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Research article

The Effect of O_2 Flow Rate on Nanostructured TiO_2 Thin Films Prepared by Reactive DC Magnetron Sputtering with OAD Technique

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Abstract

In this project, we explored how different oxygen flow rates influenced the creation of TiO_2 nanostructures in thin films using magnetron sputtering preparation with oblique angle deposition (OAD) technique. The experiment involved oxygen flow rates of 20, 40, 60, 80 and 100 sccm along with a constant argon flow at 20 sccm. Morphological analysis by FE-SEM was performed to determine film thickness and deposition rate. In a subsequent stage, thin films thickness was confirmed to be 100 nm. After coating, specimens were annealed at 300°C for 2 h using various O_2 flow rates. FE-SEM revealed morphological changes, GIXRD to explore crystal structures, and UV-Vis spectrophotometry to measure light transmittance. The results showed an optimal oxygen flow rate at 60 sccm, with annealed specimens exhibiting anatase structure and promising light transmittance of 73-83%.

Keywords: nanostructured TiO_2; oblique angle deposition technique; OAD; oxygen flow rate; reactive DC magnetron sputtering

1. Introduction

Titanium dioxide (TiO_2) stands as a versatile material with widespread applications across various industries. In the beauty and cosmetics industry, it serves as a key ingredient in sunscreens and cosmetics due to its ability to block UV rays. In air pollution treatment, TiO_2 plays a crucial role in catalyzing reactions to purify air. Additionally, its use extends to product coatings for enhancing durability and applications like solar cells in the electronics industry (Binas et al., 2017; Wei et al., 2023)

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Thin-film deposition of TiO_2 refers to the process of forming a thin layer of titanium dioxide (TiO_2) on a substrate. TiO_2 is a semiconductor material with applications in fields such as photocatalysis, solar cells, sensors, and protective coatings. The deposition of TiO_2 can be done through various methods, including: Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Atomic Layer Deposition (ALD) and Sol-Gel Deposition. These deposition techniques can yield different nanostructures, such as nanorods, nanowires, or compact/porous films, depending on the specific process parameters. (Venkatachalam et al., 2013)

Oblique angle deposition (OAD) magnetron sputtering is a specialized technique used in thin film deposition processes. In traditional magnetron sputtering, material is deposited onto a substrate in a perpendicular fashion, resulting in a film with a columnar structure. However, in OAD magnetron sputtering, the deposition angle is oblique, meaning that the material is deposited at an angle rather than perpendicular to the substrate surface. This oblique deposition angle leads to unique morphologies and properties in the deposited thin films. OAD can be used to create nanostructured thin films with controlled porosity, surface roughness, and optical properties. By adjusting the deposition angle, substrate rotation, and other process parameters, researchers and engineers can tailor the characteristics of the deposited films for various applications such as optical coatings, photovoltaics, sensors, and microelectronics. Overall, OAD magnetron sputtering offers a versatile approach to engineer thin film structures with enhanced functionalities, making it a valuable technique in materials science and engineering (Kwon et al, 2015).

The exploration of TiO_2's applications and the role of OAD in the deposition process displays the interdisciplinary nature of this research. The ability to tailor nanostructures through precise techniques opens avenues for advancements not only in air pollution treatment but also in diverse industries relying on the unique properties of TiO_2. As technology continues to advance, further refinements in deposition techniques promise even more tailored and efficient applications across various sectors.

This project was centered on depositing TiO_2 nanorods (NRs) via the magnetron sputtering system with an OAD of 85°, argon and oxygen gas were alternatively applied under various conditions. The impact of as-deposition (ASD) and annealing was explored, and quantitative data and crystallinity analysis for all specimens were presented. The O_2 flow rate plays a role in the crystalline structure and phase formation of the TiO_2 film. It can affect the transition between different phases such as anatase, rutile, or amorphous phases. Controlling the oxygen flow rate allows for tuning the crystallinity of the film, which in turn influences its optical, electrical, and photocatalytic properties.

