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The influence of substrate temperature on properties of Cu-Al-O films deposited using the reactive ion beam sputtering method

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Abstract. For the first time, Cu-Al-O films were grown using the reactive ion beam sputtering at temperatures ranging from 80 to 380 °C in 50 °C increments. Correlations between the properties of as-grown films measured by X-ray diffraction, energy dispersive X-ray spectroscopy, atomic force microscopy, Fourier transform infrared spectrometry and optical transmission measurements have been discussed. It was shown that the increase of substrate temperature caused formation of the $CuAlO_2$ phase. Additional optimization of technological parameters of growth and post-growth temperature annealing are necessary to obtain single-phase $CuAlO_2$ films.

Keywords: Cu-Al-O films, XRD, optic properties, FTIR, morphology.

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1. Introduction

Everyone every day faces with touch screens, displays and other devices that typically include optically transparent conductive layer such as In_2O_3:SnO_2 (ITO) with *n*-type conductivity or its alternative transparent conductive films (TCF) such as ZnO doped by donor impurity or fluorine-doped tin oxide SnO_2:F (FTO) [1]. Development of deposition technology of optically transparent conductive oxides that have large electronic bandgap (>3.1 eV) and high *p*-type (hole) conductivity, opens the doors for development of flat-panel displays, UV light-emitting diodes heterojunctions, solar cells and transparent semiconductor devices as well as transparent electronics (TE) [2]. Consequently, the synthesis of *p*- and *n*-type conductivity semiconductors with a bandgap higher than 3.1 eV is an urgent task to create TE devices [3]. Delafossite-$CuAlO_2$ films have a large bandgap (about 3.5 eV) and exhibit *p*-type conductivity and high transparency in the visible region of spectrum [2, 4].

The diverse famous physical and chemical deposition methods such as magnetron sputtering [5], pulsed laser deposition [6], plasma-enhanced chemical vapour deposition [7, 8], sol–gel [9] have been used for $CuAlO_2$ films deposition. The reactive ion beam sputtering (RIBS) is considered to be the most interesting growth method due to a good films adhesion, its high deposition rates, films uniformity of over large areas of the substrates and very smooth surface of deposited films, which is important for optoelectronic applications. However, to our best knowledge, the influence of technological parameters on structure and optical properties for $CuAlO_2$ grown by RIBS method has not been studied yet in details.

It should be noted that the actual problem of $CuAlO_2$ films growth is formation of thermodynamically stable unwanted phases such as Cu_2O, CuO, Al_2O_3 and $CuAl_2O_4$ [10]. Our paper devoted to solution of this problem via careful investigation of the substrate temperature influence on structure, optical properties, elemental composition, morphology and optical properties of Cu-Al-O thin films deposited on Si (111) and glass substrates by RIBS.

2. Experimental procedure

2.1. Sample preparation

The reactive ion beam sputtering method of floatable alloyed Al-Cu target (with purity 99.99 at.%) with atomic ratio of 1:1 was used for growing $AlCuO_2$ films on Si (111) and glass substrates. In our experiments, such parameters as oxygen-argon composition in a vacuum chamber (1:3) with the pressure $4\cdot10^{-4}$ Torr, accelerating voltage (5 kV), beam current (125 mA), target-substrate distance (3 cm) and deposition time (90 min) maintain fixed. We change only the substrate temperature within the range 80 to 380 °C by the steps of 50 °C.

2.2. Characterization

The structure of the films was investigated using a DRON-3M diffractometer, equipped with a scanning and recording the computer system of the diffraction pattern using the Bragg–Brentano focusing with monochromatic Cu-K_α radiation. The sample transmission spectra were recorded on a computerized monochromator LOMO12. The surface morphology of deposited films was studied using atomic force microscope (AFM) (Quadrexed NanoScope IIIa Dimension 3000, Digital Instruments / Bruker, USA) in the tapping mode. The elemental analysis was carried out with ZEISS EVO 50 XVP SEM by using the energy dispersive X-ray spectroscopy (EDX) furnished INCA 450 (OXFORD Instruments). Fourier transform infrared spectrometry (FTIR) was carried out using the IR microscope Nicolet 6700 equipped with a motorized objective table.

