The Effect of Various Annealing Cooling Rates on Electrical and Morphological Properties of TiO2 Thin Films

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Abstract—This paper investigates the effect of various postannealing cooling rates on structural and electrical properties of Titanium Dioxide (TiO2) thin films. TiO2 thin films were deposited on a silicon substrate using DC magnetron sputtering technique. After annealing TiO2 thin films at 600°C, to investigate the effect of different cooling rates on TiO2 thin films, samples were cooled down from 600°C to room temperature under 3 different rates: 2°C/min, 6°C/min, and 8°C/min. The Surface morphology, crystal structure, and electrical properties of the samples were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and Four-point probe (FPP) techniques. It is found that the rate of decreasing temperature after annealing can affect the morphology structure and electrical resistivity of TiO2. The sample with 2°C/min cooling rate has the largest grain size and highest electrical resistivity, while the sample with 8°C/min cooling rate has the smallest grain size and lowest electrical resistivity.

Keywords: TiO2, annealing, electrical properties, thin film, cooling rate
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1. INTRODUCTION

TiO2 as one of the most thermally and chemically stable semiconductors has been widely studied in many researches [1–6]. Due to its interesting chemical, electrical, and optical properties [7, 8], it has been widely used in many applications such as solar cells [9], photocatalysis [10], and gas sensors [11]. Also, because of its low electrical resistivity, TiO2 is prevalently used as the material for microelectronic devices [12]. TiO2 thin film can be fabricated using various methods, namely chemical vapor deposition (CVD), ion beam deposition, sol gel dip, plasma enhanced chemical vapor deposition, RF magnetron sputtering, and DC magnetron sputtering [13, 15].

Since DC magnetron sputtering is a more controllable deposition technique which provides more uniform coated thin layers [16], in our study we fabricated TiO2 thin film samples using this method. TiO2 exists in 3 different crystal phases: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [17, 18]. Rutile compared to other phases has more stability, while anatase and brookite are metastable and can be easily transformed to anatase by heat [19, 20]. Annealing at 600°C creates rutile phase in annealed TiO2 [21].

Recent studies reported the effect of heat treatment and annealing time and temperature on structural, mechanical, and optical properties of TiO2 thin films [22–25]. Also, another research has studied light harvesting and efficiency in solar cells [26] and electrical properties of TiO2 [27]. According to [28], different annealing rates (ramped from room temperature to 450°C) can affect the surface roughness of TiO2 thin films. Authors of [28] showed that the slowest rate has the lowest roughness and the largest size of islands.

Another study investigated the effect of ultra-fast annealing on the electrical properties of TiO2 Polycrystal thin films. They annealed the TiO2 at 550°C (with 10K/min ramp) for 1 hour and at 460°C (with 300 K/min ramp) under oxygen treatment and fast cooling after annealing. The total ultra-fast treatment, including heating and cooling was done in 5 minutes. Ultra-fast annealed TiO2 showed lower resistivity compared to the resistivity of the standard annealed TiO2 [29].

In an effort to control the semi conductivity of TiO2, we modified the annealing process by controlling the cooling rate after annealing. We showed different cooling rates after annealing TiO2 thin films changed the electrical properties. In Chapter 2, the sample preparation procedure is presented followed by the experimental results and discussions presented in Chapter 3 and the conclusions in Chapter 4.

2. EXPERIMENTAL PROCEDURE

TiO2 thin films were coated on silicon a substrate by DC magnetron sputtering technique at room tempera-
perature. Before deposition, the 1 cm × 1 cm silicon substrates were cleaned in an ultrasonic bath for 10 minutes. Argon (99.99% pure) as the sputtering gas and high-purity oxygen (99.99%) were used with the composition from pure argon to pure oxygen. Ti target and substrate distance was fixed at 35 mm. Sputtering chamber was evacuated to $p = 2 \times 10^{-5}$ Torr and the pressure of working gas was kept at $p = 2 \times 10^{-2}$ Torr, with discharge current and electric discharge potential of 200 mA and 500 V, respectively. After deposition, by using Dektak3 surface profile measurement system, 35 nm thickness was measured for all samples.

The TiO$_2$ thin films were annealed at 600°C [30–32] for 10 minutes, after which point, the temperature was decreased to room temperature under three different cooling rates; 2°C/min, 6°C/min, and 8°C/min. XRD, AFM, and FPP measurement methods were employed to analyze the effect of the aforementioned cooling rates on electrical and morphological properties of TiO$_2$ thin films, presented in the ensuing chapter.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1. XRD Results

Figure 1 shows the XRD measurement results of TiO$_2$ thin films cooled at different rates (2°C/min, 6°C/min, and 8°C/min) after annealing. The X-Ray pattern was measured by CUKA 1 source and 1.5 Å wavelength, scanning $2\theta$ in range of 30° to 75°. The main peak around 69° is attributed to the Silicon (400) substrate (reference code: 00-033-1381).

As expected, annealing TiO$_2$ at 600°C produced the rutile phase [21]. The XRD spectra indicates that all the samples consist of TiO$_2$ rutile phase peak with (112) preferred orientation as the shoulder at the right side of Si peak.

For the TiO$_2$ thin film cooled at 8°C/min, this phase was observed at $2\theta = 69.22$° with lower intensity and tetragonal structures. With decreasing cooling rate, the intensity of the rutile phase increased. Obvious increased intensity of the TiO$_2$ peak rutile phase (112) (reference code: 01-084-1284) peak for 6°C/min sample is observed compared to 8°C/min sample. In addition, XRD data show multi-crystal structure including Ti$_3$O$_5$(203) (reference code 01-082-1137) with monoclinic structure, and TiO$_2$(221) (reference code: 01-084-1284) rutile phase with tetragonal structures.

