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Structural, vibrational and photodegradation properties of $CuAl_2O_4$ films

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Abstract. Cu–Al–O thin films were grown on Si (111) substrates by using the reactive ion-beam sputtering (RIBS) method within the temperature range 80 to 380 °C. The effect of thermal annealing of Cu–Al–O films under various regimes of cooling on the microstructure, morphology, optical properties and photocatalytic activity were examined. The properties of annealed Cu–Al–O films were studied using atomic force microscope (AFM), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectrometry (FTIR). The X-ray diffraction patterns show appearance only $CuAl_2O_4$ phase after thermal annealing of Cu–Al–O thin films at 900 °C. Raman scattering confocal measurements have also confirmed the presence of CuO phases in annealed Cu–Al–O samples. AFM results have indicated that the greatest RMS roughness is observed in $CuAl_2O_4$ films after temperature annealing under the fast cooling regime. Photodegradation of $CuAl_2O_4$ films was investigated using methyl orange as model pollutant. Present results indicate that $CuAl_2O_4$ photocatalysts are potential candidate for the practical application in photocatalytic degradation of organic compounds.

Keywords: Cu–Al–O films, XRD, optical properties, FTIR, photocatalytic degradation.

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1. Introduction

The copper aluminate nanocomposites have attracted a great interest due to their low cost, thermal stability, non-toxic, high electrical and optical resistance characteristics that make them promising for various applications in microelectronics (optical, electronic and magnetic devices) up to catalysis and biosensors [1–3]. The ternary oxide copper aluminate ($CuAl_2O_4$) is *p*-type semiconductor with a bandgap 1.77...2.3 eV [4], which can be used as a potential photocatalyst for degrading toxic water-soluble organic dyes within the range of visible
light [5]. Such properties of copper aluminate as hydrophobicity, low surface acidity make them promising catalytic or carrier materials for substituting the more traditional systems [6].

These properties can be used, for example, to decompose methyl orange (MO). It is an organic azo dye widely used in various branches of industry, for example, printing, textile and photography. Its release into environment is not only toxic to aquatic life, but it is carcinogenic to humans. The removal of azo dyes is of great significance to water purification. In the recent years, photocatalytic degradation was attractive as a promising tool for removal of azo dyes and organic impurities from waste water. Photocatalytic materials could effectively eliminate many stable non-biodegradable dyes, as compared with the traditional method of processing [7].

The main scientific and technological challenge is deposition of $CuAl_2O_4$ films with a good quality and homogeneity. Earlier, $CuAl_2O_4$ films were tried to be deposited using several methods, namely: magnetron sputtering [4], pulsed laser deposition [8], plasma-enhanced chemical vapour deposition [9, 10], and sol-gel method [11]. However, all these contain additional unwanted oxide phases. In recent years, the reactive ion-beam sputtering (RIBS) method becomes attractive technique for growing the films, because of its advantages of producing pure and ultrafine films at low temperatures. It is considered to be the most interesting

growth method due to a good adhesion of coatings, its high deposition rates, film uniformity over large areas and very smooth surface of deposited films, which is very important for the optoelectronic applications. However, the researches devoted to deposition of $CuAl_2O_4$ films by using the RIBS method are known up to now.

It is very important to pay attention to the topical problem of deposition single-phase materials in Cu–Al–O system that is inclined to easy formation of thermodynamically stable unwanted phases such as Cu_2O, CuO, Al_2O_3 [12]. Our previous investigation [13] was devoted to the substrate temperature influence on the structure, elemental composition, morphology and optical properties of $CuAlO_2$ thin films deposited on Si (111) and glass substrates by using the RIBS method. The influence of such technological approach as the cooling regime after thermal annealing in the ambient atmosphere on the structural, optical and catalytic properties for $CuAl_2O_4$ films grown using the RIBS method has not been studied yet in details.

Therefore, the main purpose of this paper is to demonstrate the influence of the thermal annealing in air and regimes of cooling rate on the microstructure, elemental composition, and optical properties of Cu–Al–O thin films and on the photocatalytic performance of the synthesized $CuAl_2O_4$ films for the case of degradation of methyl orange.

