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## ***In situ* tracking the phase change in metastable copper oxide thin film via thermal oxidation**

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**ABSTRACT:** Phase change (PC) materials such as metal oxides possess high fundamental and applied importance for modern memory, sensor, and photonic devices. However, revealing the kinetics and mechanisms of PC, as well as achieving the reversible and irreversible PC regimes are still a challenge. Here we report on 200 nm films of metastable Cu<sub>4</sub>O<sub>3</sub> obtained by magnetron sputtering. *In situ* structural and optical analyses during air annealing revealed the thermal induced phase change from Cu<sub>4</sub>O<sub>3</sub> to CuO. Combination of X-ray diffraction and optical transmittance with heating up to 450 °C allowed us to explore the phase change rate, and then to correlate it with classical nucleation and crystal growth mechanism. We have also revealed two regimes of PC, possessing reversible 12 % (1.42 to 1.25 eV) and irreversible 220 % (1.25 to 2.75 eV) direct bandgap tuning by temperature. The results, thereby, pave the way for controllable transformation of copper oxide thin films to achieve the desired microstructure and its functionality.

Phase change (PC) materials, driven by temperature, pressure or electric/magnetic field, possess high fundamental<sup>1</sup> and applied importance<sup>1</sup> for modern memory, sensor, and photonic devices.<sup>2,3</sup> Occurring for different time scales from seconds to nanoseconds with high repeatability or in irreversible manner, the PC leads to significant changes in magnetic, electrical and optical properties of corresponding phase change materials, which are then read electronically or optically.

Herein, the strict criteria of high crystallinity, scalability, environmental stability and integration into existing microelectronic devices are imposed on such phase change materials.<sup>4</sup> In this regard, multicomponent inorganic materials (GeSnTe, AgInSbTe)<sup>5-7</sup> and metal-oxides,<sup>8-11</sup> whose fabrication is possible thanks to universal deposition methods,<sup>12</sup> occupy an important place for such devices. Nevertheless, one of the most common metal (Cu) oxide, produced scalably in the form of crystalline thin films and exhibiting PC upon elevated temperature, yet remains poorly investigated.

The structural stability of copper oxide thin films upon 300 °C, 350 °C and 400 °C during 4 h has been investigated,<sup>13</sup> revealing the PC process (conversion of metastable Cu<sub>4</sub>O<sub>3</sub> into CuO at 350 °C). Later,<sup>14</sup> these processes have been described numerically using *ab initio* density functional theory. Also, the PC of Cu<sub>4</sub>O<sub>3</sub> into CuO at 410 °C (in air) and 450 °C (in Ar) using high-temperature Raman analysis has been confirmed.<sup>15</sup> Such PC process in copper oxides upon local laser radiation has been also investigated.<sup>16</sup> In favor of this, experimental and numerical analysis of the Raman spectra of CuO and Cu<sub>4</sub>O<sub>3</sub> also confirmed a close relationship between their Raman modes;<sup>17</sup> however, leaving aside the questions about the phase change rate and the possibility of achieving reversible and irreversible PC regimes.

In this letter, we experimentally demonstrate *in situ* thermal induced PC from metastable mixed-valence Cu<sub>4</sub>O<sub>3</sub> to CuO at 300 – 350 °C in air, associated with oxidation. Combination of X-ray diffraction (XRD) and optical transmittance spectroscopy with heating up to 450 °C allowed us to explore the phase change rate for copper oxide thin films, and then to correlate it with classical nucleation and crystal growth mechanism.

Paramelaconite (Cu<sub>4</sub>O<sub>3</sub>) thin films have been deposited on glass substrates by magnetron sputtering in reactive Ar-O<sub>2</sub> atmospheres. The copper target (50 mm diameter and a purity of 99.99%) has been sputtered using a pulsed-DC power supply (Pinnacle+ Advanced Energy). The current applied to the Cu target was fixed to 0.3 A, the off time and the frequency were 4 μs and 5 kHz, respectively. The oxygen flow rate introduced into the chamber was fixed to 10 sccm to

selectively deposit pure  $\text{Cu}_4\text{O}_3$  phase. During the deposition, the argon flow rate has been set at 25 sccm. The films were deposited without additional heating of the substrate holder. The total pressure during the sputtering run was 0.5 Pa. The thickness of the  $\text{Cu}_4\text{O}_3$  thin films was fixed to 200 nm (deposition duration of 4 minutes). The structure of the films was studied by X-ray diffraction in  $\theta/2\theta$  mode with a  $\text{Co K}\alpha$  radiation ( $\lambda_{\text{Co}} = 0.178897$  nm). This diffractometer was equipped with a heating cell Domed Hot Stage (DHS1100) from Anton Paar to perform *in situ* annealing in air. Transmission electron microscopy (Philips CM 200) was used to check the film microstructure. Optical properties were deduced from UV-visible spectrometry (Varian Cary 5000) equipped with a heating cell (Linkam) to *in situ* heat the films in air from room temperature to 450 °C.

