

Growth mechanism of Co:TiO₂ thin film deposited by metal organic chemical vapor deposition technique

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Abstract. In this research, we investigated the growth mechanism of cobalt-doped titanium dioxide (Co:TiO₂) films. Thi Co:TiO₂ thin films were grown on the n-type silicon substrate. The films were grown by metal organic chemical vapor deposition method. The growth temperature was varied of 325°C – 450°C. The films were characterized by SEM. Using Arrheniu's equation, it is known that the activation energy value of film growth is positive in the range of temperature of 325°C – 400°C and negative in the range of temperature of 400°C – 450°C. These results show that the decomposition rate in the range of temperature of 325°C – 400°C is due to diffusion phase of precursor gas. On the other hand, the decomposition rate decreased in the range of temperature of 400°C – 450°C because the precursor gas decreased, and the surface chemical reaction was high.

1. Introduction

TiO₂ is an interesting material. It has many properties that can be applied in various fields. TiO₂ has a high refractive index and dielectric constant [1]. TiO₂ is also chemically stable. Pigment, absorbent, catalyst supports, filters, coating, and dielectric material commonly used TiO₂ [2]. In the recent times, TiO₂ has a high potential for environmental purification, decomposition of carbonic acid gas, and hydrogen gas generation [2]. Besides as a semiconductor, TiO₂ doped by cobalt (Co:TiO₂) demonstrate ferromagnetic properties at room temperature. These ferromagnetic properties allow us to use Co:TiO₂ as sprintronic devices [3].

Many techniques can used to grow TiO₂ thin film. These techniques are atomic layer deposition, MBE (molecular beam epitaxy), PLD (pulsed layer deposition), DC and RF Sputtering, and MOCVD [4][5][1][6][7]. Each technique has special advantages, but MOCVD possible to grow epitaxial film, deposit film selectively, and control the growth parameter simplicity so MOCVD is a powerful technique [7].

The effect of growth temperature on the structural and morphological quality of Co:TiO₂ thin films deposited on Si(100) substrate by MOCVD technique has been done by Saripudin et al [8]. The



morphological quality and the growth rate of Co:TiO₂ thin film as a function of temperature was pictured. However, the growth mechanism of Co:TiO₂ thin films was not explained. The activation energy of film growth also was not evaluated. In this research, we focused on the growth mechanism of Co:TiO₂ thin film. The activation energy of film growth was then evaluated by Arrhenius's equation.

2. Experimental Method

In this research, thin films of cobalt-doped TiO₂ were grown on Si(100) substrate by MOCVD method. A TTIP (Titanium Tetra Iso-Propoxide) was used as TiO₂ precursor, other while Co(TMHD)₃ was used as Co precursor. A THF (Tetra Hidrofuran) was used to make a Co solution.

TTIP of 20 mL was mixed by Co(TMHD)₃ of 900 mg and THF of 20 mL into the bubbler tube. The mixture of TTIP, Co(TMHD)₃, and THF in the bubbler tube was then heated at a constant temperature of 100°C. The vaporized TTIP and Co(TMHD)₃ of 0,3 kg/cm in partial pressure were driven by argon gas into the reactor chamber with 70 sccm in speed. A silicon substrate has been embedded on a heater disc in the reactor. The disc was heated until a constant temperature, that is, 325°C, 350°C, 375°C, 400°C, or 450°C. Each film was grown along 120 minutes with the total pressure of the reactor chamber was 2×10^{-3} torr. The details of the growth parameters of Co:TiO₂ thin films were listed at **Table 1**.

Table 1. The detail of the growth parameters of Co:TiO₂ thin film.

No.	Parameters	Value	Unit
1	Total pressure of the reactor chamber	2×10^{-3}	torr
2	Growth time	120	min
3	Argon gas (carrier) speed	70	sccm
4	Growth temperatures	325 - 450	°C
5	Bubbler tube temperature	100	°C
6	Pressure of the vaporized TTIP and Co(TMHD) ₃	0,30	kg/cm ²

Each film was characterized by SEM (JEOL type JSM-6510LA) to know the film morphology and the film thickness. The thickness of each film was measured and, by knowing the growth time, we calculated the rate of film growth. To evaluate the energy activation of film growth, we used Arrhenius's Equation, that is

$$r = Ae^{-\frac{E_A}{RT}} \quad (1)$$

where r is the rate of growth, A is the frequency factor for reaction, R is universal gas constant, T is temperature of growth, and E_A is activation energy.

3. Results and Discussion

SEM photograph of Co:TiO₂ films for various temperature growths resulting in this research is shown in **Figure 1**. The left-side of the photograph is SEM of film's surface, other while the right-side photograph is SEM of film's cross-section. These SEM photographs show, generally, that all film's surface look roughly with a relatively homogeneous grain.

