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Study of sol-gel Cu-doped Al_2O_3 thin films: structural and optical properties

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Abstract. We present a study of of copper-doped Al_2O_3 films prepared by sol-gel deposition. The films were spin-coated on Si and quartz substrates and a high-temperature treatment was conducted in the range 500 – 800 °C in oxygen or nitrogen. The impact was followed of the annealing procedures on the $Al_xCu_{1-x}O_3$ films's properties. XRD was used to determine the films' structure; it revealed a mixture of amorphous and crystalline phases. Optical characterization was performed by UV-VIS spectroscopy. The sol-gel films prepared are very transparent. The band gaps of the Al-Cu-O films were estimated from the optical data, with the values ranging from 3.4 to 4.8 eV depending on the Cu content, the annealing and the gas ambients.

1. Introduction

Aluminum oxide is a technologically important material due to its high transparency in a wide spectral range (from UV to mid-IR), and its stability with good electrical and mechanical properties. Al_2O_3 can be used as dielectric and sensing layers and optical films [1]. Various physical and chemical procedures have been employed in the synthesis of mixed metal oxide films, including pulsed laser deposition, sputtering, e-beam evaporation. [2, 3]. The sol-gel method proposed for preparation of $Al_xCu_{1-x}O_3$ films is a cost-effective technology, with advantages such as control of the composition and homogeneity, and a possibility of coating substrates of complex shapes [4].

In this paper we report a study of Cu–Al–O thin films prepared by a sol-gel technology from sols with different concentration of the Cu precursor followed by an annealing treatment. The XRD analysis revealed the structure of and the phases in the films studied. The vibrational properties were investigated by FTIR spectroscopy, while the optical transmittance and reflectance were measured by UV-VIS spectrophotometry. The dependence of the optical band gaps on the annealing temperature was also determined.

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2. Experimental

The sol solution for Al_2O_3 deposition was synthesized using alumina-sec-butoxide and isopropyl alcohol. Acetylacetone was used as a chelating agent. The resulting solution 0.4M $Al(C_4H_9O)_3$ was aged by stirring for 1h at 50 ^oC. The Cu sol was prepared by dissolving Cu acetate in ethanol (0,2 M concentration) with monoethanolamine as a complexing agent. The two solutions were mixed as described in table 1; the films prepared from the corresponding sols are referred to in the text by the sol name. The mixed sols were stirred by a magnetic stirrer at 50^{o}C/2 hours.

Table 1. Preparation of mixed sols for deposition of $Al_xCu_{1-x}O_3$ films.

Sol name	Al	AC0,2	AC0,4	AC0,6	AC5	AC10
Al sol (ml)	20	19,8	19,6	19,4	15	10
Cu sol (ml)	-	0,2	0,4	0,6	5	10

The layers were deposited by spinning at 2000 rpm on Si and quartz substrates. The preheating treatment was conducted at 300^{o}C/30 min; the annealing was carried out at temperatures from 500 to 800^{o}C for 1 hour in O_2 or N_2 ambients. The XRD spectra of the films were recorded by a Bruker D8XRD diffractometer at a grazing angle of 2^o and a step of 0.1^o for 8 s per step. The optical measurements were performed by a UV-3600 Shimadzu spectrophotometer in the range 185 – 900 nm.

3. Results and discussion

The phase composition of the samples was identified using the XRD patterns shown in figure 1. The undoped Al_2O_3 films and the $Al_xCu_{1-x}O_3$ films with low Cu content manifested featureless spectra, an