Figure 1a demonstrates the structure of as-deposited 200 nm thick film corresponding to tetragonal  $\text{Cu}_4\text{O}_3$  phase with a single diffraction peak at 41.56° corresponding to (202) plane (diffractogram labelled “Room temperature”). Next, to confirm that the fabricated metastable mixed-valence  $\text{Cu}_4\text{O}_3$  film undergoes the PC upon heating in air atmosphere, we have performed *in situ* XRD analysis with heating up to 450 °C. As one can see in Figure 1a, elevating temperature allows  $\text{Cu}_4\text{O}_3$  to transform into CuO phase with 300 °C temperature threshold. In details, at room temperature and during the heating up to 250 °C, single XRD peak at 41.56° (with slight shift to 41.75°), corresponding to (202) crystallographic orientation of the pure tetragonal  $\text{Cu}_4\text{O}_3$  phase, has been detected. At the temperature of 300 °C and higher, a new XRD peak at 45.11°, corresponding to the (111) plane of monoclinic CuO phase, has been appeared, suggested that the film annealed at 300 °C (or higher) is biphased:  $\text{Cu}_4\text{O}_3 + \text{CuO}$ . Further increase of the temperature supports the progressive transformation from tetragonal  $\text{Cu}_4\text{O}_3$  to monoclinic CuO phase (Figure 1b), corresponding to an increased number of oxygen per copper ions. Nevertheless, even at a higher temperature (up to 450 °C) we still detect the  $\text{Cu}_4\text{O}_3$  phase (broaden XRD peak at 41.45°) due to the fact that the full transition should occur at a higher temperatures (500 °C).<sup>18</sup>

To confirm the smooth PC process (i.e., the overlapping of the copper oxide phases), we have also performed transmission electron microscopy (TEM) for the film heated up to 300 °C. Figure 1c,d demonstrates that two phases can exist simultaneously in neighboring regions of the film.

Since the PC process is associated with a change in the oxidation state of copper, it should take a certain time at specific environment conditions. Therefore, time-resolved spectroscopy is required to explore the PC rate in air. For this, we have utilized a time-resolved optical transmittance spectroscopy with heating up to 450 °C (UV-visible spectrophotometer equipped with a heating device). Figure 2a demonstrates the PC in terms of evolution of the optical transmittance,  $T$ , of the film. The increase of the temperature lowers the transmittance and yields the PC at 350 °C, being in a good agreement with XRD data in Figure 1a. Further analysis of  $T$  spectra showed that the shape of  $T$  curves remain the same upon heating up to 350 °C, while the transmittance dropped by 10 %. Herein, the cooling of the films from 350 °C to room temperature is accompanied by a reversible change in  $T$  spectra. However, upon heating above 350 °C (Figure 2a), a threshold change in the shape of  $T$  spectrum and the transmittance (by 20 %) is observed. Then, the cooling the film to room temperature is associated with a constant shape of  $T$  spectrum, confirming the irreversible transformation of  $\text{Cu}_4\text{O}_3$  into  $\text{CuO}$  (Figure 2b).

To reconstruct the evolution of the bandgap,  $E_g$ , of copper oxide thin film<sup>19,20</sup> during the PC process, the Tauc method has been used by plotting  $(\alpha hv)^n$  as a function of  $A(hv - E_g)$  where  $\alpha$  is the absorption coefficient of the thin film with specific thickness,  $d$ , and  $n = 0.5$  and  $2$  (for direct allowed and indirect allowed transitions, respectively) are utilized to plot  $E_g$  (Figure 2c). As one can see in Figure 2c,d, the indirect bandgap of  $\text{Cu}_4\text{O}_3$  thin film (before 350 °C) varies reversibly from 1.42 eV to 1.25 eV, being in a good agreement with previous results.<sup>19</sup> However, crossing the temperature of 350 °C, the bandgap value shifts from 1.25 to 2.75 eV, corresponding to  $\text{CuO}$  state.<sup>19,20</sup> Subsequent cooling of  $\text{CuO}$  film to room temperature retained 2.75 eV direct bandgap value.