For 2°C/min sample, rutile phase peak (112) has a higher intensity compared to the other two samples. The intensity enhancement can be seen in Ti$_3$O$_5$(203) and TiO$_2$(221) peaks as well. This result shows that slowing down the cooling rate after annealing TiO$_2$ creates better crystallization and phase stability.

The average grain size can be calculated by XRD data and the Scherrer Equation [33]:

$$D = \frac{k\lambda}{\beta\cos(\theta)},$$

Table 1. Crystal size of TiO$_2$ with different ramp rates (2°C/min, 6°C/min, and 8°C/min)

| Sample | Position (2θ) | FWHM (θ) | Crystal size (nm) |
|--------|---------------|----------|-------------------|
| 8°C/min | 69.04(112)    | 1.14     | 0.93              |
|        | 69.22(112)    | 3.43     | 0.82              |
|        | 32.83(203)    | 6.87     | 1.24              |
| 6°C/min | 65.77(221)    | 13.75    | 0.83              |
|        | 32.83(203)    | 9.16     | 1.19              |
|        | 69.32(112)    | 1.14     | 0.93              |
| 2°C/min | 65.88(221)    | 9.16     | 1.09              |
|        | 32.96(203)    | 6.87     | 1.24              |
in which, D is the grain size in nm, k is the shape constant (0.9), \( \beta \) is the peak full width-of-half-maximum (FWHM), \( \lambda \) is the X-ray wavelength (1.54 Å), and \( \theta \) is the diffraction angle.

The results indicate that by speeding up the cooling rate, grain sizes were decreased. Table 1 represents the measured grain size of samples.

3.2. AFM Results

Surface morphology and roughness of TiO\(_2\) thin films with different cooling rates (2\(^\circ\)C/min, 6\(^\circ\)C/min, and 8\(^\circ\)C/min) after annealing were evaluated by AFM imaging. Figure 2 presents the AFM images of TiO\(_2\) thin films with a ramping rate of (a) 2\(^\circ\)C/min, (b) 6\(^\circ\)C/min, and (c) 8\(^\circ\)C/min. The correlation between the increased grain size and the lower cooling rate observed in the XRD results is also discernible in the AFM data.

Surface roughness obtained from AFM is presented by root mean square (Rq) [34, 35]. According to the AFM results, surface roughness was measured as 1.862 nm, 2.002 nm, and 2.294 nm for 8\(^\circ\)C/min, 6\(^\circ\)C/min, and 2\(^\circ\)C/min cooling rates, respectively. It is observed that when the cooling rate decreases, both the grain size and surface roughness increase. Also, densification in lower rates leads to higher grain size. This effect can be seen in Fig. 3.

3.3. FPP Results

The FPP technique was used to measure the resistivity of different TiO\(_2\) thin films.

Surface resistivity (\( \rho_s \)) can be calculated via Equation (2) [36]:

\[
\rho_s = \left( \frac{1}{\ln 2} \right) f \left( \frac{R_t + R_z}{2} \right),
\]

where, \( f \) is Vander Paw factor that depends on the position of electrical connection and can be calculated by Eq. (3):

\[
f = 1 - \frac{\ln 2}{2} \left( \frac{R_z - R_t}{R_t + R_z} \right)^2.
\]

Electrical resistivity can be calculated by \( \rho = t \rho_s \), in which \( t \) is the thickness of the thin film taken to be 35 nm in this study.

Equation (4) describes Electrical conductivity (\( \sigma \)) that has a reciprocal relationship with the resistivity (\( \rho \)).

\[
\sigma = \frac{1}{\rho}.
\]

As seen from Eq. (4), there is an inverse relationship between electrical resistivity and conductivity.
Figure 4 illustrates measured resistivity and calculated conductivity of TiO$_2$ thin films with different cooling rates. Increasing the cooling rate leads to decreased surface roughness and increased conductivity. Also, resistivity was measured as 80, 125, 185 $\mu$Ω for TiO$_2$ thin films with the cooling rate of 8°C/min, 6°C/min, and 2°C/min, respectively.

According to the AFM and XRD data, the lowest cooling rate has the highest roughness and grain size, improved crystallite, higher oxidation phase, and highest resistivity of 185 $\mu$Ω. Compared to other samples, the samples cooled at 2°C/min rate demonstrates the most improved crystallite and semiconducting properties which leads to the highest resistivity. In addition, increasing grain size leads to decreasing grain boundary and hence conductivity [37]. The clump shape of grains and valleys between the clumped grains reduce the movement of charge carriers.

Lower oxidation phase, weaker semiconducting properties and smaller grain sizes of 6°C/min and 8°C/min sample lead to the decrease of the electrical resistivity. The decrease in grain size enhances the electron mobility and consequently increases the conductivity. 8°C/min sample has the lowest grain size and lowest resistivity of 80 $\mu$Ω and the sample with 6°C/min rate has 123 $\mu$Ω resistivities.

4. CONCLUSIONS

In this work the effect of different cooling rates (2, 6, and 8°C/min) after the annealing process on morphological and electrical properties of TiO$_2$ thin film coated on silicon substrate fabricated by DC magnetron sputtering technique was investigated. It has been observed that slowing the ramping rate increased the grain size, roughness, and conductivity of TiO$_2$ thin films. 2°C/min rate has the largest grain size, surface roughness, semiconducting properties, and improved crystallite and resistivity of 185 $\mu$Ω, while the highest cooling rate of 8°C/min has the lowest grain size and resistivity of 80 $\mu$Ω and, consequently, the highest conductivity. A resistivity of 123 $\mu$Ω was measured for the sample cooled at 6°C/min.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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