3. Results and discussion

The effect of substrate temperature increasing on structure of Cu-Al-O films was studied using XRD measurements (Fig. 1). It was found that the films, deposited under substrate temperature within the range 80 to 280 °C, are composed of crystalline CuO, Cu_2O and $CuAl_2O_4$ accordingly with JCPDS cards number 65-2309, 65-3288 and 78-1605, respectively. When the substrate temperature reaches 280 °C $AlCuO_2$ begins to form, having the most intense diffraction peak (101) with the interplanar distance of 0.243 nm (accordingly with JCPDS cards number 77-2494). Also, it should be noted that all deposited Cu-Al-O films have *p*-type conductivity as confirmed by thermoelectric studies but have high resistivity (about $3\cdot10^4$ Ohm·cm) caused by multi-phases nature of as-grown films (Fig. 1).

The transmittance spectra for prepared Cu-Al-O samples in the wavelength range 300…1100 nm are presented in Fig. 2. There is also transmittance of a glass substrate used in deposition of Cu-Al-O samples with the edge close to 300 nm, which testifies that a glass substrate does not influence on optical properties of prepared Cu-Al-O samples and determination of the bandgap value. Fig. 2 shows that optical properties are greatly affected by the substrate temperature. As the temperature increases, we observed the blue shift of the absorption edge as well as increase in transparency of as-grown Cu-Al-O films, which entirely confirms the conclusion already obtained from XRD data, namely: at a low substrate temperature formation of such oxides with the bandgap lower than 3.2 eV (like CuO, Cu_2O or $CuAl_2O_4$) is dominating. When the substrate temperature comes up to 380 °C, formation of wide bandgap oxide ($CuAlO_2$) prevails over formation of other oxides (Fig. 2).

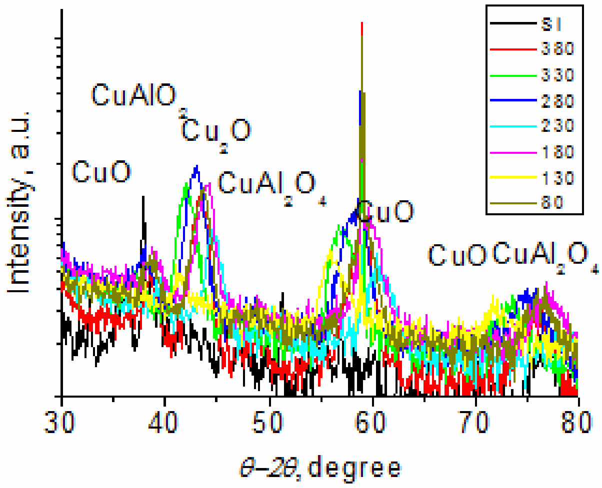


Fig. 1. X-ray diffraction patterns of Cu-Al-O films deposited at diverse substrate temperatures.

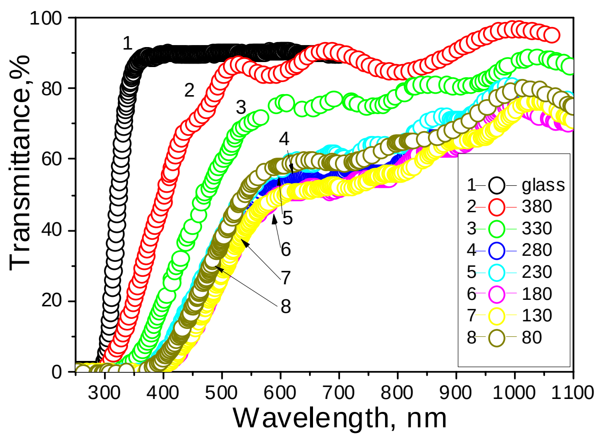


Fig. 2. The transmittance spectra of Cu-Al-O samples deposited at various substrate temperatures.