To shed light on the phase change rate, we have set the heating temperature at 325 °C and recorded the evolution of  $T$  spectra over time with 2 min steps (Figure 3a). As one can see, the PC occurs nonlinearly: The transmittance drops by app. 20 %, while the shape of  $T$  spectrum also changes as in the case of PC occurring at 350 °C (Figure 2b). Then, we have estimated the intensity of the transmittance at 750 nm over time (Figure 3b). Assuming that the  $\text{Cu}_4\text{O}_3$  to  $\text{CuO}$  transformation occurs layer by layer, we have introduced the transformation rate  $\tau = d_{\text{CuO}} / (d_{\text{CuO}} + d_{\text{Cu}_4\text{O}_3})$ , where  $d_{\text{CuO}}$  and  $d_{\text{Cu}_4\text{O}_3}$  denote the thickness of transformed  $\text{CuO}$  and residual  $\text{Cu}_4\text{O}_3$  layers, respectively, and  $d_{\text{CuO}} + d_{\text{Cu}_4\text{O}_3} = d = 200$  nm as the film thickness is constant. Given that, the total transmittance  $T$  can be expressed as  $T = \exp\{-d \alpha\} = I / I_0 = (I / I_{\text{Cu}_4\text{O}_3 / \text{CuO}}) \times (I_{\text{Cu}_4\text{O}_3 / \text{CuO}} / I_0) = T_{\text{Cu}_4\text{O}_3} \times T_{\text{CuO}}$ , where  $I_{\text{Cu}_4\text{O}_3 / \text{CuO}}$  is the light intensity between  $\text{CuO}$  and  $\text{Cu}_4\text{O}_3$  layers (and  $T_{\text{Cu}_4\text{O}_3}$ ,  $T_{\text{CuO}}$  correspond to the transmittance of the  $\text{Cu}_4\text{O}_3$  and  $\text{CuO}$  layers, respectively), we can express the transmittance as  $T = T_{\text{Cu}_4\text{O}_3} \times T_{\text{CuO}} = \exp\{-d_{\text{Cu}_4\text{O}_3} \alpha_{\text{Cu}_4\text{O}_3} - d_{\text{CuO}} \alpha_{\text{CuO}}\} = \exp\{-(1-\tau) d_{\text{total}} \alpha_{\text{Cu}_4\text{O}_3} - \tau d_{\text{total}} \alpha_{\text{CuO}}\}$  and, hence, the transformation rate  $\tau$  is equal to  $(\alpha_{\text{Cu}_4\text{O}_3} - d^{-1} \ln(T)) / (\alpha_{\text{CuO}} - \alpha_{\text{Cu}_4\text{O}_3})$ . Assuming that the transformation rate equals 0 and 1 before and after the PC, the absorption coefficients of  $\text{CuO}$  and  $\text{Cu}_4\text{O}_3$  part of the film are equal to  $d^{-1} \ln(1/T_{\text{end}})$  and  $d^{-1} \ln(1/T_{\text{start}})$ , respectively, where  $T_{\text{start}}$  and  $T_{\text{end}}$  determine the transmittance before and after the PC at a specific wavelength. Therefore, we have obtained the relation between the transmittance,  $T$ , and transformation rate  $\tau = \ln(T_{\text{start}}/T) / \ln(T_{\text{start}}/T_{\text{end}})$ . Using this relation, we have replaced the transmittance of  $\text{Cu}_4\text{O}_3$  at a wavelength of 750 nm in Figure 3b (black curve) with the transformation rate as a function of time (Figure 3b, red curve).

Finally, these results (Figure 3b) allowed us to utilize an Avrami equation  $\tau = 1 - \exp\{-kt^n\}$  to describe the  $\text{Cu}_4\text{O}_3$  to  $\text{CuO}$  transformation.<sup>21</sup> Figure 3c demonstrates that the dependence of the transformation rate as  $\log(-\ln(1-\tau))$  over time,  $t$ , provides the following parameters of the equation:  $n = 2.31 \pm 0.07$  and  $k = (1.23 \pm 0.27) \cdot 10^{-4}$ . The Avrami exponent ( $n$ ) depends on the nucleation and the growth of the  $\text{CuO}$  layer. Its value close to 2 confirms the TEM results (Figure 1c), i.e. a diffusion controlled oxidation step occurring in two dimensions.

