

STRUCTURE AND MORPHOLOGY OF CU-OXIDES FILMS DERIVED FROM PLD PROCESSES

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Copper oxides were prepared by thermal oxidation of copper PLD films: i) in air at 260 °C ii) in oxygen atmosphere at 300 °C ($P_{O_2}=6\times 10^{-3}$ Torr) and 700 °C ($P_{O_2}=1.5\times 10^{-4}$ Torr) respectively; iii) deposition of copper oxides with a pulsed laser from a Cu target at 700 °C ($P_{O_2}=1.5\times 10^{-4}$ Torr). Silicon wafers were used for substrates. The oxides' properties related to the oxidation temperature have been investigated by FTIR, micro-Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. The films oxidized at lower temperatures show copper excess and also the presence of Cu_2O_3 . Thermal oxidation of PLD Cu films at 700°C in oxygen and Cu-oxides films grown from a Cu target at $T_s=700^\circ C$ yield a mixture of CuO and Cu_2O in the terminal surface of the samples as revealed by Raman spectroscopy measurements. The sample grown through ablation of Cu in oxygen at 1.5×10^{-4} Torr exhibits well defined Cu_2O crystallites on top of a smooth CuO film, as shown by SEM imaging. Their sizes range between 1 μm and 5 μm and their shapes are typical for Cu_2O .

(Received April 22, 2011; Accepted May 3, 2011)

1. Introduction

Nature yields copper oxides Cu_2O and CuO as cuprite and tenorite, respectively [1]. Cu_2O is a reddish p-type semiconductor with a cubic crystallographic structure and an energy gap of 2.1 eV. The absorption coefficient in the visible range and the good electrical properties make Cu_2O one of the most interesting phases of copper oxides. CuO is a black semiconductor with a monoclinic structure and is reported to have a 1.4 eV direct gap of the charge-transfer type.

Copper oxides were grown by PLD in oxygen at different pressures and at various substrate temperatures (300-700 °C), using different geometries [2], targets (e.g. copper metal or a copper oxide) and substrates such as Si and MgO [3], [4], [5]. The results highlight different structural properties (nature of phases, orientation of crystallites, in-plane epitaxial relationships, etc.) depending on the growth conditions and the substrate, which was used.

With this work, we have attempted to draw a comparison between copper oxides (CuO and Cu_2O respectively) films prepared in different ways: post growth thermal oxidation of PLD Cu films, either in air or oxygen, and PLD Cu-oxide films grown from pure copper targets in reactive (oxygen) atmosphere. The influence of process parameters on structure and morphology of the films are mainly investigated.

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2. Experimental

Four samples are considered for this study, as listed in Table 1. Copper films were grown by PLD, from pure copper targets, on n-type silicon substrates. Samples C1-C3 were oxidized post-deposition, either in air or oxygen atmosphere. Sample C4 is a copper oxide film on Si obtained directly by PLD, in reactive (O_2) atmosphere. All PLD processes were carried out in a PVD Products workstation, using an excimer laser CompexPro 201(Coherent) ($\lambda=248$ nm, $\tau=20$ ns, repetition rate 10 Hz, $F=8$ J/cm²), on substrates held at room temperature ($T_s=22^\circ\text{C}$), except C4, for which $T_s=700^\circ\text{C}$. The process conditions are given in Table 1.

Table 1. PLD process parameters and oxidation conditions.

Sample	Type	No. of pulses	Atmosphere	Pressure	$T_s[^\circ\text{C}]$	$T_a[^\circ\text{C}]$
C1-post anneal	oxidised Cu film	20 000	air	atmospheric	22	260
C2-post anneal	oxidised Cu film	50 000	oxygen	6×10^{-3} Torr	22	300
C3-post anneal	oxidised Cu film	50 000	oxygen	1.5×10^{-4} Torr	22	700
C4-oxide growth	Cu-oxide film	25 000	oxygen	1.5×10^{-4} Torr	700	-