2. Materials and Methods

This experiment consisted of two parts. In the first part, the objective was to study the deposition rate of thin films with a fixed deposition time of 30 min. In the second part, the focus was on studying the annealing process at 300°C under various O_2 flow rate at constant deposition rate and thickness of 100 nm.

2.1 The deposition rate of thin films at a constant deposition time of 30 min

In this process, we demonstrated how to determine the deposition rate by utilizing thickness data obtained from the sputtering process, wherein the oxygen flow rates were 40, 60, 80, and 100 sccm. All specimens were subjected to a 30 min operation.

Subsequently, each specimen underwent characterization analysis using SEM to measure thickness for the calculation of the deposition rate.

2.1.1 Sample preparation

Si substrate and glass slide were cut into a rectangular shape with dimension of 1 x 4 cm for the Si substrate and dimensions of 1 x 1 inch for the glass slide. Both the Si substrate and the glass slide were cleaned using ultrasonication in isopropanol, acetone, and distilled water bath for 15 min each. After cleaning, the substrates were dried under nitrogen flow. Once dry, the substrates were loaded into the deposition chamber, with the Si substrate positioned horizontally and the glass slide was placed adjacent to it. The anode angle was set to 85°, and precise alignment was ensured by verifying the desired angle.

2.1.2 Preparation of sputtering process

In the sputtering process, the deposition rate, specific parameters and conditions were determined. The material used for deposition was high-purity titanium (Ti) at a concentration of 99.999%. The flow rate of argon (Ar) during the process was set at a constant 20 sccm, while the flow rates of oxygen (O_2) varied across the different conditions of 40, 60, 80, and 100 sccm. These variations allow for an exploration of the impact of different oxygen flow rates on the deposition process. The base pressure maintained during the process was an ultra-low level of 8.0×10^{-6} mbar, contributing to a controlled and stable environment. The power input was set at 300 W, influencing the energy supplied to the system. The total deposition time was standardized at 30 min, ensuring consistency across experiments. Additionally, the flow-on time for both argon and oxygen was set at 20 s each, introducing a periodicity in the gas flow that contributeed to the dynamic nature of the sputtering process.

2.1.3 Calculation of films thickness

All specimens underwent characterization using scanning electron microscopy (FE-SEM; Hitachi S-8030). The objective was to measure the thickness of the TiO_2 nanorod (TiO_2 NRs) thin films obtained through the sputtering process. The program employed for thickness measurement was SemAfore. The thickness was measured at approximately ten different points on each specimen. Subsequently, the average of the thickness was calculated by the equation;

$$\text{Deposition rate} = \frac{Thickness}{Time}$$

2.2 The deposition time at a constant thickness of 100 nm and annealing process

2.2.1 Sample preparation and sputtering process

In this experiment, the setup closely mirrored the initial process, except for variations in the experimental conditions. As per the first process, the specimens were prepared following the same parameters and dimensions. The Si substrate and glass slide were arranged in the prescribed manner, and the anode angle was set at 85°. However, the conditions for the sputtering process in this experiment differed and are detailed as follows. The material used remained high-purity titanium (K.J. Lesker, 99.999%). The flow rates of argon (Ar) were held constant at 20 sccm, while oxygen (O_2) flow rates of 40, 60, 80, and 100 sccm were applied, providing a range of conditions for investigation. The flow-on time for both argon and oxygen was set at 20 s each. The base pressure was maintained at an ultra-low level of 8.0 × 10^{-6} mbar, ensuring a controlled environment for the sputtering process. The power input remained at 300 W, influencing the energy supplied to the system. Notably, the deposition time varied in this experiment. This variation in deposition time allowed for an exploration of how different time durations impacted the resulting thin films.