In order to determine the optical bandgap value, we first calculated the absorbance coefficient of the films using the known relation $\alpha = \ln(1/T(\lambda))/d$. Then, the bandgap value E_g was calculated from α by fitting the following expression $\alpha = A(h\nu - E_g)^{1/2}$ that is valid for direct bandgap transition. The obtained results are shown in Fig. 3. We observed two linear segments: first at low substrate temperature from 130 to 230 °C, where the bandgap value E_g increased slowly from 2.9 to 3.22 eV, and second, from 280 to 380 °C, where E_g increased significantly from 3.22 to 4 eV, respectively. A large difference in E_g over temperature range leads us to conclusion that the prepared Cu-Al-O samples contain several different phases with diverse optical properties, which correlates with XRD results. The main phase of $CuAlO_2$ starts to form only at high substrate temperatures. Cu-Al-O samples grown at the substrate temperature 380 °C have the bandgap values approximately near 4 eV, which correspond to the E_g value of $CuAlO_2$ reported in the paper [11]. These high-temperature films have a good optical quality (transparency over 80% and abrupt band edge), which is important for TCO applications.

Composition of the deposited Cu-Al-O films was estimated using the EDX analysis. Fig. 4 shows typical EDX spectrum of Cu-Al-O film deposited on Si substrate. In some samples, availability of Ar impurities up to 2.44 at.% was observed. No other contamination was found. The values of measurement errors in determination of atomic composition for O, Cu and Al were ±0.2 at.% [12].

The influence of substrate temperature on elemental distribution of as-grown Cu-Al-O films is shown in Fig. 5. For our technological parameters, all the Al-Cu-O films were deposited under oxygen-rich condition (oxygen in films was more than 50 at.%). It was found that with increasing the substrate temperature the Al/Cu stoichiometric ratio in films gradually decreases from 3.18 for the samples deposited at the substrate temperature 80 to 1.49 °C for the samples deposited at the temperature 380 °C. Obviously, this improvement of Al/Cu stoichiometric ratio with substrate temperature enhancement leads to formation of $CuAlO_2$, which was also shown using XRD and optical measurements. Improvement of the rest technological parameters for the reactive ion beam sputtering method is needed to obtain single-phase $CuAlO_2$ films.

FTIR spectroscopy is useful method for studying film composition and also for founding the chemisorbed contaminations [13]. Fig. 6 represents the FTIR spectrum of as-grown Cu-Al-O films grown at various substrate temperatures. In these spectra, the weak absorption peaks within the range 630…635 cm^{-1} and intense weak absorption peaks within the range 960…1045 cm^{-1} are observed. These weak absorption peaks are associated with Cu-O and Al-O vibrations in CuO, Cu_2O, $AlCu_2O_4$ and $AlCuO_2$ films [14-18]. The intense absorption peak was also observed in the FTIR spectrum of Si substrate (Fig. 6) and attributed to Si-O vibration [19]. Also, these reflectance spectra of Cu-Al-O films reveal the absence of good resolved peaks associated with chemisorbed contaminations on the surface of films, because in the full wavelength range the FTIR spectra of Cu-Al-O films repeat the FTIR spectrum of Si substrate (Fig. 6).

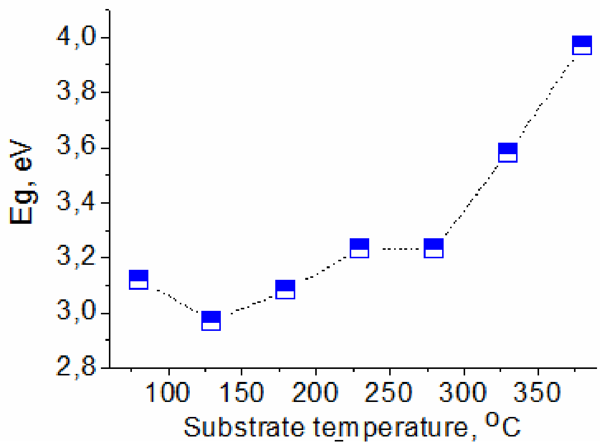


Fig. 3. The dependence of the optical band-gap of Cu-Al-O films on the substrate temperature.

