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LOW TEMPERATURE SOL-GEL TECHNIQUE FOR PROCESSING Al-DOPED ZINC OXIDE FILMS

V.I. Kondratiev[1*], I. Kink[1,2], A.E. Romanov[1,3]

[1]Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

[2]Estonian Nanotechnology Competence Centre, Riia 142, 51014 Tartu, Estonia

[3]Ioffe Physical Technical Institute, RAS, 26 Polytekhnicheskaya, St. Petersburg 194021, Russian Federation

*e-mail: kondraty@ut.ee

Abstract. In this work, Al-doped Zinc Oxide (AZO) films are prepared by sol-gel method. Films are highly transparent with transmittance over 90 % at 550 nm. Film parameters are studied varying film thicknesses. Different substrates are used, such as technical glass or Si. Typical film thicknesses are less than 500 nm. In order to optimize the technology for processing of transparent electrode materials based on AZO, influence of aluminium content, annealing time/temperature and annealing environment on the film resistivity are studied. For film characterization 4-probe resistance method, optical spectrophotometry, SEM and energy-dispersive X-ray spectroscopy, are used.

1. Introduction

Transparent conductive films (TCF) are usually fabricated from transparent conductive oxides (TCO). TCFs in the form of doped metal oxides are used in the modern optoelectronic devices such as light-emitting diodes, solar cells and flat panel displays [1, 2]. TCF properties have significant influence on the performance of these devices. For this reason, the manufacturing process and the properties of TCFs are required to be improved.

Tin-doped indium-oxide (ITO) has become a TCO standard and nowadays is broadly used for mass production of TCFs. However, ITO is expensive and a shortage of indium may occur in the near future because of the limited World indium reserves [3]. A group of materials has been proposed as ITO alternatives. This group includes fluorine doped tin oxide, aluminium doped zinc-oxide (AZO) and gallium doped zinc-oxide. ZnO-based TCOs are cheaper and due to their electrical and optical properties are capable to replace ITO for transparent electrode applications [2].

To date, doped ZnO films are manufactured by various methods: RF magnetron sputtering [4], pulsed laser deposition [5], electron-beam evaporation [6], molecular beam epitaxy [7, 8], chemical vapor deposition [9], spray pyrolysis [10], sol-gel [11–15], and others. Comparing to other methods, sol-gel process has several benefits. It is simple, non-vacuum and low cost technique that does not require utilization of complicated and expensive equipment. This process gives opportunity to produce small and large area coatings of desirable shape at relatively low temperatures. Moreover, there is an easy way to control solution concentration, doping level, homogeneity in sol-gel procedure. Usually, result films are uniform and have high purity. However, it is necessary to find and use the optimized processing parameters that are required for minimization or elimination of effects related to film shrinkage and film cracking.

In 1994 Tang and Cameron describe preparation of AZO films by sol-gel method [14]. Tsuchiya et al. employed dip-coating process and investigated electrical properties of the film [16]. Ohyama et al. described effects of the heat-treatment conditions and crystal orientation of the ZnO films [17] and analyzed the relationship between preparation parameters and film resistivity [13]. Schuler and Aegerter investigated the influence of the multilayer deposition process [18]. Alam and Cameron varied annealing temperature and dopant concentration and in result got low resistivity films [12]. Wang et al. investigated the effects of annealing and dopant concentration on the structural, electrical and optical properties of the films [11]. They use rapid thermal annealing techniques in argon atmosphere. Srivastava and Kumar studied effect of aluminium doping on the morphology, electrical resistivity and optical behavior of AZO films [15]. Wide overviews on TCO prepared by sol-gel methods and about ZnO properties have been presented by Znaidi [19] and by Janotti and Van de Walle [20]. However, there are still many open questions remaining, e.g. as noted by Znaidi [19] very close experimental procedures can give different crystallographic orientation and properties of the films.

In the current work, AZO films were prepared by the sol-gel method. In order to optimize the technology for processing of transparent electrode materials based on AZO, dependence of resistivity and transmittance of Al-doped films from aluminium content, time/temperature of annealing and annealing environment were studied.