These nuanced changes in experimental conditions were aimed at providing a comprehensive understanding of the influence of varied oxygen flow rates and deposition times on the characteristics of the deposited thin films. The utilization of the SemAfore program (an internet program) for thickness measurement was intended to contribute to the quantitative analysis of the outcomes.

2.2.2 Characterization

In this process, all specimens underwent characterization using scanning electron microscopy (FE-SEM; Hitachi S-8030) and grazing incident x-ray diffraction (GI-XRD; Rigaku TTRAX III) using Cu Kα radiation operated at 50 kV and 300 mA to analyze their structural properties. It was measured in 20°- 60° (2θ) angular region with scanning rate of 2°/min. The characterization focuses on the as-deposition (ASD) state. The Si substrate was subjected to SEM and XRD analyses to provide insight into its surface morphology and crystallographic structure. Additionally, the optical transmission was determined by a UV-Vis-NIR spectrophotometer (Agilent Cary 7000) ranging from 200 to 2000 nm.

2.2.3 Annealing process

All samples were annealed at same temperature of 300°C for 2 h. The objective was to induce a phase change in TiO_2 from the amorphous phase to the anatase phase. The annealing process was performed using an electric ceramic kiln machine. This systematic approach allowed for a comprehensive understanding of the effects of annealing on the structural and morphological properties of the TiO_2 thin films.

3. Results and Discussion

3.1 The deposition rate of TiO_2 nanorods at a constant deposition time of 30 min

The cross section of TiO_2 nanorods by SEM technique are shown in Figure 1. Thickness and deposition rate graphs are shown in Figure 2. The distinct results were revealed for various oxygen flow rates. TiO_2 NRs at O_2 flow rate of 40 sccm exhibited a deposition rate of 5.05 nm/min, while at 60 sccm, the deposition rate was 4.9 nm/min. The deposition rate decreased slightly to 4.45 nm/min at 80 sccm, and at 100 sccm, it registered at 4.7 nm/min. These findings provide a detailed understanding of how varying oxygen flow rates influenced the deposition rate of TiO_2 nanorods, offering valuable insights for optimizing thin film fabrication processes. In Figure 2a, when O_2 flow rate was increased, thin films thickness decreased because the higher O_2 flow rate led to an increase in reactive oxygen species in the sputtering chamber. As the oxygen flow rate increases, more oxygen

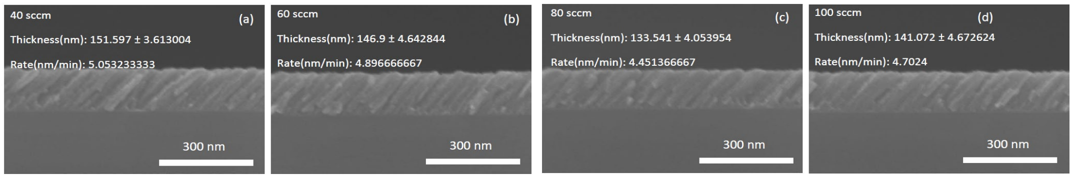


Figure 1. SEM cross section of TiO_2 nanorods at various O_2 flow rates: (a) 40 sccm, (b) 60 sccm, (c) 80 sccm, and (d) 100 sccm

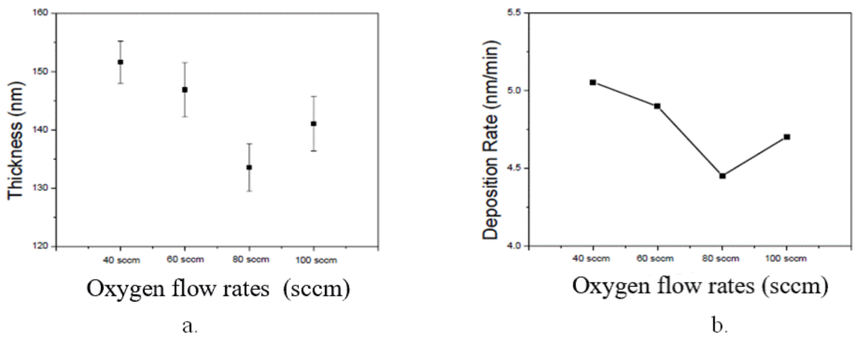


Figure 2. TiO_2 nanorods at various O_2 flow rates (a) Thickness (b) Deposition rate