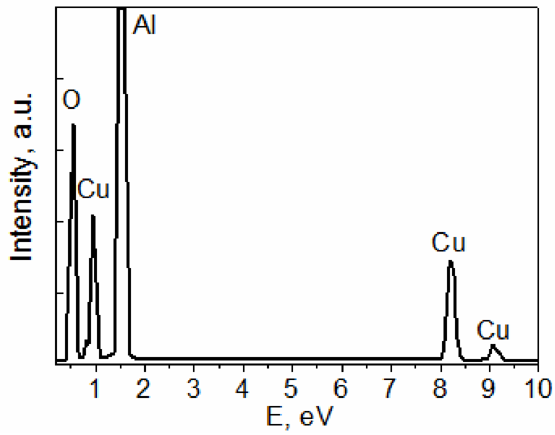


Fig. 4. Energy dispersive X-ray spectrum of Cu-Al-O films deposited under the substrate temperature 380 °C.

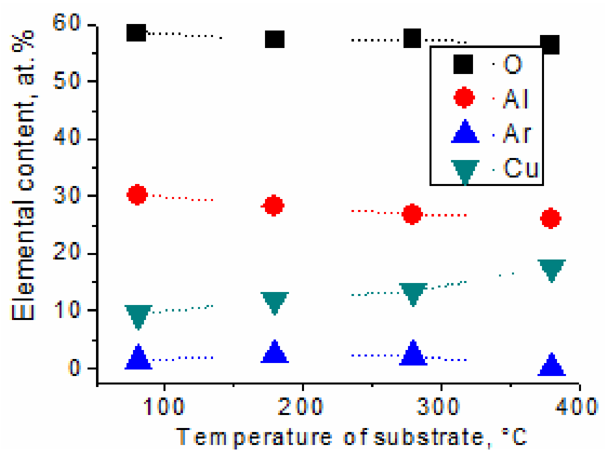


Fig. 5. The dependence of elemental content in the as-grown Al-Cu-O samples on the substrate temperature.

