1. Szymon KIEŁCZAWA, 2. Artur WIATROWSKI

Wrocław University of Science and Technology
Faculty of Electronics, Photonics and Microsystems
ORCID: 1. 0000-0003-4315-7385; 2. 0000-0002-8594-2384

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Specific method of deposition of aluminium-doped zinc oxide thin films on flexible glass substrates

Abstract. *In this paper, we report specific method of controlling magnetron sputtering process by parameter named by the power supply manufacturer as "circulating power". That parameter may be used to determine sputtering mode (metallic, transient, dielectric). Basing on the circulating power characteristics the AZO thin films were deposited onto conventional (non-bendable) and bendable glass substrates. The films were characterized by high optical transmittance (over 80% in visible light spectrum) and low resistivity, which was in range of 10^{-3} Ω·cm.*

Streszczenie. *W artykule przedstawiono specyficzną metodę sterowania procesem rozpylania magnetronowego za pomocą parametru nazwanego przez producenta zasilacza "mocą krążącą", który użyto do określenia modu rozpylania (metaliczny, przejściowy, dielektryczny). Na podstawie charakterystyk mocy krążącej cienkie warstwy AZO zostały naniesione na konwencjonalne oraz giętkie podłoża szklane. Warstwy te posiadały dużą transmisją światła (powyżej 80% w zakresie widzialnym światła) oraz niską rezystywnością (na poziomie 10^{-3} Ω·cm).* ***Specyficzna metoda osadzania cienkich warstw tlenku cynku domieszkowanego glinem na elastycznych podłożach szklanych.***

Keywords: *magnetron sputtering, reactive sputtering, transparent electronics, flexible coatings*
Słowa kluczowe: *rozpylanie magnetronowe, rozpylanie reaktywne, transparentna elektronika, powłoki elastyczne*

1. Introduction

Aluminium-doped zinc oxide (AZO) films are prominent and low-cost alternatives to indium-tin-oxide (ITO) for transparent conducting oxide (TCO) films in applications like antireflective coatings for solar cells, transparent electrodes for solar cells, liquid crystal displays (LCD) or light emitting diodes (LED) [1-5]. Such TCO coatings should meet expectations of the highest possible optical transmission (in general more than 80% in visible spectrum is acceptable) and the lowest sheet resistance (suitable materials should offer relatively low resistivity, lower than 10^{-4} Ω·cm) [6]. It is known that ITO is the most commonly used as a transparent conducting oxide nowadays, due to its high conductivity and high optical transmittance in visible spectrum. However, its toxic nature [7] and high costs led to attention being drawn to alternative materials e.g. AZO, although its sensitivity to moisture is noticeable drawback.

The AZO thin films, which meet the TCO requirements may be obtained by various techniques, including PVD techniques and in particular by magnetron sputtering [8, 9]. Due to low cost of apparatus and high process repeatability magnetron sputtering is one of the commonly used PVD techniques. However, in order to achieve desired (the TCO suitable) properties of AZO films it is necessary to conduct deposition processes in the unstable transition mode of the magnetron source operation. The second problem is the need of use of relatively high deposition temperatures (over 200ºC), that is the major problem in case of deposition films onto flexible (plastic) substrates.

The necessity of substrate heating may be substituted (to some extend) by the usage of post-annealing of the films, but still the significantly positive results require post-annealing in 200-300ºC [13]. Nevertheless, the high power impulse magnetron sputtering (HiPIMS) method has been proposed [10]. The HiPIMS uses the power supplied by high current density impulses with low duty cycle. The alteration from standard magnetron sputtering to HiPIMS leads to higher plasma density and that in turn offers opportunity to reduce the temperature of substrate [11]. Summarizing the issue of deposition temperature there are some technological possibilities to be chosen.

The above mentioned first problem, connected with the operation of magnetron source in the transition mode is even multiplied by the hysteresis effect that occurs while mode of magnetron operation changes among dielectric-transient-metallic. Such behaviour makes it difficult to control the sputtering process both to maintain the transition mode and provide constant deposition rate. The O_2 flow ratio has significant impact on sputtering mode and the deposition rate is characterized by hysteresis, with the respect to the reactive gas flow ratio (O_2). This kind of behaviour induce changes in deposition rate with the changes of the reactive gas flow. As it was said before to achieve the high-quality (the TCO quality) of AZO films with high deposition rate, it is needed to control sputtering conditions precisely in transition region mode of magnetron operation [12] where even small fluctuations of the technological parameters can lead to significant changes of properties of deposited films.