molecules are available to react with the sputtered titanium atoms. This can lead to the formation of a titanium oxide layer (TiO_2) on the surface of the titanium target itself, creating a "poisoned" target effect. The oxide layer on the target is harder and more resistant to sputtering than pure titanium, which reduces the sputtering yield. As a result, fewer titanium atoms are ejected from the target and deposited on the substrate, leading to a thinner film. (Ogwu et at., 2005). From Figure 2b, when the O_2 flow rate was increased, the deposition rate decreased because in reactive sputtering, the introduction of oxygen gas (O_2) is crucial for the formation of TiO_2 films. However, an excessively high O_2 flow rate (≥100 sccm) can alter the dynamics of the sputtering process. The reactive gases may compete with sputtered Ti atoms for surface sites on the substrate, leading to reduced deposition efficiency and, consequently, a decrease in the deposition rate (Tachibana et al., 2000).

3.2 The deposition time at a constant thickness of 100 nm

This variation in deposition time allows for an exploration of how different time durations impact the resulting thin films. For varying the O_2 flow rate from 40, 60, 80 and 100 sccm, the deposition times calculated from equation 1 were 19 min 47 s, 20 min 25 s, 22 min 28 s and 26 min 16 s, respectively. However, the angle and thickness of TiO_2 films increased when the O_2 flow rate increased because the longer deposition times increased the thin film thickness (Figure 3a and 3b). The increase in deposition time allowed more TiO_2 to accumulate, leading to an increase in the film thickness. This thicker film can affect the angle of nanorods by promoting a more vertical growth pattern due to the increased amount of material available for deposition, which can enhance the overall thickness of the TiO_2 films. However, the opposite was seen for length. The length of TiO_2 nanorods decreased