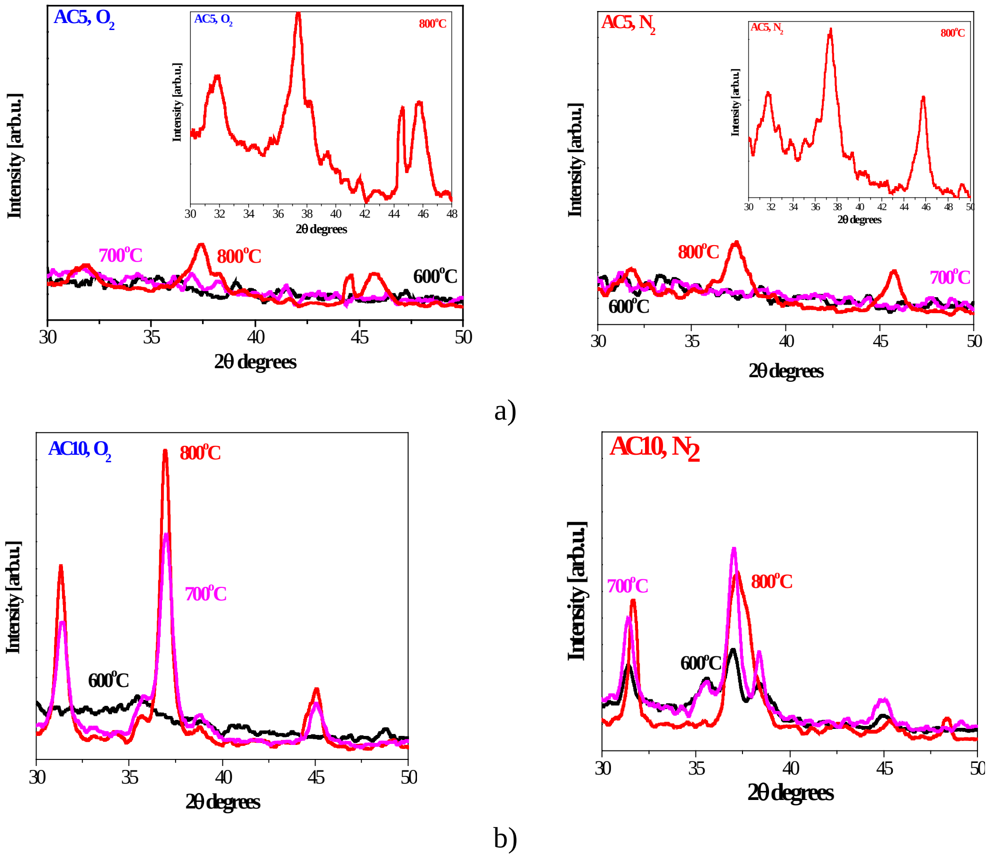


Figure 1. XRD spectra of $Al_xCu_{1-x}O_3$ films annealed at 600, 700 and 800^{o}C in O_2 and N_2 ambient; a) films obtained from sol AC5 and b) from AC10.

indication of an amorphous structure, independent of the annealing temperature and ambient. The XRD analysis of $Al_xCu_{1-x}O_3$ films obtained from sols AC3 and AC4 after annealing at 500 ^oC in O_2 and N_2 revealed spectra without any XRD peaks, a sign of an amorphous structure. Broad XRD lines began to appear as the annealing temperature was raised, revealing some amorphous fraction still present even after a 800 ^oC treatment. A considerable difference was seen for the films obtained from sols AC5 and AC10. The AC5 films remained amorphous up to 700 ^oC regardless of the gas ambient (figure 1a). The inset shows the enlarged XRD lines of AC5 films treated at 800^oC. The two lines (31.9^o and 37.3^o) are due to reflections (006) and (101) of $CuAlO_2$ (JCPDS 00-009-0185), the line (46°) is assigned to γ-Al_2O_3 [5]. The peak at 44.5^o, appearing only for a film annealed in oxygen, is related to $CuAl_2O_4$ (JCPDS 01-078-0556). $CuAlO_2$ is the predominant phase in $Al_xCu_{1-x}O_3$ films (sol AC5) with no CuO or Cu_2O phases.

