Titanium Dioxide Thin Films as Methane Gas Sensors

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***Abstract*— TiO_2 thin film was deposited onto n-Si substrate at 100 °C by using a sputtering method, and the film was annealed in air atmosphere at range of 500 °C–1000 °C. The structural and morphological properties of the all films were investigated by X-ray diffraction and atomic force microscope. The gas sensor with interdigitated platinum electrodes was fabricated with photolithographic techniques using the as-deposited and annealed TiO_2 thin films as an active material. The sensitivity of the sensors was determined by altering the conductivity of the sensor material under methane gas with various concentrations at different working temperatures. It was determined that the fabricated sensor using as-deposited TiO_2 thin film with 10-nm particle size has high sensitivity and fast response/recovery time. The sensor operated at 50 °C had also sensitive to the methane gas and its detection performance increased with temperatures. It was observed that the fabricated sensors exhibited reproducible and stable results.**

***Index Terms*— Titanium dioxide, sputtering, annealing, methane, gas sensors.**

I. Introduction

TITANIUM dioxide (TiO_2), especially in thin film form is widely preferred as a semiconductor material because of its unique properties [1]–[6]. It is widely used in gas sensing applications as well as several electro-optical devices [4]–[6]. In recent years, a large number of studies have reported the extraordinary sensitivity of TiO_2 towards methane gas [7]–[10]. TiO_2 has also been preferred as a material for gas sensors due to its low resistivity to the reduced driving power of the sensor. In addition, TiO_2 shows good sensing properties to CO [11], ethanol [12] and H_2 [13].

Metal oxide-based gas sensors normally operate at elevated temperatures. Most of the existing research focused on the optimization of the TiO_2 thin film deposition in order to improve the sensing properties of gas sensors as well as their operation at low temperatures for lower power consumption. However, further research and development studies are needed to improve the sensor performance. TiO_2-based gas sensors can operate in low temperatures owing to the stability of TiO_2, which is an important feature of the device. Especially, in industrial applications, low operation of the sensor is preferred due to high operation temperature increases electrical power consumption [14].

A gas sensor is generally characterized with its sensitivity, detection limit, response/recovery time, life cycle and stability, etc [15]. Sensing capability of a metal-oxide gas sensor is mainly related with changing of their conductivities depend on interaction between gas and adsorbed oxygen ions on surface of the metal-oxide [16]. In addition, grain size and microstructure of the sensing materials affect the sensitivity of the sensor [17]. Resistivity of the metal-oxide films decreases with increasing grain size which become larger by deposition and annealing temperature. Moreover, high temperature ($>$ 600 °C) treatments can cause phase changing of TiO_2 thin films. As known, TiO_2 has anatase (tetragonal) phase at lower deposition or annealing temperatures ($<$ 600 °C) while rutile (tetragonal) and brookite (orthorhombic) phases at high temperatures [18]. Therefore, in case of production of sensor using TiO_2 treated with high temperature, possibility of changing of the crystal phase need to be considered. In similarly, at high working temperatures ($>$ 600 °C), the phase of TiO_2 film can also be changed.

There are many processing techniques that can be used to prepare TiO_2 thin films such as chemical vapour deposition (CVD) [19], sol-gel [20], electron-beam evaporation [21], pulsed laser deposition [22], liquid deposition [23], direct current (DC) and radio frequency (RF) magnetron sputtering [24]–[27], plasma oxidation [28] and screen printing [29], etc. Among these techniques, magnetron sputtering is a preferable technique for industrial applications because of its low cost and large-scale deposition capability. The properties of the TiO_2 thin films depend not only on the preparation techniques but also on the deposition conditions [30]. High-quality metal oxide based thin films can be obtained by the optimization of the deposition parameters such as sputtering pressure, power, gas flux, and film thickness [31]. In addition, the thermal annealing of the obtained films is effective in increasing the crystallinity thereof.