2. Experimental procedure

Two different AZO solutions were prepared (subsequently called as routes #1 and #2). For the synthesis zinc acetate dihydrate [$Zn(CH_3CO_2)_2 \cdot 2H_2O$] (Sigma-Aldrich, assay ≥99.0 %), 2-methoxyethanol [$C_3H_8O_2$] (Sigma-Aldrich, assay ≥99.5 %), ethanolamine [MEA, C_2H_7NO] (Sigma-Aldrich, assay ≥99 %), aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] (Sigma-Aldrich, assay ≥98 %), ethanol (C_2H_5OH, assay ≥99) were used.

Route #1: Zinc acetate dihydrate and aluminium nitrate nonahydrate were dissolved in ethanol. Zinc acetate dihydrate concentration in solution was 0.07 mol/L. In routes #1 and #2 aluminium nitrate nonahydrate was used as Al-dopant precursor, with various concentration of Al/Zn. The solution was refluxed in magnetic stirrer at 80 °C for 3 h with various stirring speed to get a clear solution. After that, the solution remained stable for several hours.

Route #2: Zinc acetate dihydrate was dissolved in 2-methoxyethanol. Solution concentration was 0.75 mol/L. Then it was refluxed in magnetic stirrer at 73 °C. After 35 min ethanolamine was added to prevent forming precipitation in the solution. The molar ratio of ethanolamine/zinc was 1:1. The solution was refluxed in magnetic stirrer for about 2 hours. Aluminium nitrate nonahydrate was added. Solution was stirred at the same temperature for about 1 hour. The solution was stable and clean for a long time (visible differences were not noticed after several months).

Before deposition the glass and Si substrates were ultrasonically cleaned in acetone and/or methanol for 10 minutes and dried in a flowing nitrogen gas. For both routes a spin-coating deposition technique was used. The substrates were rotated at speed 3000 r/min and ~170 µl of solution was dropped on the substrates. The coated substrates were heated at 250-260 °C (drying) for 10 min in air after each coating. By repeating this procedure the films with different thickness were obtained. As the last step the films were annealed at 500 °C in air or Ar for hour. Heating and cooling from 25 °C to 500 °C was with rate 2 °C per min.

The flowchart that shows the procedure used for preparing aluminium doped zinc oxide is given in Fig. 1.

The sheet resistivity of ZnO films was measured by using a four-probe method (Keithley 2400 sourcemeter). Film transparency was measured using by Spectrophotometer V-570 Jasco. The thicknesses were measured using electron microscopy (Helios NanoLab,

FEI). Element analysis was performed using energy dispersive x-ray spectroscopy (EDS Oxford Instruments).

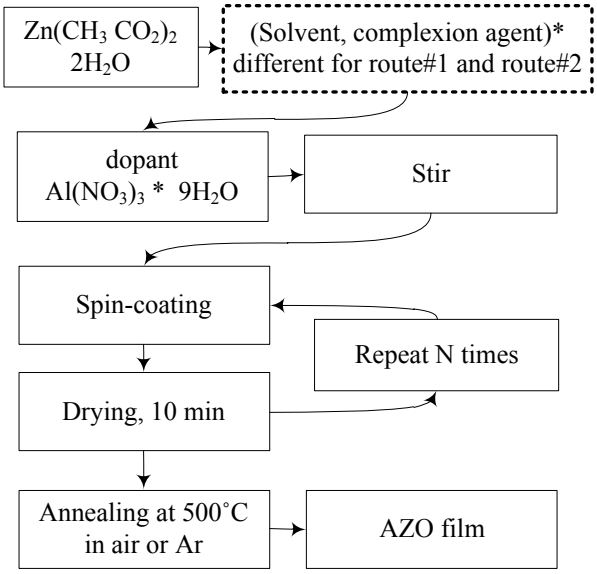

Fig. 1. AZO thin film preparation by the sol–gel technique.
* For route #1 - C_2H_5OH, for route #2 - $C_3H_8O_2$+ C_2H_7NO.

3. Results and discussions

A number of samples were prepared under different conditions in order to determine optimal process parameters. Table 1 presents data for various samples from route #1 and #2.

Table 1. Preparation parameters of AZO films.

Route	Stirring speed, rpm	Substrate rotation speed, rpm	Drying temperature, °C	Annealing temperature, °C	Number of layers
#1	300 – 1500	3000	260	500	1 - 5
#2	1000	3000	250	500	1 - 5

In the ethanol solution stirring speed has a significant influence on the film quality. More uniform film surfaces are achieved when stirring at 1500 rpm as compared to e.g. 300 rpm. In ethanolamine and 2-methoxyethanol solution the uniform surfaces are achieved with lower stirring speed.

