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Studies of Hydrogen Gas Sensing Properties of Anatase TiO_2 Thin Films Prepared by Magnetron Sputtering

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Abstract:
Titanium dioxide thin films were deposited on sapphire substrates by reactive dc magnetron sputtering method. The prepared thin films were then annealed in air at various temperatures (600 – 800 °C) to achieve crystalline thin films having anatase phase. The comb-like Pt electrodes, with a distance of 10 μm, were prepared on the top of the films to measure the electrical and gas sensing properties. The films prepared in this work showed high electrical response for various concentrations of H_2/air, ranging from 20 to 10 000 ppm. The response was tested in the working/operating temperature range 150 – 350 °C and it was observed that these thin films are the most sensitive at temperatures below 200°C.

Key words: crystalline thin films, anatase phase, hydrogen gas sensors, operating temperature,

Introduction

Thin films and nanostructures based on titanium dioxide are extensively studied for various applications because of their multifunctional nature. Among MOS (metal oxide semiconductors), the stability of titanium dioxide in harsh environment makes it a good candidate for gas sensing applications [1], which have been already reported many times in last decades [2, 3, 4, 5]. Despite having excellent sensing properties and high stability, MOS gas sensors have problems with selectivity and are usually more suitable for higher operating temperature sensing applications i.e. above 150 °C [6, 7]. An ongoing trend in the sensor technology is focused on preparing smart sensors with reduced operating temperature and thus lower power consumption. The demand of such sensors is increasing e.g. for usage in hydrogen fuel cells leakage detection in automobile industry or mobile battery-powered gas detection devices.

Experimental

In the present work, TiO_2 thin films were prepared by reactive dc magnetron sputtering method from Ti target [2, 3]. The thickness of the thin films was determined from SEM image in cross-section to be 100 nm. The films were then annealed in air at temperatures 600 °C, 700 °C and 800 °C for 1 hour. We have used X-ray Diffraction technique and Atomic Force Microscopy to study the crystal structure and surface topography of the thin films.

The same gas sensing experimental setup, as described in Ref.2 and 3 was used here to measure resistance *R* of TiO_2 thin films up to 10^{11} Ohms. The films were exposed to various concentrations of H_2 in technical air at operating temperatures from 150°C to 350°C and the resulting changes in the resistance were recorded.

The comb-like platinum electrodes were prepared on TiO_2 thin films to measure the electrical resistance. In preparing platinum comb-like electrodes, first 20 nm thick Pt film was deposited by dc magnetron sputtering. Then direct optical lithography and subsequent Ar ion beam etching was used to pattern comb-like micro-structures. The distance between electrodes was 10 μm. Different steps involved in preparing these electrodes are shown in fig.1.

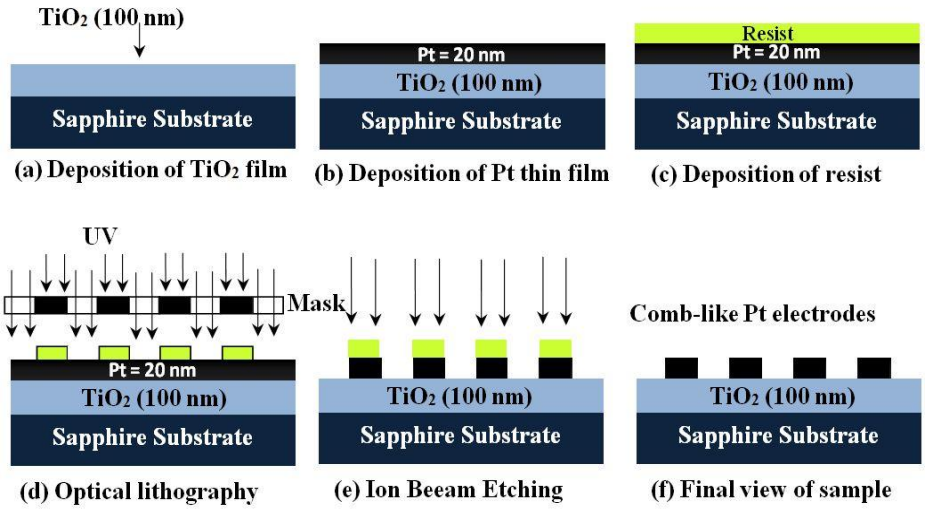

Fig. 1. The figure illustrates the different steps involved in preparation of Pt electrodes.