The AC10 films exhibit a different behavior (figure 1b), as clear XRD lines for films annealed at 600 ^oC in N_2 are seen; for the films treated in O_2, crystallization starts after annealing at 700 ^oC. Three XRD lines (31.9^o, 35.6^o, 37.3^o) are due to $CuAlO_2$ (JCPDS 00-009-0185; JCPDS 04-007-5000), and a weak line, to $CuAl_2O_4$. A feature at 38.3^o corresponds to tenorite CuO (JCPDS 00-003-0867). Rise of the temperature to 700^oC leads to the same XRD lines, but with a greater intensity. Annealing at 800 ^oC in O_2 results in a well-crystallized AC10 film with no $CuAl_2O_4$ phase. The AC10 film treated in N_2 shows a lower intensity of the lines, together with additional peaks related to the (104) and (009) orientations of $CuAlO_2$ and a line at 48.3^o assigned to cuprite Cu_2O (JCPDS 00-005-0067). The XRD study further reveals that $CuAlO_2$ is the phase found predominantly in the AC5 and AC10 films. Similar XRD results for Al-Cu-O films were reported in [4]. It must be noted that the $CuAlO_2$ films are studied due to their low electrical resistivity, high optical transparency in the visible region, the existence of a photovoltaic effect and a field emission effect; it is thus known as a multi-functional p-type semiconductor [3].

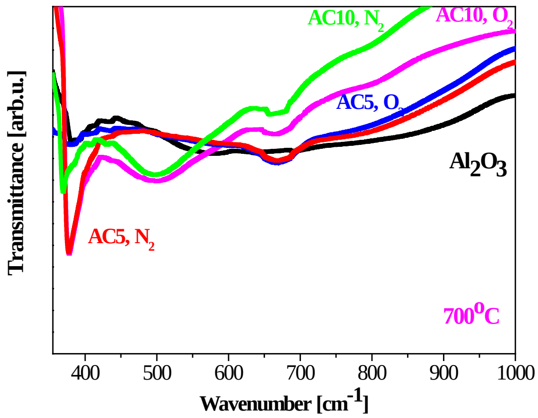
Table 2 presents the crystallite sizes as determined by the Debay-Scherrer equation from the XRD line of $CuAlO_2$. As is seen, for AC5 films the peak is relatively weak and the crystallites are very small. In the AC10 films, the crystallites become bigger as the annealing temperatures is raised; the crystallites are larger for samples annealed in N_2 compared to those annealed in O_2.

The sol-gel $Al_xCu_{1-x}O_3$ films were compared to pure Al_2O_3 by FTIR spectroscopy. The absorption bands around 3400 – 3700 cm^{-1} are related to O-H stretching vibrations; their intensity decrease with the annealing. The line at 2350 cm^{-1} is due to CO_2 from atmospheric contamination, while the weak band at 1585 cm^{-1} is assigned to the COO stretching vibration. The FTIR analysis was focused on the spectral range 350 – 1000 cm^{-1}, where the characteristic metal-oxygen vibrations can be detected. The detailed FTIR studies of the films from the sols AC0,2-0,6 (small Cu concentrations) reveal that the Cu additive affects the shapes and the intensity of the IR lines without the appearance of new absorption bands connected to Cu-O bonds. Thus, the FTIR spectra of sol-gel films with a higher copper content (sols AC5 and AC10) are given in figure 2. The spectra of the preheated samples show a difference in the absorption bands shapes and intensity for all lines attributed to Al-O bonds.

Table 2. Crystallite size as estimated from XRD data ($CuAlO_2$).

Material	Annealing	2θ, (006)	Crystallite size, [nm]
AC5	600^oC, N_2	31.73	18.1
	700^oC, O_2	31.37	18.4
	700^oC, N_2	31.37	25.9
	800^oC, O_2	31.45	15.3
	800^oC, N_2	31.60	38.8
AC10	800^oC, O_2	31.90	5.8
	800^oC, N_2	31.83	8.3

The annealing at 500 and 600°C in O_2 and N_2 (not shown here) led to the detection of new weak bands around 500 cm^{-1}, which can be due to Cu-O bonds. The high temperature treatments at 700 and 800 °C resulted in FTIR spectra with stronger differences from pure Al_2O_3. The absorption bands at 660 and 440 cm^{-1} in all spectra are due to Al-O stretching vibrations of AlO6 and to bending vibrations of AlO4. The main absorption peaks at 370 cm^{-1} become stronger for AC5 and AC10 films compared to the Al_2O_3 film. A clear absorption line at 490 cm^{-1} appears in the spectra of AC10 films treated at 700 and 800 °C and for AC5 films at 800 °C; this band is related to Cu-O bonds, an indication of a CuO phase. The presence of a small CuO fraction in these films was detected by XRD. Other interesting features are a weak line at 615 cm^{-1} and a clear band at 640 cm^{-1} for AC5 films and AC10 films annealed at 800 °C in O_2 and for AC10 in N_2. These bands are assigned to Cu(I)-O bonds in Cu_2O. The cuprite was not seen in the XRD spectra, but it might be in an amorphous state or below the XRD sensitivity. Similar FTIR results for $CuAlO_2$ films were reported in [6]. The FTIR bands are broad, indicating an amorphous and disordered structure, thus confirming the XRD results. The small Cu contents lead to negligible changes in the films' structure, similarly to the case of Al_2O_3 films. Higher amounts of the copper additive results in the formation of a new phase ($CuAlO_2$).



