ions from the target. Indeed, it is known that also high energy bombardment by negative ions can influence the microstructure [47], and the film texture [48, 49] of oxide thin films. This mass spectrometry study assists in narrowing down the parameter space for crystalline CuO thin films.

2. Experimental

A stainless steel cylindrical sputtering chamber of 30 cm in diameter and 70 cm in length was evacuated to a base pressure of $2 \times 10^{-4}$ Pa using a combination of a turbomolecular pump backed-up by a rotary pump having an effective pumping speed of 250 l/s. A copper target of 2 inch in diameter (Testbourne, 99.999% purity) was fixed on a home built magnetron and powered by a Hüttigler 1500 DC power supply. The substrate (single crystal (100) silicon cleaned according the RCA procedure) was placed opposite to the copper target at a perpendicular distance of 10 cm. The substrate was neither intentionally heated nor cooled. Experiments were performed at constant discharge current (0.2, 0.3, 0.4, or 0.5 A). Oxygen and argon (purity 99.9%) were introduced in the vacuum chamber through mass flow controllers (MKS Instruments). Experiments were performed at constant argon pressure (0.3, 0.5, or 0.8 Pa), or at constant total pressure (0.3, 0.5, 0.7, or 1.0 Pa). In the latter set of experiments, the argon flow was reduced when the oxygen flow was increased to maintain a constant total pressure. The pressure during the experiments was measured by a capacitance gauge (CMR 375, Pfeiffer Vacuum). The film thickness was measured using a surface contact profilometer (Talystep Taylor-Hobson). The deposition rate was calculated by dividing the measured thickness by the deposition time. The phase analysis is performed based on X-ray diffraction (Bruker D8 Advance), using Cu Kα radiation, in the Bragg-Brentano setup using LynxEye linear detector. Additional characterization of the phase was based on far infrared spectra obtained with a Bruker Vertex 80v FTIR spectrometer. The film density was measured with X-ray reflectometry (XRR) performed on a Bruker D8 Advance with a scintillation detector and Cu Kα radiation. The energy flux was measured with a passive thermal probe [50] under the same experimental conditions as during the deposition. The aperture (300 μm diameter) of an energy resolved mass spectrometer (Hiden Analytical EQP1000) was placed at the same position of the substrate to measure the energy distribution of the negative oxygen ions.

3. Results

3.1. Process conditions

To study the influence of oxygen on the discharge conditions, the oxygen flow was stepwise increased until a maximum value of 50 standard cubic centimeter per minute (sccm), and was then stepwise decreased to reach the initial discharge conditions. Simultaneously the discharge voltage and the total pressure were recorded. This kind of experiment results for a large number of target material/reactive gas combinations in a hysteresis of the process parameters as a function of the reactive gas flow, especially at low pumping speeds [51]. However, as the used pumping speed (minimum 120 l/s, maximum 250 l/s) is rather high, no hysteresis effects were observed. In one series of experiments, the pumping speed was deliberately decreased to 16 l/s (at a constant argon pressure of 0.3 Pa, and a discharge current of 0.3 A). Even under these extreme conditions, the hysteresis was not pronounced with the first critical flow at 3.8 sccm and the second at 3.2 sccm. Therefore, to discuss these working conditions, it is better to express them as a function of the oxygen fraction $f_{O_2}$ in the plasma. This parameter is determined from the ratio between the oxygen partial pressure $P_{O_2}$ and the total pressure $P_{tot}$, i.e. $f_{O_2} = P_{O_2}/P_{tot} = P_{O_2}/(P_{O_2} + P_{Ar})$. As the argon flow and the pumping speed are known, the oxygen partial pressure can be calculated from the difference between the total pressure and the argon pressure. The discharge voltage and the deposition rate change when the oxygen fraction in the plasma is altered (see Fig. 1).

Initially, both the discharge voltage and the deposition rate increase with increasing oxygen fraction, while at higher oxygen fractions the opposite behavior is observed. As can be observed from Fig. 1, the deposition rate decreases before the discharge voltage drop. This trend doesn’t depend on the process conditions, i.e. current, argon (or total) pressure. The oxygen fraction at which the maximum in the discharge is observed shows a clear trend on the studied deposition parameters.

3.2. Energy flux measurements

As the texture and phase formation can be affected by the energy per arriving atom (EPA), both the deposition rate and the total energy flux towards the sample were measured.

To convert the deposition rate to an atomic flux the film density was determined with XRR. The EPA as a function of the oxygen fraction is presented for the different experimental conditions in Fig. 2. For oxygen
fractons lower than 0.35 the deposition conditions hardly affect EPA. Indeed, with increasing discharge current also the energy flux increases, resulting in a minor effect of the discharge current on the EPA. As the contribution of the sputtered atoms to the total energy flux is relatively small, the effect of the argon pressure on the EPA is also small. At higher oxygen fraction the deposition rate decreases (see Fig. 1) due to target poisoning which explains the increase of the EPA.