In this work, gas sensors based on TiO_2 thin films, which were deposited on n-Si substrate by RF magnetron sputtering method, were fabricated with Pt interdigitated electrodes. To identify the effect on the film structure and the sensing

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capability of the sensor for methane gas, the grown film was annealed at different temperatures (500–1000 °C) by conventional thermal annealing (CTA) in air atmosphere. In addition, the gas sensing properties of the fabricated device were measured in an air and methane gas ambient by using current–voltage (I–V) measurement system. We noticed that the sensor exhibits good sensing properties to methane gas at low temperature as 50 °C.

II. Experimental Method

A. The Preparation and Analysis of the TiO_2 Thin Films

The TiO_2/n-Si thin film was prepared by radio frequency (RF) magnetron sputtering system (NANO-VAK) in an argon (Ar) gas atmosphere. A Titanium dioxide ceramic disk with 0.125 thickness and 99.9% purity was used as a target. A two-inch diameter of TiO_2 target has been directed with 45° angle with respect to the substrate. The base pressure was 2×10^{-6} Torr. During the deposition, the rotation speed and pressure was kept at 5 rpm and 10^{-3} mTorr, respectively. The distance between the target and substrate was about 8 cm. In addition, the RF power was set at 150 W and the temperature of the substrate was maintained at 100 °C. The thickness of the growth film was measured a thickness meter as insuite. After the deposition, the thickness of the film was measured with a stylus type profile meter as 170 nm. The obtained TiO_2 thin film was annealed in the air from 500 to 1000 °C. The structural properties of the films were investigated by X-ray diffraction (XRD). The surface topography of the films was analyzed by Atomic Force Microscope (AFM). In addition, the tape test was applied for examining of the mechanical stability of the films. For this, a piece of adhesive tape was firmly placed over the films and was then removed. After these operations for both of Pt electrodes-heater and TiO_2 films, the material transfers from the films to surface of the tape was not observed under 20x power microscope.

B. Fabrication of Pt Interdigitated Electrodes and Heater

The TiO_2 gas sensor with Platinum (Pt) contact electrodes was then fabricated by using traditional photolithographic techniques. Pt electrodes and the resistor for heater were deposited onto front and back surface of the as-deposited film with RF magnetron sputtering, respectively. The thickness of the interdigitated electrodes was 500 nm and its line width was 50 μm which was formed as seen in Fig.1(a).

The back side was used for heater fabrication which has the thickness of 1000 nm. Fig.1(b) shows the heater surface of the sensor. Active area of the sensor was 3 mm x 3 mm. The schematic representation of the fabricated sensor was given in Fig.2.

Then, the fabricated device was tested both under the air and the methane gas at different temperatures (50–200 °C) with current–voltage (I–V) measurements.

III. Results and Discussion

The structural properties of the TiO_2 thin films were analyzed by X-ray diffractometer (XRD) system. Fig.3 shows the

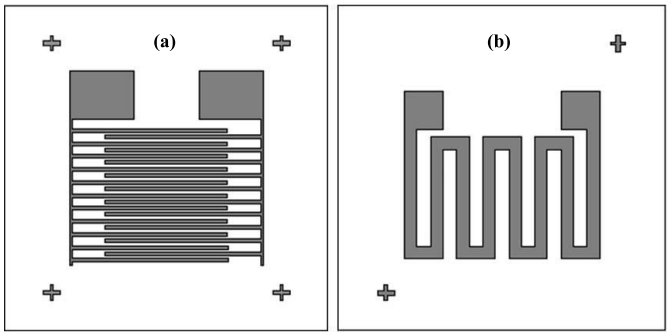

Fig. 1. Sensor's photomasks: (a) interdigitated Pt electrodes and (b) Pt resistor for heater.

