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Quantitative Analysis of Oxygen Content in Copper Oxide Films using Ultra Microbalance

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Abstract. Copper oxide films were prepared on quartz substrates through electron beam physical vapor deposition in a vacuum chamber, and the films were observed using X-ray diffraction (XRD) and scanning electron microscope (SEM). The oxygen content of the films were analyzed using an ultra microbalance. Results indicated that when the substrate was heated to 600℃ and the oxygen flow rate was 5 sccm, the film was composed of 47% Cu and 53% Cu2O (mass percent), and the oxidation ratio of copper was 25%. After the deposition process at the same condition, i.e. the substrate at temperature of 600℃ and blowed by oxygen flowrate of 5 sccm，then in-stu annealed at 600℃ in low oxygen pressure of 10 Pa for 30 minutes, the film composition became 22% Cu2O and 78% CuO (mass percent), and the oxidation ratio of copper greatly increased to about 88%.

Keywords: copper oxide films, oxygen content, quantitative analysis, ultra microbalance
PACS: 74.70.-b, 74.72.-h 81.05.Bx

INTRODUCTION

The properties of functional metal oxide thin films are controlled to a large degree by the oxygen content. For example, oxygen content influenced the electrical and optical properties of indium tin oxide (ITO) films [1]. Optical properties of ZnO films was affected significantly by the oxygen content [2], and the main property of some cuprate superconductors with pervoskite structures depend on the oxygen content of Cu-O planes [3]. Oxygen content affects the crystal structure [4] and electronic structures [5] of $YBa_2Cu_3O_{7-\delta}$ superconductors obviously, and superconductivity disappears at the orthorhombic-to-tetragonal transition that occurs near =0.65. The oxygen content also has influence on the luminescence of Er-doped amorphous SiOx thin films [6].

In order to improve the manufacture process and to obtain high property films, it is important to understand the accurate oxygen content of functional metal oxide films. But it is difficult to determine the oxygen content quantitatively using traditional analysis methods. Zhang [7] used atomic force microscopy(AFM)，X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) methods to characterize the variations in microstructures and compositions at the initial oxidation stage of copper film. Mayer [8] studied the oxidation and protection behavior in copper and copper alloy films using rutherford backscattering spectrometry (RBS), TEM and Normalized resistance measurement, and Zhu [9] investigated the influences of oxygen partial pressure and gas flow rate on the structures and properties of Cu_2O thin films, but all of the above results did not give the quantitative oxygen content. RBS is one of the most frequently used techniques for quantitative analysis of thickness and composition of thin films near the surface region [10-12], Ren [13,14] determined the oxygen content of high Tc superconducting films using RBS methods, but the determination accuracy can be influenced by the choice of the primary energy, which affects the scattering cross section. The quantitative analysis of oxygen content in indium tin oxide (ITO) target material with electron probe micro-analyzer (EPMA) needs to utilize the standard sample experiment to get the calibration curve [1], and the intensities of characteristic peak can be influenced by the crystal instruction, this is especially acute when we analyze the light element such as oxygen [15]. Auger electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) method needs calibrate the sensitivity factor, which perhaps leads to appearance of error of measurement [16, 17]. In addition, all XPS, RBS, EDX, AES, and EPMA are surface micro region analysis method, and surface heterogeneity affects the accuracy of measure result unavoidably.

Because copper element is used widely in most kinds of films, and when the oxygen content of the copper oxides films is different, the mass of the films should be different. In this paper, we tried to measure the mass change using an ultra microbalance which has enough sensitivity, and then the amount of the oxygen content in the copper oxides films could be calculated. The accuracy of the ultra microbalance was testified using quartz crystal oscillator thin

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film controller, and the mass of the samples at different stage was measured (before deposition, after deposition and after annealing treatment) using an ultra microbalance, X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to analyze the as deposited films. This research provided a new method to determine the mass of oxygen element in oxide thin films.

EXPERIMENTAL PROCEDURE

The depositions were carried out in the IMCAS-MEBPVD system [18], and in order to maximize the oxidation degree of the deposited copper films in stu, an oxygen chamber was designed to improve the oxygen pressure near the substrate. The structural diagram of substrate heater, oxygen chamber and rotation device is shown in Fig. 1.

The copper oxide thin films were deposited on double side polished quartz glass substrates using electronic beam evaporation method, and the size of the substrates was about 15mm×15mm×0.5mm. Just before deposition, the substrates were degreased in acetone and ethanol and dried in air and their mass were measured using ultra microbalance (METELLER XP2U) before and after film deposition. The substrate was heated to 600℃, and the O2 (5sccm) gas was introduced into the “oxygen chamber” through a mass flow controller (MFC), where the oxygen pressure in the “oxygen chamber” was about 0.1Pa. The evaporation rate of copper was monitored and controlled to 1.8Å/s by a quartz crystal thin film controller (INFICON XTC/2), and the final thickness showed in the controller was approximately 6000A. During the deposition process, the substrate holder rotated along the axis with a rate of 80r/min, and the deposited copper film followed with oxidation in the “oxygen chamber” immediately, and so on. In order to use our method to analyze the oxygen content quantitatively, two kinds of samples were prepared under different conditions.