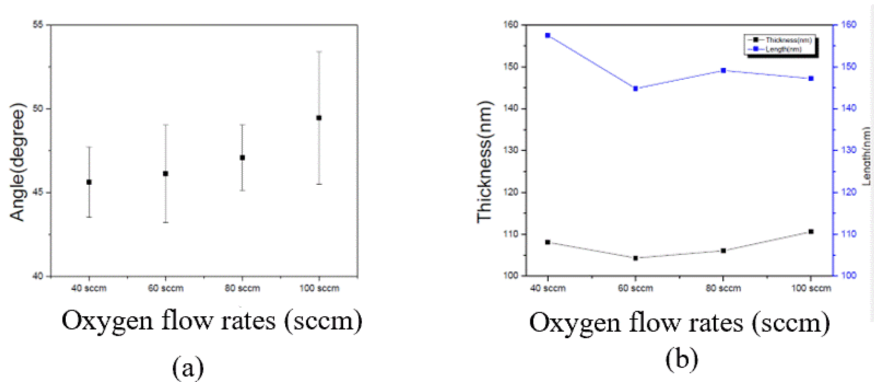


Figure 3. TiO_2 nanorods by various O_2 flow rate (a) Angle (b) Thickness

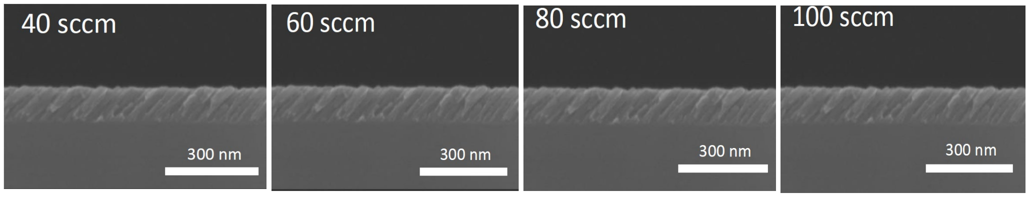
with increase in O_2 flow rate (Figure 3a and 3b). The reaction between titanium and oxygen involves the incorporation of oxygen atoms into the titanium lattice, resulting in the formation of TiO_2. This process can lead to a reduction in the overall size or length of the TiO_2 structure, especially if the oxidation reaction results in the removal of titanium atoms or a rearrangement of the crystalline structure (Khan et al., 2023). Additionally, the thermodynamics of the reaction may play a role. The conditions created by higher O_2 flow rate, such as elevated temperature, may favor the formation of a more compact or stable TiO_2 structure, contributing to the observed decrease in length (Hanaor et al., 2011). From these results, TiO_2 thickness of 100 nm was selected for the next experiment due to the thickness, as the thickness across all conditions started at a minimum of 100 nm.

3.3 Annealing process

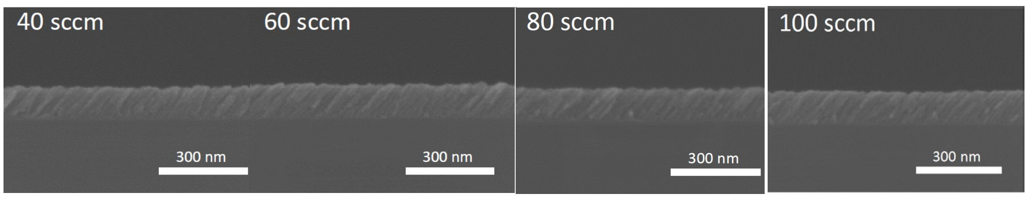
Annealing is a heat treatment process used to alter the physical and chemical properties of materials. The annealing process was conducted at temperatures of 300°C with various O_2 flow rates, shown as SEM images presented in Figure 4. The objective was to induce a phase change in TiO_2 from the amorphous phase to the anatase phase. The temperature of 300°C is often chosen because it is within the temperature range where the transformation from the amorphous phase to the anatase phase is thermodynamically favorable. The specific choice of temperature is based on the desired properties and application of the material.

After the annealing process, the length and thickness of TiO_2 also increased (Figure 5). This was because during annealing, the amorphous TiO_2 undergoes a phase change from the amorphous phase to the anatase phase, which is a crystalline structure. The transition to a crystalline structure can lead to the rearrangement and packing of atoms in a more ordered manner, resulting in an increase in overall dimensions (Castrejón et al., 2019).

The crystal structure was investigated using grazing ıncident x-ray diffraction (GIXRD). It was observed that the unannealed specimens displayed a polymorphic crystal structure as shown in Figure 6a. In contrast, specimens annealed at 300°C revealed the TiO_2 anatase structure in the principal planes (101), (004), (200), (105), and (211), corresponding to the 2θ of 25.4°, 37.9°, 48.12°, and 59.34°, respectively (Jalali et al., 2020), as shown in Figure 6b.



(a)



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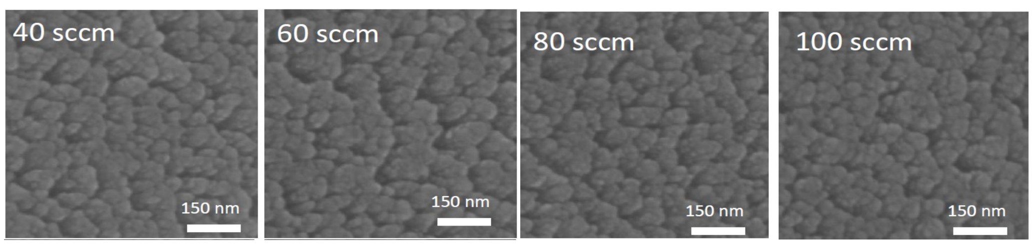


(c)