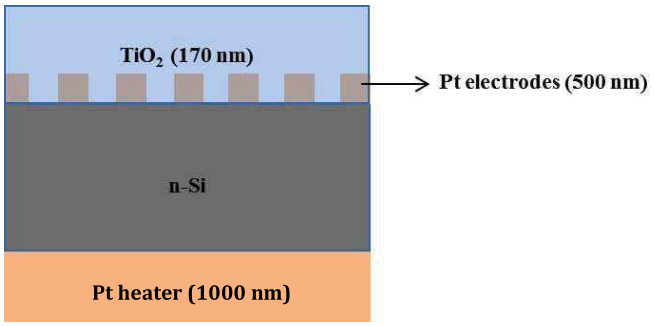

Fig. 2. Schematically fabricated TiO_2 thin film gas sensor.

XRD patterns of the films at 100 °C and various other annealing temperatures. The as-deposited film (100 °C) shows peaks corresponding to the reflections from anatase (101), (103) planes at $2\theta = 25.2°, 36.9°$, respectively. In addition, while the annealing temperature is at lower temperatures ($\leq$ 600 °C), the films are still in anatase phase as seen in the figure. At 700 °C, the films exhibited a mixed phase of anatase and rutile. The crystal structure of the films converted into the rutile phase with the increase of the annealing temperature. After annealing at higher temperatures ($\geq$ 800 °C), the (110), (200), (210) diffraction peaks from rutile structure were observed at $2\theta = 27.4°, 39.1°, 44.0°$, respectively. These peaks indicated that the structure at high temperature fully converted into the rutile phase. In addition, the peaks had become more intense and sharp, as well as it is seen that full width half of maximum (FWHM) values were listed in Table 1.

The grain size of the films was calculated from the FWHM values using the Scherrer's formula:

$$D = \frac{0,9.\lambda}{cos\theta}. \quad (1)$$

Where, D is the grain size, 0.9 is the constant (K), λ is the wavelength of X-ray (= 1.540598 Å), B is the line width (FWHM) and θ is the Bragg angle. The obtained grain sizes of the films varied depending on the annealing temperatures were given in Table 1. The smallest grain size (10.48 nm) was obtained in the as-deposited film. In addition, the grain size of film annealed at 500 °C very close to as-deposited one. The grain size obtained for the rutile phase was larger than that for the anatase phase. The grain size in the rutile phase increased with the increase in annealing temperature and it reached 57.01 nm at 1000 °C.

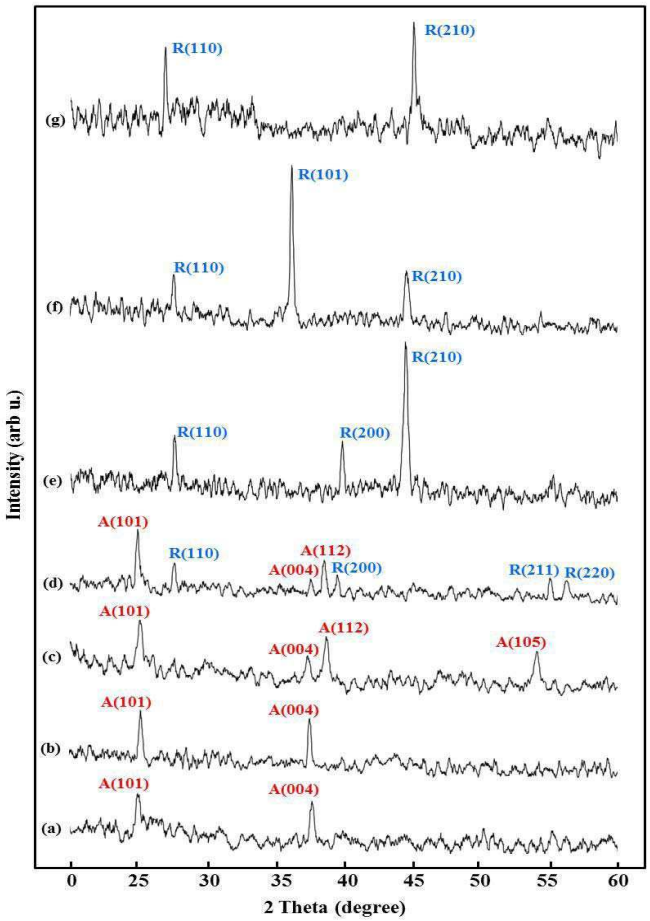

Fig. 3. XRD patterns of the TiO_2 thin films: (a) as-deposited, and at various annealing temperatures (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C and (d) 1000 °C.