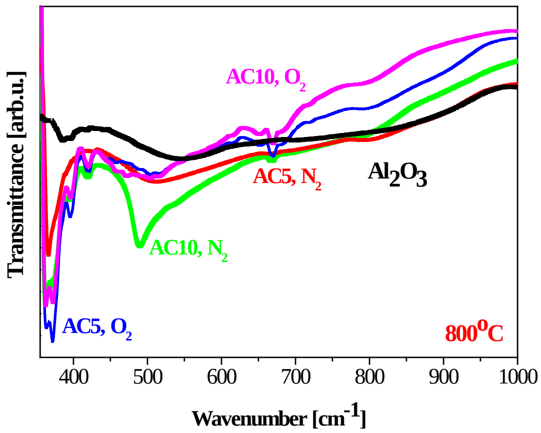


Figure 2. FTIR spectra of sol-gel Al_2O_3 and $Al_xCu_{1-x}O_3$ films annealed at different temperatures in oxygen and nitrogen ambient.

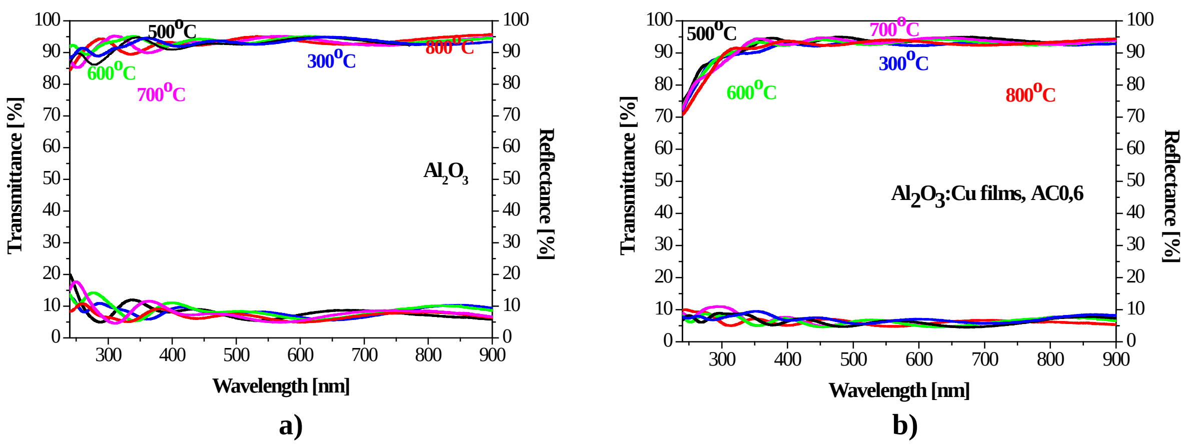


Figure 3. UV-VIS transmittance and reflectance spectra of; a) Al_2O_3 films and b) $Al_xCu_{1-x}O_3$ films obtained from the sol AC0,6.