The films from route #1 were deposited on the silicon substrates for the thickness and element analysis measurements. To get desirable film thicknesses (see Table 2) varying numbers of layers were deposited. Each deposited layer had approximately similar thickness ≈ 110±35 nm.

Table 2. The films properties: thickness, route #1.

Annealing	Number of layers	Thickness, nm	Drying, °C	Annealing, °C
Before	1	150	260	-
	3	230	260	-
	5	540	260	-
After	5	150	260	500 Air

After annealing the thickness of the film decreased from 550 nm to 150 nm (Fig. 2), so film thickness depends on the annealing. Concentration of oxygen in films increased and concentration of carbon in films decreased.

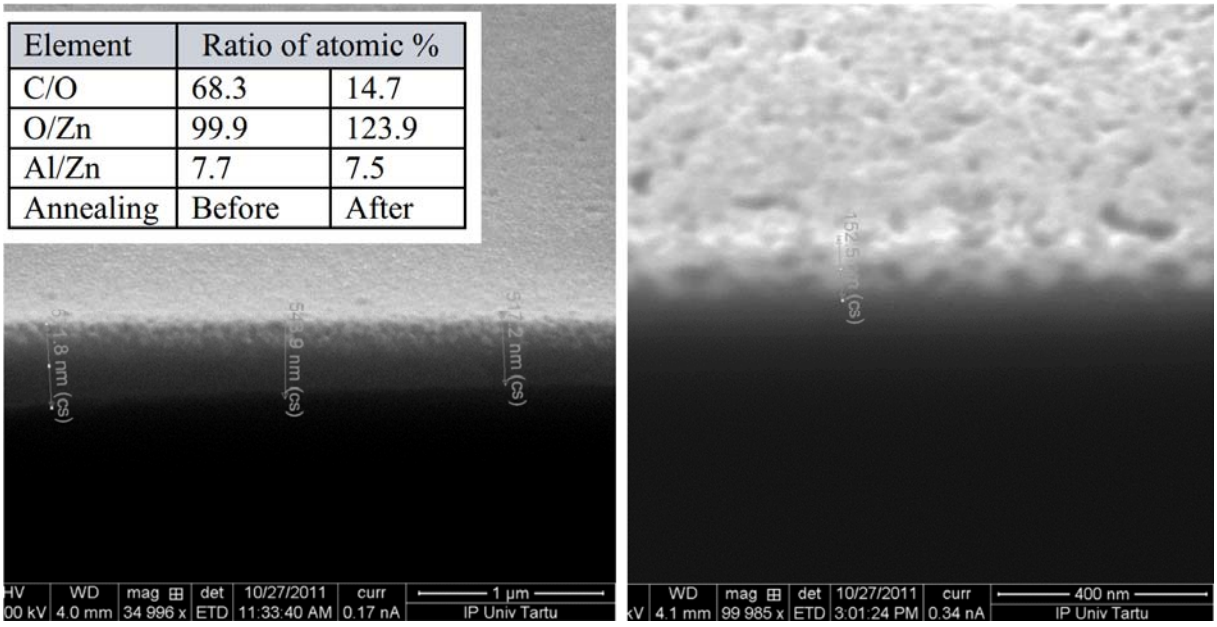

Fig. 2. AZO films. Thickness of the 5-layer film was 540 nm and ~150 nm before (left) and after (right) annealing, respectively (route #1).

ZnO-based film resistivity is strongly dependent on dopant concentration and annealing temperature [11]. Other factors play secondary role. For these reasons aluminium was selected as dopant in order to provide low specific resistance. Temperature of annealing was changed from 300 °C to 500 °C (Fig. 3). After annealing at 400 °C films were more uniform.

Concentration of $Al(NO_3)_3 \cdot 9H_2O$ precursor was varied in wide range. Part of the samples was additionally annealed in Ar. It was noticed that annealing in Ar decreases the resistivity up to ~50-100 times than annealing in air (see Table 3).

Table 3. Experimental results of ZnO films application on a glass substrate.