TABLE I
STRUCTURAL RESULTS OBTAINED FROM XRD DATA

*T_S(°C)	**T_A(°C)	FWHM (B)	2θ (DEG)	Grain Size (nm)
100	-	0.136	26.83	10.48
100	500	0.123	25.10	11.54
100	600	0.097	25.16	14.64
100	700	0.092	25.00	15.43
100	800	0.082	27.59	17.41
100	900	0.081	36.33	18.01
100	1000	0.025	26.83	57.01

*T_s = Substrate temperature; **T_A = Annealing temperature

Thermal annealing has a strong influence on the surface morphology of thin films [32], [33]. To understand this effect, the surface morphology of the films was analyzed by using the AFM measurements. Fig.4 shows the three dimensional (3D) AFM images of the as-deposited and annealed films at different temperatures. It was seen from the images that the surface quality of the TiO_2 films was very good without any cracks. One of the most important results is that the grains of the films changed from column to nubbly and were of close-packed structure. The pure rutile film annealed at 1000 °C has a substantially smooth surface with equiaxed grains, as

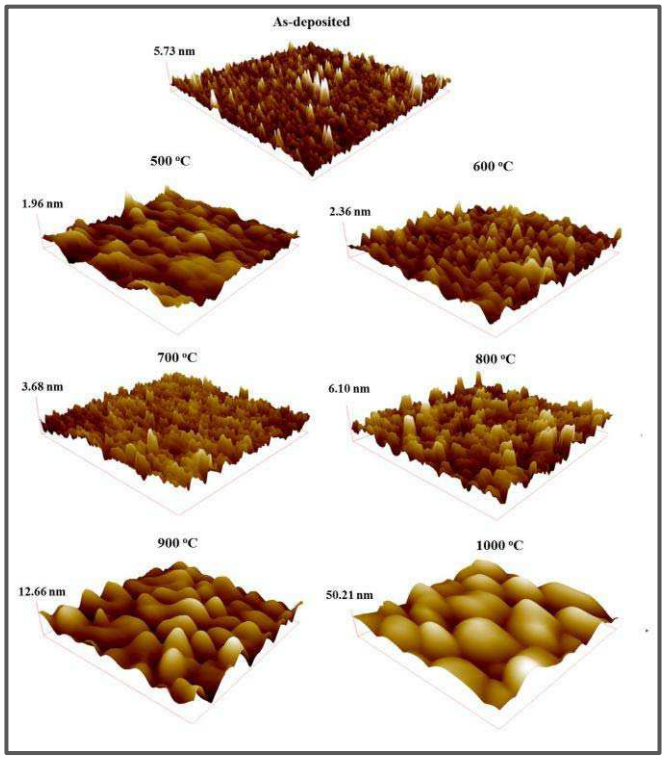

Fig. 4. AFM images of the TiO_2 thin films. The scan area is $1 \times 1 \mu m^2$ in all the images

TABLE II
RMS VALUES WITH DEPENDING ON TEMPERATURE FROM AFM DATA

*T_S(°C)	**T_A(°C)	RMS (nm)	Grain Size (nm)
100	-	0.172	13.20
100	500	0.229	18.22
100	600	0.279	22.64
100	700	0.436	23.40
100	800	0.900	34.41
100	900	1.898	51.70
100	1000	7.426	122.50

*T_s = Substrate temperature; **T_A = Annealing temperature

seen in Fig.4. X. H. Xu et al. observed the column structure of anatase films by AFM and they similarly reported that the rutile films exhibited a surface morphology of equiaxed grains without distinct boundaries [31].