2. Experimental procedure

2.1. Sample preparation

The reactive ion-beam sputtering method of floatable alloyed Al–Cu target (with the purity 99.99 at.%) with atomic ratio of 1:1 was used for growing Al–Cu–O films on Si (111) substrates. In our experiments, such parameters as oxygen-argon composition in vacuum chamber (1:3) with pressure $4\cdot10^{-4}$ Torr, accelerating voltage 5 kV, beam current 125 mA, target-substrate distance 3 cm and deposition time 90 min were fixed. The substrate temperature was in the range 80...380 °C with the step close to 50 °C. After that, the obtained films were annealed at 900 °C for 3 hours under ambient conditions. The first series was cooled in the regime of slow rate (for 3 h), and the second one was done at the fast rate regime (for 15 min).

2.2. Characterization

The structure of the films was investigated using the DRON-3M diffractometer, equipped with a scanning and recording computer system of the diffraction pattern by using the Bragg–Brentano focusing with monochromatic Cu-K_α radiation. The surface morphology of deposited films was studied using the atomic force microscope (AFM) (Quadrexed NanoScope IIIa Dimension 3000, Digital Instruments / Bruker, USA) in the tapping mode. The elemental analysis was carried out using the scanning electron microscope (SEM) ZEISS EVO 50 XVP SEM using the energy dispersive X-ray (EDX) spectrum analyzer INCA 450 (OXFORD Instruments). Fourier transform infrared spectrometry (FTIR) was carried out using the IR microscope Nicolet 6700 equipped with a motorized objective table. The transmittance of the methyl orange solution was measured with the spectrophotometer based on LOMO MDR12 equipped with Hamamatsu detector S1336.

2.3. Photocatalytic experiment

The photocatalytic activities of the rapidly cooled Cu–Al–O films were investigated for degradation of MO used as a model waste water contaminant. MO has two absorption peaks in distilled water at 270 and 465 nm, respectively. The absorbance at 465 nm was chosen to monitor the effect of photocatalysis on the degradation of MO, because it was conformed to the Lambert–Beer law at concentrations ranging between $2\cdot10^{-3}$ and $1\cdot10^{-5}$ M [14]. The initial concentration of MO was chosen $3\cdot10^{-5}$ M as optimal. For experiments, the Si wafers covered by $CuAl_2O_4$ films with area near of 1×1 cm^2 were immersed in 3 mL of aqueous solution of MO. Before illumination, the investigated $CuAl_2O_4$ films hold in MO aqueous solution for 30 min in the dark to achieve an adsorption–desorption equilibrium. Then, the $CuAl_2O_4$ films were exposed to UV Hg lamp having the electric power 200 W for 3, 6, 9, 12 h. The change in the concentration in each degraded solution was monitored by measuring the transmittance of MO aqueous solution at the wavelength 465 nm. The distilled water was used as the reference sample.

3. Results and discussion

The influence of substrate temperature on the elemental distribution of as-grown Cu–Al–O films is shown in Fig. 1. It was found that Al/Cu atomic ratio in our Cu–Al–O films gradually increases from 1.49 up to 3.18 with increasing substrate temperature from 80 to 380 °C. The increase of Al/Cu atomic ratio favors formation of highly pure $CuAlO_2$ or $CuAl_2O_4$ films, while its decrease leads to formation of $CuAlO_2$ films with the additional CuO phase that was confirmed by XRD in [15] for the samples annealed at 900 and 950 °C. The paper [15] also implies that diffusion of CuO into the Al_2O_3 matrix occurs slowly at low growth temperatures.

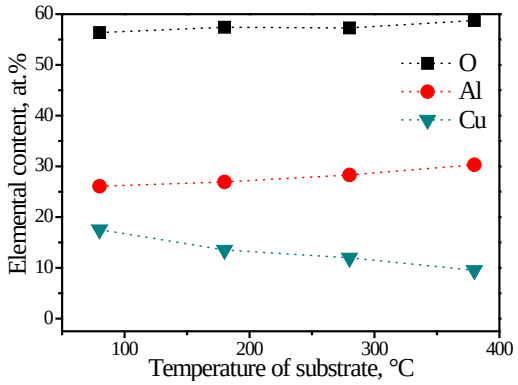

Fig. 1. Dependence of elemental content on the substrate temperature in the as-grown Al–Cu–O films.

