Comparison of gas sensor properties by producing ZnO thin films with different techniques

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ZnO thin films were produced by conventional sol-gel spin coating technique and a novel technique of sol-gel magnetic spin coating. Structural, surface and optical properties of ZnO thin films produced by both techniques were investigated comparatively. The setup and investment costs of the thin film deposition techniques were compared. The use of the produced ZnO thin films as gas sensors has been tested in the gas control and detection system.

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1. Introduction

Rapid technical advancements have made it easier to obtain materials and energy, allowing high-quality items to be processed easily and fast. The necessity of lowering energy, investment, and raw material costs has developed as a means of achieving competitive advantage. Furthermore, hazardous chemicals emitted into the medium as a result of industrialization have a harmful impact on human health. With appropriate conditions and costs, it is necessary to detect, filter, and eliminate the harmful effects of gases. The need to reduce high energy costs and eliminate environmental damage raises interest in renewable energy sources such as geothermal, wind, and solar energy, which are alternatives to limited-reserve fossil fuels. Electronic wearable textile solutions that are durable, light, and low-cost can now be developed, with the goal of improving user comfort and living standards without causing disruption. Semiconductor thin film coating technology can be used to make advanced smart fabrics, artificial skins and nerves, medicinal materials for surgical applications, and flexible textile sensors. Flexible solar cells, tactile sensors, flexible displays, organic transistors, portable electronics, and gas sensors all utilise semiconductor thin film technologies. Semiconductors can be made using a variety of thin film techniques, including non-vacuum electroplating [11], spray pyrolysis [12], vapor annealing Sintering [13], magnetron sputtering [14], atomic layer deposition [15], and spin coating. In this study, ZnO thin films were produced by conventional technique spin coating and a novel technique of magnetic spin coating. Structural, surface and optical parameters of ZnO thin films produced by both techniques were investigated comparatively. The setup and investment costs of the techniques, as well as the m^2 unit costs of the thin films produced, were compared. The use of the produced ZnO thin films as gas sensors has been tested in the gas control and detection system.

2. Materials and methods

In this study, a microscope slide was chosen as the glass surface to be coated and cut in size of 10 x 10 mm. After cleaning and rinsing in an ultrasonic bath, it was dried and made ready for use as a substrate for thin film deposition.

Sol-gel solutions of different concentrations were prepared for deposition of thin films. The sol-gel solution was prepared with Zn(CH3COO)2.2H2O (zinc acetate dihydrate) as reagent, 2-methoxyethanol as solvent and monoethanolamine (MEA) as a stabilizer. The optimum sol-gel solution was prepared by changing parameters such as solvent amount, ZnO reagent amount, mixing time and temperature, stabilizer amount, waiting time. The prepared sol-gel solution was deposited on glass substrates with the different speed rotating mechanical spin coating device shown in Fig. 1 and with the heatless, high speed rotating magnetic spin coating device shown in Fig. 2. In the spin coating and magnetic spin coating techniques, the solution was spread homogeneously on the substrates by rotating at different speeds and thin films were deposited.