Figure 4. SEM cross-section images of TiO_2: a) Before annealing, b) after annealing, and c) SEM top view of TiO_2 after annealing

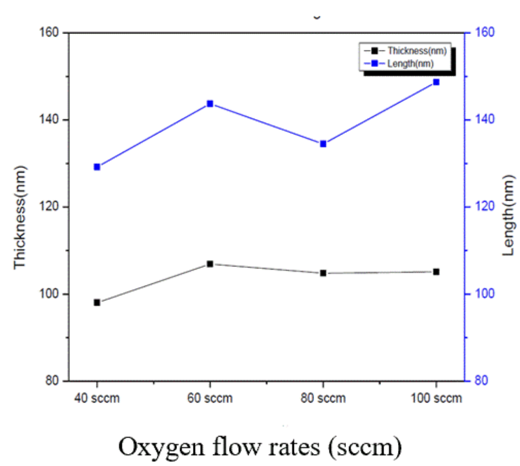
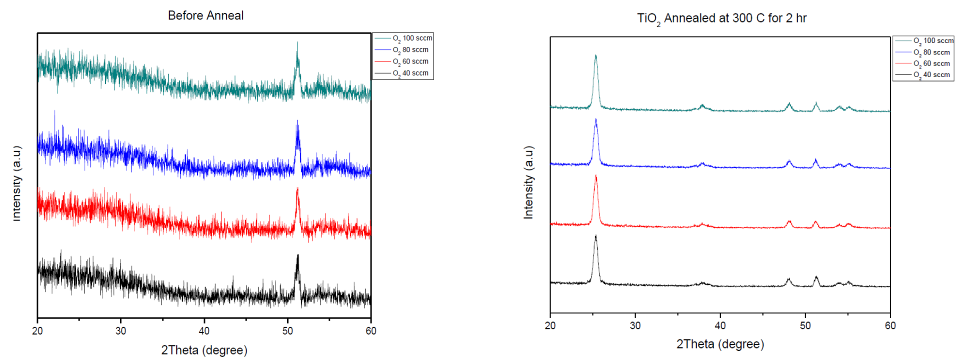


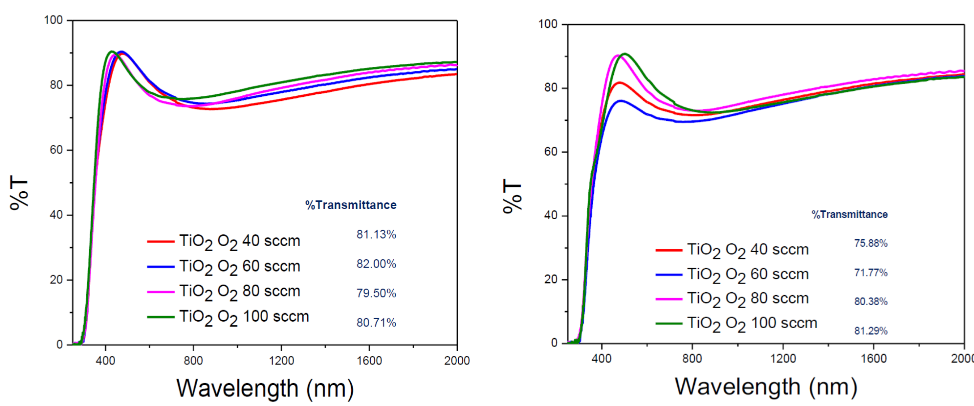
Figure 5. Thickness and length of TiO2 at various O_2 flowrates after annealing process



a b

Figure 6. XRD results of TiO_2 at various O_2 flowrates (a) before (b) after annealing