In this paper a certain approach is presented to give an example of another way to control the process of reactive deposition of AZO films by the means of magnetron sputtering. This approach involves the use of easy-to-make two-element target and the use of a specific pulsed-resonant power supply [14].

2. Experimental

The sputtering system used for sputtering processes and deposition of Al_xZn_yO films consisted of a custom-made circular magnetron source WMK-100 equipped with originally self-invented two-element Zn/Al target and a Medium Frequency pulsed (100 kHz) power supply Dora Power Systems. The sputtering processes and deposition of the sample thin films were conducted at total pressure in the vacuum chamber of about $2 \cdot 10^{-3}$ mbar. The sample thin films were deposited during reactive process in a mixture of argon and oxygen with the oxygen partial pressure of about $7 \cdot 10^{-4}$ mbar and the discharge power was about 150 W. Substrates of the Corning glass were used: standard (7059, 700 µm thick) and flexible (Willow® Glass, 200 µm thick).

The two-element Zn/Al target was prepared by pressing the circular Al rings (Al wire with diameter of 2 mm) into the milled grooves of the 100 mm Zn disc surface. The thickness of the Zn disc was 9 mm. The Al rings were fitted tight inside the disc to ensure low thermal resistance and prevent wires from melting. Basing on preliminary sputtering processes the number of three Al rings was chosen and all rings were placed inside the race-track zone (Fig. 1) [9].

The MF DPS power supply is a pulsed current source with the sinusoidal-shaped current waveform. The resonant power stage of this unit offers a non-common parameter named by the manufacturer as a circulating power, P_C. When the impedance of magnetron source discharge decreases (e.g. in case of increase of secondary electron emission coefficient from the target surface) then the circulating power of the DPS power supply increases. The value of the ion-induced secondary electron emission coefficient changes its value for many materials then such material became oxidized. This makes the circulating power a useful parameter which is related with the condition of the surface of the target, i.e. circulating power is related with the mode of sputtering – metallic, transient, dielectric. With this relationship between circulating power and the target surface condition it is possible to control the reactive process or to estimate the target surface condition during the sputtering process [14].

With respect to the magnetron sputtering processes discussed in this paper we assumed that the flow of the discharge current applied only to the race-track area (race-track power density was about 4.5 W/cm^2). Because of that assumption we considered that the changes of the circulating power were caused exclusively by the changes of sputtering mode of only that part of the target which was the race-track area.

2.1 Details of the target

The view of the prepared target (after reactive sputtering processes) and its dimensions are given in Fig. 1 and Fig. 2, respectively. The race-track zone was sharply visible between the border areas covered by dark-brown non-stoichiometric oxides (Fig. 1). The inner and outside radii of the race-track zone were about 21 and 39 mm, respectively (Fig. 2) and the area of the race-track zone was 3392 mm^2.

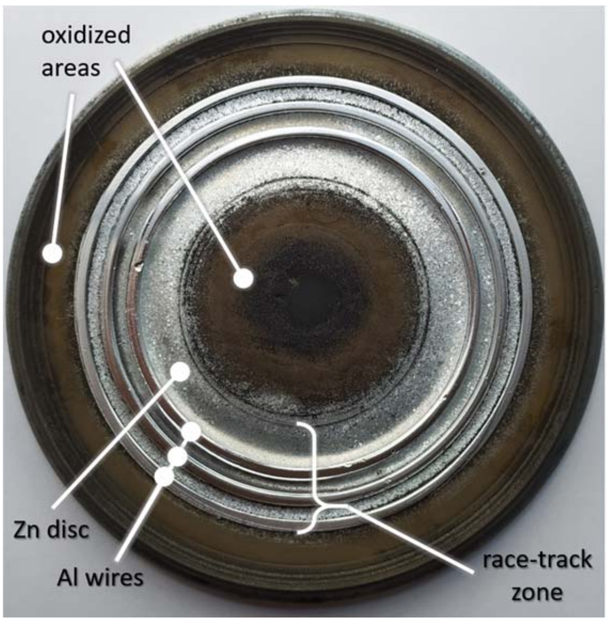

Fig. 1. The Zn/Al target showing arrangement of Al inserts. Target after reactive sputtering processes indicates the race-track zone and oxidized areas.