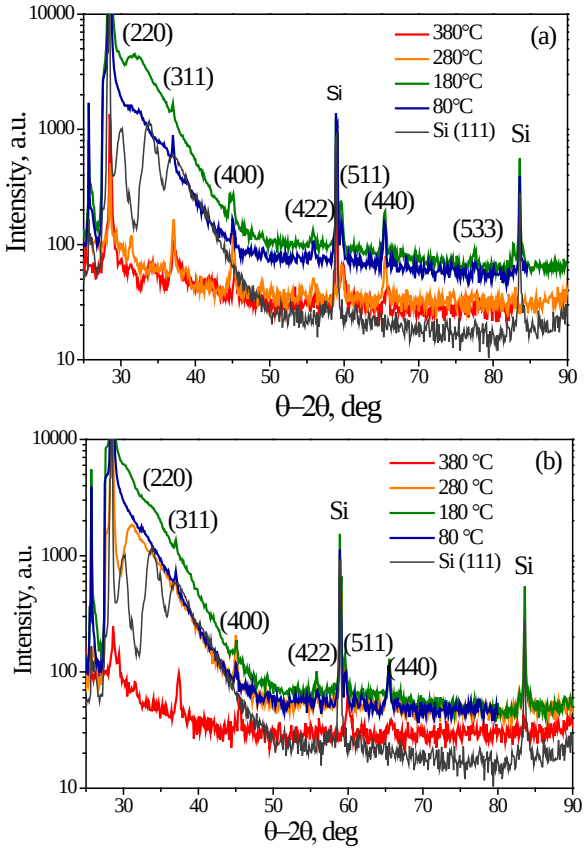

Fig. 2. X-ray diffraction patterns of the annealed $CuAl_2O_4$ films deposited on Si at diverse substrate temperatures and cooled at fast regime (a) and slow regime (b). (Color online)

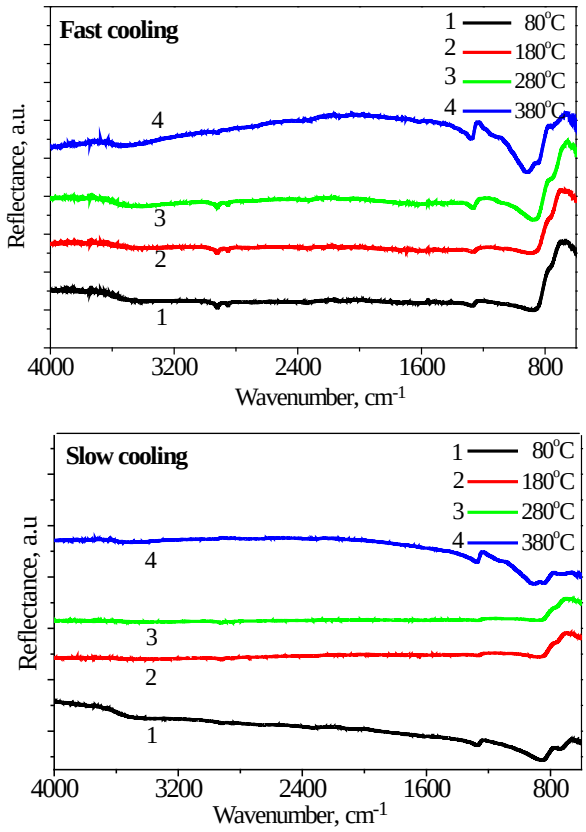

Fig. 3. The observed FTIR spectra of annealed Al–Cu–O films deposited at diverse substrate temperatures in the following regimes: fast cooling; slow cooling.

The crystallinity and Al/Cu atomic ratio in the films was significantly improved, when the temperature was raised to 380 °C. Improvement of the technological parameters for RIBS is necessary to obtain single-phase Cu–Al–O films. The effect of different regimes for cooling rate after annealing at 900 °C on the structure of Cu–Al–O films was studied by XRD measurements (Figs 2a and 2b). It was found that the films deposited at substrate temperature within the range 80 to 380 °C and then annealed at the temperature 900 °C are composed of crystalline $CuAl_2O_4$ [16] in accord with JCPDS cards number 78-1605. XRD measurements have confirmed single-phase formation of $CuAl_2O_4$ with the XRD diffraction peaks from (220), (311), (400), (422), (511) and (440) planes [17]. It is worth to note that no additional peaks of any other phases were found in the XRD pattern corresponding to the films under study. When increasing the substrate temperature up to 280…380 °C, the corresponding diffraction peaks (220), (311) become stronger, apparently, due to the growth of crystallites [18].