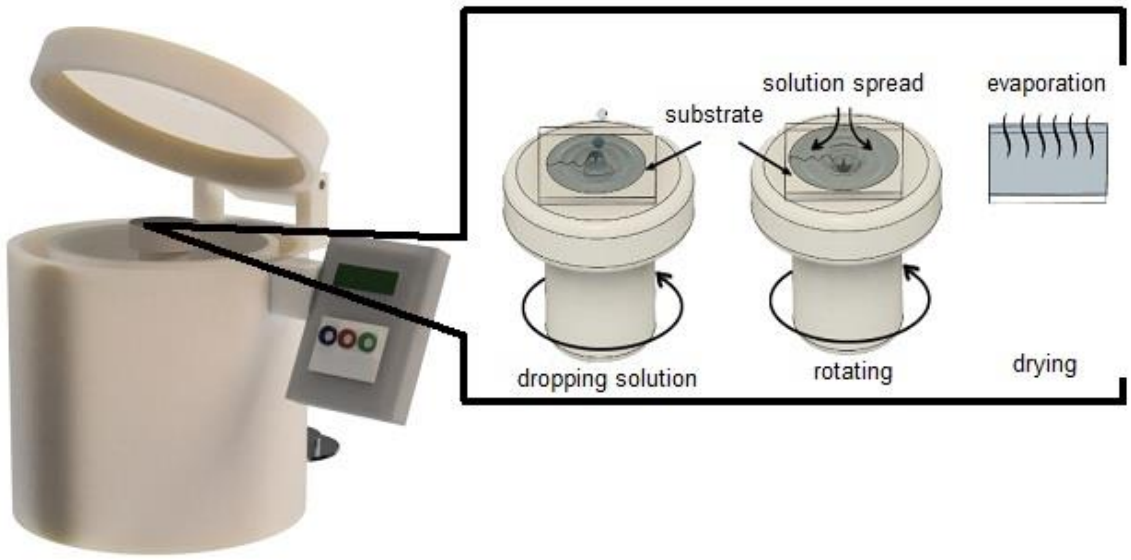

Fig. 1. Spin coating technique

The process steps of the spin coating technique are given in Fig. 1 and the magnetic spin coating technique in Fig. 2. In both techniques, the coating process begins with the dropping of the prepared solution onto the substrate surface. The homogeneous distribution of the dripping solution on the substrate and draining excess solution is provided by spining the substrates at different speeds. The spinning process is stopped and the thin films deposited on the substrates are dried. Multi-layer films are created by repeating the processes for each film layer. The deposited films are annealed to ensure crystallization.

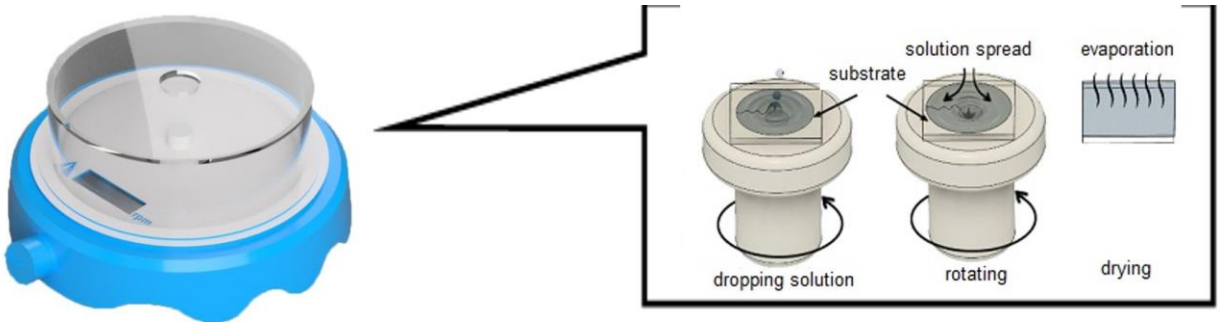

Fig. 2. Magnetic spin coating technique

In the dip coating technique, the spin of the substrates is done with a vacuum platform, while in the magnetic spin coating technique, the spin of the substrates is done with a magnetic platform. The dip coating technique spin platform is larger than the magnetic spin coating technique and can be used to coat larger substrates.

In spin coating techniques; the structures of the films to be produced can be easily diversified by changing parameters such as film thickness, rotation speed, rotation time, number of coating layers, solution volume and annealing temperature.

Thin film deposition trials were carried out for the ZnO series with Spin coating and Magnetic Spin coating devices. It was observed that the dropping solution did not spread to the surface in 10 µL, and the amount of solution expelled in 20 µL was high. The amount of working drop solution was determined as 15 µl. Coating trials were carried out at spin speeds of 1000 rpm, 2000 rpm and 3000 rpm. The number of layers of the films was tried as 3, 6 and 9 layers. It was observed that the solution was optimally spread on the substrates at 3000 rpm and 9 layers. ZnO thin films were prepared by keeping these determined parameters constant. The thin films produced were annealed at 300, 400 and 500°C. Crystallization started on the surface at 300 °C and 400 °C, but a completely homogeneous structure was not formed. The ideal annealing temperature was determined as 500°C. Structural, surface and optical properties of ZnO thin films were examined and compared according to deposition techniques.

3. Results and discussions

The produced ZnO thin films are given in Table 1 by naming them according to the production techniques.

Table 1. Serial names of thin films according to production techniques

Technique	Serial
Spin coating	A
Magnetic Spin coating	B

Structural properties of ZnO thin films were investigated by PANALYTICAL Impregnating X-Ray Diffraction (XRD) device. As the operating conditions of the device, 45 kV voltage and 40 mA current were applied. Scanning speed was selected as 2 degrees/min, CuKα beam with a wavelength of 1.5406 Å was used and samples were examined at the limit values of $30°\leq 2\theta \leq 80°$. The comparative XRD spectrum of ZnO thin films is given in Fig 3. When examining x-ray diffraction patterns of thin films; Compared with the ICDD (International Center for Diffraction Data): 98-003-1052 card for hexagonal ZnO. When both spectra are examined, it is seen that the structure formed is very similar to each other. Both films obtained are polycrystalline and hexagonal ZnO structures. In the A and B series; The (010), (002), (011), (012), (110), (013) and (112) planes of the ZnO structure were determined, respectively. The peak intensities of the B series are slightly higher than the A series.

