Growth of TiO$_2$:Au thin films on Si substrates by Spin coating method

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Abstract. Thin titanium dioxide: gold (TiO$_2$:Au) films are grown on n-type Si(100) substrates by spin coating, using 97% pure titanium (IV) isopropoxide [TTIP, Ti(O(C$_3$H$_7$)$_3$)$_4$] as a metal-organic precursor and powdered gold oxide (Au$_2$O$_3$) as a dopant. The Au$_2$O$_3$ was dissolved in tetrahydrofuran (C$_8$H$_8$O) to a concentration of 0.2 M, and this was then mixed with the TTIP in a 1:4 ratio. This experiment used a TTIP buffer layer to reduce lattice mismatch between the substrate and the film. The growth temperature was varied from 400°C to 550°C with an interval of 50°C during deposition of TiO$_2$:Au films, in which the experimental results show that the grown film exhibited rutile (002) (R (002)) crystal planes for all temperature conditions. In addition, while the films were grown at a temperature of 400°C and 450°C showed anatase (211) planes, the layers realized with a temperature of 450°C and 550°C exhibited rutile (200) planes. Increasing the amount of Au incorporation within a film will decrease its bandgap energy. The 500°C films showed a crystalline domain size in the R (002) plane of around 20.38 nm, making it a promising candidate base material for use in carbon monoxide (CO) gas sensors.

1. Introduction

Semiconductor technology has developed very rapidly, from the discovery of semiconductor materials to processing them and their application as gas sensors. The gas sensors in common use today are based on tin dioxide (SnO$_2$), but this has lower sensitivity and is less stable than titanium dioxide (TiO$_2$). Thus, in the last decade, both pure TiO$_2$ and TiO$_2$ doped with other elements have been intensively investigated for use in optical sensors and electrochemical devices [1, 2, 3, 4]. Such TiO$_2$ materials are the most promising candidates for creating the next generation of gas sensors.

Gas sensors generally take the form of thick or thin films. The main advantages of thin-film-based sensors are their small size, simple construction, low cost, lightweight, and low power consumption. However, some work is still needed to increase their performance, such as improving their operating temperature range, stability, measurement accuracy, cost, ability to detect high gas concentrations, and reproducibility [2].

Thin TiO$_2$ films have been studied for use as carbon monoxide (CO) gas sensors [5, 6, 7]. Although TiO$_2$ is characterized as a semiconductor material, it is also the most corrosion-resistant metal, highly reactive, able to form a very stable oxide on its surface, and, of course, easy to find in Indonesia.
However, its sensor performance indicates that a dopant material is needed to control the sensor's sensitivity and selectivity [1, 3, 8]. Doping it with transition elements can strengthen the metal-oxygen interactions and weaken the metal-metal interactions [3, 9]. Gold (Au) is both unreactive and highly conductive and can thus be used as a good conductor [9, 10]. This study, therefore, investigates the use of gold oxide (Au$_2$O$_3$) to dope TiO$_2$ with the aim of improving CO gas sensor sensitivity and selectivity.

Thin films can be grown by either chemical or physical methods. Previous studies have reported the growth of thin TiO$_2$ films by physical methods such as ion implantation [10, 11], the sol-gel method [2, 4, 9, 12, 13, 14], DC Magnetron Sputtering [3], the facile in-situ method [3].

This research is a continuation of our previous work growing thin TiO$_2$ thin films on Si (100) substrates by the spin-coating method [15]. Other studies have used a 97% pure titanium (IV) isopropoxide precursor [TTIP, TiO(C$_2$H$_5$)$_4$] [16, 17, 18]. This study, however, takes the novel approach of using a TTIP buffer layer to reduce the lattice mismatch between the Si substrate and TiO$_2$ film. Also, the TiO$_2$ films are doped with powdered Au$_2$O$_3$ dissolved in tetrahydrofuran (THF,OC$_3$H$_7$), which again is a new approach.