FTIR spectroscopy is a useful method for studying films composition [19]. FTIR studies were carried out in the reflection mode, because Si substrates were not transparent. The FTIR spectra of annealed at 900 °C Al–Cu–O films that were previously grown at diverse substrate temperatures are presented in Fig. 3. The faint absorption peak around 3100...3500 cm^{-1} was caused by the OH longitudinal vibrations of the adsorbed water molecules. The broad band below 1000 cm^{-1} is attributed to the characteristic metal-oxygen vibrations in the Cu–Al–O films [20]. The appearance of additional metal–oxygen stretching frequencies within the range 550...850 cm^{-1} for annealed films is associated with the vibrations of Cu–O, Al–O, and Cu–O–Al bonds [21] or Al–O–Al longitudinal vibrations in $CuAl_2O_4$ [17]. The absorption peaks in the spectral range around 1300 and 2900 cm^{-1} are attributed to vibrations of Si–O bonds and associated with chemisorbed organic contaminations on the films' surface [22].

The film surface morphology and roughness were characterized using AFM. To characterize the surface roughness, we used the root mean square (RMS) value in nanometer determined from 2.5×2.5 μm AFM images. Fig. 4 demonstrates that annealed films have a very uniform surface. The grain size decreases from 55…60 down to 38…40 nm with increasing the substrate temperatures (Fig. 5a). The calculated by Gwyddion software RMS roughness of $CuAl_2O_4$ films increases with substrate temperature enhancement from 80 °C up to 380 °C: for as-grown samples from 0.39 up to 1.37 nm; for annealed slowly cooled samples from 2.81 up to 6.67 nm and fast cooled from 3.29 up to 14.73 nm. These results have indicated that the greatest RMS roughness observed in $CuAl_2O_4$ films after temperature annealing in the fast cooling regime.

