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Authors	Szymon Kiełczawa, Artur Wiatrowski, Milena Kiliszkiewicz, Witold Posadowski and Jaroslaw Domaradzki
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ORCID® iDs	Szymon Kiełczawa - https://orcid.org/0000-0003-4315-7385; Artur Wiatrowski - https://orcid.org/0000-0002-8594-2384; Milena Kiliszkiewicz - https://orcid.org/0000-0003-0612-3573; Witold Posadowski - https://orcid.org/0000-0003-0872-142X; Jaroslaw Domaradzki - https://orcid.org/0000-0002-4707-6817

Application of two-element Zn-Al metallic target for deposition of aluminum-doped zinc oxide - analysis of sputtering process and properties of obtained transparent conducting films

Szymon Kiełczawa*, Artur Wiatrowski, Milena Kiliszkiewicz, Witold Posadowski, Jarosław Domaradzki

Wrocław University of Science and Technology,
Faculty of Electronics, Photonics and Microsystems
Janiszewskiego 11/17, 50-372 Wrocław

*corresponding author: szymon.Kielczawa@pwr.edu.pl

Abstract

This article presents an analysis of the reactive magnetron sputtering process using a two-element Zn-Al target, with a particular focus on its application for deposition of AZO (aluminum-doped zinc oxide) layers for transparent electronics. The research encompasses the deposition of AZO layers on standard Corning 7059 glass and flexible Corning Willow® glass. In order to determine optimal process conditions, a detailed analysis of the target surface state was conducted based on the ratio of working gas to reactive gas (argon/oxygen). Significant influence of the sputtering atmosphere ratio on the Al/Zn atomic ratios in the deposited AZO layers was observed, subsequently affecting their optical and electrical properties. Layers deposited in an atmosphere with an 80/20 ratio (argon/oxygen), corresponding to a surface target mode close to the dielectric mode, exhibited a high light transmission coefficient in the visible range (averaging 84%) and high layer resistivity ($47.4 \cdot 10^{-3}$ Ωcm). On the other hand, layers deposited in an atmosphere with an 84/16 ratio (argon/oxygen), corresponding to a surface target state close to the metallic mode, showed low resistivity ($1.9 \cdot 10^{-3}$ Ωcm) and a light transmission coefficient in the visible range at 65%. The most promising results were obtained for layers deposited in an atmosphere with an 82/18 ratio (argon/oxygen), characterized by both high light transmission (83%) and low layer resistivity ($1.4 \cdot 10^{-3}$ Ωcm).

1.Introduction

Sputter deposition is one of the methods for obtaining thin films which allowing control over the deposition process throughout its duration. The kinetic ejection of atoms or molecules from the target surface leads to the deposition of the target material (which serves as the cathode of the system) or the reaction product of the cathode material with a reactive gas. The origins of this method can be traced back to the 1970s, and due to its advantages, it has been continuously developed and improved over the subsequent decades [1-3]. The sputtering process itself is dependent on the pressure inside the process chamber (usually in the range of 10^{-3} mbar), the type of working gas, the target material, the presence of a reactive gas, and the power supplied to the magnetron. However, despite many variables, magnetron sputtering remains one of the most widespread industrial methods for thin film deposition, primarily due to its high repeatability, cost-effectiveness, and the quality of the obtained films.

Zinc oxide doped with aluminum (AZO) has attracted particular interest as a potential substitute for indium tin oxide (ITO) in transparent conductive oxides (TCO) applications. The TCO applications require the conductive oxides that should exhibit high optical transparency in the visible range (often exceeding 80% for films up to 200 nm in thickness) and low resistivity (resistivity should be less than 10^{-3} Ω·cm). The ITO is currently the most commonly used TCO material, but due to its toxicity and high production costs attention has turned to search for alternatives. Materials based on zinc-oxide (ZnO) are studied, and in particular AZO, which is characterized by good long-term electrical stability, low resistivity and a high transmission coefficient [4]. ZnO is a wide bandgap semiconductor (3.30 eV), making it well-suited for optical requirements of TCO. However, the carrier concentration of ZnO is about 10^{6} cm^{-3} at room temperature, which is lower than that of practical TCO layers [5]. To meet the electrical requirements for TCO, ZnO needs to be doped with other elements, such as aluminum. Doping widens the range of applications for this material, which is widely used in thin-film electronics, LED diodes, solar cells, and gas sensors [6-11]. For the sputter deposition of thin AZO films the sintered powder targets of ZnO/Al_2O_3 are commonly used, with aluminum oxide content typically ranging from 1-7% [12,13]. Aluminium doping of ZnO allows for the generation of additional electrical carriers while maintaining its optical transparency in the visible light range. The Kroger-Vink equation (1), presented by Gao and Banerjee, describes the process of obtaining AZO with simultaneously release of electrons into the conduction band of the material, thus increasing its conductivity [14]:

$$Al_2O_3 \xrightarrow{2ZnO} 2Al_{Zn} + 2O_O^X + 2e^- + \frac{1}{2}O_2 \uparrow \tag{1}$$

The bandgap width is another crucial property for TCO because it determines the transparency of the layer for electromagnetic waves. For ZnO, the bandgap is approximately 3.30 eV, corresponding to a cut-off wavelength of 375 nm [15]. As a result, ZnO is transparent across visible spectrum. However, doping ZnO to improve its electrical properties leads to a change in the width of the bandgap and, consequently, a change in the light transmission coefficient. This change depends on the type of dopant and its percentage content in the layer [5, 14, 16].