3.3. X-ray analysis

X-ray analysis was performed on each sample, and the data is presented as a contour plot in Fig. 3 for the samples deposited at a constant discharge current of 0.3 A, and an argon pressure of 0.3 Pa.

Similar contour plots were obtained for each studied condition. The contour plot shows the logarithm of the measured X-ray intensity divided by the film thickness (color scale) as a function of the diffraction angle (horizontal axis), and the oxygen fraction (vertical axis) as measured during deposition. To facilitate the interpretation, the contour plot is 4 times repeated, and the peak positions for one of the detected phases are shown per individual contour plot: copper (a), cuprite (b), parameleconite (c), and tenorite (d).

One observes a gradual transition from pure copper (no oxygen addition), over cuprite and parameleconite, to tenorite with increasing oxygen fraction. So, as soon as oxygen was introduced into the chamber, the cuprite (111) reflection was observed together with the (111) and (200) Bragg reflection for Cu. At an oxygen fraction of approximately 0.18, pure cuprite films with a strong preferred orientation in the [100] direction were deposited. Pure parameleconite films (see (020), (022), and (220) Bragg reflections) were successfully synthesized at the oxygen fraction close to 0.27. When oxygen fraction is higher or equal to 0.32, only the tenorite phase was detected. As mentioned before, the same trend is observed for all deposition conditions. An overview is given in Table 1.

XRD was also used to study a full-width at half-maximum (FWHM) and the (111) peak position of the tenorite (CuO) Bragg reflection for constant EPA (approx. 50 eV/at) conditions. The FWHM as a function of the peak position are shown in Fig. 4. Two series of experiments are in view. Constant current (0.3 A) experiments at different total pressure are indicated in greenish markers. Red to yellow markers are used for constant pressure experiments at different discharge currents. The marker size is proportional with the film thickness (see markers scale bottom right). It is seen that FWHM decreases with increasing pressure, but hardly changes with increasing discharge current. As the deposition rate is the function of the oxygen fraction, the film thickness could influence this latter observation. Therefore, films with different thickness were deposited under the same conditions (EPA = 50 eV/at, $P_{\text{tot}} = 0.7 \text{ Pa}, f_{\text{D}} = 0.26, I = 0.3 \text{ A}$). The influence of the film thickness on the FWHM and the peak position for the same Bragg reflection is presented in Fig. 4b. A clear trend is observed, but the effect of the film thickness on both the FWHM and the peak position is small for films thicker than 200 nm. This latter statement excludes a possible influence of the film thickness on the results presented in Fig. 4a.

3.4. FTIR

As discussed by several groups, the phase analysis solely based on X-ray analysis is difficult as many Bragg peak positions are close to each other [2, 3, 24, 34]. As reported by Debbichi et al. [52] based on first principle calculations, the Raman and the infrared spectra for parameleconite have a clearly different fingerprint as compared to those cuprite and tenorite. Therefore, Fourier transform infrared (FTIR) analysis was performed. FTIR absorption spectra were recorded using an uncoated Si wafer as background. Fig. 5a summarizes the FTIR data for thin films deposited at the same conditions as in Fig. 3. In our case, at room temperature, the strong infrared absorption bands of CuO at 610, 147 cm$^{-1}$ [53] were observed in the cuprite films. All the reported bands of the Cu$_2$O [52] and the CuO [52, 54] phase were observed. The FTIR analysis confirmed the XRD results and clearly distinguished these three oxide phases. For sake of completeness, the XRD patterns of the films consisting of a given pure phase are shown in Fig. 5b.

3.5. Energy resolved mass spectrometer measurement

The negative ion mass spectrum (not shown) measured at a high oxygen fraction of 0.3 (at an argon pressure of 0.3 Pa, and a discharge current of 0.3 A) allowed to identify several negative ion species: O$_2^-$, O$_3^-$, Cu$^-$, Cu$_2$O$^-$, and CuO$_2^-$. The ion signal intensity of O$^-$ was at least one order in magnitude higher than the other species. Therefore, we have limited the energy analysis to this ion ($m/q = -16$). Fig. 6 displays the ion energy distribution of the negative oxygen ions for different oxygen fractions during experiments performed at a constant argon pressure of 0.3 Pa and at a discharge current of 0.3 A.

The ion energy distributions show multiple peaks which can be explained from the decomposition of more complex ions as explained in Mahieu et al. [55] The peak positions are mainly defined by the discharge voltage as the emitted ions are accelerated over the cathode sheath. We also observe a change of the intensity of the high energetic (350 to 650 eV) ions as a function of the oxygen fraction. The ion energy distribution was integrated over this energy region accounting for the energy dependency of the acceptance angle of the spectrometer [55, 56]. The result is shown in Fig. 7. The integrated count rate increases with the oxygen fraction until it stabilizes at a given oxygen fraction which does not coincide with the oxygen fraction at which the discharge voltage becomes maximal.