	№ layers	Drying, °C	Annealing, °C		$R_{\square}$, 10^6 Ω/□
			in air	in Ar	
Route #1	5	260	300 1 h	-	50-100
	5	260	400 1 h	-	
	5	260	500 1 h	-	
	5	260	300 1 h	500 1h	80
	5	260	400 1 h		0.9
	5	260	500 1 h		2
Route #2	3	250	500 1 h	-	2
	3	250	-	500 10 min	0.12
	3	250	-	500 1h	0.030

In route #2 solvent (ethanol (C_2H_5OH)) was replaced by 2-methoxyethanol ($C_3H_8O_2$) and ethanolamine (MEA, C_2H_7NO) was added. Solution was colorless, but after spin-coating

films turned yellow. After drying some samples were totally cracked, in contrast with others (Fig. 4). The non-cracked samples were annealed in air or in Ar. Films had uniform surface without particles on the surface.

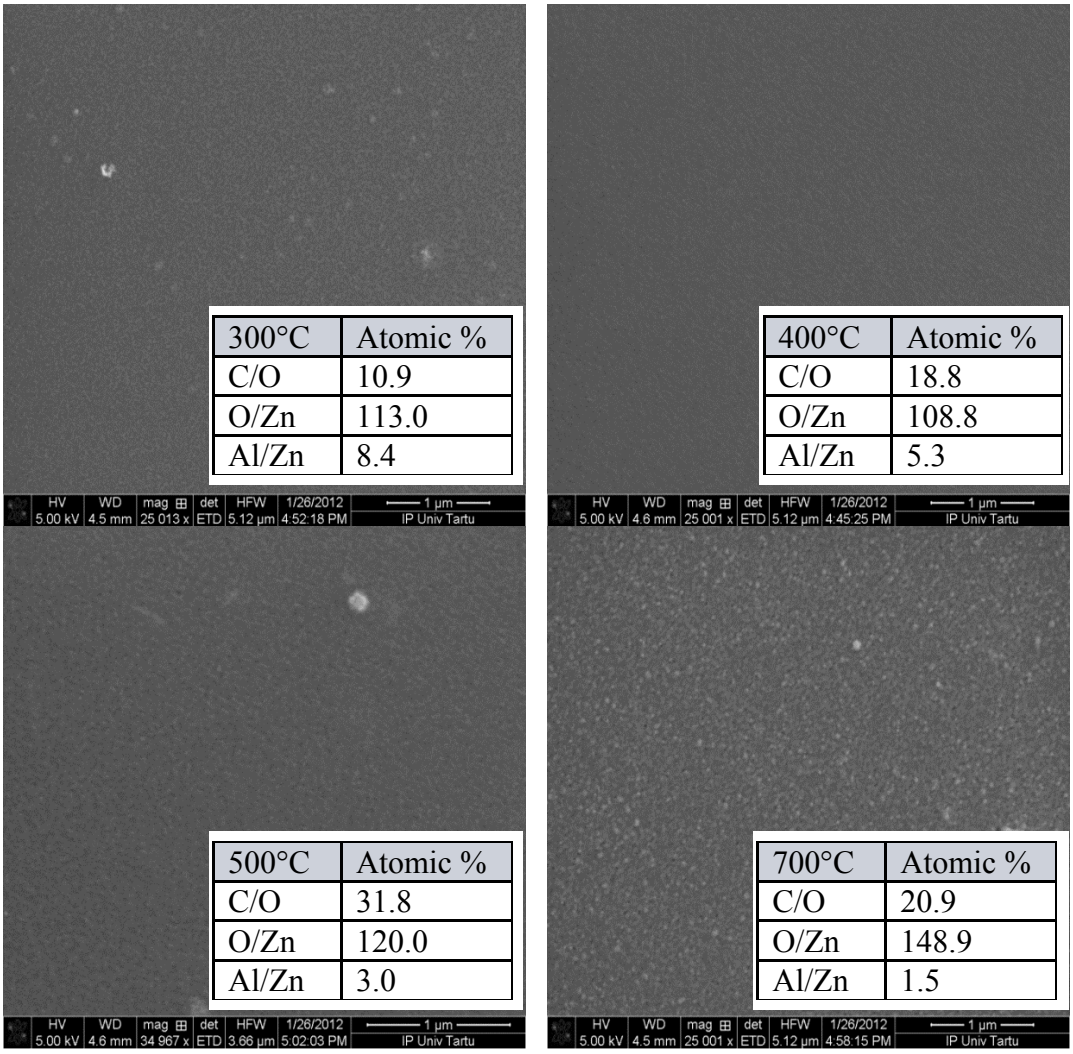

Fig. 3. ZnO:Al films after annealing at 300,400,500,700 °C for 1 hour in air. Films have 5 layers (route #1).