ZnO exhibits asymmetry in its ability to being doped with type n and type p dopants. Doping with type p is a significant challenge and the reason of this challenge is not clear. It might be attributed to high activation energy of acceptors, low solubility of p-type dopants, and the induction of a self-compensation process during doping, leading to the formation of high concentrations of compensating donors or the creation of defects [17]. On the other hand, numerous experiments have been conducted on doping with n-type dopants. It has been demonstrated that these dopants are incorporated into the zinc lattice sites. At these zinc lattice sites, these elements act as shallow donors with an ionization energy of about 57 meV, which decreases with increasing donor density. This effect is governed by the overlap of wave functions with the conduction band of the zinc lattice, causing all donors to be ionized even at low temperature. It has been shown that ZnO doping with Ga and specifically with Al results in the lowest resistivity. This is due to the fact that the covalent radii of Ga and Al are similar to the covalent radius of Zn [18].

The aim of this study was to investigate the use of a two-component Zn-Al metallic target as an alternative to commercially available, relatively expensive sintered targets of ZnO/Al_2O_3. Article discusses the considerations regarding target's surface condition and the influence of the discharge power parameters on sputtering process. Selected structural, electrical and optical properties of the obtained AZO films are presented and discussed.

2. Experimental

Sputtering system

Al_XZn_YO layers were deposited using a vacuum system equipped with rotary vane and diffusion pumps, the ultimate pressure of the vacuum chamber was about $1 \cdot 10^{-5}$ mbar. The sputtering system consisted of circular planar magnetron source equipped with self-designed two-component Zn-Al metallic target (100 mm in diameter) [19] and medium frequency (100 kHz) resonant type power supply from Dora Power Systems (DPS) [20].

The two-component Zn-Al target was prepared by inserting three aluminum rods (2 mm in cross-section diameter) into the grooves prepared in a 9 mm thick zinc target. The locations for aluminum inserts were chosen within the race-track erosion zone basing on previous experiments [19] and considerations described in this paper.

The medium-frequency power supply DPS is a source of sinusoidal-shaped current pulses of about 10 μs in duration. The resonance power-stage of the DPS power supply is characterized by a specific parameter called circulating power, denoted as P_C by the manufacturer. When the impedance of the magnetron discharge decreases (e.g., when the secondary electron emission coefficient from the target surface increases) then the circulating power value of the supply increases [21]. This parameter is useful for monitoring the sputtering process, because the secondary electron emission coefficient changes as the target surface begins to be covered with an oxide compound. Therefore, in case of the reactive sputtering, the P_C parameter of the DPS power supply may be used as a technological indicator that represents the degree of oxidation of the target's surface (some prior calibration of P_C is needed).

Deposition processes

Reactive sputtering processes were carried out in an atmosphere of argon and oxygen at the total pressure of $1.5 \cdot 10^{-3}$ mbar. Firstly, the oxygen partial pressure was established in the chamber via needle-type dosing valve and then argon was added via another valve to reach the given total pressure. The ionization gauge was used for pressure measurements. The argon/oxygen content ratio was varied and ratios of 80/20, 82/18 and 84/16 are reported in this paper, to demonstrate the occurrence of optimal conditions for obtaining AZO films with the best TCO properties. The given argon/oxygen ratios resulted in the P_C parameter value of: 80, 60 and 40 W for the Ar/O_2 ratios of 80/20, 82/18 and 84/16; respectively. The discharge power was kept constant at the value of 150 W. Substrates were placed 60 mm above the target, at a radial distance of 67 mm from the center point of the target. Additionally the substrates were tilted 45° form horizontal position to face the target. Such geometry and discharge power resulted in deposition rate of about 8 nm/min. The films were deposited for 15 minutes on different substrates: standard glass Corning 7059 (thickness 700 µm), flexible Corning Willow® Glass (100 µm and 200 µm thickness) and amorphous silica substrates. No additional heating of the substrates was introduced.

Measurements

During the deposition processes, the optical emission spectrum of the plasma was measured using an Ocean Optics spectrophotometer (QE65000 type). Subsequently, using the SpectraWiz software from StellarNet Inc., the emission lines corresponding to Zn, Al, Ar, and O atoms were indicated.
The surface morphology of the films was determined based on the analysis of Atomic Force Microscope measurements (Nanosurf C3000), while their chemical composition was measured using Energy Dispersive Spectroscopy (Bruker Quantax). The surface resistance was measured using a four-point probe (Jandel Engineering Ltd.) and a source-meter (Keithley 2611A type). The tips of four-point probe were co-linear with a distance of 1 mm between tips. Optical properties were determined based on the light transmission spectrum. Light transmission characteristics were measured using a coupled halogen-deuterium lamp and Ocean Optics spectrophotometers (type QE65000 for VIS and NIR256 for NIR) in the wavelength range from 300 nm to 2000 nm.

