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FABRICATION OF P-TYPE TRANSPARENT OXIDE FILMS WITH DELAFOSSITE STRUCTURE BY SOL-GEL PROCESSING

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Abstract. $CuAlO_2$, $CuAl_{1-x}Mg_xO_2$, $CuCrO_2$, $CuCr_{1-x}Mg_xO_2$ and $CuAl_{0.5}Cr_{0.5}O_2$ thin films were deposited on quartz substrates by sol-gel processing using spin coating technique. The elemental compositions, synthesis mechanisms, optical transmittance and resistivity of prepared films were studied. $CuAl_{0.5}Cr_{0.5}O_2$ films had the best characteristics under lower temperature of synthesis. Optical transmittance of $CuAl_{0.5}Cr_{0.5}O_2$ reached 70 % in visible region. The resistivity of $CuAl_{0.5}Cr_{0.5}O_2$ was 0,4 kΩ·cm and was stable with time. Thus, $CuAl_{0.5}Cr_{0.5}O_2$ films may have potential applications for transparent optoelectronics as p-conductivity transparent oxides.

Keywords: p-type transparent oxide films; quartz substrate; delafossite structure; sol-gel processing.

1. Introduction

Transparent conductive oxide films of n-type conductivity are widely used as transparent conductive electrodes in optoelectronic devices: LEDs, photodetectors, solar panels, to increase their productivity [1]. Nowadays, the industry of thin-film oxide films is focused on the development and production of thin-film materials of p-type conductivity. The preparation of p-type conductivity transparent films will significantly expand the boundaries of thin-film structures applications and lead to the development of "transparent" thin-film optoelectronics based on a transparent p-n heterojunction. Transparent oxide films of p-type conductivity have only recently attracted an attention of researchers due to the complex technology of such materials preparing. The interest in materials with the delafossite structure appeared after first p-type $CuAlO_2$ thin film was fabricated in 1997 [2, 3]. However, until now, in terms of their electrical characteristics, these films are inferior to the well-proven n-type thin oxide films, such as aluminum-doped zinc oxide (AZO) and indium-doped tin oxide (ITO) [4, 5]. Currently, the problem is to increase the conductivity of the p-type oxide films with decrease the cost of production technology owing to reducing process temperature. At present, the main methods for fabricating films of the delafossite structure are the pulsed laser deposition method, magnetron sputtering and electron beam sputtering [6, 7]. At the same time, the method of films preparing from solutions, namely the sol-gel method [8-14], could become an alternative competitive approach for the production of such materials.

In this paper, we describe the sol-gel processing of Cu (I) -based delafossite oxides on quartz substrates and comparison their optical and electrical characteristics.

2. Experimental and results

Different sol solutions were examined for each structure $CuAlO_2$, $CuAl_{1-x}Mg_xO_2$ (x=0.01), $CuCrO_2$, $CuCr_{1-x}Mg_xO_2$ (x=0.05) and $CuAl_{0.5}Cr_{0.5}O_2$. The molar ratio of Mg to Cu in each solutions was determined by the x value and then the molar ratio of Al species was equal to the (1-x) value. To yield a homogeneous solution the prepared sol stirred at room temperature for 5 hours. The fused quart plates with 15 mm in diameter were used as substrate. The film was deposited layer by layer on substrate at a speed of 4000 rpm for 20 s. Each layer was preheated for at to remove organic resides. Ten layers were deposited for each film. Finally, deposited films were annealed for several hours at 900-1150 °C in air or argon.

For $CuAlO_2$ films precursor solution consisted of $Cu(CH_3COO)_2 \cdot H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, 2-Methoxyetanol. The molar ratio of Cu/Al was 1.2:1. The concentration of solution was 0.4 M. The film was annealed in argon for 4 hours at 1200 °C. At annealing in air the phase $CuAlO_2$ was not obtained.

For $CuAl_{1-x}Mg_xO_2$ (x=0.01) films the solution was prepared by dissolving mixtures of $Cu(CH_3COO)_2 \cdot H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and isopropanol. The molar ratio of Cu/Al was 1:1. The concentration of solution was 0.2 M. The film was annealed in air for 4 hours at 1200 °C.

For $CuCrO_2$ films the solution was prepared by dissolving mixtures of $Cu(CH_3COO)_2 \cdot H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, 2-Methoxyetanol. The molar ratio of Cu/Cr was 1:1. The concentration of solution was 0.2 M. The film was annealed in air for 1 hours at 1000 °C.

For $CuCr_{1-x}Mg_xO_2$ films the solution was prepared by dissolving mixtures of $Cu(CH_3COO)_2 \cdot H_2O$ + $Cr(NO_3)_3 \cdot 9H_2O$ + $Mg(NO_3)_2 \cdot 6H_2O$ + 2-Methoxyetanol. The molar ratio of Cu/Cr was 1:1. The concentration of solution was 0.2 M. The film was annealed in air for 1 hours at 1000 °C.