Results

In our previous works [2, 3], we have reported that the annealing temperature at which the phase transition – from Anatase to Rutile for TiO_2 thin films prepared in our laboratory by dc magnetron sputtering method – took place was 700 °C – 800 °C. In this work we limited our research to only anatase thin films annealed up to 800 °C.

AFM topography was used to study the surface roughness and grain size of the films. AFM images are shown in Fig. 2, which indicates that as deposited thin film is a denser one with very fine grains.

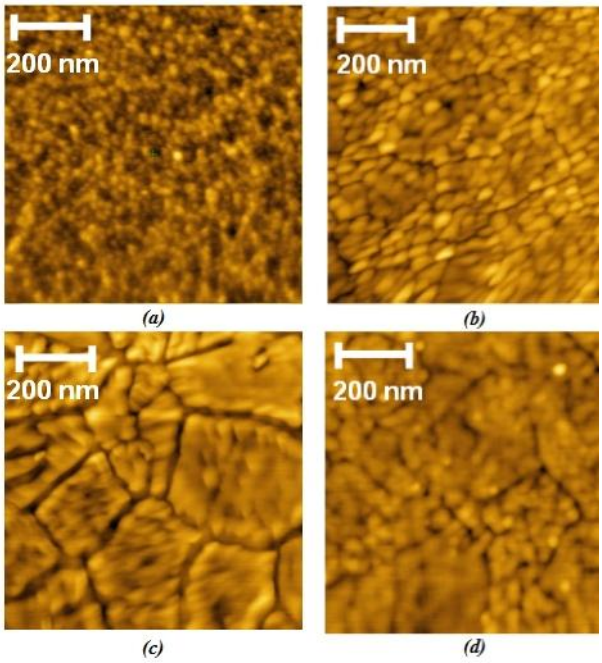

Fig. 2. AFM topography of the TiO_2 thin films, as deposited (a), annealed at 600°C (b), annealed at 700°C (c) and 800 °C (d).

It was observed that the grain size and the surface roughness tended to increase with the increase in the annealing temperature (see Fig. 2), which is in accordance with the previous works [1, 2, 3, 4].

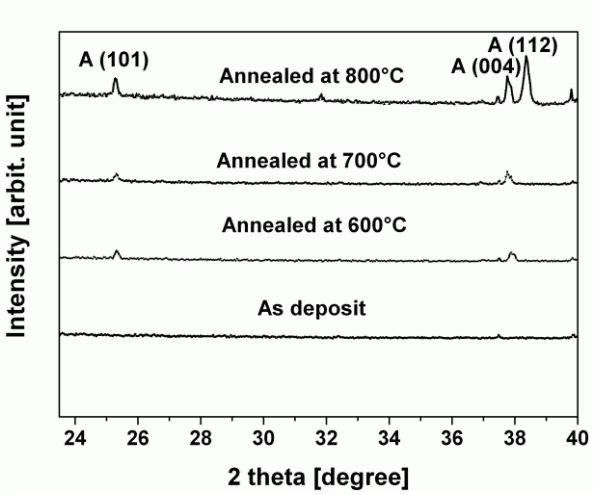

Fig. 3. XRD pattern of as deposited TiO_2 thin films and films annealed at various temperatures (600, 700 and 800 °C).

From XRD measurements it was confirmed that the as deposited thin film showed amorphous structure with no visible peaks of anatase or rutile. The TiO_2 is mostly in the anatase phase for thin films annealed at 600 ºC, 700 °C and 800 °C, with preferential growth along A(101) and A(112) plane (Fig. 3).