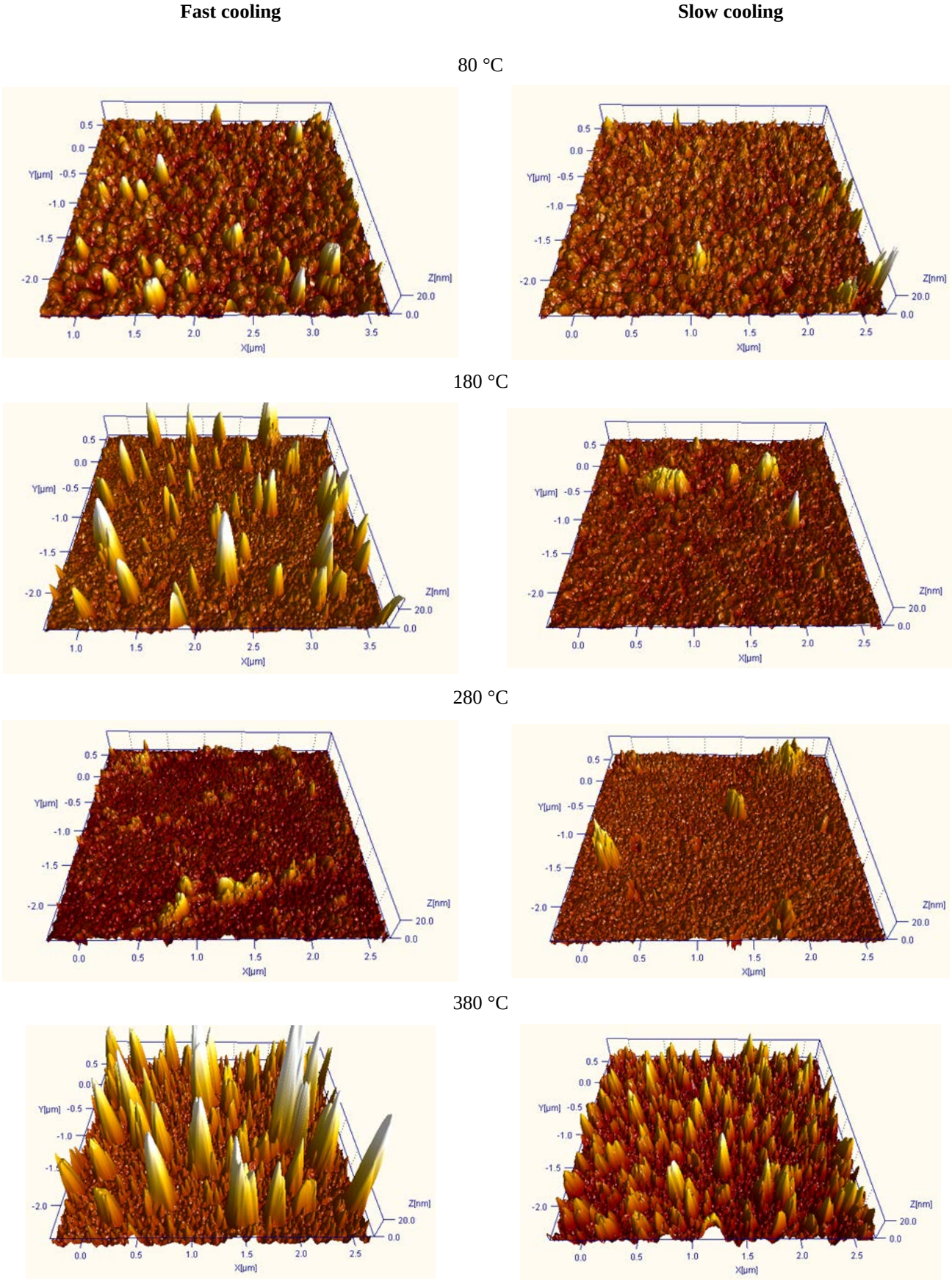

Fig. 4. AFM 3D images of surface morphology for annealed Cu–Al–O films deposited at 80, 180, 280, and 380 °C.

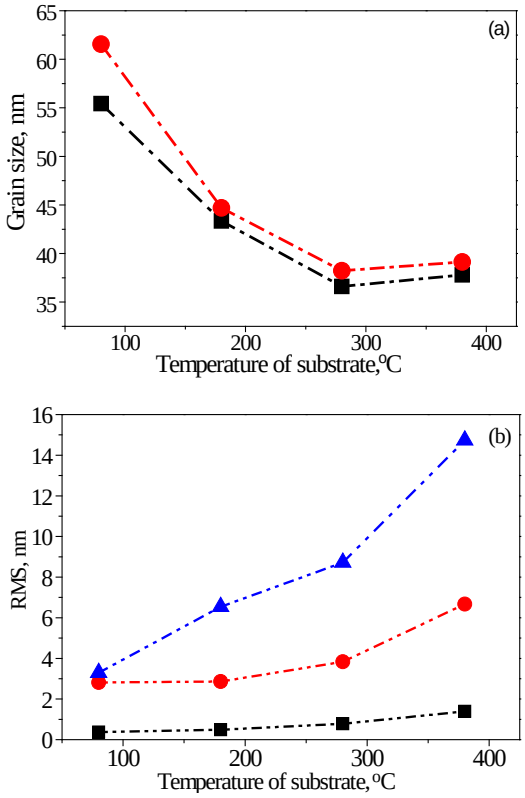

Fig. 5. Temperature dependences of (a) grain sizes (■ – slow cooled, ● – fast cooled) and (b) RMS values (■ – as-grown, ● – slow cooled, ▲ – fast cooled) of annealed $CuAl_2O_4$ films.

The Raman spectroscopy is a powerful method for the characterization of chemical and crystal structure and phase evolution for thin films. Fig. 6 shows the micro-Raman spectra of annealed and cooled in the fast rate regime Cu–Al–O films in dependence on the substrate temperatures. For the Cu–Al–O films, several peaks at 232, 288, 343, 361, 484, 593, 624, 708 and 761 cm^{-1} were observed. The strong Raman peaks at 288, 343 and

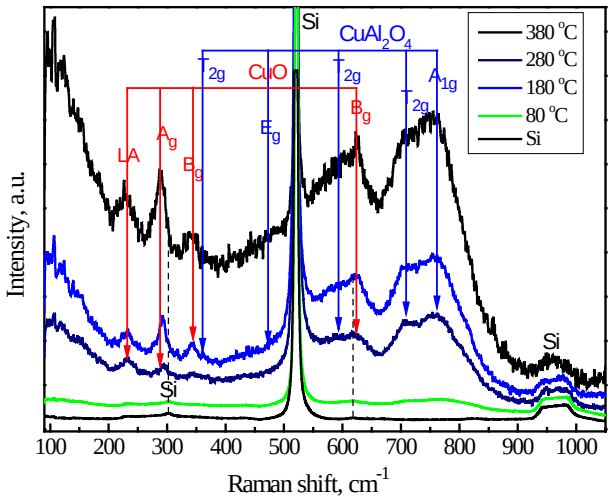

Fig. 6. Raman spectra of the annealed Cu–Al–O films deposited at 80, 180, 280, and 380 °C. (Color online)