The thin TiO$_2$:Au films are then characterized regarding their crystal structure, morphology, electrical properties, and optical properties at various deposition temperatures. This morphology features homogeneous nanometer-scale granules growing perpendicular to the substrate plane. This work is expected to result in thin TiO$_2$:Au films optimized for use as a base material in CO gas sensors.

### 2. Method

Thin TiO$_2$:Au films were grown on Si (100) substrate using spin-coating. First, the substrates were cleaned in acetone for 5 minutes, then with methanol for a further 5 min before being terminated with 10% hydrofluoric acid mixed with de-ionized water for 2 min to remove the natural layer of silicon dioxide (SiO$_2$) from the substrate surface. Finally, the substrates were dried by spraying them with nitrogen (N$_2$) gas (99.999% pure).

The precursors were prepared by dissolving the Au$_2$O$_3$ dopant in TTIP (97% pure, Sigma Aldrich Chemical Co., Inc.). Powdered Au$_2$O$_3$ (99.99% pure, Sigma Aldrich Chemical Co., Inc.) was used for doping and was dissolved in a THF solvent at a concentration of 0.2 moles/L to obtain a liquid dopant, which was then mixed with the TTIP solution in a 1:4 ratio. The precursor was then dripped in 0.2 mL drops onto the substrate, which had been attached to a disc spinner. This caused a thin TTIP buffer layer to form, coating the substrate. The spinner used in this study span at rates of (1500–3000) rpm for 1 min, producing films of different thickness depending on the rotation rate: higher rotation rates gave thinner films.

After growth, the thin film morphology and crystal structure were characterized by scanning electron microscopy (SEM) (Jeol JSM 6360LA) and X-ray diffraction (XRD) using Cu Ka ($\lambda = 1.5406$ Å) radiation (Philips PAN Analytical 'X' Pert Pro PW3071). The optical properties were characterized by the reflectance method, and the electrical properties were characterized by the I-V method, while the chemical composition for thin films was determined by the analysis of the energy dispersive x-ray (EDAXS) (Jeol JSM 6360LA).

### 3. Results and Discussion

Figure 1(a) shows an SEM cross-section image of a thin TiO$_2$: Au film deposited at 400°C. As shown in Figure 2(a), this exhibits three crystal planes: rutile (002) (R (002)), anatase (211) (A (211)), and Si (400). There are no clearly visible boundaries between the grains, implying that these boundaries have not formed properly [19] and thus suggesting that this film is in an amorphous phase. Figure 1(b) shows an SEM cross-section image of a TiO$_2$:Au film deposited at 450°C with a thickness of about 0.2 µm. As shown in Figure 2(b), the resulting grains exhibit rutile (200) (R (200)), A (211), R (002), and Si (400) crystal planes. Figure 1(c) shows an SEM cross-section image of a TiO$_2$: Au film deposited at 500°C with a thickness of about 0.4 µm. As shown in Figure 2(c), the resulting grains indicate the formation of single-phase R (002) and Si (400) crystal planes, suggesting that the film
grew epitaxially on the Si substrate. When the deposition temperature was raised to 550°C (Figure 1(d)), the resulting material exhibited R (200), R (002), and Si (400) crystal planes (Figure 2(d)). The film consisted of columnar granules, but the grain boundaries were not clearly visible, again implying that these boundaries had not formed properly [19] and suggesting that the film was in an amorphous phase.

Figure 1. SEM images showing the surface morphologies and cross-sections of thin TiO$_2$:Au films deposited at (a) 400°C, (b) 450°C, (c) 500°C, and (d) 550°C.

Figure 2 shows the characterization of the crystalline structure of TiO$_2$: Au thin films grown at temperatures (400-550)°C.

Figure 2. XRD patterns of thin TiO$_2$: Au films deposited at (a) 400°C, (b) 450°C, (c) 500°C, and (d) 550°C.