The optical transmittance and reflectance spectra were recorded in the 240 – 900 nm spectral range for sol-gel Al_2O_3 and $Al_xCu_{1-x}O_3$ films. The Al_2O_3 films exhibit a very high transmittance (~94 %) (figure 3a). The $Al_xCu_{1-x}O_3$ films with a smaller Cu content manifest an optical behavior very similar to that of Al_2O_3 with a slightly lower transmittance (figure 3b). For these films, no absorption edge is observed in the spectral range studied. These results are supported by the structural studies, where the characteristics of the films with a small Cu content differ slightly from those of Al_2O_3 films. Raising the Cu content results in quite different optical characteristics (figure 4). The change in the optical properties is explained by the existence of a new phase, namely $CuAlO_2$, as revealed by the XRD analysis. The AC5 films show a transparency around 87 % (at 550 nm) after an annealing up to 700 ^{o}C in both gas ambient. After a high temperature treatment at 800 ^{o}C, the transparency decreases and absorption bands appear at 450 nm (O_2 annealed films) and at 440 nm (N_2).

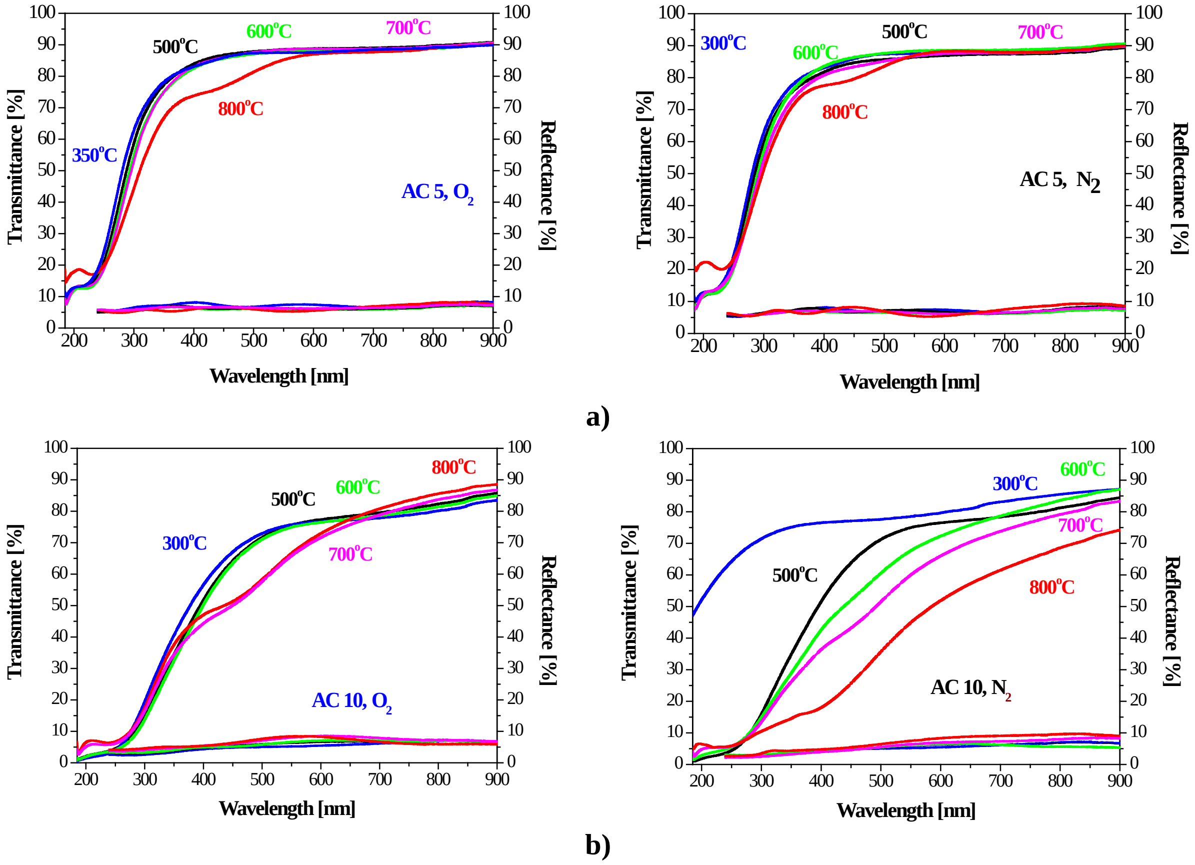


Figure 4. Transmittance and reflectance spectra of $Al_xCu_{1-x}O_3$ films; a) films obtained from the sol AC5 and b) AC10 films annealed at different temperatures.