1) Sample A: films were deposited at 600℃ with 5 sccm oxygen flow rate;
2) Sample B: films were deposited at 600℃ with 5 sccm oxygen flow rate, and then in-stu annealed at 600℃ in 10 Pa oxygen partial pressure for 30 minutes.

After deposition, sample A and sample B were post-annealed in a thermal furnace under air ambient at 530℃ for 60 minutes. Mass of the samples at different stages (before deposition, deposited with film, in-stu annealing treatment and post annealing treatment) were measured using ultra microbalance, and the surface morphology of the films were examined using scanning-electron microscopy(SEM), and the crystal structure were investigated by X-ray diffraction (XRD, Rigaku D/max 2100H) with a CuKa radiation (λ= 0.1542 nm).

RESULTS AND DISCUSSION

Surface Morphology and Crystal Structure

The film surface morphology of sample B is shown in Fig. 2a, and Fig. 2b shows the surface morphology of sample B after post annealing treatment in air ambient at 530℃ for 60 minutes. It can be seen that the film is compact and uniform, no cracks is observed. The surface morphology of sample A is similar to that of sample B.

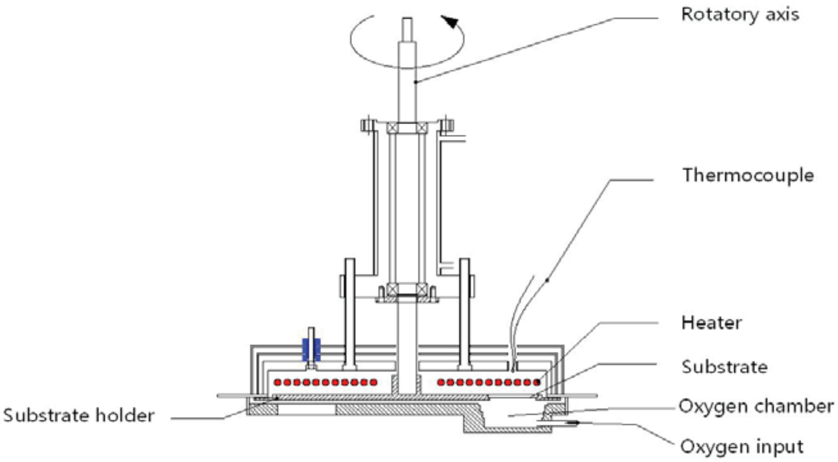

FIGURE 1. Structural diagram of substrate heater, oxygen chamber and rotation device.

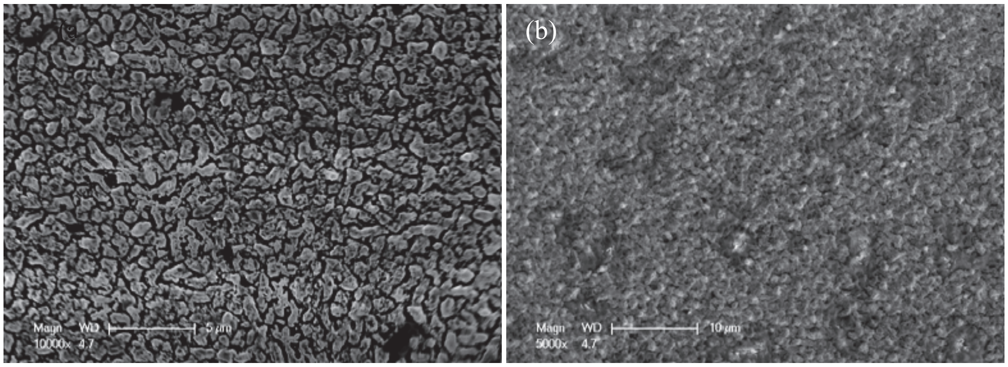

FIGURE2. Surface morphology of sample B (a) and that after post annealing treatment at 530℃in air for 60 minutes (b).

Curve A in Fig. 3 shows the XRD patterns of the film of Sample A, and three peaks correspond to Cu (111), Cu (200) and Cu2O (111), which means that the film of sample A is consisted of mixed copper (Cu) and cuprous oxide (Cu2O) phases. The composition of the film is similar to that of Walter's result [19]. When sample A is post annealed in air at 530℃ for 60 minutes, the XRD patterns of the film is shown as Curve A-2 in Fig. 3, two peaks correspond to (-111) and (200) peak of cupric oxide (CuO) phases, indicating that Cu and Cu2O is completely oxidized to CuO, and the film is composed of pure CuO. The composition of the film is similar to that of Figueiredo's result [20].