The structural properties were investigated by FTIR, Raman spectroscopy, and EDS analysis. The morphology was observed by scanning electron microscopy (SEM). The SEM imaging and EDS analysis were performed with a Philips ESEM 30 microscope, at an acceleration voltage of 15 kV, to allow a better check of the films' surfaces. Atomic force microscopy (AFM) was done in order to investigate the surface topology, operated in ac mode. The FT-IR spectra were acquired by means of a Perkin Elmer Spectrophotometer-Spectrum 100, using a specular reflectance accessory at an angle of 60 deg. in the range 450 - 4500 cm⁻¹. The number of scans was 32 in all measurements and the measurement error was $\pm 0.1\%$. Micro-Raman unpolarised spectra were collected in the backscattering geometry with a LABRAM HR 800 (Horiba-Scientific) spectrometer using a 633 nm laser excitation source from 130 to 1800 cm⁻¹. The laser spot size was 1 μm , the laser power at the samples' surfaces was 15 mW and the resolution of the measurement 0.5 cm⁻¹.

3. Results and discussion

The FTIR spectra taken on the four samples listed in Table 1 are shown in Fig.1.

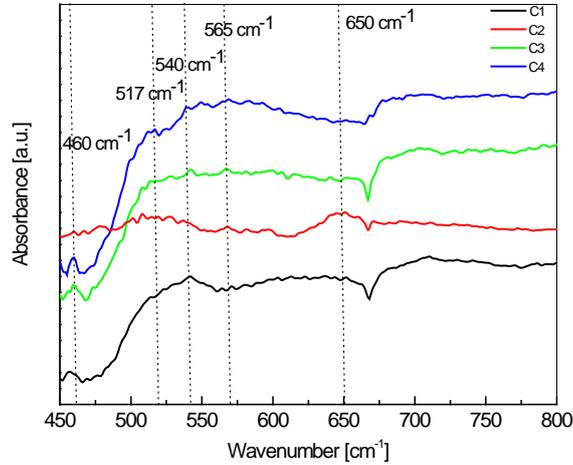


Fig. 1. FTIR specular reflectance spectra of Cu oxides samples deposited on Si substrates. CuO phase is shown through the absorption bands around 480, 520 and 540 cm^{-1} . The broad peak $\sim 640 \text{ cm}^{-1}$ is due to sub-peaks belonging to Cu_2O .

The bands at about 480 cm^{-1} , 520 cm^{-1} and 540 cm^{-1} can be associated with CuO [6], [7] whereas the wide absorption band around 640 cm^{-1} is attributed to Cu_2O [8]. The sample C1, which suffered in air oxidation at 260 $^\circ\text{C}$, shows two major peaks around 460 and 540 cm^{-1} , corresponding to the CuO phase. Formation of both CuO and Cu_2O phases has been reported at 280 $^\circ\text{C}$ [9]. The three important peaks that appear in the C2 spectrum (480, 517, and $\sim 650 \text{ cm}^{-1}$) indicate the presence of both CuO and Cu_2O . The spectra for C3 and C4 samples are totally characterized by CuO IR absorptions. Micro-Raman spectroscopy has been used in support of the FTIR measurements [10]. The spectra of all samples are displayed in Fig. 2. The peaks around 520 cm^{-1} and 640 cm^{-1} have been attributed to Cu_2O by several groups [11-14], and the peak at about 280 cm^{-1} has been associated with CuO [11]. The spectra of samples C1 and C2 look quite similar, suggesting a mixture of Cu_2O (lines at 517 and 640 cm^{-1}) and Cu_3O_2 through the peaks at about 195 cm^{-1} and 860 cm^{-1} [11]. The samples C3 and C4 exhibit a pronounced peak around 300 cm^{-1} that can be trusted to be the 280 cm^{-1} line slightly shifted, due to the very small crystallites in the films. Still, the sample C3 shows peaks belonging to both Cu_2O and CuO, although the FTIR results are specific to CuO.