624 cm^{-1} correspond to A_g, $B_g(1)$ and $B_g(2)$ phonon modes of the CuO phase [23, 24]. For CuO, only three optical phonon modes $A_g + 2B_g$ are Raman active. The change (3…5 cm^{-1}) in peak positions of A_g, $B_g(1)$ and $B_g(2)$ phonon modes with increasing the substrate temperature reflects strain and size effects that act to confine the lattice vibrations in the radial directions resulting in a shift in A_g and B_g symmetries [25]. The well-defined peak at 232 cm^{-1} was attributed to the bandboundary LA phonon [26] or spin-phonon coupling [24]. The enhancement of the substrate temperature leads to increasing the intensity of CuO-related Raman scattering modes. This fact correlates with the observed results for the elementals distribution inside Cu–Al–O films, which is presented in Fig. 1. Therefore, to deposit single-phase $CuAl_2O_4$ films by using RIBS, more favorable is choosing the low-temperature range of substrate temperatures.

Other Raman peaks in Fig. 6, which are located at 361, 484, 593, 708 and 761 cm^{-1}, are related to $CuAl_2O_4$. It should be noted that $CuAl_2O_4$ is an inverse spinel, which exhibits the cubic structure. In this structure, the oxygen anions form a cubic close-packed sub-lattice surrounded by Cu^{2+} and Al^{3+} cations occupying tetrahedral and octahedral positions, respectively. $CuAl_2O_4$ is related to the $Fd\bar{3}m$ space group, which predicts five active Raman modes, namely, $\Gamma = A_{1g} + E_g + 3T_{2g}$ [27]. The wide Raman peaks observed at 361, 593 and 708 cm^{-1} correspond to T_{2g} phonon mode of $CuAl_2O_4$ as a result of Cu–O vibrations. The peak at 761 cm^{-1} could be assigned to A_{1g} that represents the vibrations of M_t–O_4 tetrahedron (M_t, tetrahedral cation) [28]. The weak E_g mode at about 450 cm^{-1} corresponds to the bending mode of Al–O tetrahedron. The great width of the high-frequency band could be caused by the presence of different cation–anion bond lengths in $CuAl_2O_4$ [29].

3.1. Photocatalytic studies

The mechanism for MO degradation by photocatalysis has been described by He Y. *et al.* [30, 31]. At the beginning, $CuAl_2O_4$ semiconductor is photo-excited to generate electron (e^-_{CB})-hole (h^+_{VB}) pairs. Water molecules are then split into H^+ and the oxidizing OH• (hydroxyl OH^- ions) due to the presence of the valence band holes. Then, hydroxyl ions also inject electrons into the valence band holes (of $CuAl_2O_4$) to form OH•. OH• is the main oxidant for the degradation of MO molecules in water. OH• attaches to the aromatic ring of MO, and later finds multiple substitutions. The intermediate could be further attacked by OH• and subsequently could break into smaller molecules generating CO_2 and H_2O at the end of reaction. Electron from the conduction band is scavenged by an O_2 molecule to generate superoxide radical $O_2^{\bullet-}$, however, they have a minor role to play in the photocatalytic oxidation process. Therefore, photo-irradiation was necessary to achieve the better degradation within a short time and it would help to reduce the reaction time and to increase degradation rate [17].

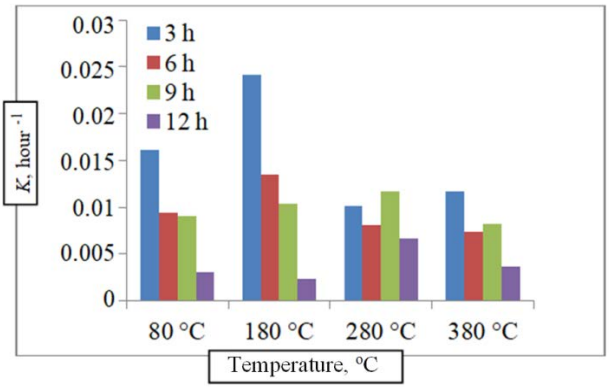

Fig. 7. Degradation rate constants of MO in the presence of $CuAl_2O_4$ films under UV Hg lamp irradiation. $K = -\ln(C_0/C)/t$, K – degradation rate constant, C_0 – initial concentration, C – concentration at certain time, t – reaction time.

