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Layer-by-layer deposition of transparent AZO coatings on polymer surfaces in a DC magnetron discharge

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Abstract. The method of layer-by-layer deposition of transparent conductive AZO coatings on transparent polymer substrates (acrylic and polycarbonate) from two metal targets was presented. For the deposition of the ZnO layer, a metallic Zn target was sputtered in a mixture of working gases Ar and O_2 (2:1). The alloying layer was prepared by a metallic Al target sputtering in Ar gas. The required ratio of the dopant in the ZnO:Al structure was achieved by varying cycle times of Al and ZnO layer deposition. The samples showed surface resistance as low as $R_s^{min} \sim 10$ Ω/□ and resistivity as low as $\rho^{min} \sim 3 \cdot 10^{-6}$ Ω·m coupled with a high level of optical transparency.
Keywords: AZO, magnetron sputtering, metal target, TCO.

1. Introduction

At the moment, the most common methods of magnetron deposition of transparent conductive AZO coatings involve sputtering of a sintered ceramic Al:ZnO target with a certain percentage of Al dopant, or sputtering of separated ceramic ZnO target and metallic Al target, where the parameters of the magnetron discharge determine the fluxes of the dopant (Al) and the main compound (ZnO). To realize the deposition on transparent polymers (plastics), it is necessary to use pulsed magnetron power supply systems (HiPIMS, L-HiPIMS), or to operate in low-power mode with frequency modulated DC or RF magnetron power supplies [1–4].

Another approach to deposit transparent conductive AZO coatings with a magnetron is to sputter two separated metallic targets (Zn and Al) in an argon-oxygen mixture of working gases. This is a rather complicated process, since in order to control the conductivity and transparency of the growing coating, it is necessary to tune the fluxes of oxidizable metallic Zn and alloying Al within certain ranges. Keeping in mind the sputtering rate of the oxidized Zn target and the sputtering rate of the doped Al target, the ratio of the Zn (ZnO) to Al fluxes should be about 11:1. This ratio can be achieved by using different power ratios for each of magnetrons with Zn target and Al target, respectively.

In this work, we used cycle-style deposition of ZnO layers with an almost completely oxidized Zn target in a working mixture of Ar and O_2, and Al layers with a metal Al target in Ar working gas. We used a single power supply with a minimum power of 100 W for two different magnetrons. This method enabled us to control the amount of ZnO and Al deposited in each layer, instead of controlling the ratio of the fluxes of sputtered atoms from two different targets. Prepared transparent plastic substrates with deposited layers of transparent AZO were comparable to the coatings obtained as a result of the classical processes of AZO deposition from a sintered ceramic ZnO:Al target and from a sintered ceramic ZnO target with a metallic Al target for doping in terms of optical transparency and electrical conductivity.

2. Experimental setup

A confocal magnetron sputtering system (Fig.1) based on two magnetrons of the Magneto-3GABS type (Pinch, LLC) was used for the deposition of coatings in this work. An aluminum target (purity 99.99 % wt., Girmet, LLC) was installed on one of the magnetrons, and a zinc target (purity 99.975 % wt., Girmet, LLC) was installed on the other one. The targets were circular with diameter of 75 mm and thickness of 2 mm each. In these magnetrons, it is possible to change the degree of unbalance of the magnetic field by tuning the configuration of the magnet packs. For the

AZO coating deposition, the configuration yielding maximum density of the ion current on the substrate was set initially and was not changed during further operation.

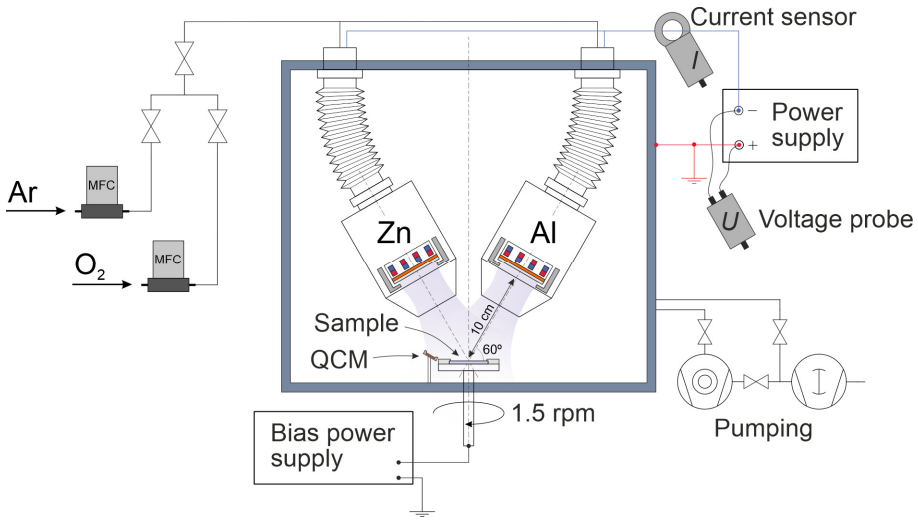

Fig.1. Confocal magnetron sputtering system.

Single APEL-M-5PDC-800 DC power supply was used to power the magnetrons. All work was carried out at a minimum power of 100 W (in power stabilization mode). Ultimate residual pressure in the chamber was $1 \cdot 10^{-6}$ Torr. The working pressure for both the Ar + O_2 gas mixture and pure Ar was 0.1 Pa. The gas mixture was prepared by digital gas flow controllers Bronkhorst El-Flow. High purity argon (99.998 %) and high purity oxygen (99.99 %) were used. In the case of working with a metallic zinc target, a gas ratio of 2:1 (Ar:O_2) was used. The installation was equipped with a rotating sample stage with the possibility of applying a bias potential.