3. Considerations about sputtering conditions

Two-element Zn-Al target

The surface view of the two-component Zn-Al target, after several dozen of sputtering processes, is presented in fig.1. A distinct erosion zone (race-track region) could be observed, along with dark brown areas covered with non-stoichiometric oxides. The dimensions of erosion zone listed below were similar with prior results [21]. This showed that the geometrical factors of sputtering of such two-component target are not a subject of significant changes. The inner and outer radii of the erosion zone were measured to be of about 15 and 39 mm, respectively, resulting with a total erosion zone area of about 4069 mm². The approximate geometry of the erosion zone, suitable for the deposition of AZO films, was estimated experimentally on the basis of previous tests. There were three aluminium circular inserts (rods) located within the erosion zone. The diameter of cross-section of each rod was 2 mm and the radii of their placement were successively 29, 33 and 38 mm (fig.1). Therefore the zinc area of the erosion zone was of about A_{Zn} = 2813 mm². The erosion depth of the Zn area was about 0.9 mm, so it was assumed that the Zn area was flat. The influence of the circular cross-section of the aluminium inserts (rods), in accordance to the angular dependence of the ion-induced sputtering yield, was taken into account during considerations and the equivalent aluminium area was calculated to be of about 5 times larger than given by the physical dimensions of inserts. The aluminum rods were slightly flattened during the process of pressing them into the grooves in a zinc disc, so the multiplication factor was assumed to be not greater than 3. The outer aluminium rod was placed on the border of the erosion zone. This fact of reduced efficiency of sputtering was taken into account and multiplication factor was reduced to 1.5 for this rod. The equivalent aluminium area of the erosion zone was finally estimated to be of about A_{Al} = 3050 mm². The estimated areas of Zn and Al, together with the sputtering yield of Zn, Al and their oxides, were used for the considerations about conditions of sputtering of two-element Zn-Al target.

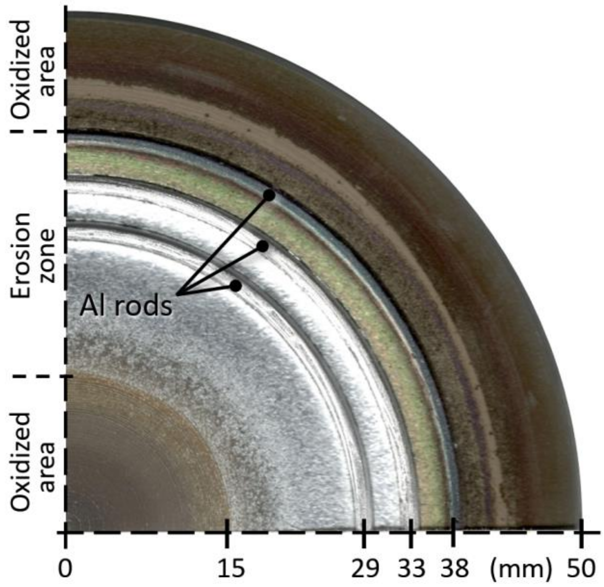

Figure 1. A sectional view of the two-component Zn-Al metallic target, dimensions of erosion zone and placement of the aluminium rods are given.

The wear pattern profile of the target showed that its sputtering in regions located over the magnetic poles was very low (oxidized areas in fig.1), making these regions insignificant for considerations about sputtering conditions. In these regions the target was observed to be constantly poisoned and this condition persisted even after short-term transition into fully argon sputtering. Basing on these observations it was assumed that considerations about sputtering conditions (induced by the changes of the argon/oxygen ratio) may be simplified and finally may be related to the erosion zone only (fig.1). With that simplified approach the discharge current was conducted by the area of erosion zone only, resulting in the target power density (the erosion zone power density) of about 3.7 W/cm^2. The energy of sputtering ions was determined from the oscillogram of anode-cathode voltage. To ensure the repeatable ignition of discharge the supply pulses of the DPS power unit had an amplitude up 1.2 kV, with the mean value of about 500 V. Therefore, it was assumed that sputtering ions had the energy of

500 eV. Basing on the Ar/O_2 ratios it was assumed that discharge current was composed of the argon ions only. In accordance with literature data, the sputtering yields (molecules, atoms per one ion) induced by argon ions were approximately 5 and 0.5 as well as 0.9 and 0.2 for the Zn and ZnO as well as for Al and Al_2O_3, respectively [22, 23].

If the target operates in oxygen-rich atmosphere then its surface is completely oxidized, which is known as the dielectric sputtering mode. In such case both, the zinc and aluminium areas of the erosion zone are oxidized. For reported investigations this sputtering condition of the erosion zone (Al_2O_3, ZnO) is marked as point D in fig.2. For simplicity, a homogeneous distribution of the discharge current density over the erosion zone can be assumed. With such an assumption, the ratio of sputtered Al_2O_3/ZnO particles is determined by the ratio of effective aluminum surface area A_{Al} times Al_2O_3 sputtering yield to zinc surface area A_{Zn} times ZnO sputtering yield. For ease of comparison, it is convenient to use the ratio of Al/Zn in the flux to the substrate, which in this case is approximately 80/100. The films obtained for such sputtering condition of the target were transparent, but showed high resistivity, which is not suitable for the use as a TCO.