In this work, we have demonstrated that depending on the temperature and the oxidation time, it is possible to obtain the phase change for the metastable oxide  $\text{Cu}_4\text{O}_3$ , that is either reversible or irreversible. The reversible/irreversible nature of this PC is closely linked to the crystallographic nature of the oxide. At low temperatures, the oxidation of  $\text{Cu}_4\text{O}_3$  to  $\text{CuO}$  does not occur and the thin film remains composed of the metastable form of copper oxide. The reversible variation of the direct bandgap is solely due to the thermal effect leading to a progressive decrease in the gap with increasing temperature. This process is therefore reversible. On the other hand, for higher oxidation temperatures (or for long annealing times), oxygen can diffuse from the annealing atmosphere inside the  $\text{Cu}_4\text{O}_3$  film and oxidize it gradually and irreversibly into  $\text{CuO}$  phase.

In summary, we have fabricated 200 nm films of metastable  $\text{Cu}_4\text{O}_3$  by magnetron sputtering. *In situ* structural and optical analysis revealed the thermal induced phase change from  $\text{Cu}_4\text{O}_3$  to  $\text{CuO}$  phase at 300 – 350 °C in air atmosphere, associated with oxidation. Combination of X-ray diffraction and optical transmittance spectroscopy with heating up to 450 °C allowed us to explore the phase change rate, and then to correlate it with classical nucleation and crystal growth mechanism. We have also revealed two regimes of PC, possessing reversible 12 % (i.e., 1.42 to 1.25 eV) and irreversible 220 % (i.e., 1.25 to 2.75 eV) direct bandgap tuning by temperature. The results, thereby, pave the way for controllable transformation of copper oxide thin films to achieve the desired microstructure and its optical functionality.

#### AUTHOR DECLARATIONS

Conflict of Interest: The authors have no conflicts to disclose.

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## Author Contributions

Y.K.: Data processing.

S.M.: Data acquisition

P.B.: Data acquisition

V.A.M.: Writing

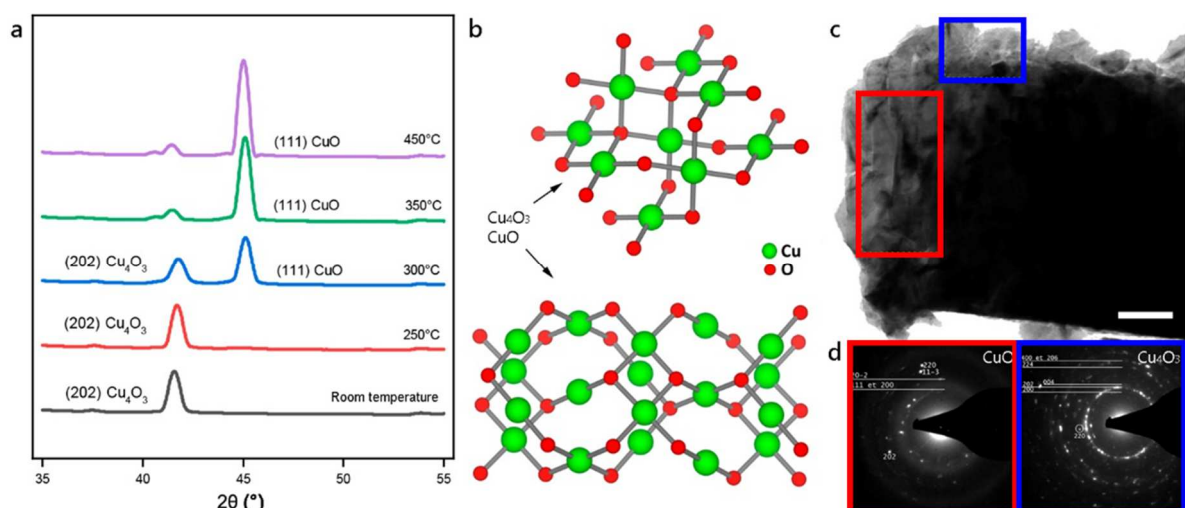
J.-F.P.: Conceptualization, data acquisition, and writing.