In sensing mechanism, firstly the oxygen is adsorbed at the surface of the thin film while capturing the electrons from the near-surface layer of the film resulting in formation of the depletion layer. The reaction at the surface of sensing layer will be determined by the nature of gas to be detected and the operating

temperature. Like H_2 is a reducing gas and generally TiO_2 is n-type semiconductor, so the resistance is decreased upon the exposure of H_2 gas. The H_2 molecules react with adsorbed oxygen by the chemical reaction: O^- *(ads)* + H_2 = H_2O *(des)* + e^-. This process releases captured electrons back to the thin film surface accompanied by the reduction in the depletion layer width and drop in the resistance of the sensor.

Typically, the thin films prepared in this work showed the electrical resistance change up to 3 orders of magnitude for 300 ppm at operating temperature 150°C (Fig.4).

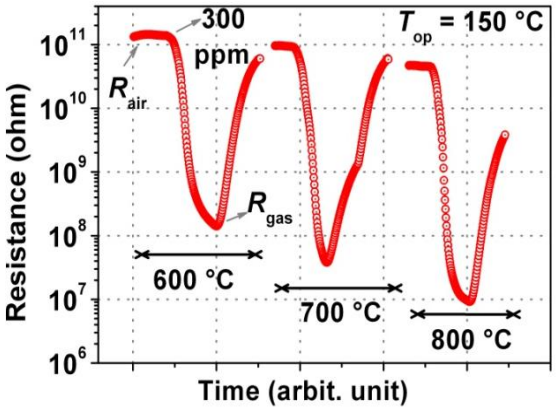

Fig. 4. The dynamic responses of thin films annealed at various temperatures (600, 700 and 800 °C) for 300 ppm concentration of H_2/air, recorded at 150°C operating temperature.

Comparison for various annealing temperatures is shown in the Fig. 4. Increasing the annealing temperature of the TiO_2 thin film in the range from 600 to 800 °C have not any significant effect on the relative resistance change of when H_2/air gas is introduced to the films. However, the resistivity of the thin film slightly decreases in correlation to the annealing temperature what might be related to the formation of larger grains at higher annealing temperatures and thus occurrence of less grain boundaries to scatter the transport (Fig. 2).

Relative resistance changes ΔR (R_{air} - R_{gas}), at a given concentration C [ppm], were evaluated by the equation:

$$S = (1/C)^*(\Delta R/R_{gas}) \qquad (1)$$

where S is the sensitivity of the gas sensor. The sensitivity vs. operating temperature graph was plotted from obtained *RT*-curves in air and gas for various concentrations (Fig. 5). It has been shown that the sensitivity decreases with increase in operating temperature in the range 150 - 350 °C at all measured concentrations.

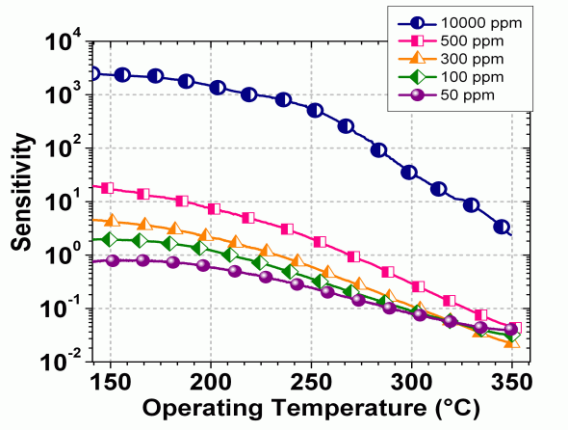

Fig. 5: The plot of sensitivity as a function of the operating temperature for the TiO_2 thin films annealed at 600 °C.

The Fig. 6 shows the plot of the response and recovery time with H_2 gas concentration. All the thin films have compartively fast response time and recovery time for a given concentration change. These times are in range of a few minutes up to 20 minutes for 90% of relative change in the resistance. Response time is maximal for lowest concentrations (below 100 ppm) when the recovery time is shortest. On the other side, response time is shortest for highest concentrations (over 5 000 ppm) when the recovery time is maximal. However, the sum of the response and the recovery time for an actual concentration is always nearly the same (~15 min). This behaviour is given only by the method of measurement and have nothing to do with dynamics of the gas-sensor interaction as we have already discussed elsewhere [2].