If the oxygen content is decreased, it is possible to reach a state where the erosion zone is not fully oxidized, which is known as the transient sputtering mode. In case of our two-element Zn-Al target the transient mode of sputtering may be considered in yet another way. Since zinc has a higher sputtering yield than aluminium, the sputtering condition of the erosion zone is likely to be such that the aluminium part operates in the dielectric mode and the zinc part operates in the transition mode. The zinc oxide that forms is continuously removed and the metallic zinc surface is exposed. This is a particular state of dynamic equilibrium and, in fact, there can be a different degree of oxidation of the zinc part of the erosion zone. In fig.2 there are indicated three such cases, marked as T_1, T_2, T_3. Each of these cases was obtained by varying the argon/oxygen content ratio: of 80/20 (T_1), 82/18 (T_2) and 84/16 (T_3). The boundary state could be a sputtering condition of the erosion zone in the form of Zn, Al_2O_3. For such a sputtering condition the ratio of Al/Zn in the flux to the substrate is of about 9/100. For a sintered AZO target made of ZnO/Al_2O_3 98:2 wt%, sputtered in argon [24, 25], the Al/Zn ratio in the flux to the substrate is approximately 3/100. It may be noted that the convergence of these ratios indicates that our considerations about sputtering of two-element Zn-Al target seem to be quite likely.

The opposite transient situation of the erosion zone of a two-element metallic Zn-Al target, i.e. a sputtering condition of the erosion zone in the form of ZnO; Al, is rather unlikely to occur. In addition, in case of such a sputtering condition the flux of Al/Zn to the substrate is of about 195/100, which does not seem to be applicable for the deposition of transparent AZO films.

Monitoring of sputtering conditions with DPS power supply

The resonance power stage of the DPS power supply is characterized by a specific parameter called circulating power, denoted as P_C by the manufacturer. At a given output power value (discharge power value, P_E) the value of P_C depends on the load impedance [20]. With respect to the sputtering process in an atmosphere of which argon/oxygen ratio can be changed, the value of P_C may be used as the indicator of target's surface condition (metallic, oxidized) if only there is a difference in the ion-induced secondary electrons emission coefficient between metallic and oxidized state of the target's surface. Fortunately many metals and their oxides exhibit such properties [26], including Zn/ZnO and Al/Al_2O_3. To illustrate the P_C specifics, fig.2 shows the $P_C(P_E)$ dependences for a solid Zn target (9 mm thick) sputtered in an argon/oxygen atmosphere of ratio: 100/0 (blue line, filled squares) - metallic mode; 0/100 (blue line, open squares) - dielectric mode. For a given discharge power the oxidation of the zinc target significantly changes the value of P_C. Additionally, in that figure there are the $P_C(P_E)$ dependences shown for solid Al target (9 mm thick) sputtered in an argon/oxygen atmosphere of ratio: 100/0 (red line, filled circles) - metallic mode; 0/100 (red line, open circles) - dielectric mode. The oxidation of the aluminium target changes the P_C value even more significantly with comparison to the zinc target. In fact, to monitor the sputtering condition of the target, it is not important to know the value of the ion-induced secondary electron emission coefficient. It is sufficient that the sputtered element has a higher emission of secondary electrons in the oxidized state than in the metallic state – in such case an increase of P_C value is present with oxidation of the target.

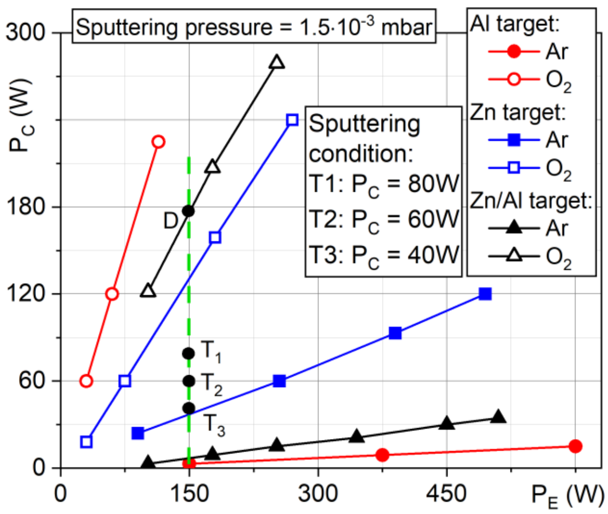

Figure 2. The circulating power P_C dependence on discharge power P_E at different target material and composition of the sputtering atmosphere. Technological points D and T_{1-3} are described in section 3.