To avoid film cracking the substrates were additionally ultrasonically cleaned in acetone and in plasma cleaner for 10 min. Three layers were deposited and heated at 250 °C (drying). After annealing in Ar for 1h the films had approximately the same resistivity and transmittance.

After annealing in air for 1 hour films had resistivity $2 \cdot 10^6$ Ω/□ (see Table 3). It is 25-50 times better that was with route #1. After annealing in Ar for 10 min films had resistivity $0.12 \cdot 10^6$ Ω/□. Longer annealing in Ar (1h) improved electrical properties even more. Resistivity decreased to about $0.03 \cdot 10^6$ Ω/□.

In the articles the resistance of the film is represented as sheet resistance [21] or as resistivity [22]. According to four-point probe measurements [23] resistivity is calculated with following equation:

$$\rho = R_{\square} t = \pi \cdot t \cdot V \cdot F / (\ln(2) \cdot I), \quad (1)$$

where ρ is resistivity [Ω-cm], $R_{\square}$ is the sheet resistance [Ω/□], t is the film thickness [cm], V is the voltage [V], I is the current [A], F is the correction factor.

Figure 5 shows dependence $\rho(R_{\square})$ for films with different thickness.

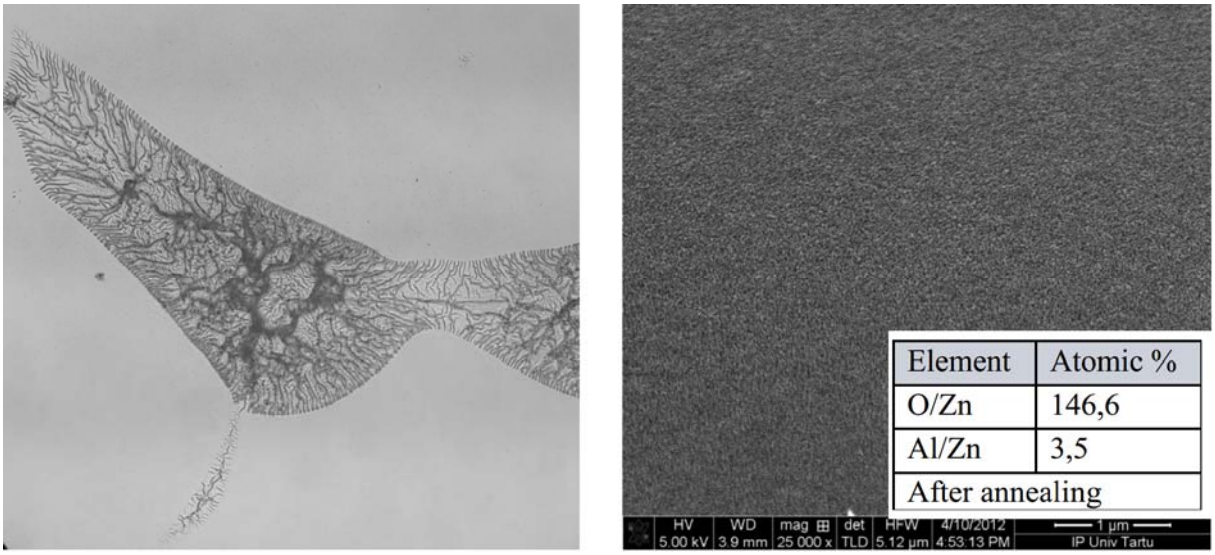

Fig. 4. Totally cracked film, optical microscope image (left). Ideal film after annealing at 500 °C in Ar for 10 min, thickness ~250 nm, route# 2, SEM image (right).