The root mean square (RMS) values of the surface roughness of the films were measured to understand the surface uniformity at nanoscale. Increasing the annealing temperature led to the increment of surface roughness. The increase in roughness as the annealing temperature increases is associated with the increase in grain size. Hence, the film annealed at 1000 °C has the highest roughness with values of 7.726 nm, as seen in Table 2 and Fig.4. The grain size and RMS values increased, as expected both of AFM and XRD results, as can be seen in Fig.3 and Fig.5. It was observed that the grain size was exponentially increased with annealing. In addition, although the films annealed at the interval of 800-1000 °C have rutile phase, the crystallite size of the film annealed at 1000 °C

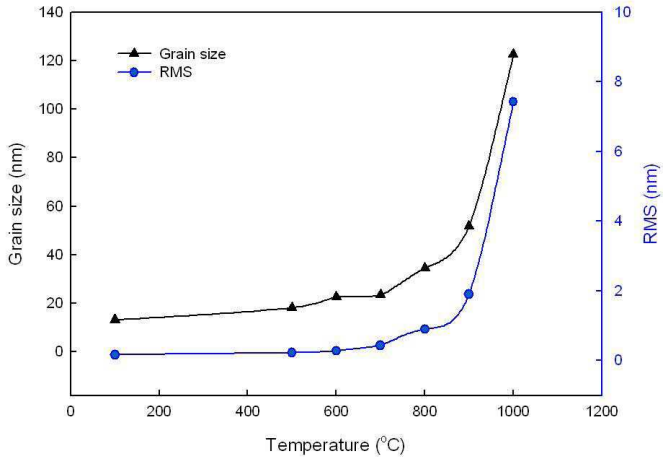

Fig. 5. Grain size and RMS values of the as-deposited and annealed TiO_2 thin films.

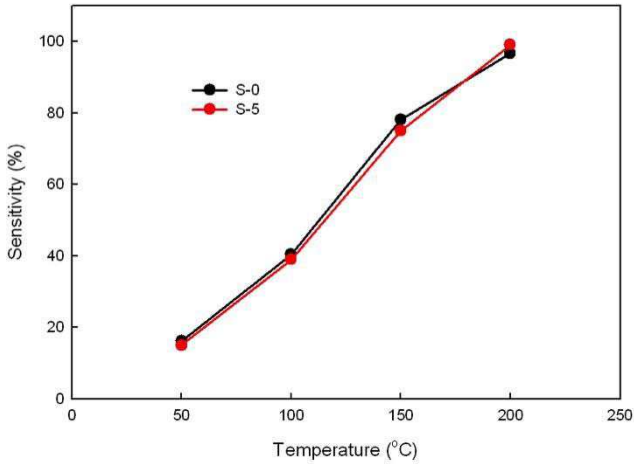

Fig. 6. The relation between the detection sensitivity and operation temperature of the sensor under 1000 ppm methane gas (S-0: as-fabricated and S-5: after 5 month later).

significantly increased as a result of completed coalescence process at this temperature.

As well known, metal oxide thin films can be used for the sensing of the several hazardous gases such as methane, propane, CO, etc. Sensing mechanism of chemical gas sensors based on the n-type metal-oxide thin films is primarily related with variation of active layer conductivity under hazardous gases [34], [35]. Changing of their electrical properties interested in adsorption of oxygen by trapping an electron from the conduction band of the metal-oxide semiconductor. At the working temperature of the sensor below 150 °C ionized molecular (O_2^-) form of the oxygen can be exist while above this temperature atomic (O^-, O^{2-}) forms is dominated [36]–[38].