The radii of placement of Al wire rings were set to 29, 34 and 38 mm (Fig. 2). The Al wires took a part of the area of the race-track equal to 364, 427, 477 mm^2, resulting in the total area of the race-track taken by the Al wires of about A_{Al} = 1268 mm^2. The remaining area of the race-track zone was the Zn area of about A_{Zn} = 2123 mm^2.

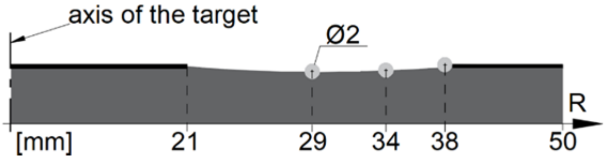

Fig. 2. The cross-section of the Zn/Al target showing dimensions, drawing not in scale.

Since the surface of the wires was not flat the dependence of sputtering yield on the angle of incidence of argon ions was taken into account. As a result of that dependence each single Al wire was sputtered with higher efficiency than the flat surface. Assuming that the incidence of argon ions was perpendicular to the magnetron cathode then the shape of the wire caused the multiplication of the sputtering yield of material from wires. For the circular cross-section of the wires this multiplication was calculated to be of about 5 times. Because the wires were misshapen during operation of pressing into the milled grooves than the actual multiplication factor was of about 3. The erosion of the zinc part of target in the race-track zone was negligible (less than 0.5 mm) and therefore the area with the Zn was assumed to be flat.

3. Results and discussion

With respect to the details of the two-element Zn/Al target given in section Experimental the circulating power characteristics were determined and considerations about mode of sputtering were conducted. Basing on made observations the processe of AZO deposition was performed and transmission and resistivity of obtained films were measured.

3.1 Circulating power characteristics

The most useful characteristic of the circulating power is its dependence on effective power P_E (i.e. discharge power) at given set of technological parameters, e.g. target material and thickness, pressure and composition of sputtering atmosphere. In Fig. 3. presented are the curves of $P_C(P_E)$ dependence for 9 mm thick targets made of Al (red lines) and Zn (blue lines) sputtered in the atmosphere of argon – metallic mode (filled square symbols) and oxygen – dielectric mode (filled circle symbols). As it was described in the introductory section, at fixed target material, oxidation of its surface causes the increase of the P_C if only the oxide of the target metal has a higher value of the secondary electron emission coefficient than the metallic target. In case of Al and Zn such relation takes place and therefore sputtering processes of these materials (as individual targets and two-element target) are suitable to be controlled by the circulating power.

At fixed partial pressure of reactive gas (set before the start of sputtering process) the mode of sputtering may be changed by the discharge power change. In general low discharge power results then in the dielectric mode of magnetron operation, because the sputtering yield of compound is lower than the rate of formation of this compound. On the contrary, high discharge power results in the metallic mode of magnetron operation, because intense bombardment of the target by the argon ions makes it impossible for the target (race-track zone) to be oxidized. As the discharge power is increased then the change of the sputtering mode from dielectric mode to metallic mode occurs rapidly at certain discharge power, so the transition mode cannot be easily established. For example the $P_C(P_E)$

curve for the process of sputtering of Al target in 90%/10% mixture of argon/oxygen is given in Fig. 3 – red line with star symbols; red arrow shows no intermediate points within the region of the transition mode. The transition mode of sputtering can be established if the operating point of magnetron source is shifted from the metallic mode, e.g. as a result of the discharge power decrease. Such shift is not so rapid and intermediate points within the region of the transition mode are obtainable. Such approach is presented in the next section, regarding the sputtering of two-element Zn/Al target.

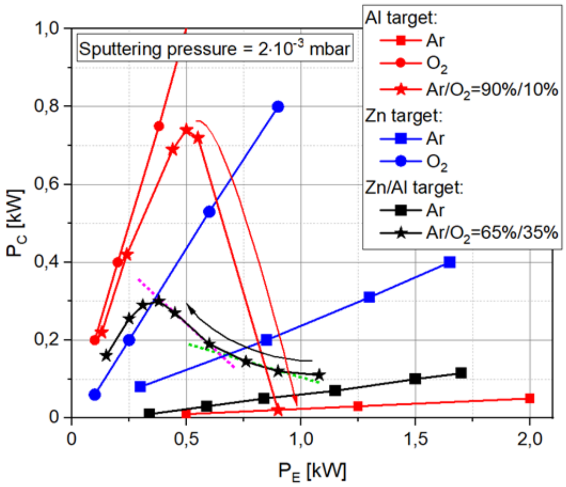

Fig. 3. The circulating power P_C dependence on discharge power P_E at different target material and composition of the sputtering atmosphere.