To present a possible influence of the negative ions on the film growth, it is better to normalize the count rate by the incoming metal flux to the substrate. This gives us, at least in a relative way, information about the number of high energy O$^-$ ions per incoming metallic particle that impinge on the growing oxide thin films. The incoming metal flux was calculated using the deposition rate and the density of the film. When the data shown in Fig. 7 are normalized by arriving metal atom, we find a power law behavior of the normalized count rate as a function of the oxygen fraction in the discharge. A similar result was obtained for an experiment performed at a constant discharge current (0.3 Pa) and a constant argon pressure (0.3 Pa). Table 2

![Fig. 2. The energy per arriving atom (EPA) as a function of the oxygen fraction for the different experimental conditions (see also Table 1). Experiments performed at the constant argon pressure are represented by a circle, while the constant total pressure experiments are indicated by a square.](image-url)
summarizes the fitting data.

4. Discussion

The discharge voltage behavior finds its origin in the formation of an oxide layer on the target surface and can be attributed to a change of the ion induced secondary electron emission yield [57]. The initial increase in the discharge voltage can be explained from the low secondary electron emission due to suboxide formation on the target surface [58], and the higher effective ionization energy for O\textsubscript{2}. We observe that once the discharge voltage starts to decrease, only tenorite (CuO) films can be grown (see Fig. 1 and Table 1) which indicates that the deposited thin film cannot further consume oxygen, and hence further the target oxidation should occur, i.e. a higher fraction of the target gets covered by CuO, which is expected based on its electronic structure to have a higher electron yield than Cu, and the other copper oxides. Further increasing the oxygen fraction results in full target poisoning, with the typical feature of a lower deposition rate. It is also interesting to remark that the integrated count rate for O\textsuperscript{−} ions (Fig. 7) shows the same trend. This is not surprising as the negative ion yield scales with the electron yield. So, at \( f_{O_2, \text{Int}} \), the integrated count rate has not reached its maximum yet, which indicates that the target is not fully

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**Table 1**

<table>
<thead>
<tr>
<th>I (A)</th>
<th>( P_{Ar} ) (Pa)</th>
<th>( P_{tot} ) (Pa)</th>
<th>( f_{O_2} )</th>
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</thead>
<tbody>
<tr>
<td>0.3</td>
<td>&lt; 0.15</td>
<td>0.16-0.19</td>
<td>0.25-0.27</td>
</tr>
<tr>
<td>0.3</td>
<td>&lt; 0.13</td>
<td>0.16-0.19</td>
<td>0.27-0.29</td>
</tr>
<tr>
<td>0.4</td>
<td>0.3</td>
<td>0.17-0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3</td>
<td>0.17-0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>0.3</td>
<td>0.5</td>
<td>&lt; 0.15</td>
<td>0.23</td>
</tr>
<tr>
<td>0.7</td>
<td>&lt; 0.07</td>
<td>0.10-0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>1.0</td>
<td>&lt; 0.07</td>
<td>0.08-0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>0.3</td>
<td>0.5</td>
<td>&lt; 0.10</td>
<td>0.11-0.16</td>
</tr>
<tr>
<td>0.8</td>
<td>&lt; 0.08</td>
<td>0.10-0.13</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The entries in bold are values at the deposition condition of \( P_{tot} \) which indicates the total pressure.

**Fig. 3.** Overview of the X-ray patterns for thin films deposited at an argon pressure of 0.3 Pa, and a discharge current of 0.3 A. Each contour plot represents the same data, and shows the intensity divided by film thickness (color scale) as a function of the diffraction angle (X-axis), and the oxygen fraction (Y-axis). The full lines refer to the peak positions for copper (a), cuprite (b), paramelaconite (c), and tenorite (d). The striped lines are related to the used Si(100) substrate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
poisoned, and can uptake more oxygen. It is not in the scope of the paper to discuss in detail the poisoning behavior, but from the above discussion, it is clear that the discharge voltage can serve as an easy guideline to define the oxygen fraction required to obtain tenorite films (Fig. 1).