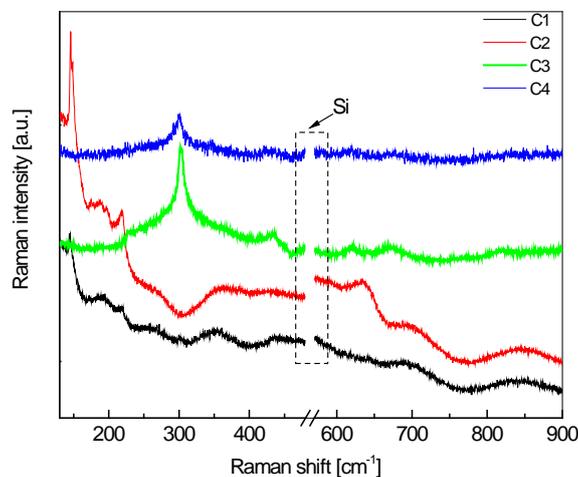


Fig. 2. Raman spectra of C1, C2, C3 and C4. The region around 520 cm^{-1} is hidden on purpose

because of the strong Si signal.

Since Raman spectroscopy is a surface sensitive technique, we believe that sample C3 has a “gradient” composition from down to top of the film, with the terminal surface composed of a mixture of CuO and Cu₂O, the latter being dominant. This is also the case of the sample C4, where the Cu₂O specific Raman lines are extremely weak in comparison with those of C3. The EDS analyses of the four samples are given in the corresponding insets in Fig. 3, showing also copper excess in all films except C4. It is to remark the striking difference in the morphologies of the films, which obviously originates from the growth conditions and the resulting chemical structures. The EDS analyses performed on the well-structured and quite large crystallites in Fig. 3 d (sample C4) give a different composition than in the smooth film areas. The crystallites are typical for Cu₂O phase, as it is mentioned in *Mineral Data Publishing, version 1 (2001-2005)*, i.e. cubic, octahedral, and dodecahedral crystals, which may be highly modified as hair-like capillary forms, with square section, reticulated, tufted and matted. The inter-crystallites film areas are clearly CuO. The other three samples show the usual PLD droplets, with various surface densities and diameters. The smoothest surface with the smallest droplets corresponds to C3, (see the AFM results in Fig. 4). The sample C1 had shown too rough for AFM investigations.

Among the samples C1, C2 and C3, which all originate from PLD Cu films, C2 and C3 should have similar thickness values according to the identical number of laser shots. The lower oxygen pressure and higher annealing temperature have led to a smoother surface of the sample C3. Concerning the composition, it seems that Cu₂O phase is formed mainly at the samples surfaces, with the best evidence in C4, where large typical Cu₂O crystallites have grown on top of the CuO film. A way to explain that could be the normal change in thermal conductivity along with the turning of the Cu film into CuO film. A thermal gradient is obviously established between the interface layer and the growing terminal surface, which eventually succeeds in the growth of large Cu₂O crystallites.