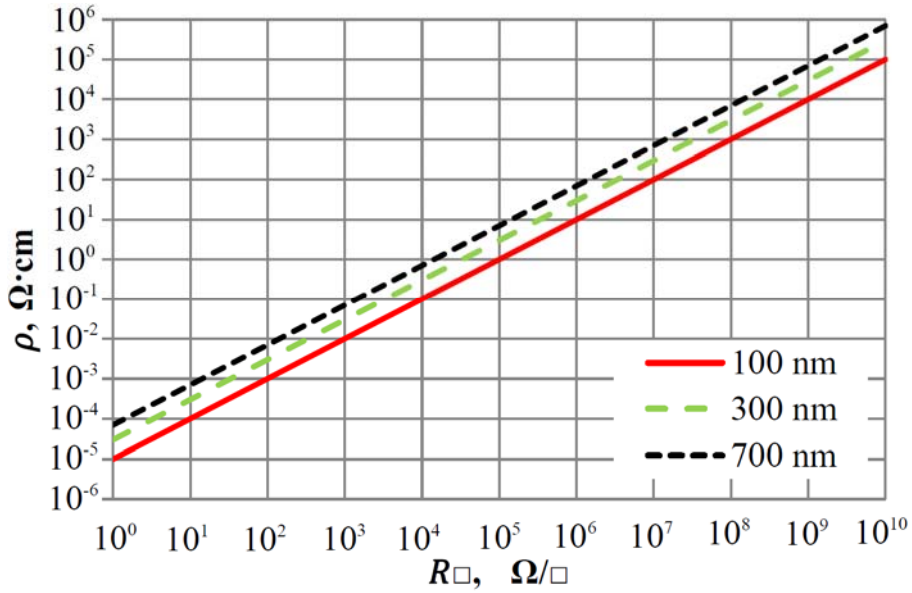

Fig. 5. Dependence $\rho(R_{\square})$ for films with different thickness.

To perform the optical measurements, the films were deposited on glass substrates. The typical transmittance spectra are shown in Fig. 6. The average value of transmittance is over 90 % at 550 nm. With increasing film thickness (numbers of layers) the transmittance became lower. After annealing it was better, because film became thinner.

Films from route #1 and 2 have similar spectra in wavelength range 370-900 nm (Fig. 7). Films from route# 2 have higher level of transmittance in the near-UV region than films from route# 1. For route# 2 annealing in Ar improves transmittance slightly.

In the Fig. 8 transmittance spectra of the films are shown. Glass substrate was cleaned in ultrasonic bath (glass type I) and cleaned by plasma cleaner (glass type II). Glass transmittance spectra were the same in both cases. Films were deposited on glass substrates (type I and II) and annealed in Ar for 1 h. Finally, the films had the same transmittance spectra.

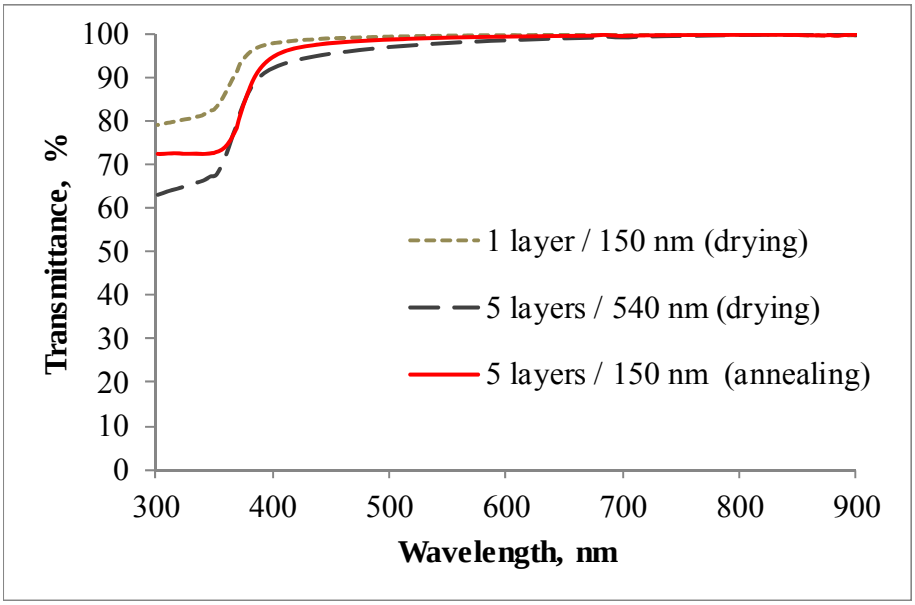

Fig. 6. Transmittance of the samples with different thickness (annealing in air), route# 1.