We suppose that the activity of photocatalyst must be increased with increasing roughness of the films. Therefore, the fast-cooled films were selected for photocatalytic experiments. To quantitatively describe the reaction kinetics of the MO degradation, a pseudo-first order equation $C = C_0 \exp(-Kt)$ (where C_0 is the initial concentration of the methyl orange, C is the concentration at a given moment of time (t) and K – degradation constant) was used appropriate for low dye concentrations [32]. MO solutions are very stable and do not degrade under visible or UV lights, except when being assisted by a suitable photocatalyst [33]. The dependence of $\ln(C_0/C)$ against irradiation time was plotted from which the constant of degradation rate K was calculated. The diagram in Fig. 7 demonstrates the dependence of K values on time and substrate temperature under UV irradiation. As can be seen, the degradation rate constant of MO is decreased with increasing the substrate temperature and diminish with the time. We supposed that this fact is related with decreasing the surface conductivity for $CuAl_2O_4$ films grown at higher temperatures. Improvement of the specific surface of $CuAl_2O_4$ films by thermal annealing and with adjustment of optimal cooling conditions can make these films suitable for photocatalytic applications. The greatest K value of MO degradation was observed for the samples grown at 180 °C after 3-hour irradiation.

4. Conclusions

The effects of thermal annealing as well as of cooling regimes (fast and slow ones) on the microstructure, morphology, and optical properties of Cu–Al–O films deposited at different substrate temperatures (80...380 °C) by using the RIBS method were investigated with XRD, EDX, FTIR, Raman scattering and AFM. It has been found that the increase of substrate temperature indicates what properties of Al/Cu ratio in as-grown Cu–Al–O films leads to. XRD studies confirm formation of single-phase $CuAl_2O_4$ films at both regimes of cooling after thermal annealing at the temperature 900 °C in air for 3 hours. However, Raman scattering examinations have shown the presence of CuO phases was found especially at the highest substrate temperatures. The RIBS method enables to obtain very smooth surface with RMS roughness of the Al–Cu–O films close to 0.37...1.39 nm. It has been found that application of fast cooling regime allows obtaining the $CuAl_2O_4$ films with an improved specific surface. The improvement of the specific surface inherent to $CuAl_2O_4$ films with thermal annealing in the fast cooling regime can make these films suitable for photocatalytic applications. Additional optimization of technological parameters of the growth method and post-growth temperature annealing is necessary to form the single-phase $CuAl_2O_4$ films and for the enhancement of value for their photocatalytic parameters providing decomposition of dangerous pollutions.

Acknowledgements

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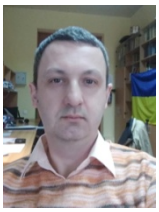

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Структурні, коливальні та фотокаталітичні властивості плівок $CuAl_2O_4$

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Анотація. Тонкі плівки Cu–Al–O вирощено на підкладках Si (111) методом реактивного іонно-променевого розпилення (RIBS) при температурі підкладок у діапазоні від 80 до 380 °C. Вивчено вплив термічного відпалу плівок Cu–Al–O при різних режимах охолодження на мікроструктуру, морфологію, оптичні властивості та фотокаталітичну активність. Властивості відпалених плівок Cu–Al–O вивчали за допомогою атомно-силової мікроскопії (AFM), енерго-дисперсійної рентгенівської спектроскопії (EDX) та інфрачервоної спектрометрії з Фур'є перетворенням (FTIR). Рентгенограми свідчать про те, що після термічного відпалу при 900 °C наявною є лише фаза $CuAl_2O_4$. Конфокальні вимірювання комбінованого розсіювання підтверджують також наявність фаз CuO у відпалених зразках Cu–Al–O. Результати AFM показали, що найбільша середньоквадратична шорсткість поверхні спостерігається у відпалених плівках $CuAl_2O_4$, отриманих у режимі швидкого охолодження. Фотокаталітичні властивості плівок $CuAl_2O_4$ досліджували за допомогою барвника метилового оранжевого як модельного забруднювача. Отримані результати вказують на те, що $CuAl_2O_4$ є потенційним кандидатом для практичного застосування при дослідженні фотокаталітичної деградації органічних сполук.

Ключові слова: плівки Cu–Al–O, XRD, оптичні властивості, FTIR, фотокаталітична деградація.