For $CuAl_{0.5}Cr_{0.5}O_2$ films precursor solution consisted of $Cu(CH_3COO)_2 \cdot H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$ + $Cr(NO_3)_3 \cdot 9H_2O$. The molar ratio of Cu/Al/Cr was 1:0.5:0.5. The concentration of solution was 0.2 M. The film was annealed in air for 1 hours at 1000 °C.

The thickness of one deposited layer was 20-40 nm. The total thickness of films was 0,2-0,4 μm.

The electrical resistivity of films was measured by 4-probe method with used source meter Keithley 2450. Optical absorption measurements of films were performed with fiber spectrometer AvaSpec-2048.

Figs. 1-5 illustrate the transmittance of $CuAlO_2$ (S1), $CuAl_{1-x}Mg_xO_2$ (x=0.01) (S2), $CuCrO_2$ (S3), $CuCr_{1-x}Mg_xO_2$ (x=0.05) (S4) and $CuAl_{0.5}Cr_{0.5}O_2$ (S5) thin films in the range 300-1200 nm.

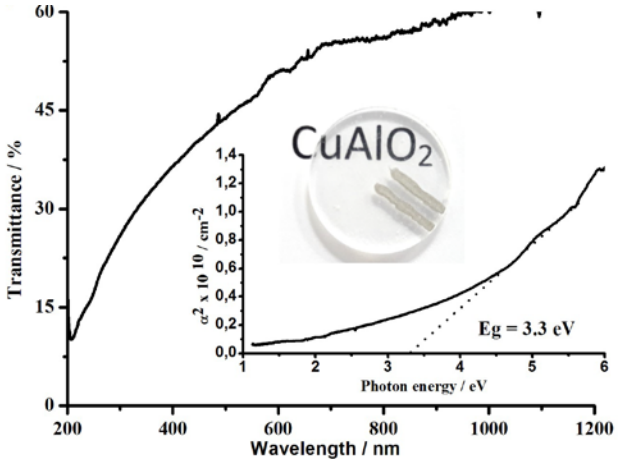

Fig. 1. Optical transmittance of $CuAlO_2$ (S1). The insets show the $CuAlO_2$ optical band gaps calculated by Tauc's relation.

The average transmittance of the samples S1, S2, S3, S4 and S5 at 400-800 nm were 41 %, 50 %, 36 %, 26 %, and 53 %, respectively.

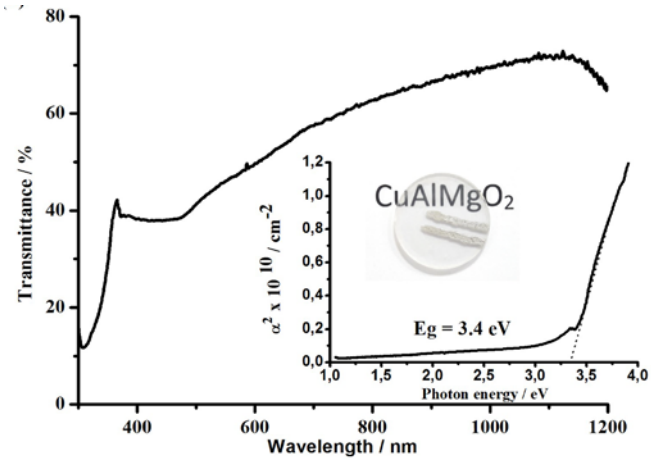

Fig. 2. Optical transmittance of $CuAl_{1-x}Mg_xO_2$ (x=0.01) (S2). The insets show the $CuAl_{1-x}Mg_xO_2$ (x=0.01) optical band gaps calculated by Tauc's relation.

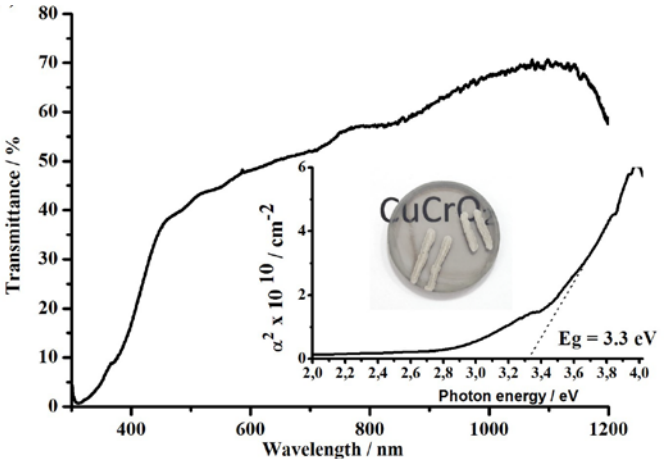

Fig. 3. Optical transmittance of $CuCrO_2$ (S3). The insets show the $CuCrO_2$ optical band gaps calculated by Tauc's relation.