XRD pattern of film of sample B is shown as curve B in Fig. 4. One X-ray diffraction peak (111) of Cu_2O and three peaks (-111), (200) and (-113) of CuO are observed, indicating that the film is consisted of mixed Cu_2O and CuO. When sample B is post annealed in air at 530℃ for 60 minutes, the XRD pattern of the film is shown as curve B-2 in Fig.4, only two X-ray diffraction peaks (-1,1,1) and (200) of CuO are measured, which means that the Cu_2O in the sample B is oxidized to CuO completely.

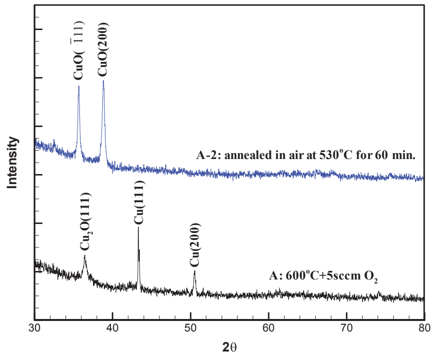

FIGURE 3. XRD patterns of the film on sample A and that after post annealing treatment at 530℃ in air for 60 minutes (A-2).

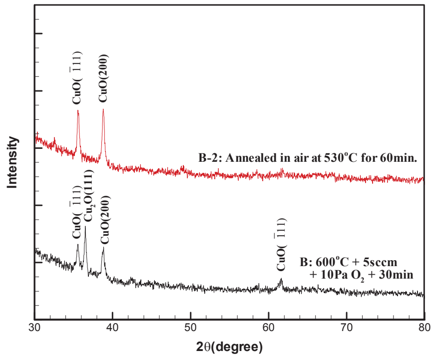

FIGURE 4. XRD patterns of the film on sample B and that after post annealing treatment at 530℃ in air for 60 minutes (B-2).

Quantitative Analysis of Oxygen Content

Accuracy Calibration of the Ultra Microbalance

The accuracy of the ultra microbalance (METELLER XP2U) is calibrated using a quartz crystal thin film controller (INFICON XTC/2). Thin film of BaF_2 is deposited on the quartz crystal by thermal evaporation of BaF_2 powder, where the quartz crystal oscillator probe is mounted right above the evaporation source. The mass of the quartz crystal (m_0) and the mass of the quartz crystal with BaF_2 film (m_1) is weighed using the ultra microbalance, and the mass of the deposited film (m) can be obtained according to the equation $m = m_1 - m_0$.

On the other hand, the mass of the deposited film can be calculated from the film thickness (t) recorded by the thin film controller, the density of the BaF_2 ($\rho = 4.89\text{g/cm}^3$) and the area of the film ($A = 0.535\text{cm}^2$) according to the equation $m_{cal} = \rho A t$.

The results are shown in Table 1, it can be seen that the measured mass of the deposited film is found in excellent agreement with the calculated mass, so the ultra microbalance can be used to analyze the oxygen content in the copper oxide films.

Quantitative Analysis of the Oxygen Content in Copper Oxide Films

We define the oxidation ration of Cu element (δ) as the mole ratio of oxygen to copper, and the nominal expression of copper oxide can be written as CuO_δ , then

$$\delta = \frac{m_O / M_O}{m_{Cu} / M_{Cu}} . \tag{1}$$

In equation (1), m_O is the mass of oxygen element in the film, M_O is the mole mass of oxygen ($M_O = 16$). m_{Cu} is the mass of copper element in the film, M_{Cu} is the mole mass of copper ($M_{Cu} = 63.54$), then equation (1) can be written as

$$\delta = 3.97 \times \frac{m_O}{m_{Cu}} . \tag{2}$$

According to the definition of oxidation ratio, when the deposited film is Cu_2O , the $\delta = 0.5$, and when the deposited film is CuO , the $\delta = 1$.

The mass of sample A and sample B before film deposition (m_0), after film deposition (m_1) and after post annealing in air (m_2) are measured using ultra microbalance, and the results are shown in Table 2.

TABLE 1. Comparison of the calculated mass and the measured mass of BaF_2 film.

Sample Number	Film Thickness t (Å)	Mass of the Quartz Crystal m_0 (μg)	Mass of the Quartz Crystal with Film m_1 (μg)	Calculated Mass of the Film $m_{cal} = \rho A t$ (μg)	Measured Mass of the Film $m = m_1 - m_0$ (μg)	Deviation (%)
1	8617	90072.3	90297.3	225.43	225.0	0.19
2	11350	90240.5	90539.1	296.93	298.6	0.56

TABLE 2. Mass of sample A and sample B at different stages.