As the Zn and Al targets showed a change in P_C due to oxidation, it was expected that the two component Zn-Al target would also show this tendency. With respect to the current investigations in fig.2 there are the $P_C(P_E)$ dependences shown for two-component Zn-Al target sputtered in argon/oxygen atmosphere of ratio: 100/0 (black line, filled triangles) - metallic mode; 0/100 (black line, open triangles) - dielectric mode. In this paper reported are the results obtained at the discharge power of P_E=150 W, which is marked in fig.2 with dashed green line. At such discharge power the full oxidation of the sputtering zone of the target resulted in the P_C value of 180 W. On the other hand the metallic state of the sputtering zone resulted in the P_C value of about 10 W. As it was estimated in the previous section the AZO films suitable as TCO are likely to be deposited while the two-element target is operating in the transient mode. It was concluded that the sputtering condition of the erosion zone may be needed in the form of Zn, Al_2O_3 to obtain the ratio of Al/Zn in the flux to the substrate to be comparable with the ratio calculated for the sintered AZO target made of ZnO/Al_2O_3 98:2 wt%. Such a sputtering condition may be achievable rather far from the fully oxidized state. All the estimations made indicated that, for a fixed discharge power of 150 W, the composition of the process atmosphere (argon/oxygen ratio) should be adjusted in such a way that the P_C should have a value in the range of 30-90 W. The argon/oxygen ratio was varied and ratios of 80/20, 82/18 and 84/16 are reported in this paper. In fig.2 there are shown technological points T_{1-3} that correspond to given argon/oxygen ratio. The given argon/oxygen ratio resulted in the P_C parameter value of (fig.2): 80, 60 and 40 W for the Ar/O_2 ratios of 80/20 (point T_1), 82/18 (point T_2) and 84/16 (point T_3); respectively. The AZO films, described in the following sections, were obtained at these sputtering conditions, to demonstrate the occurrence of optimal conditions for obtaining AZO films with the best TCO properties. The effect of hysteresis influenced the sputtering process. Because of that the desired argon/oxygen ratio was obtained with specific procedure - firstly, the oxygen partial pressure was established in the chamber via needle-type dosing valve and then argon was added via another valve to reach the given total pressure. After the sputtering process was started the oxygen partial pressure was adjusted to obtain the desired P_C value and the shutter was opened to start the deposition. If the P_C value changed during deposition then the oxygen partial pressure was changed to restore the desired P_C value. This suggests that an automatic regulation loop could be established by linking the dosage of oxygen with the desired P_C value, using a similar approach to previous investigations about deposition of Al_2O_3 [27].

4. Results

Transmission of light

A key performance parameter of films to be suitable for TCO applications is the light transmission, particularly in the visible light range. Light transmission characteristics of as-deposited films at sputtering conditions T_{1-3} (indicated in fig.2) are shown in fig.3. For comparison, the transmission spectra of the substrates alone (Corning 7059 glass , Corning Willow® Glass) are also shown in fig.3.

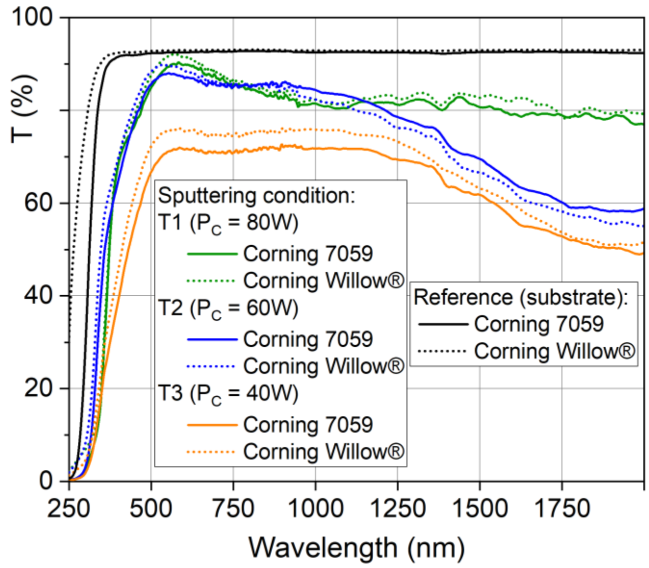

Figure 3. Transmission spectra of obtained AZO films

The AZO film obtained at sputtering condition T_1 (Ar/O_2 ratio of 80/20) had a transmission higher than 80% in the 450-2000 nm wavelength range (flexible glass substrate). The film deposited on standard glass substrate had a slightly lower transmission coefficient, especially in the 1000-2000 nm wavelength range (77%). The transmission coefficient value did not fluctuate significantly throughout the measured range for both substrate types. The highest value of transmission coefficient (of about 90%) was found in the 525-600 nm wavelength range. In the visible wavelength range, the average transmission of light was calculated to be approximately 84%. The AZO film obtained at sputtering condition T_2 (Ar/O_2 ratio of 82/18) had a transmission higher than 80% in the 450-1150 nm wavelength range for both substrate types. Within this range the results were found to be similar to the film obtained at sputtering condition T_1. That resulted in the calculated average transmission of light in the visible wavelength range to be of about 83%. A significant decrease in the transmission was observed for wavelengths longer than 1250 nm, but it did not decline below 55% up to 2000 nm. Such an observed decrease in transmittance in the near-infrared range was caused by the conductive property of the charge carriers in AZO [28-30]. The AZO film obtained at sputtering condition T_3 (Ar/O_2 ratio of 84/16) had the lowest (of all samples) light transmission over the entire measured range. In the 450-1150 nm range it had a transmission of approximately 70%. In the visible wavelength range, the average transmission of light was calculated to be of about 67%. Similarly to the sample obtained at sputtering condition T_2, the transmission significantly decreased for wavelengths above 1250 nm. However, it did not decrease below 50% up to 2000 nm. Results of transmission measurements are summarized in table.1, together with the calculated values of the fundamental absorption edge (the cut-off wavelength).