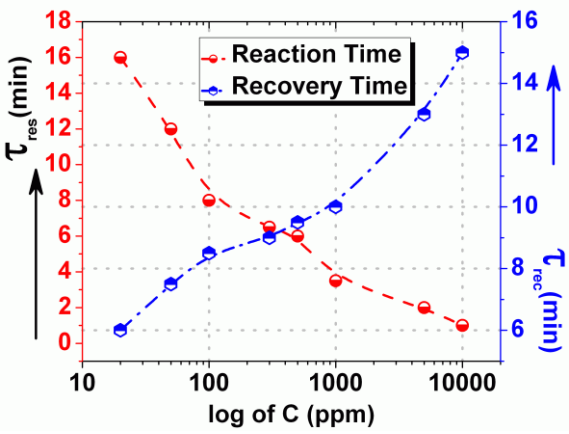

Fig. 6. The graph shows the concentration (log of C) dependence of response time (τ_{res}) and recovery time (τ_{rec}) for TiO_2 thin films annealed at 600°C and measured at 150°C. The times were estimated for the 90% relative change in the resistance from its stabilized value

Finally, the Fig. 7 shows the comparison of dynamic responses to various concentrations of H_2/air gas at higher operating temperature (350 °C). The trend of sensitivity fall (Fig. 5) is noticeable when the films exposed to 10 000 ppm as the films showed change in the resistance comparable to the change at lower operating temperature (150 °C) when exposed to only 300 ppm (Fig. 4). It is interesting to note that despite of different grain sizes and roughness of the thin films (Fig. 2), there is not significant variation in gas sensing properties due to different annealing temperatures of the thin film up to 800 °C.

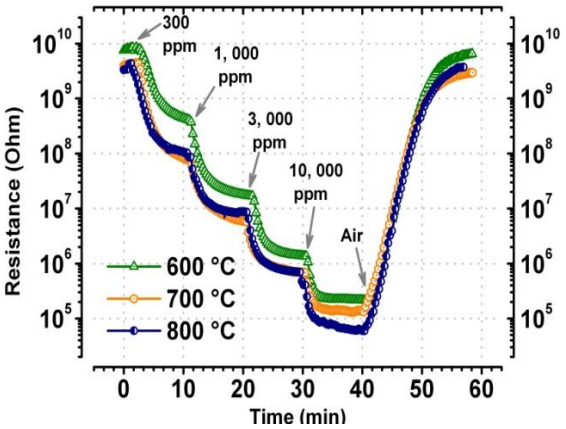

Fig. 7. The typical dynamic response for films annealed at 600 °C, 700°C and 800°C, measured at Top = 300 °C. The plot shows the dynamic changes in the electrical resistance upon the introduction of various concentrations of H_2 gas ranging from 300 ppm to 10,000 ppm for every 10 minutes.

Conclusion

The reported nanocrystalline TiO_2 thin films were prepared by reactive dc magnetron sputtering and subsequently annealed at temperatures 600 ºC, 700 °C and 800 °C. The films showed only anatase phase with relatively small grains (below 0,3 μm). The comb-like Pt electrodes were prepared on the top of the films by depositing 20 nm Pt layer followed by direct optical lithography and ion-beam etching. The change in the resistance upon the exposure to 300 ppm H_2/air gas at operating temperature 150 °C was more than 3 orders of magnitude with response/recovery time up to 16 minutes. We have not found any significant trend in the variations of gas sensing properties with annealing temperature in spite of the fact that grain size and roughness varies considerably. Finally, it has been shown that the sensitivity of the films decreases for all measured gas concentrations (20 – 10 000 ppm) with increasing operating temperature in the range 150 °C – 350 °C.

Acknowledgements

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