3.2 Considerations about sputtering of the Zn/Al target

The presented considerations were conducted under four important assumptions: i) the discharge current was the argon ions current only, ii) the argon ions current was directed only to the area of the race-track zone, iii) the current density of argon ions was constant over whole area of the race-track zone, iiii) the energy of incident argon ions was 500 eV. Basing on the literature data the sputtering yields induced by the argon ions were found to be of about 5/0.5 and 0.9/0.2 atoms/ion for the Zn/ZnO and Al/Al_2O_3, respectively [16, 17].

The $P_C(P_E)$ dependence for sputtering process of two-element Zn/Al target in argon atmosphere is depicted in Fig. 3 - black line with filled square symbols. This dependence is located between the dependences for sputtering of the single-element Zn and Al targets - Fig. 3 lines with filled square symbols blue and red, respectively. That shows that two-element target behaves like a sum of two elements weighted by their area A_{Zn} and A_{Al}.

The $P_C(P_E)$ dependence for reactive sputtering process of two-element Zn/Al target is depicted in Fig. 3 - black line with star symbols; black arrow shows that intermediate points within the region of the transition mode are obtainable. With that observation the values of circulating and discharge power may be used to identify the desired setpoint, that allows deposition of good quality AZO films. Moreover, such setpoint may be the parameter for stabilization in the closed loop e.g. by changing the inflow of the reactive gas, as it was described for Al_2O_3 films [15].

Starting the sputtering of Zn/Al target at high discharge power the mode of sputtering is metallic – if the discharge power is higher than about 1 kW then the $P_C(P_E)$ dependence for reactive sputtering becomes in fact the $P_C(P_E)$ dependence for sputtering of Zn/Al target in argon atmosphere only (Fig. 3, black line with filled square symbols). Metallic mode results in the ratio of sputtered Al/Zn atoms of about 0.32/1; calculated as the area A_{Al} multiplied by the sputtering yield of Al and the geometrical factor (mentioned in section Details of the target) to the area A_{Zn} multiplied by the sputtering yield of Zn. The films obtained at such conditions are opaque dark-grey and therefore do not meet basic requirements for TCO.

Once the discharge power is decreased below about 800 W then the intensity of the sputtering is decreased and some areas of the race-track zone became oxidized – what is clearly indicated by the increase of the circulating power value – the operating point of the magnetron enters the transition mode. Because the sputtering yield of Al and Zn differs greatly (0.9 and 5, respectively) it is highly likely that the Al part of the race-track zone becomes oxidized first. With such assumption one unique state of the transition mode may be considered – Al area fully oxidized (dielectric mode) and Zn area not oxidized (metallic mode). That state results in the ratio of sputtered Al_2O_3/Zn molecules/atoms of about 0.072/1; calculated as the area A_{Al} multiplied by the sputtering yield of Al_2O_3 and the geometrical factor to the area A_{Zn} multiplied by the sputtering yield of Zn. The calculated ratio of Al/Zn atoms directed to the substrate was about 0.029/1. This unique state may be localized at the point of P_E=0.65 kW, P_C=0.18 kW; where the discussed $P_C(P_E)$ curve changes its slope – green dot line to magenta dot line. The films obtained at such conditions are light-grey with the resistivity in the range of about 10^{-1}–10^{-2} Ω·cm.

Further decrease of the discharge power (below the 0.65 kW) makes the increase of the circulating power faster – the Zn area of the race-track (that is larger than A_{Al}) zone becomes oxidized.

With the discharge power lower than 0.25 kW the discussed $P_C(P_E)$ curve points out the dielectric mode of sputtering, but one keep in mind that sputtering atmosphere was Ar/O_2=65%/35% and therefore the role of argon ions in the sputtering of the target was predominant. Assuming dielectric state of the race-track zone the ratio of sputtered Al_2O_3/ZnO molecules was of about 0.89/1; calculated as the area A_{Al} multiplied by the sputtering yield of Al_2O_3 and the geometrical factor to the area A_{Zn} multiplied by the sputtering yield of ZnO. The calculated ratio of Al/Zn atoms directed to the substrate was about 0.7/1.