Electrical properties – resistivity

Measurements of the sheet resistance were performed for as-deposited samples. The sheet resistance together with the film thickness were used to calculate the resistivity of AZO films and calculations results are summarized in table 1. The AZO films with the lowest resistivity (close to the 10^{-4} $\Omega\cdot$cm range) were obtained at sputtering condition T_2 (Ar/O_2 ratio of 82/18).

Table 1. Electrical and optical parameters of obtained AZO films

Sample		Film thickness (nm)	Sheet resistance (Ω)	Resistivity $\cdot 10^{-3}$ ($\Omega\cdot$cm)	Cut-off wavelength (nm)	Transmittance (average value for visible range) %	Figure of merit ($1/\Omega\cdot$cm)
Substrate	Ar/O_2 ratio %						
standard glass (Corning)	T_1 (80/20)	88	5391	47.4	326	84	4
	T_2 (82/18)	116	121	1.4	306	83	110
	T_3 (84/16)	123	157	1.9	305	65	7
flexible glass (Willow)	T_1 (80/20)	88	3896	34.3	300	86	6
	T_2 (82/18)	116	100	1.2	294	85	167
	T_3 (84/16)	123	135	1.7	295	70	17

To evaluate the TCO quality of the deposited films, the Figure of Merit (FOM) was calculated. This provided a valuable metric, taking into account both electrical and optical properties of films, using the modified Haacke formula FOM = T^{10}/ρ [31]; where T is the average light transmittance in the visible spectrum and ρ is the resistivity of the film (Ωcm). The highest FOM values were obtained for films deposited at sputtering condition T_2 (Ar/O_2 ratio of 82/18). Additionally, positive influence of the substrate was observed, which resulted in the sample made on flexible glass having the best optical and electrical properties.

Surface properties and elemental composition

Deposited films were diagnosed using SEM microscopy for surface imaging (fig.4) and EDS measurements. The surface morphology was diagnosed basing on the AFM scans (fig.5). Table 2 presents the quantitative results of these measurements. Both SEM and AFM scans, showed that the surface of the films, deposited in each of the three sputtering conditions (T_1, T_2, T_3), had a smooth surface. Rare aggregations of material were found only on the sample T_2 (standard glass). The EDS images showed uniform distribution of elements over the whole area of samples, no imprints of the geometric distribution of Zn-Al elements from the target were present on the samples. It can be concluded that the distance between the target and substrate, together with the geometric features of deposition process, were sufficient for the discharge plasma to cause mixing of sputtered material.

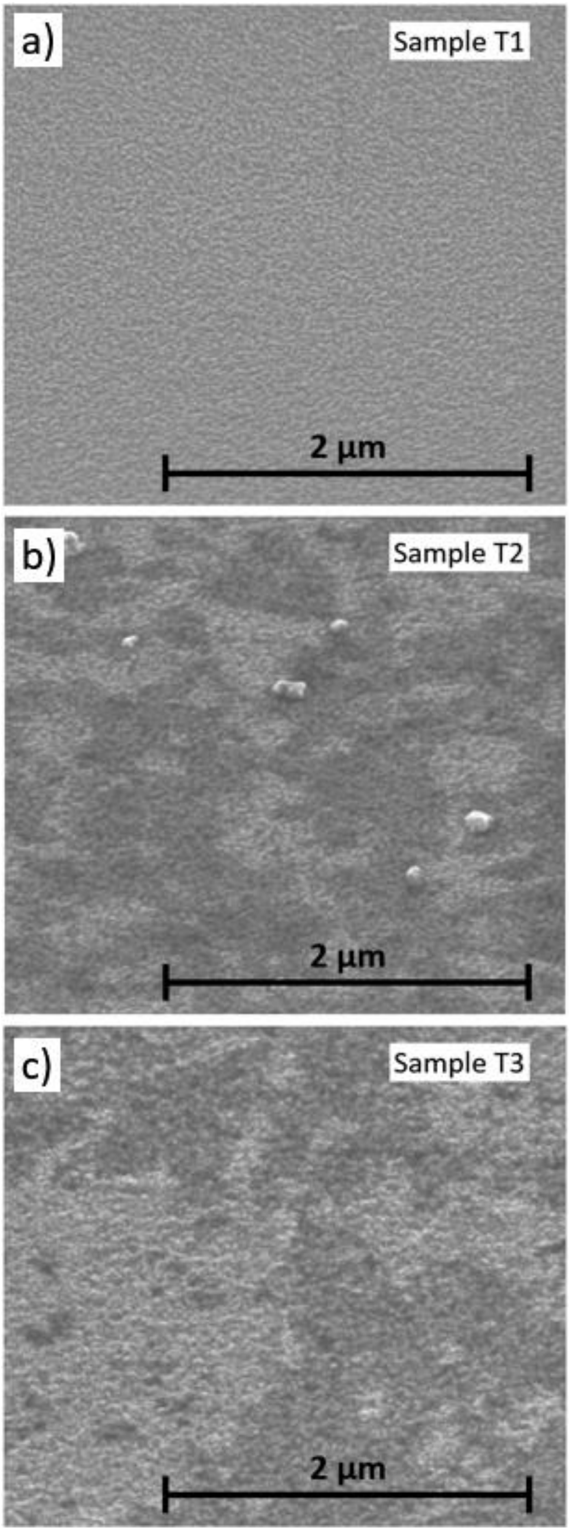

Figure 4. SEM scans of obtained AZO films deposited on standard glass substrates.