The AC10 films display a lower transparency; different optical properties are obtained depending on the gas ambient. For the O_2 ambient, these films have a transmittance around 77 % (550 nm) after annealing in the 300 – 600 ^{o}C range. The films treated at 700 and 800 ^{o}C show absorption features at 490 nm. The AC10 films in N_2 manifest a clear tendency of transparency reduction from 79 % (300 ^{o}C, 550 nm) to 45 % (800 ^{o}C). The reflectance is between 9 – 10% in the entire spectral range studied. The absorption observed at 450 – 490 nm in the transmittance spectra of some $Al_xCu_{1-x}O_3$ films is attributed to the presence of Cu_2O nanoparticles [7]. The presence of the Cu_2O phase was not detected by the XRD measurements, but was found by the FTIR study.

The optical band gaps estimated from the spectrophotometric data are given in figure 5. The optical band gap values for the preheated samples are 4,63 eV for the AC5 films and 4,06 eV for the AC10 films. It can be seen that in the AC5 films the optical band gap slightly decreases with the annealing temperature, with the films treated in nitrogen possessing higher values. The AC10 films are characterized by significantly lower values. The values reported for $CuAlO_2$ films are in the range 3,38 – 3,80 eV [8,9], some authors [3] quote the value of 4.7 eV. In our case, the films' structures are with mixed crystalline and amorphous fractions, the $CuAlO_2$ phase being predominant according to the XRD results. The broadening observed of the band gap of the AC5 films can be related to the smaller particle sizes (table 2), i.e., the quantum confinement effect of a size dependency of the band gap that is often found in semiconductors.

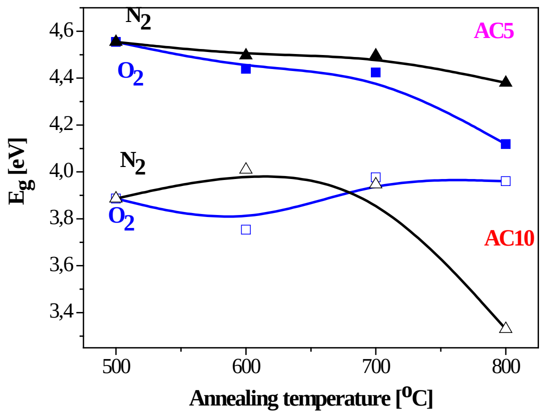


Figure 5. Optical band gaps of $Al_xCu_{1-x}O_3$ films.

4. Conclusions

The Al_2O_3 and Cu doped Al_2O_3 films were successfully prepared by a sol-gel technology and spin coating. The influence was studied of the amount of the copper additive. Increasing the copper incorporation leads to $Al_xCu_{1-x}O_3$ films with a predominant $CuAlO_2$ crystalline phase with small inclusions of CuO and A_2O_3. The optical properties depend on the copper amount, the annealing temperature and the gas ambient.

References

[1] Li X, Chen Q, Sang L, Yang L, Liu Z and Wang Z 2011 *Phys. Procedia* **18** 100
[2] Prasanna S, Mohan R, Jayakumar S, Kannan M and Ganesan V 2012 *Thin Solid Films* **520** 2689
[3] Zhang Y, Liu Zh, Zang D and Feng L. 2014 *Vacuum* **99** 160
[4] Banerjee A, Chattopadhyay K K and Joo S W 2011 *Physica* B*: Cond. Matter.* **406** 220
[5] Musil J, Blažek J, Zeman P, Prokšová Š, Šašek M and Čerstvý R 2010 *Appl. Surf. Sci.* **257** 1058
[6] Saha B, Thapa R and Chattopadhyay K K 2009 *Mater. Lett.* **63** 394
[7] Massera J, Choi J, Petit L, Richardson M, Obeng Y and Richardson K 2008 *Mater. Res. Bulletin* **43** 3130
[8] Lu Y M, He Y B, Yang B, Polity A, Volbers N, Neumann C, Hasselkamp D and Meyer B K 2006 *Phys. Status Solidi* C **8** 2895
[9] Zhang Y, Liu Z, Zang D Y, Che X S, Feng L P and Bai XX 2013 *J. Phys. Chem. Solids* **74** 1672