The literature data indicate that AZO films suitable for TCO applications in photovoltaics are deposited by sputtering from targets composed of 2–4% Al metal incorporated in ZnO [18], what results in Al/Zn content ratio of about 0.1/1 and in turn the ratio of Al/Zn atoms directed to the substrate of about 0.4/1 (assuming the dielectric state of the target surface). With respect to those literature data the process of sputtering of the two-element target should be set between the unique state of transient mode and the dielectric state of the whole race-track zone, i.e. discharge power should take the value between 0.6 and 0.15 kW. Within this range the films with the best transmission and lowest resistivity were obtained at the discharge power of about 0.16 kW. According to $P_C(P_E)$ curve such value indicates operation of magnetron source almost with the fully oxidized target, which was needed to reduce the number of Zn atoms sputtered from the target. In the light of conducted considerations about sputtering of the Zn/Al target it suggests that A_{Al} should be increased, e.g. by addition of another aluminium wire ring.

3.3 Deposition of AZO films

At the discharge power of 0.16 kW the AZO films of 70 nm in thickness were deposited with the deposition rate of about 14 nm/min. The substrates were located 100 mm above the target, 60 mm off-axis [9]. No intentional heating of the substrates was used, and the films were not annealed after deposition process. The transmission spectra of obtained films are presented in Fig. 4 and the calculated mean transmission in visible spectrum is given in Tab. 1, together with the resistivity. The mean transmission in visible spectrum was greater than 80% and the resistivity of about $2–4·10^{-3}$ Ω·cm. The film deposited onto flexible glass shown slightly better values probably due to higher temperature of the substrate – as the Willow® glass was thinner it probably reached the higher temperature than the Corning 7059.

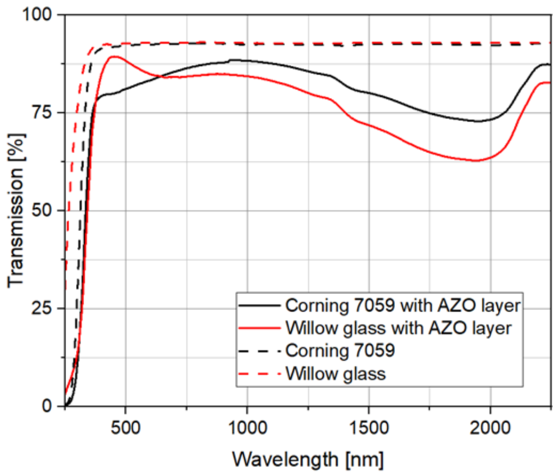

Fig. 4. Results of investigation on optical transmission.

Table 1. The basic parameters of obtained AZO films

Substrate	Resistivity [Ω·cm]	Mean transmission in visible spectrum
Corning 7059	$4·10^{-3}$	83%
Corning Willow	$2·10^{-3}$	86%

4. Conclusions

The thin films of AZO are promising for TCO applications, especially because acceptable electrical parameters may be obtained at room temperature, what is important for flexible (plastic) substrates.

The deposition of AZO films by the means of sputtering of two-element Zn/Al target [9] was discussed in this paper in terms of sputtering mode determination. Further detailed investigations will include the use of Optical Emission Spectroscopy to verify is it really so that one material is oxided first, because of the difference in sputtering yields.

Basing of the relation between the circulating power and the discharge power it was possible to control the AZO deposition process. Once the dependence of circulating power on the discharge power was known then the mode of sputtering was determined exactly during the deposition process. The sample AZO films were deposited onto glass substrates – standard Corning 7059 and flexible Corning Willow®. The mean transmission in visible spectra and resistivity reached comparable values, regardless of the substrate. What should be pointed out is the fact that obtained films met be basic TCO requirements.