The optical properties were studied with a UV-Vis spectrophotometer. Percentage of light transmittance (%T) in the wavelength range of 200 nm to 2000 nm was studied quantitatively and the results are shown in Figure 7. It was found that the unannealed specimen had a %T of 79-82% (Figure 7a), and the annealed specimen had %T of 73-83% (Figure 7b). The annealing process in air atmosphere likely enhanced the reactive of O_2 with Ti atoms, leading to the formation of the TiO_2 phase. This process demonstrated the formation of the Ti-oxide phase, which was confirmed by the high optical transmittance of the film. Especially, TiO_2 in the anatase phase is known for its high transparency and transmittance in the visible region of the electromagnetic spectrum. A higher O_2 flow rate can improve the crystallinity of the TiO_2 films, particularly promoting the formation of the anatase phase, which has high transparency and good optical properties. Better crystallinity often leads to reduced light scattering and higher transmittance. Additionally, higher O_2 flow rates can affect the growth rate and thickness of the films. Although an increase in O_2 flow rate generally decreases the deposition rate, the resulting films are often denser and more uniform, which can enhance transmittance. This property makes TiO_2 suitable for applications where optical clarity is crucial, such as in thin films or coatings (Mekkaoui et al., 2022).



a. b.

Figure 7. Optical properties of TiO_2 at various O_2 flowrate (a) before (b) after annealing

Figure 8 shows a comparison of %T of ASD (as-deposited) and 300°C annealed TiO_2 NRs. After annealing, Ti formed the Ti-oxide phase, resulting in increasing %T because before annealing the amorphous or non-crystalline structures displays light scattering, and thus reduced transparency. As titanium undergoes annealing and transforms into the TiO_2 crystalline phase, the reduction in internal structural disorder can minimize light scattering, allowing more light to pass through the material (Vargas & Rodríguez-Páez, 2017). The O_2 flow rate of 60 sccm presented with the lowest of %T, which indicated the presence of more pure Ti than TiO_2. However, after annealing, all samples showed high transmittance, indicating high levels of TiO_2.

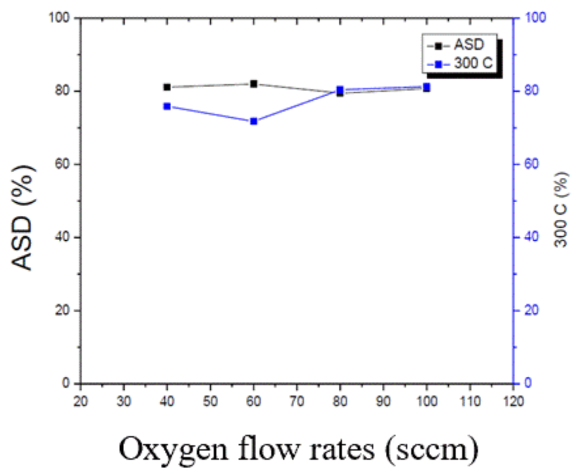


Figure 8. Comparison of %T between before annealing (ASD) and after annealing (300°C) at various O_2 flowrates

4. Conclusions

In this study, we demonstrated the successful fabrication of TiO_2 nanorods (NRs) by varying O_2 flow rate with the direct current magnetron sputtering (DCMS) and oblique angle deposition (OAD) technique. The results showed that when O_2 flow rate was increased, the thickness and deposition rate decreased which was confirmed by SEM images. GIXRD indicated that after the annealing process at 300°C for 2 h, the amorphous phase had changed into the anatase phase of TiO_2 for all samples. Additionally, after annealing, the samples showed high transmittance, indicating the high levels of TiO_2. The O_2 flow rate influenced the stoichiometry of the TiO_2 film. Controlling the oxygen flow ensures the proper incorporation of oxygen into the film during deposition. An optimal O_2 flow rate helped in achieving the desired composition of TiO_2, which was crucial for the film's properties. Then, O_2 flow rate can impact the deposition rate of TiO_2 during sputtering. Adjusting the oxygen flow helps control the film thickness. Different flow rates may result in variations in the growth rate and, consequently, the thickness of the deposited film.

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6. Conflicts of Interest

The authors declare no conflicts of interest.

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