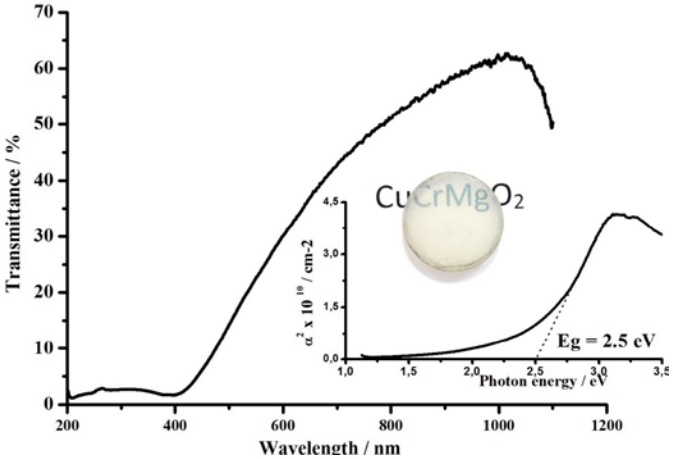

Fig. 4. Optical transmittance of $CuCr_{1-x}Mg_xO_2$ (x=0.05) (S4). The insets show the $CuCr_{1-x}Mg_xO_2$ optical band gaps calculated by Tauc's relation.

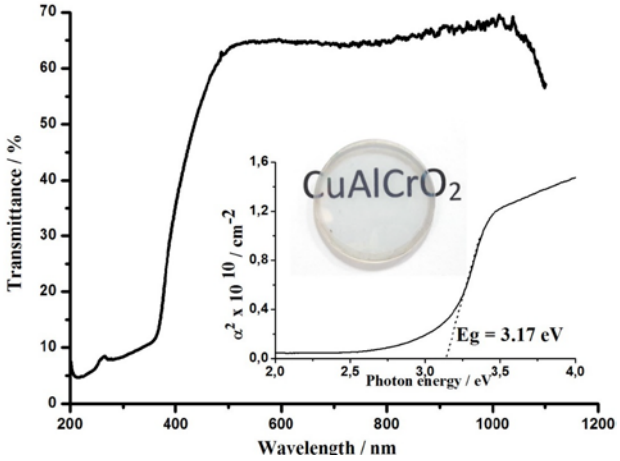

Fig. 5. Optical transmittance of $CuAl_{0.5}Cr_{0.5}O_2$ (S5). The insets show the $CuAl_{0.5}Cr_{0.5}O_2$ optical band gaps calculated by Tauc's relation.

The optical band gap was estimated by the Tauc's relation [15], expressed as

$$\alpha h\nu^n = A(h\nu - E_g^{opt}), \quad (1)$$

where A is a constant, E_g^{opt} is the band gap of the films, hν is the photon energy, α is the absorption coefficient. For a direct allowed transition, n is 2.

As shown in Fig. 1-5 (insets), for the direct transition, optical band gap of the samples S1, S2, S3, S4 and S5 were 3,3 eV, 3,4 eV, 3,3 eV, 2,5 eV, 3,17 eV, respectively.

The electrical resistivity of the films S1, S2, S3, S4 and S5 were 9 kΩ·cm, 1.8 kΩ·cm, 0.8 kΩ·cm, 0.4 kΩ·cm and 0.4 kΩ·cm, respectively.

3. Conclusions

We deposited $CuAlO_2$, $CuAl_{1-x}Mg_xO_2$, $CuCrO_2$, $CuCr_{1-x}Mg_xO_2$ and $CuAl_{0.5}Cr_{0.5}O_2$ thin films on quartz substrates by sol-gel processing using spin coating technique. Prepared films had high optical transmittance comparable to films prepared by other physics methods. Optical transmittance of $CuAlO_2$ and $CuAl_{1-x}Mg_xO_2$ films reached 60-75 % in visible region. The average transmittance for these films at 400-800 nm was 50 % and 41 %, respectively. The resistivity of $CuAlO_2$ and $CuAl_{1-x}Mg_xO_2$ were 9 kΩ·cm and 1.8 kΩ·cm, respectively. The resistivity of $CuAlO_2$, $CuAl_{1-x}Mg_xO_2$ films increased with time. The optical transmittance of $CuCrO_2$, $CuCr_{1-x}Mg_xO_2$ films was lower ~ 30-40%, when resistivity was 0,8 kΩ·cm and 0,4 kΩ·cm, respectively. Resistivity measurements showed that doping of pure $CuAlO_2$ and $CuCrO_2$ was helpful in increasing conductivity of the films. $CuAl_{0.5}Cr_{0.5}O_2$ films had the best characteristics under lower temperature of synthesis. The resistivity of $CuAl_{0.5}Cr_{0.5}O_2$ was 0,4 kΩ·cm and optical transmittance reached 70 %. The resistivity of $CuCrO_2$, $CuCr_{1-x}Mg_xO_2$, $CuAl_{0.5}Cr_{0.5}O_2$ films was stable with time. Followed on from the results we suggested that $CuAl_{0.5}Cr_{0.5}O_2$ films could be considered as perspective candidates for p-type transparent conductive oxides with the lowest resistivity 0.4 kΩ·cm and the highest transmittance under lower temperature of synthesis.

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