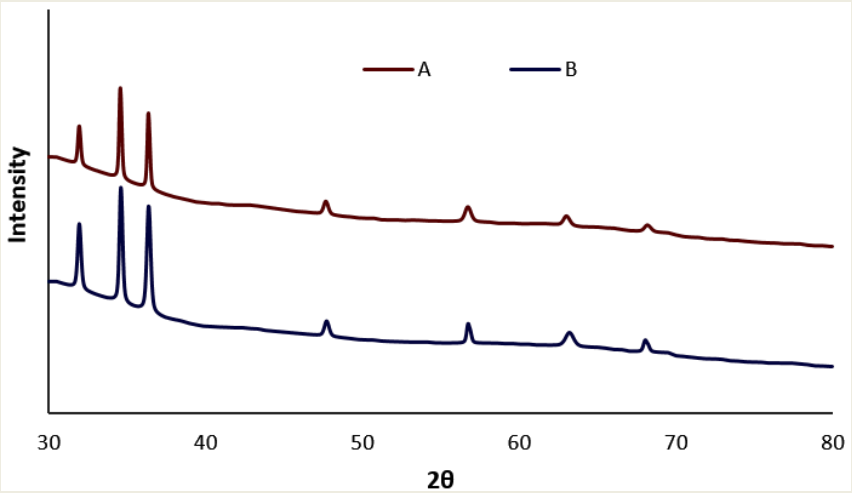

Fig. 3. Comparative XRD spectrum of ZnO thin films (color online)

The surface properties of the ZnO thin films were examined in the ZEISS Supra 40 VP electromicroscope. In this examination, the secondary electron (SE) detector of the device was used and images were obtained at 30 kx magnification. In the FESEM images of the A and B series shown in Fig. 4. It was observed that the ZnO structure produced by both thin-film coating techniques coated the substrate homogeneously in a similar way, there were no formations in the form of agglomeration and there were no voids on the surface. Thus, it was understood that the grains adhered well to each other. In addition, it is seen that the grain size of the thin films produced by the B series magnetic spin coating technique is slightly smaller than the A series.

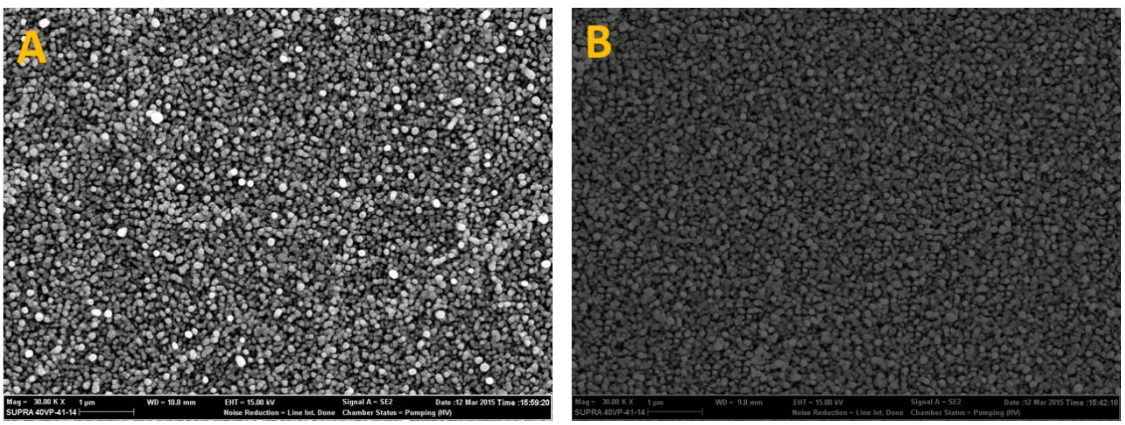

Fig. 4. SEM images of ZnO thin films at 30 kx magnification

UV-Vis Spectroscopy measurements for the optical properties of ZnO thin films were taken in the PERKIN ELMER LAMBDA 25 instrument in the wavelength range of 1100–300 nm. Using the basic absorption spectrum data obtained from UV-Vis Spectroscopy measurements, it was determined that the thin films have direct band structure. After determining that the obtained films have direct and allowed bandpass, variation graphs of (αhυ)2 vs. hυ were drawn in order to determine the band gaps. The energy values of the point where the direction of the linear parts of these graphs intersects the hυ axis at (αhυ)2 = 0 were determined as the band gaps of the films. The plots of (αhυ)2 vs. hυ of ZnO thin films are given in Fig. 5. The band gap values obtained from these curves are shown in Table 2. When the band gap values were examined, it was seen that the values of the films produced by both production techniques were very close to each other.