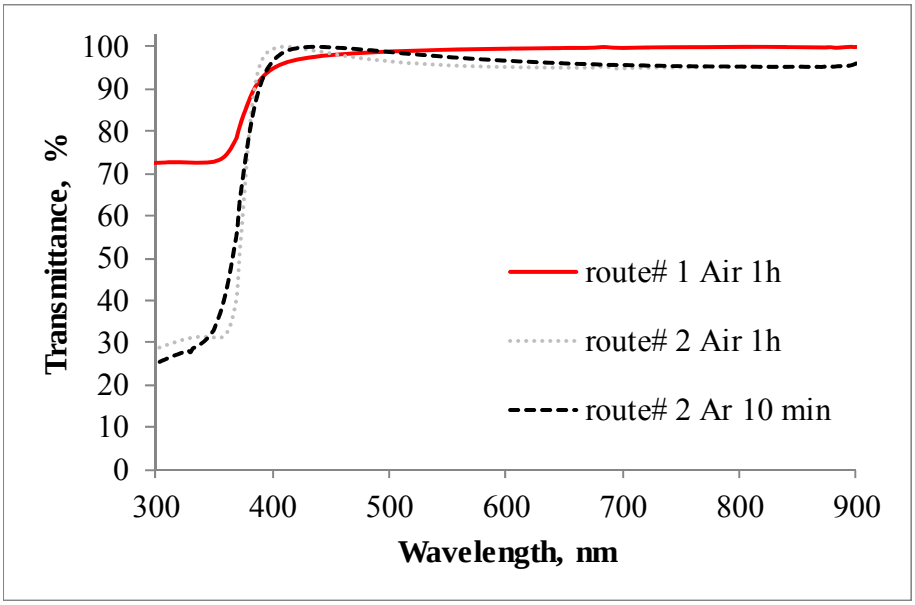

Fig. 7. Transmittance of samples from route # 1 and 2 (annealing in air/Ar). Films have 5 layers.

4. Summary and conclusions

Sol-gel process for transparent electrode material was studied with the use of various precursors. Highly transparent films of aluminium doped zinc oxide have been fabricated. Some of the precursors were found to give better quality films (from transmittance and resistivity point of view). Worst results were shown by ZnO films produced from a mixture with C_2H_5OH solvent and annealed in the air. Increasing the number of deposited layers reduces cumulative transparency. After varying several process parameters it was noticed that annealing in Ar decreases the resistivity 10-100 times compare to annealing in air. Longer exposition in Ar provides better results. ZnO-based TCOs are capable to replace ITO for transparent electrode applications due to its electrical and optical properties.

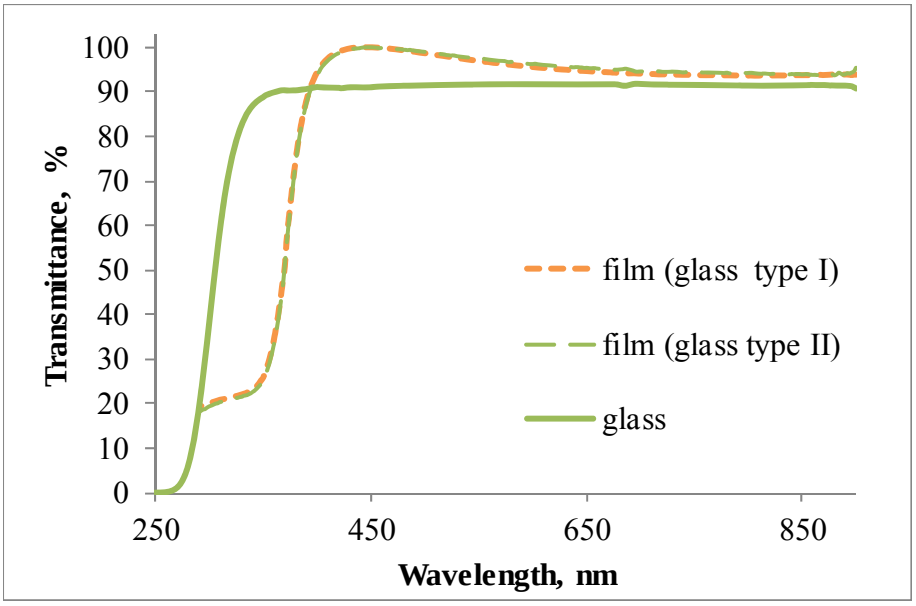

Fig. 8. Films transmittance on different substrates, route# 2.

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