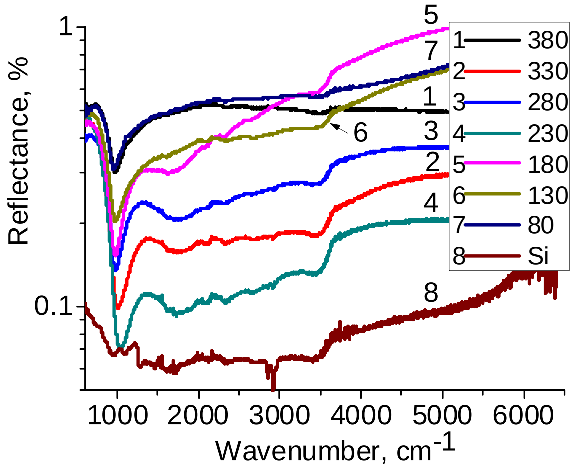
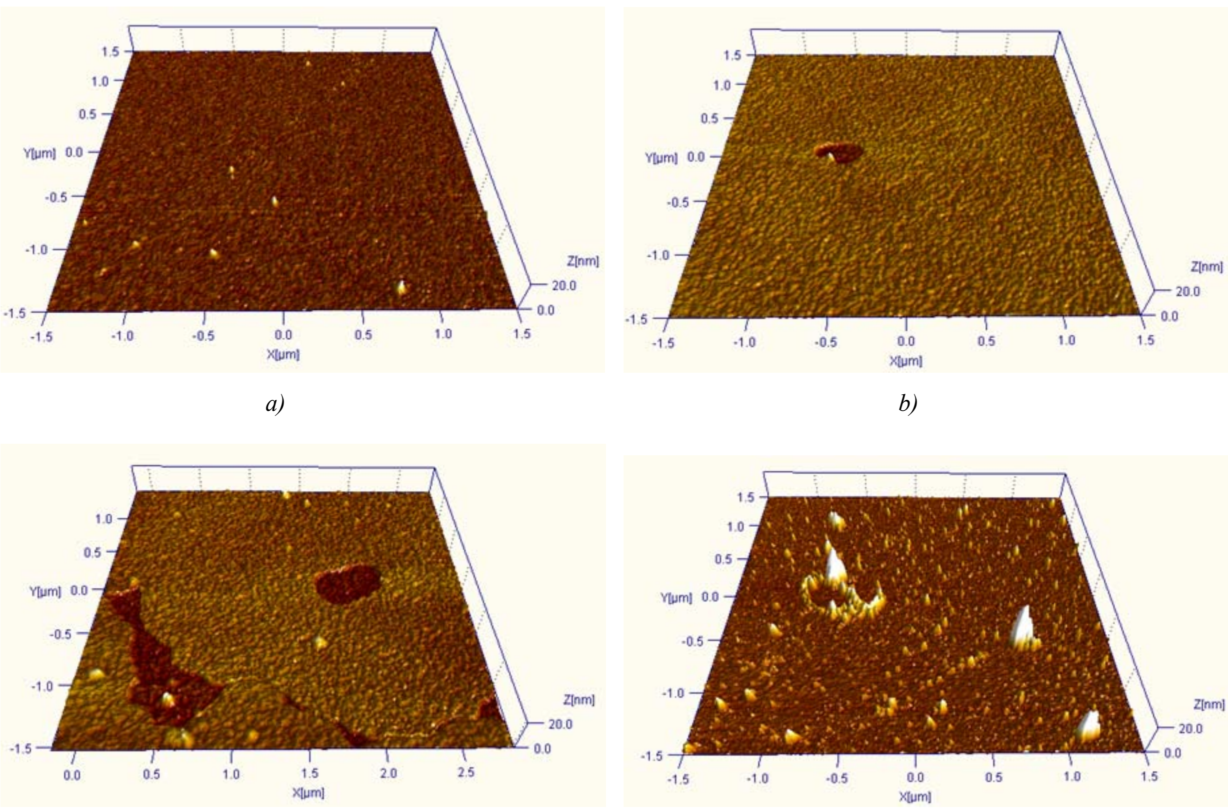


Fig. 6. The observed FTIR spectra of as-grown Al-Cu-O films deposited at various substrate temperatures. The FTIR spectrum of Si substrate is also presented.

Fig. 7 presents AFM 3D images of the Al-Cu-O films surface. The morphology of the films has polycrystalline nature with very smooth surface. The calculated using the Gwyddion software root-mean-square (RMS) roughness of the Al-Cu-O films increases gradually from 0.37 to 1.39 nm with enhancing the substrate temperature from 80 up to 380 °C, respectively. The AFM studies of Al-Cu-O films morphologies also confirm formation of diverse phases for as-grown films (Fig. 7b, c). In the case of deposition at the substrate temperature 380 °C, diverse phases are not observed (Fig. 7d).

4. Conclusions

Cu-Al-O thin films have been deposited on Si (111) and glass substrates by reactive ion beam sputtering method of floatable Al-Cu target with atomic ratio of 1:1. The effect of substrate temperatures changed in the range 80…380 °C on the properties of Cu-Al-O thin films was studied. XRD and optical transmittance measurements demonstrate that enhancement of the substrate temperature up to 280 °C leads to formation of $AlCuO_2$ phase, when the Al/Cu stoichiometric ratio approaches to unity. The RIBS method allows to obtain very smooth surface with RMS roughness of the Al-Cu-O films 0.37…1.39 nm. The aim to obtain single-phase of $CuAlO_2$ films requires the improvement of other technological parameters of the reactive ion beam sputtering method.



a) *b)* *c)* *d)*

Fig. 7. AFM 3D images of the surface morphology for as-grown Cu-Al-O films deposited at 80 (*a*), 180 (*b*), 280 (c) and 380 °C (*d*).

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