Table 2. Band gap values of ZnO thin films

Serial	Band Gap (eV)
A	3,32
B	3,41

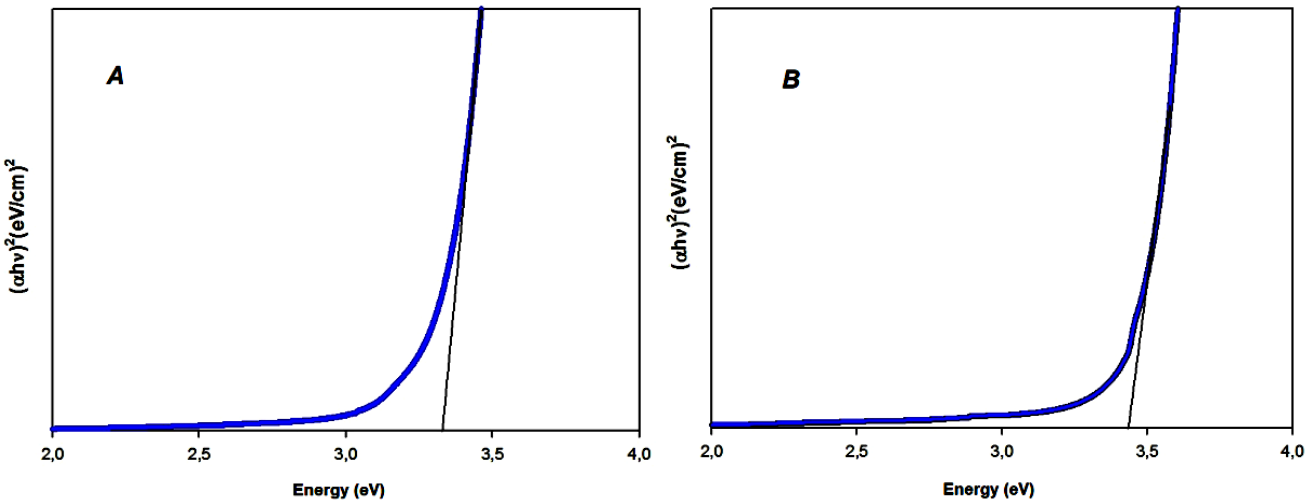

Fig. 5. The plots of $(\alpha h\upsilon)^2$ vs. hυ of ZnO thin films (color online)

4. Cost analysis

In this study, ZnO films were produced by conventional spin coating technique and alternatively developed magnetic spin coating technique. It is aimed to reduce the investment cost and energy consumption with the newly developed technique. IKA Brand, big squid White Model, unheated magnetic stirrer with a price of 374 € was used for the magnetic spin coating technique. Laurell brand WS-400-6NPP Spin Coater with a price of approximately 5000 € was preferred for the spin coating technique. When the device costs of Thin Film Production Techniques are compared, it is seen that the initial investment and maintenance costs of the Magnetic spin coating technique developed by us are quite low. The technical specifications of the devices are shown in Table 3.

Table 3. The technical specifications of the devices

	Magnetic Spin Coating	Spin Coating
Voltage	100 - 240 V	95 - 240 V
Frequency	50/60 Hz	47/63 Hz
Power input	4 W	300 W

Thin films were coated on glass substrates prepared at 100 mm^2 in nine layers. The devices were operated for average of 1 minute for each layer. The energy consumption was calculated as 6 kW/m2 for the magnetic spin coating technique and 450 kW/m2 for the spin coating technique. In addition, a vacuum pump is also operated to fix the substrates in the spin coating technique. This causes an additional energy consumption, so the energy consumption of the spin coating technique is calculated more than the magnetic spin coating technique. The magnetic spin coating technique appears to be advantageous when considering the installation and operating costs.