In addition, small grain size in the active layer has a positive role in changing the conductivity of the sensing material due to the increasing amount of conduction electrons from each grain boundary [39]. Lu et al. noticed that the response of the SnO_2-based gas sensors to 500 ppm CO increased if the grain size becomes smaller than 10 nm, and that there was no change in its sensitivity when the grain size was larger than 50 nm [40]. The similar sensitivity results were obtained for other metal oxides-based sensors: For instance, a decrease in the grain size of the WO_3-based sensing layer results in increased sensitivity [41]. Taking these findings into account, in this study, TiO_2 film (as-deposited) with $\sim$ 10 nm grain size was used as the sensor active layer.

Response (or detection sensitivity) of the sensors can be calculated as [16], [42];

$$S = \frac{R_a - R_s}{R_a} \times 100\%. \quad (2)$$

Where, R_a and R_s are the measured resistance under air and methane gas, respectively. In this study, it was aimed to determine the sensitivity of the sensors depending on the temperature, using resistivity measurements to compare the results in the air (without introducing gas) and 1000 ppm methane gas ambience. During resistivity measurements, the as-fabricated sensors were exposed to the gas at different temperatures (50–200 °C). In these conditions, resistance variation of the sensors was re-measured after five months later. The calculated response (S) of the sensors in case of as-fabricated and five months later was given in Fig. 6. The sensor prepared is sensitive to methane gas as seen in this figure. It was shown that the detection sensitivity of the sensors for these two measurements did not significantly change. As known the stability of the chemical gas sensors related the particle size in the film [39]. Our sensors provided good stability after five months. This can be explained that the maximum operation temperature of the sensor is 200 °C due to the particle size did not considerable change at lower annealing temperature as seen Table 1. It was seen that the detection sensitivity increased as the operating temperature increased. The highest response of the sensor was reached at an operating temperature of 200 °C, as % 96. In addition, the results indicate that the sensor has a good response with 16% at a low temperature as 50 °C.

Fig. 7 represents the sensitivity of the sensor with methane gas. Calculated response, from Eq.2, of the sensor as a function of concentration of the methane gas at constant temperature of 200 °C was shown inset in Fig. 7.

The average sensitivity per ppm (sensitivity/ppm) of prepared sensor was determined by slope of the response curve as 0.15. Response of the sensors was linear in the concentration range of 100–1000 ppm with $\pm$ 6% of precision.

Fig. 8 shows, as an example, recovery/response time of the sensor depends on variation of the resistivity with and without introduction of methane gas (1000 ppm) at working temperature of 200 °C. In this experiment, sensor's resistance was recorded in 2 minutes in air. Then, it was observed that resistance of the sensor sharply decreased when introduction of methane gas with concentration of 1000 ppm in air in the chamber in another 2 min. After that, when exhausting of the gas from the chamber resistance gradually decreased in about 15 second and rapidly recovered the initial value. This result indicated that fabricated sensor has a good response time. For determining of reproducibility, this process was repeated

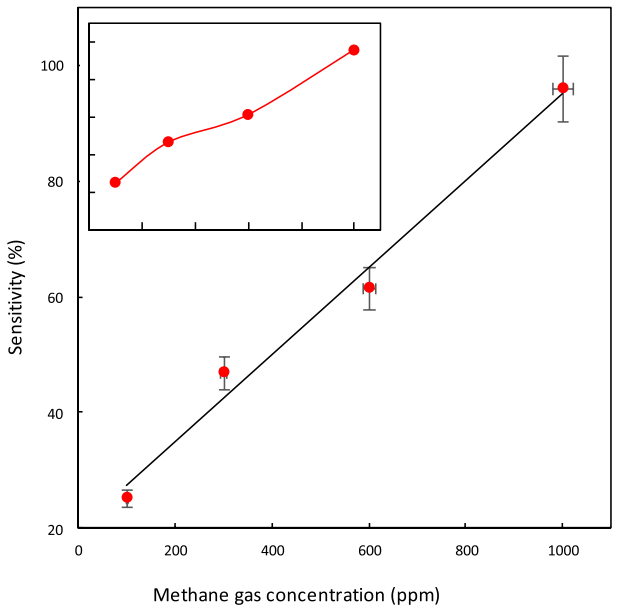

Fig. 7. Sensitivity curve of the sensor with methane gas at 200 °C. Inset represent response curve of the sensor versus the gas concentration.