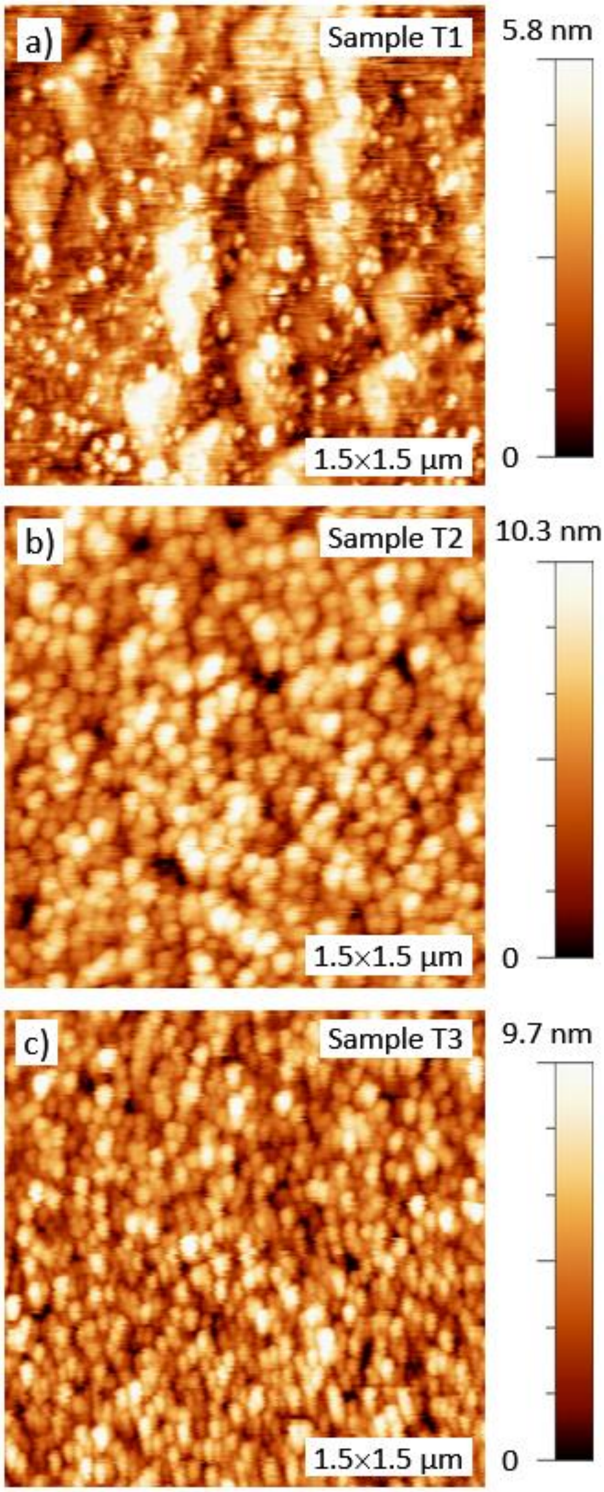

Figure 5. AFM scans of obtained AZO films deposited on standard glass substrates

Table 2. Surface properties of obtained AZO films

Sample		RMS roughness (nm)	peak-to-peak (nm)	EDS measured ratio of Al/Zn
Substrate	Ar/O_2 ratio %			
standard glass (Corning)	T_1 (80/20)	1.34	5.8	8/100
	T_2 (82/18)	1.86	10.3	7/100
	T_3 (84/16)	1.81	9.7	10/100
flexible glass (Willow)	T_1 (80/20)	1.21	5.6	8/100
	T_2 (82/18)	1.42	7.8	7/100
	T_3 (84/16)	1.61	8.5	10/100

The results summarized in the tab.2 show that the variation of the Ar/O_2 ratio did not significantly affect the surface morphology of obtained AZO films, in the studied range of Ar/O_2 ratio. However, the films had the lowest surface roughness values under T_1 sputtering condition. Unfortunately the T_1 sputtering condition resulted in the highest resistivity of obtained films (table 1).

Basing on the EDS measurements the ratio of Al/Zn atoms in the films was calculated. The resulted values were in good agreement with theoretical predictions given in section 3 (Considerations about sputtering conditions, Two-element Zn-Al target) for the boundary state of the erosion zone in the form of Zn, Al_2O_3. For such a sputtering condition the ratio of Al/Zn in the flux to the substrate was estimated to be of about 9/100.