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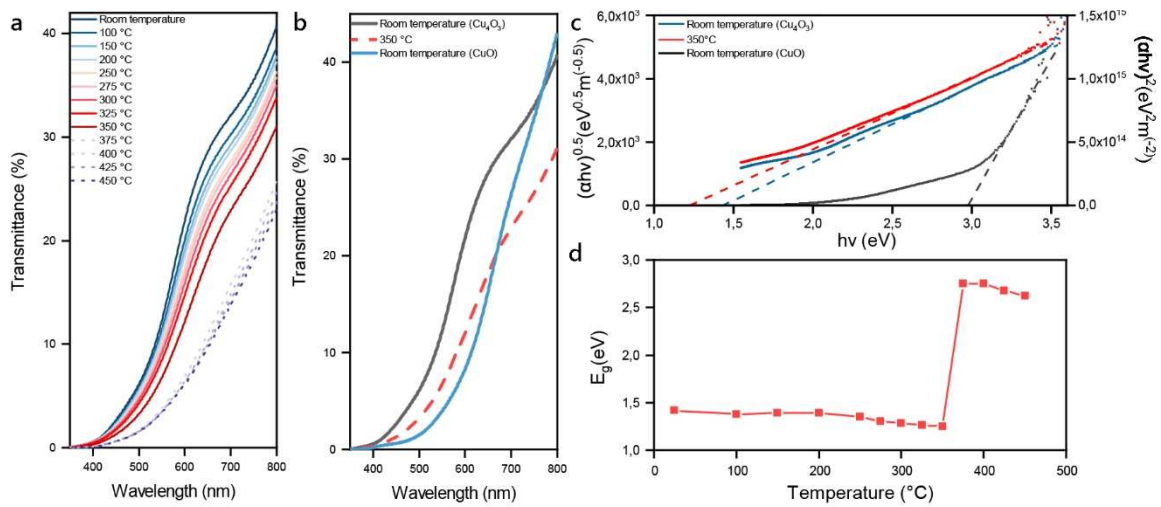


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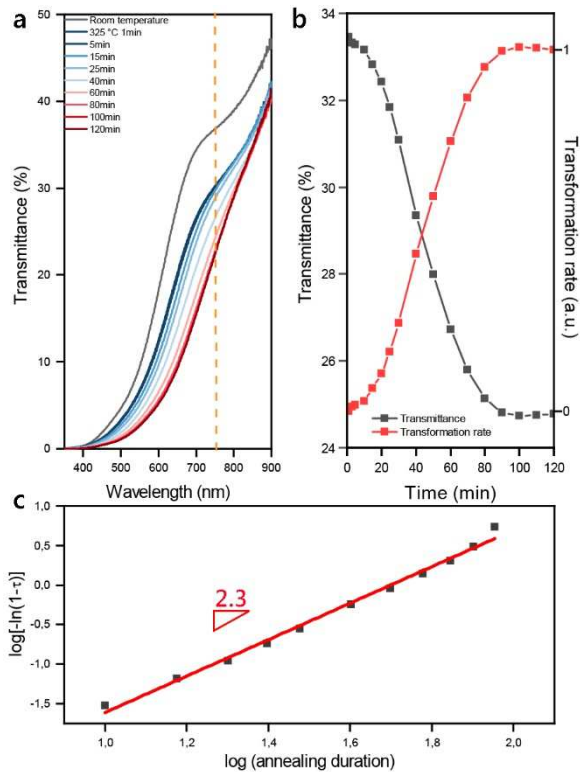


**Figure 1.** (a) XRD patterns for Cu<sub>4</sub>O<sub>3</sub> thin film undergoing oxidation in air due to temperature increase from room temperature to 450 °C. (b) Crystal structure of CuO and Cu<sub>4</sub>O<sub>3</sub> phases. (c,d) TEM micrograph and electron diffraction of a piece of Cu<sub>4</sub>O<sub>3</sub> film oxidized at a temperature of

300 °C. CuO phase is detected from the red area in (c), while the Cu<sub>4</sub>O<sub>3</sub> is from the blue area square.



**Figure 2.** (a,b) *In situ* optical transmittance spectroscopy of the thin film of Cu<sub>4</sub>O<sub>3</sub> at elevated temperature. Blue curve in (b) corresponds to CuO phase, obtained after heating to 350 °C followed by cooling to room temperature. (c) The bandgap of Cu<sub>4</sub>O<sub>3</sub> and CuO phases after the PC with corresponding evolution over the heating (d).



**Figure 3.** (a) Evolution of the copper oxide transmittance as a function of the wavelength for various oxidation duration in air at 325 °C. (b) The evolution of the transmittance and the transformation rate over time at a constant temperature of 325 °C. (c) Avrami fitting of the dependence of the transformation rate on time.