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Authors. *mgr inż. Szymon Kiełczawa, szymon.kielczawa@pwr.edu.pl; dr hab. inż. Artur Wiatrowski, artur.wiatrowski@pwr.edu.pl; Politechnika Wrocławska; Wydział Elektroniki, Fotoniki i Mikrosystemów; ul. Z. Janiszewskiego 11/17; 50-372 Wrocław.*

REFERENCES

[1] Kluth O., Rech B., Houben L., Wieder S., Scho G., Beneking C., Wagner H., Lo A., Schock W.H., Texture etched ZnO:Al coated glass substrates for silicon based thin film solar cells, Thin Solid Films 351 (1999) 247–253

[2] Yoo J., Lee J., Kim S., Yoon K., Jun Park I, Dhungel S.K., Karunagaran B., Mangalaraj D., Junsin Y., High transmittance and low resistive ZnO:Al films for thin film solar cells, Thin Solid Films 480–481 (2005) 213–217

[3] Nomoto J., Hirano T., Miyata T., Minami T., Preparation of Al-doped ZnO transparent electrodes suitable for thin-film solar cell applications by various types of magnetron sputtering depositions, Thin Solid Films 520 (2011) 1400–1406

[4] Yamamoto N., Makino H., Osone S., Ujihara A., Ito T., Hokari H., Maruyama T., Yamamoto T., Development of Ga-doped ZnO transparent electrodes for liquid crystal display panels, Thin Solid Films 520 (2012) 4131–4138

[5] Doo-Soo K., Ji-Hyeon P., Su-Jeong L., Kyung-Jun A., Mi-So L., Moon-Ho H., Woong L., Jae-Min M., Effects of oxygen concentration on the properties of Al-doped ZnO transparent conductive films deposited by pulsed DC magnetron sputtering, Materials Science in Semiconductor Processing 16 (2013), 997-1001

[6] Markvart T., Castaner L., Solar Cells: Materials, Manufacture and Operation, Elsevier, Amsterdam, 2006

[7] Nagano K., Nishizawa T., Umeda Y., Kasai T., Noguchi T., Gotoh K., Ikawa N., Eitaki Y., Kawasumi Y., Yamauchi T., Arito H., Fukushima S., Inhalation Carcinogenicity and Chronic Toxicity of Indium-tin Oxide in Rats and Mice, Journal of Occupational Health 53 (2011), 175-187

[8] Minami T., Nanto H., Takata S., Highly conductive and transparent zinc oxide films prepared by rf magnetron sputtering under an applied external magnetic field, Appl. Phys. Lett. 41(1982), 958

[9] Posadowski W., Wiatrowski A., Domaradzki J., Mazur M., Selected properties of AlxZnyO thin films prepared by reactive pulsed magnetron sputtering using a two-element Zn/Al target, Beilstein J. Nanotechnol. 13 (2022), 344–354

[10] Zubkins M., Arslan H., Bikse L., Purans J., High power impulse magnetron sputtering of Zn/Al target in an Ar and Ar/O2 atmosphere: The study of sputtering process and AZO films. Surface and Coatings Technology 369 (2019), 156-164

[11] Mickan M., Helmersson U., Rinnert H., Ghanbaja J., Muller D., Horwat D., Room temperature deposition of homogeneous, highly transparent and conductive Al doped ZnO films by reactive high power impulse magnetron sputtering, Sol. Energy Mater. Sol. Cells 157 (2016) 742–749

[12] Nishi Y., Hirohata K., Tsukamoto N., Sato Y., Oka N., Shigesato Y., High rate reactive magnetron sputter deposition of Al-doped ZnO with unipolar pulsing and impedance control system. Journal of Vacuum Science & Technology A 28 (2010), 890–894

[13] Liu C, Xu Z., Zhang Y., Fu J., Zang S., Zuo Y., Effect of annealing temperature on properties of ZnO:Al thin films prepared by pulsed DC reactive magnetron sputtering. Materials Letters 139 (2015), 279–283

[14] Posadowski W.M., Wiatrowski A., Dora J., Radzimski Z.J., Magnetron sputtering process control by medium-frequency power supply parameter, Thin Solid Films 516 (2008) 4478-4482

[15] Wiatrowski A., Patela S., Kunicki P., Posadowski W., Effective reactive pulsed magnetron sputtering of aluminium oxide – properties of films deposited utilizing automated process stabilizer, Vacuum, 134 (2016) 54-62

[16] Eckstein, W. (2007). Sputtering Yields, in: Sputtering by Particle Bombardment. Topics in Applied Physics, vol 110 (2007), Springer, Berlin

[17] Tominaga K.. Ueshiba N., Shintani Y., Tada O., High-energy neutral atoms in the sputtering of ZnO, Japanese Journal of Applied Physics, 20 (1981), 519-526

[18] Petti C.J., Hilali M.M, Prabhu G., Thin Films in Photovoltaics, in: Handbook of Thin Film Deposition, Third edition (2012), William Andrew