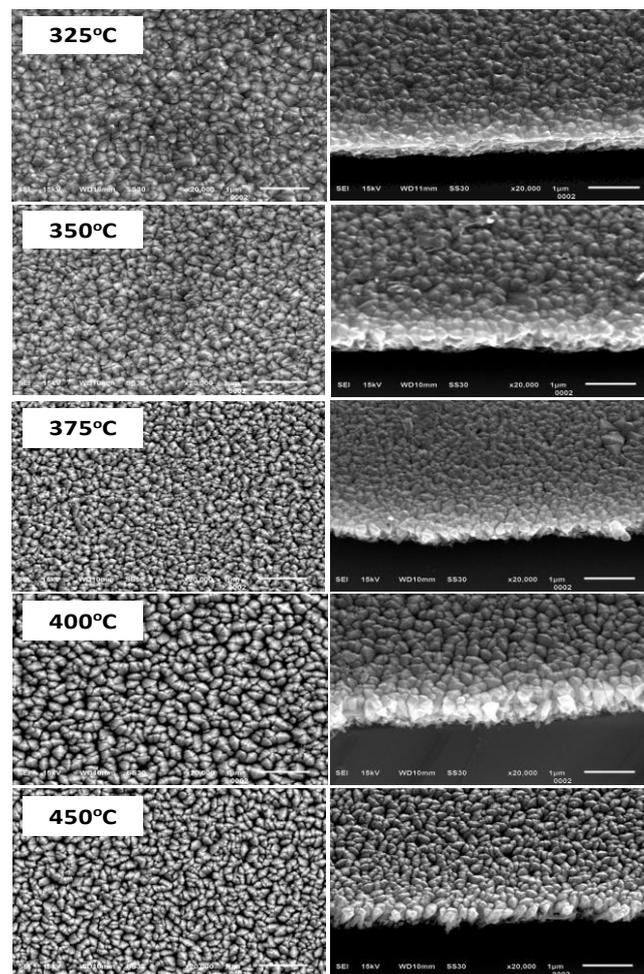


Figure 1. SEM photograph of films grown in various temperature.

SEM photograph of film's cross-section grown at 375°C – 450°C show that the film composed by like rod crystal grains. At the interface of film-substrate, crystal grains look random. These results were obtained because of competitively crystal growth so that the crystal grains formed depend on the diffusion process of surface's atomic precursor. The competitively crystal growing can be caused by various crystal grain orientations on the substrate's surface [9]. On the other hand, photographs of film's cross-section grown in the range of temperature of 325°C - 350°C show that the grain is in the random position and separated each other. It was caused by polluter covered the crystal surface that is growing.

Although the films were grown at the same growth time, the thickness of each film are different for different temperature. It means that the rate of film growth is different. The film grown at temperature of 325°C is the lowest rate of growth, that is about 2.42 nm/min. On the other hand, the film grown at temperature of 400°C is the highest rate of growth, that is about 5.33 nm/min. This fact indicated that the rate of film growth depend on the temperature of film growth.

Graph of $\ln r$ versus $1/T$ for Co:TiO₂ films is shown in **Figure 2**. By linear fitting, we get the activation energy of film growth. It is revealed that the activation energy of film growth is positive, that is 32.2 kJ/mol, for the film grown in the range of temperature of 325°C – 400°C. This result shows that the rate of film growth increased as the temperature increased. This phenomenon caused by gas phase of precursor that higher than surface's chemical reaction [4]. In the other word, deposition of film is controlled by diffusion [7].

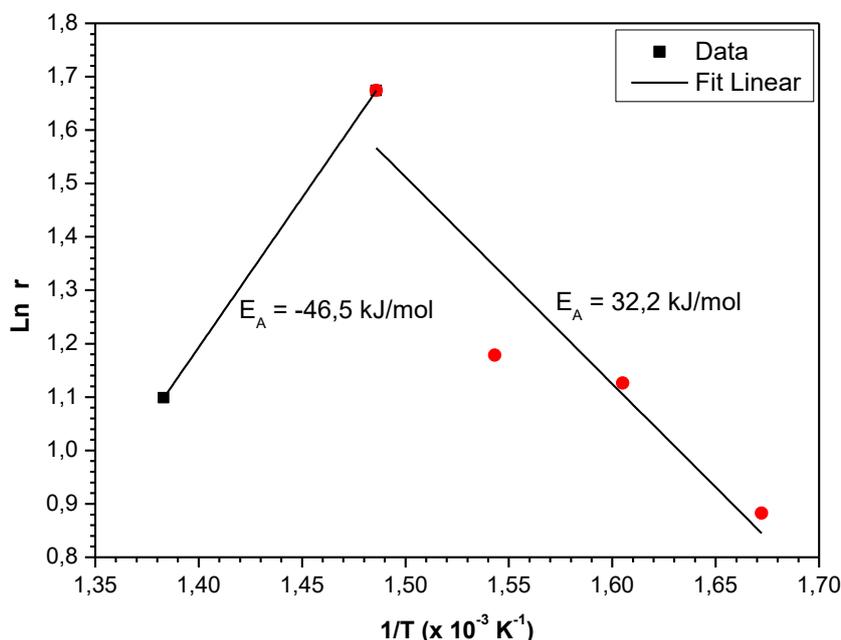


Figure 2. Graph of natural logarithm of film growth rate ($\ln r$) versus inversely temperature ($1/T$).

A different result is shown by the film grown in the range of temperature of 400°C - 450°C. Its activation energy is negative, that is -46.5 kJ/mol. This result shows that the rate of film growth decreased as the temperature of film growth increased. The decreasing tendency of the rate of film growth at the higher temperature is commonly occur. In the high temperature, the decomposition rate of film and other surface chemical reaction becomes higher. This phenomenon decreased the gas diffusion of precursor. In that situation, film deposition is controlled by kinetically deposition [7].

4. Conclusion

We have grown a series of Cobalt-doped TiO₂ thin films on the n-type silicon substrate by MOCVD method in the range of temperature of 325°C – 450°C. SEM photograph of the film shows that all film's surface look roughly with a relatively homogeneous grain. The activation energy of film growth is positive in the range of temperature of 325°C – 400°C and negative in the range of temperature of 400°C – 450°C. These results show that the decomposition rate in the range of temperature of 325°C – 400°C is due to diffusion phase of precursor gas. On the other hand, the decomposition rate decreased in the range of temperature of 400°C – 450°C because the precursor gas decreased, and the surface chemical reaction was high.

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