5. Gas sensor applications

The sensor control system, which was originally created to test the use of ZnO films produced with two

different techniques as gas sensors, is shown in Fig 6. Sensor control system; DC power supply providing constant 5V voltage, heater providing the required temperature for the activation of the material to be used as the sensor, gas chamber with the sensor gas interaction, gas resistance circuit that creates analog data of the sensor sensitivity by measuring the voltage change on it, analog digital converter that converts the obtained analog data to digital data, and It consists of a control card that controls the operation of the entire system.

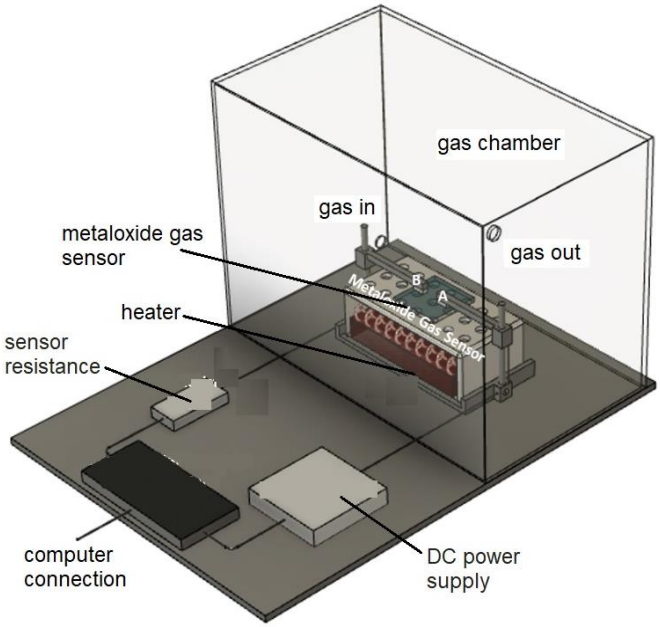

Fig. 6. Gas Sensor control system

The constant voltage of 5V from the DC power supply is supplied to the metal oxide thin film gas sensor at point A. The voltage passing through the sensor switches to the sensor resistance circuit for grounding at point B. The sensor placed on the heater in the gas chamber can operate at different temperatures. The temperature required to activate the semiconductor metal oxide thin film gas sensor is provided by the adjustable heater. The voltage on resistor varies depending on the semiconductor property and temperature. When gas is given to the medium, the voltage value on the resistor changes by increasing or decreasing depending on the structure of the semiconductor sensor. The voltage change data on the resistor is converted by the control card, the gas detection and sensitivity of the sensor is calculated.

A constant concentration of CO gas was introduced into the gas chamber. Gas detection and sensitivity of the produced ZnO gas sensors were measured. Initially, experiments were carried out at room temperature and 100°C. In the low-temperature experiments, it was determined that ZnO thin films were not activated as semiconductors and did not exhibit sensory properties. When the temperature of the thin films was at 200 °C, the data obtained from the sensor made with gasless and CO gas are shown in Fig 7.

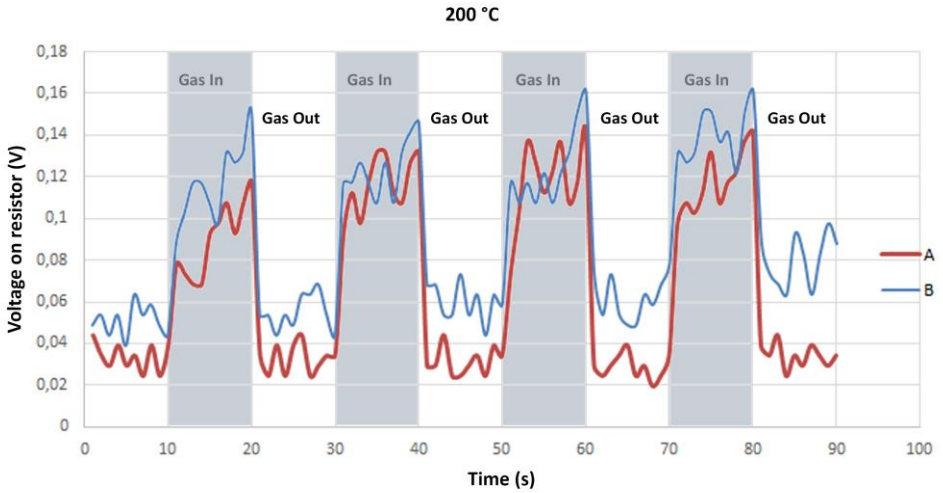

Fig. 7. ZnO gas sensor measurement values at 200 °C (color online)

The response of the gas sensor to the CO gas supplied to the gas chamber at 10 second intervals was measured. The voltage value on the resistor to which the A series is connected in gas-free medium was measured in the range of 0.02-0.04 V. Higher values of 0.04-0.06 V were found for the B series. From the ZnO thin-film gas sensors, which became active at 200 °C when CO gas was introduced into the medium, the first voltage on the resistor for the A series was measured above 0.08 V and then above 0.1 V. It was observed that the first voltage value for the B Series was 0.05 V, then this value rose above 0.15 V. This shows that both ZnO gas sensors respond to CO gas, but the sensitivity of the B Series is proportional to the voltage value on the resistor.