Sample	Mass of the Substrate m_0 (μg)	Mass of the Sample after Film Deposition m_1 (μg)	Mass of the Sample with Film after Post Annealing Treatment in Air m_2 (μg)
A	496064.2	496252.8	496286.4
B	498448.5	498659.4	498664.6

1) Quantitative analysis of oxygen content in film of sample A

The mass of the deposited film (m_f) of sample A can be calculated as

$$m_f = m_1 - m_0 = 188.6\mu g\ .$$

When the film was post annealed in air at 530℃ for 60 minutes, the film is composed of pure CuO (Fig.3), and the mass of CuO film (m_{CuO}) can be obtained

$$m_{CuO} = m_2 - m_0 = 222.2\mu g\ .$$

The mass of Cu element (m_{Cu}) in the deposited film can be calculated according to the mass of CuO (m_{CuO})

$$m_{Cu} = m_{CuO} \times \frac{M_{Cu}}{M_{Cu} + M_O} = 177.5\mu g\ .$$

The mass of oxygen element (m_O) in the deposited film can be calculated

$$m_O = m_f - m_{Cu} = 11.1\mu g\ .$$

The mass percent of oxygen element in the deposited film is about 5.9% (m_O / m_f), and that of copper element is about 94.1%.

The oxidation ratio of copper element can be calculated using equation (2)

$$\delta = 3.97 \times \frac{m_O}{m_{Cu}} \approx 0.25\ .$$

That is to say, the nominal expression of copper oxide in sample A can be written as $CuO_{0.25}$.

Because the deposited film of sample A is consisted of mixed Cu and Cu_2O, so the mass of oxygen element (m_O) belongs to Cu_2O, and the mass of Cu_2O (m_{Cu_2O}) in the deposited film of sample A can be calculated

$$m_{Cu_2O} = 99.26\mu g\ .$$

So the mass of Cu phase in the deposited film of sample A is 83.94μg.

The deposited film of sample A is composed of 89.34μg Cu, and 99.26μg Cu_2O, and the corresponding mass percentage is 47% and 53% respectively.

2) Quantitative analysis of oxygen content in film of sample B

According to the XRD result (Fig. 4), the deposited film of sample B is constituted of Cu_2O and CuO, and its mass can be calculated

$$m_f = m_1 - m_0 = 210.9\mu g\ .$$

When the sample was annealed in air at 530℃ for 60 minutes, the film is constituted of pure CuO, and its mass is

$$m_{CuO} = m_2 - m_0 = 216.1\mu g\ .$$

The mass of Cu element (m_{Cu}) in the deposited film can be calculated according to the mass of CuO (m_{CuO})

$$m_{Cu} = 172.6\mu g\ .$$

The mass of oxygen element (m_O) in the deposited film can be calculated

$$m_O = m_f - m_{Cu} = 38.3\mu g\ .$$

The mass percent of oxygen element in the deposited film is about 18.2% (m_O / m_f), and that of copper element is about 81.8%.

The oxidation ratio of copper element can be calculated using equation (2)

$$\delta = 3.97 \times \frac{m_O}{m_{Cu}} \approx 0.88\ .$$

That is to say, the nominal expression of copper oxide film in sample B can be written as $Cu_{0.88}$, and that after post annealing treatment in air is CuO.

After post annealing treatment in air, the mass gain of sample B (m_{gain}) can be calculated

$$m_{gain} = m_2 - m_1 = 5.2\mu g\ .$$

TABLE 3. The composition and oxidation ratio of deposited films of sample A and sample B.

Sample	Composition of the Deposited Film	Mass Percentage of Each Component in the Deposited Film	Oxidation Ratio of Copper Element
A	Cu, Cu_2O	Cu: 47%, Cu_2O: 53%	0.25
B	Cu_2O, CuO	Cu_2O: 22%, CuO: 78%	0.88

And the mass gain is due to the further oxidation of Cu_2O in the deposited film according to the following reaction,

$$Cu_2O + \tfrac{1}{2}O_2 = 2CuO \ . \tag{3}$$

Then mass of Cu_2O in the deposited film of sample B can be obtained, which is 46.5μg, and its mass percentage is 22%. Mass of CuO in the deposited film of sample B is 164.4μg, and its mass percentage is 78%.

The composition and oxidation ratio of deposited films in sample A and sample B are summarized in Table 3.

CONCLUSIONS

From this research, two conclusions can be obtained.

1) The ultra micro balance can be used to analyze the oxygen content of copper film quantitatively.
2) The in-situ annealing treatment of copper oxide film can improve the oxygen content significantly.

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