The surface resistance R_s of the samples was measured by the Van der Pauw method. For this, a prototype of a resistance meter was designed and manufactured. A MASTECH HY3010 unit was used as a power source. Current and voltage were measured with digital multimeters Fluke 179. The measurement scheme is shown in Fig.2.

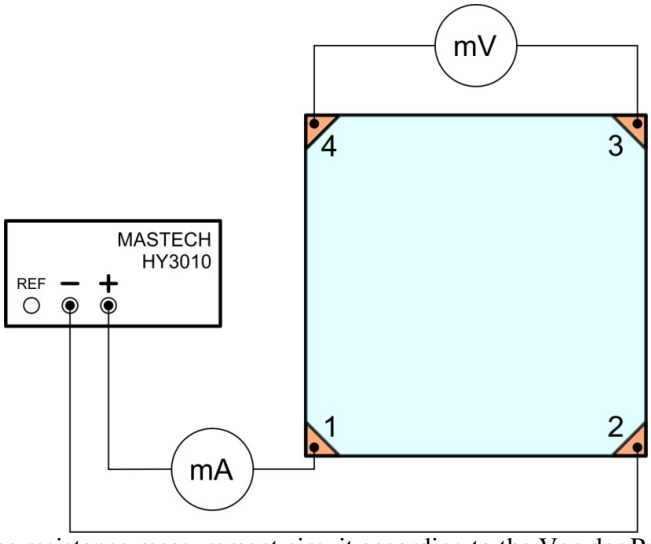

Fig.2. Surface resistance measurement circuit according to the Van der Pauw method.

The measurements were carried out in pairs for sides 1–2 and 3–4. Initially, the current was passed along side 1–2 (I_{12}), and the potential difference was measured on side 3–4 (U_{34}), then the connection was changed, and I_{23} and U_{41} were measured, respectively. The measurements were repeated several times. Surface resistance was calculated from average values:

$$R_s = \frac{\pi}{2\ln 2}\left(\left\langle\frac{U_{34}}{I_{12}}\right\rangle + \left\langle\frac{U_{41}}{I_{23}}\right\rangle\right)$$

Specific resistance was determined as $\rho = R_s \cdot d$, where d is the film thickness. The thickness of the films was estimated in reference experiments when the film was deposited on samples with an initially applied mask. After deposition, the mask was removed, and the height of the resulting step was measured using a Veeco Dektak 150 surface profiler. In the experiments, the thickness of the films was varied from 150 to 250 nm.

3. Results

As a result of the experiments, 7 different samples were selected with the best parameters of surface resistance and specific resistance. All samples were processed at a power input of 100 W. The discharge voltage of 508 V was typical for Al target sputtering in pure argon. For the sputtering of an almost completely oxidized Zn target in a working gas ratio of 2:1 (Ar:O_2), typical discharge voltage was 408 V. In all experiments, a negative bias voltage of -150 V was applied to the sample stage. The thickness of all samples was kept in the range from 150 to 250 nm.

For all selected samples, we varied the following parameters: the number of processing cycles (one cycle is ZnO deposition, followed by Al deposition); the processing time in a magnetron discharge with Al target; the processing time in a magnetron discharge with Zn target. All variable parameters can be taken into account by introducing a value equal to the ratio of the treatment time in a discharge with Al target to the time of treatment in a discharge with Zn target (t_{Al}/t_{Zn}). For all of the above listed samples, the surface resistance was measured by the van der Pauw method, and the specific resistance was calculated. The dependences of surface resistance and specific resistance on ratio t_{Al}/t_{Zn} are shown in Fig.3.

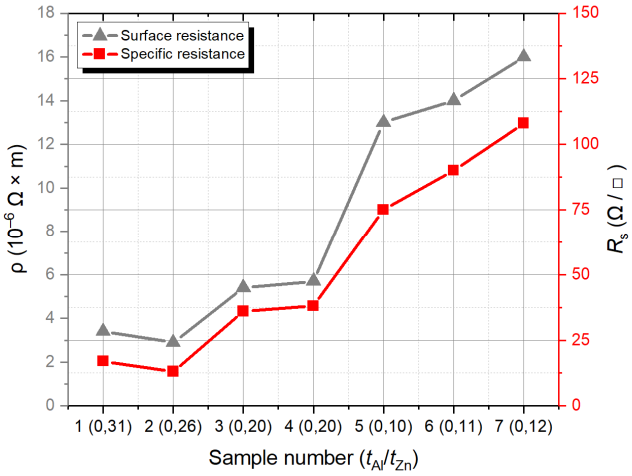

Fig.3. The dependences of surface resistance and specific resistance on t_{Al}/t_{Zn}.

Samples with a t_{Al}/t_{Zn} ratio greater than 0.33 have much lower transparency and higher resistance, so they were not shown in the graph. The best samples were obtained in the t_{Al}/t_{Zn} range from 0.26 to 0.31. For two samples with the same t_{Al}/t_{Zn} ratio, the sample with more cycles and a

shorter cycle time demonstrated lower resistance. When ZnO was deposited on Al, a sharp antireflection of a thin aluminum coating was observed.

4. Conclusion

The layer-by-layer cycle-style preparation of transparent AZO coatings on transparent plastic surfaces in a DC magnetron discharge technique was presented.

The best of the samples showed a surface resistance $R_s \sim 10$ Ω/□ and a specific resistance $\rho \sim 3 \cdot 10^{-6}$ Ω·m with a high level of optical transparency. It is comparable to the results obtained with sputtering of a sintered ceramic ZnO:Al target with a certain percentage of Al dopant, or with sputtering of a ceramic ZnO target and a separate metallic dopant Al target [1–4].

It has been shown that the best samples were obtained in the t_{Al}/t_{Zn} range from 0.26 to 0.31.

5. References

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