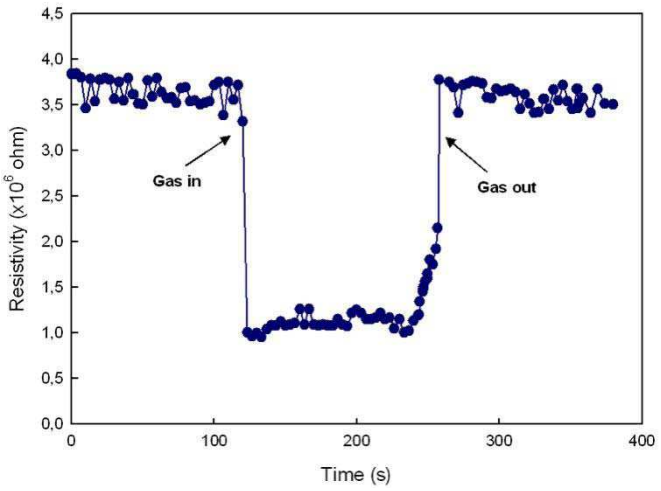

Fig. 8. Time-dependent resistivity of the sensor under 1000 ppm methane gas at the working temperature of 200°C.

5 times at 1 hour periods, and similar behavior of sensor's resistance was observed.

IV. Conclusion

We focused on both deposition of TiO_2 thin film on n-Si substrate with high crystallinity and surface morphology using RF sputtering technique, and investigation of sensitivity of the fabricated TiO_2-based gas sensor to methane gas at different operation temperatures. The TiO_2 thin film was deposited onto n-type Si(100) substrate at 100 °C and then annealed at 500–1000 °C. The structural and morphological properties of the films were investigated in detail. It was observed that the change in phase from anatase to rutile of the TiO_2 films started at above 600 °C. After 700 °C, the film was fully in rutile phase. In addition, the AFM measurements showed that the as-deposited TiO_2 film had smaller grain size and lower surface roughness than the others. The TiO_2-based gas sensor was fabricated using the as-deposited, with Pt interdigital electrodes, for the detection of methane gas. The obtained sensor was tested against methane gas at 50–200 °C. It is note that fabricated sensors with the structures were treated at higher temperature (> 600 °C) have very low sensitivity under the methane due to their particle size is not sufficiently small to the increasing amount of conduction electrons from each grain boundary [39]. Lower sensitivity of rutile phase than anatase phase is also related with lower electron mobility in rutile [43]. We point out that, in principle, annealing temperature of the TiO_2 thin film and working temperature of the sensor are different manner. However, obtained results in case of annealing at > 600 °C showed that TiO_2 sensor is not efficient above at this working temperatures as methane gas sensor.

In general, gas sensors show sensitivity at high temperatures; therefore, it is important to achieve detection sensitivity at low temperatures. In this work, the sensitivity of the sensor was also ensured at 50 °C. Our results show that the deposited TiO_2 thin films by the optimization of the deposition conditions of the sputtering process can be used for methane gas detection at low operation temperatures.

The fabricated TiO_2 gas sensors were also exhibited a good stability after five months. In addition, it is suggested that the effects of the interdigitated electrode geometry on the sensitivity of the sensor can be investigated. In this work, we aimed to develop TiO_2 thin film-based methane gas sensor, which is preferred in technology fields. This also opens the door to the development of quality sensors with low electrical power consumption thanks to its low working temperature. In near future, the nanostructured TiO_2 thin film-based gas sensor may be made sensitive to methane gas even at room temperature.

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