The combined XRD and FTIR analysis shows a gradual transition from pure Cu to CuO thin films as a function of the oxygen fraction. Under these conditions the EPA remains more or less constant (see Fig. 2). This means that neither the deposition conditions (current and pressure), nor the oxygen fraction influence the EPA. Hence, the phase formation is a pure chemical driven process. Or stated differently, despite the wide variation in process conditions shown in literature, one can expect that the same crystalline phases and similar trends in chemical compositions are observed. This latter statement partially

Fig. 4. (a) The full width at half maximum (FWHM) as a function of (111) peak position of CuO films deposited at different conditions. Two series of experiments are shown. Constant current (0.3 A) experiments at different total pressure are indicated in greenish markers. Red to yellow markers are used for constant pressure experiments at different discharge currents. The marker size is proportional with the film thickness (see markers scale bottom right). (b) The influence of the film thickness on the FWHM and the peak position. Films with different thickness were deposited under the same conditions (EPA = 50 eV/at, $P_{\text{tot}} = 0.7 \text{ Pa}$, $f_{O_2} = 0.26$, $I = 0.3 \text{ A}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (a) Overview of the FTIR absorption spectra as a function of the wave number for thin films deposited at an argon pressure of 0.3 Pa, a discharge current of 0.3 A, and a different oxygen fraction (color scale). Note that the oxygen fraction only starts at 0.18 as thin films deposited at lower oxygen fraction had a strong copper phase contribution. All the spectra are divided by the film thickness and represented in arbitrary units, and shifted by the oxygen fraction. In order to make the spectra clearer, the 100–350 cm$^{-1}$ range was artificially magnified by multiplying the spectra by a factor of 2.5. The full lines refer to the peak positions for cuprite [53], paramelaconite [52], and tenorite [52]. (b) Typical XRD pattern for each of the identified phases (cuprite, paramelaconite, and tenorite). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. The ion energy distribution for O$^-$ for different values of the oxygen fraction in the discharge. Experiments performed at constant argon pressure of 0.3 Pa and discharge current of 0.3 A.

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paramelaconite (Cu₄O₃), and tenorite (CuO) the oxygen fraction at di
function of the deposition conditions, even at constant, low EPA
experiments performed at a constant discharge current of 0.3 A. The integration of
the count rate is performed over the energy interval 350 and 650 eV. The striped lines indicate the fraction at which the discharge voltage becomes maximal.

Table 2
The normalized count rate for m/q = −16 as a function of the oxygen fraction in the discharge was fitted with a power law \( A_f \), with \( f \) the oxygen fraction.

<table>
<thead>
<tr>
<th>Condition</th>
<th>( \log A )</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 Pa, 0.3 A</td>
<td>−10.13</td>
<td>2.89</td>
</tr>
<tr>
<td>0.5 Pa, 0.3 A</td>
<td>−10.68</td>
<td>2.05</td>
</tr>
<tr>
<td>0.7 Pa, 0.3 A</td>
<td>−11.38</td>
<td>1.05</td>
</tr>
<tr>
<td>0.3 Pa, 0.3 A</td>
<td>−10.40</td>
<td>2.74</td>
</tr>
</tbody>
</table>

explains the research question raised in the introduction.

As this study is a first step in the development of multilayer thermite stacks, we are mainly interested in the growth of CuO films, and discuss in more detail these films. We observe at low EPA that all tenorite films have the same film texture, but that the full width at half maximum (FWHM) and the peak position of the (111) or the (111) peak are function of the deposition conditions, even at constant, low EPA (= 50 eV/atom). As shown in Fig. 4 at higher total pressure, the thin films have a larger crystal size (smaller FWHM). The shift towards larger Bragg angles when the total pressure is increased, is probably related to lower compressive stress. Impingement of heavy energetic species, such as reflected neutrals, sputtered atoms, and negative ions, are known to induce compressive stress which results in Bragg peak shifts towards lower angles [46]. Also, it is well known that the crystallinity of oxide thin films is influenced by negative ion bombardment [47-49, 55, 59] which can be understood from the momentum transfer of these ions to the growing film. Based on the presented results this can be quantified by studying the FWHM and the peak position as a function of the normalized count rate (see Table 2). This correlation is shown in Fig. 8.

5. Conclusion

In this work, the influence of several deposition parameters on the growth of copper oxide thin films are investigated. Cuprite (Cu₂O), paramelaconite (Cu₄O₃), and tenorite (CuO) films were successfully synthesized alongside the increasing oxygen fraction. The thermal flux measurement showed that the EPA is mainly constant during the formation of all copper oxide phases, and hence the phase formation is purely defined by the oxygen content. At constant discharge current, the discharge voltage becomes maximal at an oxygen fraction which coincides with the formation of pure CuO thin films. The film crystallinity for the latter film is influenced by negative ion bombardment. As experiments were performed at constant energy per arriving atom, it is clear that the CuO film growth is defined by momentum transfer of the negative ions towards the growing film.

Acknowledgments

The authors thank the Special Research Fund (GOA project ENCLOSE BOF2015/GOA/007/B, Ghent University) and the Research Foundation Flanders - Hercules Foundation (FWO-Vlaanderen, project number AUGE/13/13: FT-IMAGER).

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