In the experiments carried out at 200 °C in a gasless medium, it was decided to increase the temperature considering the low response of ZnO thin films. The gas sensor measurement data at 300 °C is shown in Fig 8.

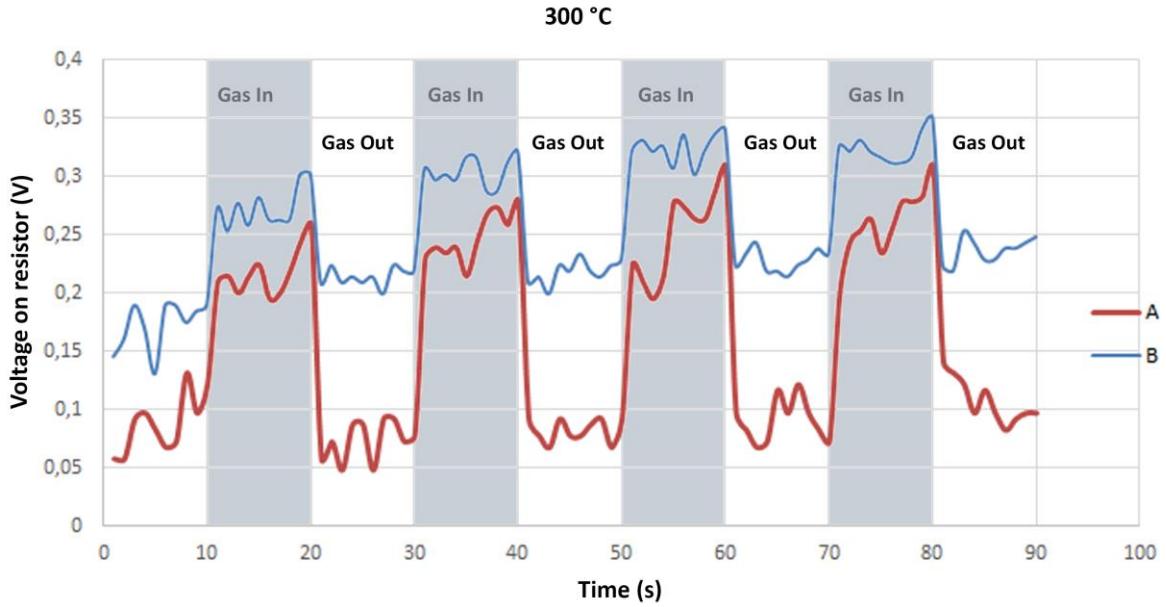

Fig. 8. ZnO gas sensor measurement values at 300 °C (color online)

While the voltage on the resistor was 0.1 V in the gasless medium for the A series at 300 °C, this value was measured as 0.17 V for the B seriesWhen CO gas was given to the medium for 10-second periods, the voltage value on the resistor increased, reaching 0.2 V for A series and 0.25 V for B series. When the data is examined, the high amount of voltage on the connected resistor shows that the semiconductor properties of B series ZnO thin films are better than the A series. In addition, the change in the voltage value on the sensor resistor when CO gas is introduced into the medium proves that ZnO thin films can be used as an alternative CO gas sensor. It has been measured that the conductivity value of the B Series is higher than the A series when there is CO gas in the environment. In the A series, the percentage change of the voltage value on the resistor is higher than the B series when passing from the gasless to the medium with CO gas.

6. Conclusions

When the studied techniques are compared, it has been determined that the magnetic spin coating technique is more efficient in terms of installation and operating costs, as well as energy consumption. It is seen that semiconductor thin films with close properties are produced with both techniques. Magnetic spin coating technique can be preferred for coatings that do not require vacuum and high speedsAs a result of the tests, it is clearly seen that ZnO thin films can be used as a gas sensor for CO gas detection. In addition, it was determined that the semiconductor and gas sensor properties of ZnO thin films increased at high temperature.

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