Optical emission of plasma (OES)

Results of studies of the optical and electrical parameters of obtained AZO films have shown, that there is a certain optimum of reactive gas dosage (given by sputtering condition T_2), which enables deposition of AZO films with TCO properties to be obtained using developed two-element Zn-Al target. When using the DORA medium frequency power supply, such point of optimum Ar/O2 ratio can be easily maintained by controlling the value of the circulating power P_C, which is read from the power supply during the sputtering process. As the DORA medium frequency power supply is used rather locally in the manufacturer's country, an OES diagnostic was undertaken to investigate whether the indication of the optimum reactive gas dosage could be realized independently of the magnetron power supply used. For sputtering processes described with the T_1, T_2, T_3 conditions, the plasma emission spectra were recorded using low-cost spectrophotometer. Spectral lines that could be clearly identified were selected in the recorded OES spectra – unfortunately, there were not many of them. Among these identified lines, we searched for those lines whose intensity varied in a characteristic way among conditions T_{1-3}, so that some mechanism for controlling the sputtering process could be proposed. In case of argon spectral lines there were found ones of excited atoms and ions which showed the minimum intensity for T2 conditions (fig.6).

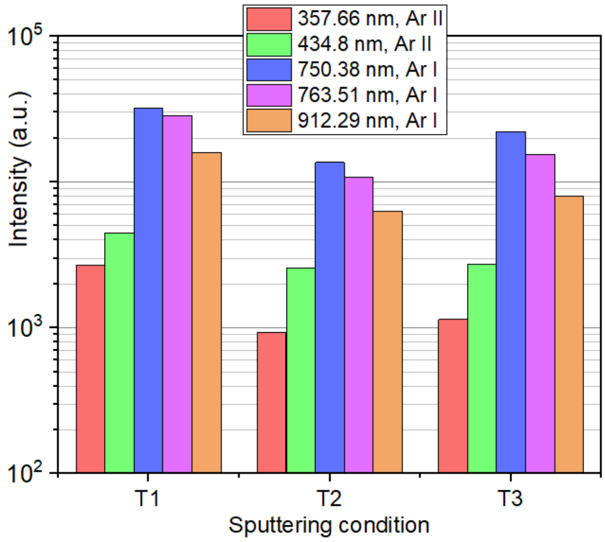

Figure 6. Selected spectral lines of argon that exhibit minimum intensity during transition of sputtering process among conditions T_{1-3}

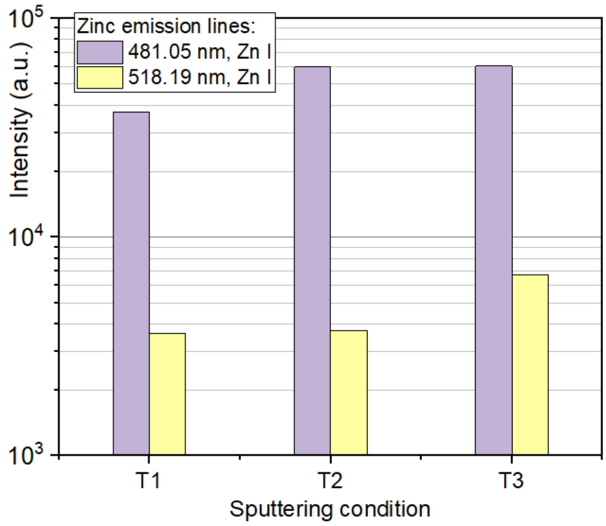

Figure 7. Intensity change of selected zinc spectral lines as a function of transition of sputtering process among conditions T_{1-3}

In case of zinc there were selected two spectral lines whose intensity varied in a characteristic way among conditions T_{1-3}. The 481.05 nm line of excited atoms indicated and intensity increase while transition from T_1 to T_2 sputtering conditions. The transition from T_2 to T_3 sputtering condition did not affected intensity of this line. On the other hand the intensity of the 518.19 nm line was not affected by the transition form T_1 to T_2 sputtering conditions, while transition form T_2 to T_3 sputtering conditions caused an intensity increase.

5. Conclusions

The AZO films were deposited using self-designed two-element Zn-Al target. It has been shown that the argon/oxygen ratio of the sputtering atmosphere influenced the Al/Zn ratio in the material flux to the substrate. The sputtering conditions of the erosion zone of the target could be influenced by the argon/oxygen ratio, i.e. by changing the oxygen flow into the process chamber. The oxygen dosage could be linked via a control loop to the electrical parameter of the power supply unit or to selected OES signal from plasma emission spectra. It was estimated that AZO films with TCO properties could be deposited if erosion zone of the target was operating at specific sputtering conditions related to transient sputtering mode. It was suggested that this specific sputtering conditions included full oxidation of aluminum part, while Zn part was in transient mode located close to the metallic sputtering mode. These specific sputtering conditions could be easily pointed using relation of discharge power and circulating power of the DPS power unit, and were linked by the relationship of $P_C/P_E \approx 0.5$. Other preliminary work has shown that this relationship was valid for the discharge power up to approximately 400 W, demonstrating that the process of deposition of AZO films from a two-element Zn-Al target seemed to be scalable. Alternatively, the OES signal could be used to controlling the sputtering process. Especially, selected argon lines were pointed to be suitable for that, because local minimum of intensity were observed.

The presented approach resulted in AZO films with resistivity of about $1.2 \cdot 10^{-3}$ Ωcm and average light transmission in the visible range of about 85%. The use of pulsed sputtering resulted in a smooth film surface with no micro-droplets, the RMS roughness was lower than 2 nm.

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7. References

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