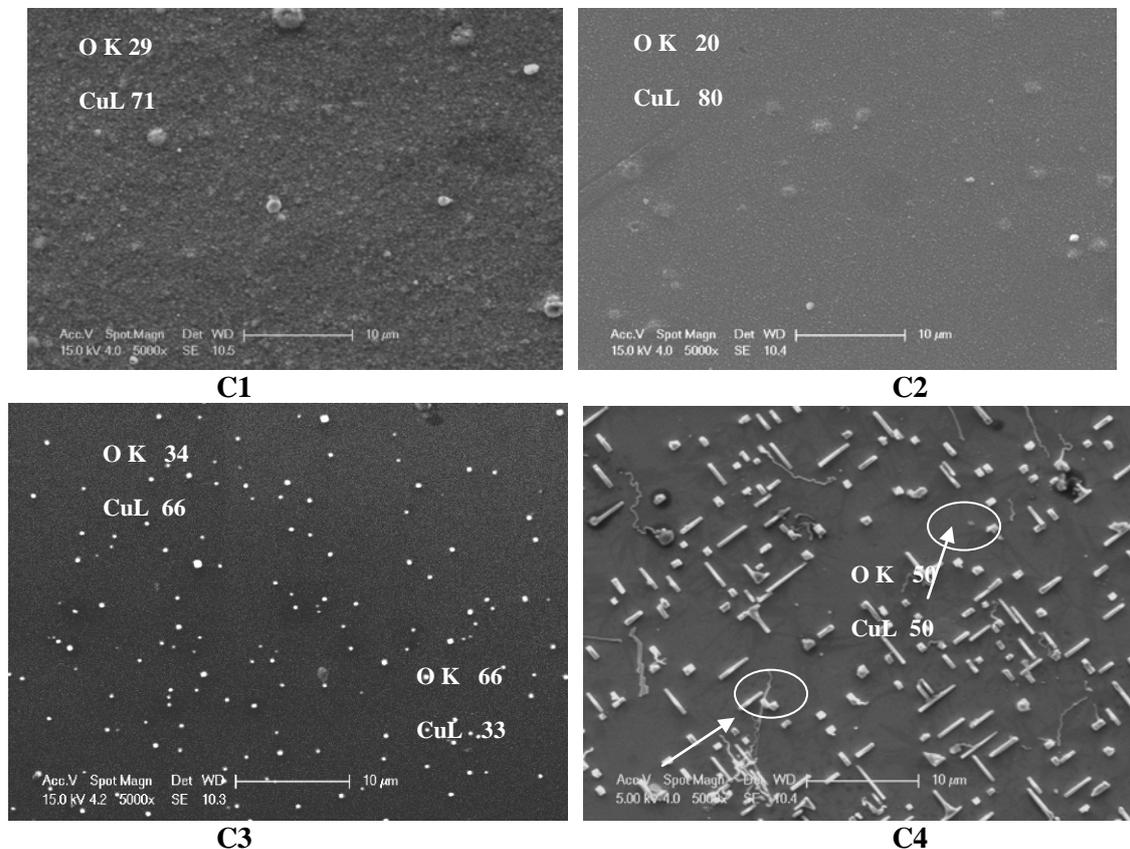


Fig. 3. SEM images of C1, C2, C3 and C4 and their corresponding EDS analyses (at%) in the insets. C4 is composed of a CuO film with Cu₂O crystallites at its terminal surface.

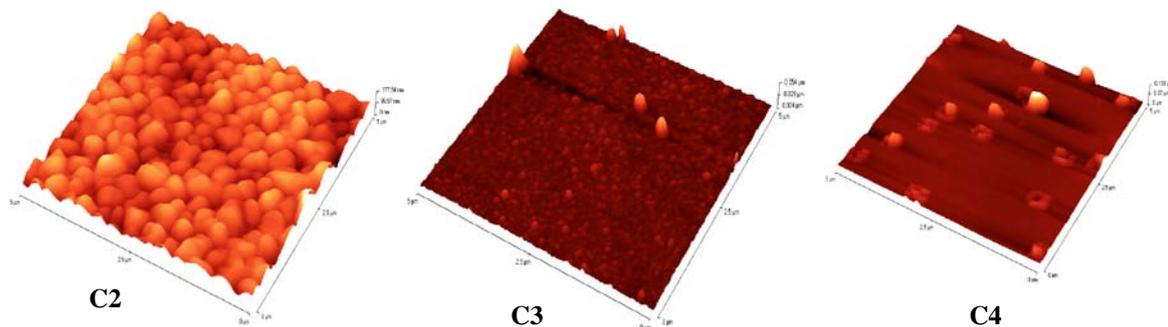


Fig. 4. AFM results for samples C2, C3 and C4. The smoothest surface is exhibit by C3.

4. Conclusions

Thermal oxidation of PLD Cu films at 700°C in oxygen and Cu-oxides films grown from a Cu target at $T_s=700^\circ\text{C}$ yield a mixture of CuO and Cu₂O in the terminal surface of the samples as revealed by Raman spectroscopy measurements. The sample grown through ablation of Cu in oxygen at 1.5×10^{-4} Torr exhibits well-defined Cu₂O crystallites on top of a smooth CuO film, as shown by SEM imaging. Their sizes range between 1 μm and 5 μm and their shapes are typical for Cu₂O. It seems that Cu₂O phase is formed mainly at the samples surfaces, whichever the Cu-oxide formation were, i.e. direct growth or post-growth annealing in oxygen providing a process temperature of 700°C. Lower oxygen pressure and higher annealing temperature have led to smoother surfaces. The films oxidized at lower temperatures, i.e. 260-300°C show copper excess and also the presence of Cu₂O₃.

Acknowledgements

This work has been carried out on funding of the PNCDI II Project FUNFOTON, Contract no. 12-111/2008 CNMP ROMANIA

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