Based on the XRD analysis of the crystal structure, the size (diameter) of the films crystalline domains can be calculated using the Scherrer equation [20]:

$$D \approx K \frac{\lambda}{B \cos \theta_B}$$

(1)
where $D$ is the crystalline domain size (diameter), $\lambda$ is the X-ray wavelength, $\theta_B$ is the Bragg angle, $B$ is the full width at half maximum (FWHM) of the selected peaks, and $K$ is a material constant whose value is less than one. A value of $K \approx 0.9$ is generally used [20].

Table 1 shows the sizes of the crystalline domains in the TiO$_2$:Au films, calculated on the basis of the growth temperature and R (002) crystal planes. The R (002) plane is said to be the dominant plane, as it forms regardless of the growth temperature. The films were grown at 450 °C, 500 °C, and 550 °C had crystalline domain sizes of approximately 27.32, 20.38, and 32.86 nm, respectively. Based on these results, the film grown at 500°C had the smallest crystalline domain size and hence the highest porosity, suggesting that it would be the best choice for use in a CO gas sensor.

| $T_{\text{growth}}$ (°C) | FWHM (nm) | $D_{R(002)}$ (nm) |
|--------------------------|-----------|-------------------|
| 450                      | 0.0576    | 27.322            |
| 500                      | 0.0768    | 20.383            |
| 550                      | 0.048     | 32.858            |

The film's optical properties were also studied, as shown in Figure 3. The film band gap grown at 400, 450, 500, and 550 °C were 3.2, 3.4, 3.5, and 3.8 eV, respectively. The oscillations in the reflectance spectra are relatively uniform, indicating that the grains have uniform surface morphologies, as confirmed by the SEM images in Figure 1.

**Figure 3.** Reflectance spectra of thin TiO$_2$:Au films deposited at (a) 400 °C, (b) 450 °C, (c) 500 °C, and (d) 550 °C.

Figure 4 shows the $I$–$V$ characteristics of the TiO$_2$: Au film was grown at 500°C. This indicates a linear relationship between current and voltage, so Ag on TiO$_2$: Au is ohmic. Figure 5 shows SEM images of the surfaces of TiO$_2$:Au films deposited at (a) 450 C, (b) 500 C, and (c) 550 C. These films' Au contents, as obtained from energy-dispersive X-ray spectroscopy (EDS) characterization, were 0.08%, 0.03%, and 0.01%, respectively. Each film had a different average grain size. The 450°C film exhibits a higher degree of roughness, whereas the 550°C film has a smoother structure than the other two films.
Figure 4. Current-voltage ($I$–$V$) curve for Ag ohmic contacts on the thin TiO$_2$:Au film deposited at 500 °C

Figure 5 shows SEM images of the surfaces of TiO$_2$: Au films deposited at (a) 450 °C, (b) 500 °C, and (c) 550 °C. These films' Au contents, as obtained from energy-dispersive X-ray spectroscopy (EDS) characterization, were 0.08%, 0.03%, and 0.01%, respectively. Each film had a different average grain size. The 450 °C film exhibits a higher degree of roughness, whereas the 550 °C film has a smoother structure than either of the other two films.

Figure 5. SEM surface images of thin TiO$_2$:Au films deposited at (a) 450 °C, (b) 500 °C, and (c) 550 °C.

The roughness of the film surface can be influenced by four factors [21]: (1) the degree of lattice parameter mismatch between the film and substrate; (2) the level of impurities in the film; (3) the homogeneity of the nucleation point distribution on the substrate surface; and (4) the growth temperature. Of these four factors, the dominant effect on the roughness of the films shown in Figure 5 is due to the amount of Au used to form stoichiometric TiO$_2$:Au at the different deposition
temperatures. In this case, the Au atoms are regarded as impurities in the TiO$_2$ material. Films with more homogeneous crystalline grains will have smoother surface morphologies.

4. Conclusion
In this study, thin TiO$_2$:Au films have been grown using titanium (IV) isopropoxide [TTIP, Ti(O(C$_3$H$_7$)$_3$)] precursor. The Au$_2$O$_3$ was dissolved in THF (C$_6$H$_{12}$O) to a concentration of 0.2 moles/L and was then mixed with the TTIP solution in a 1:4 ratio. The thin TiO$_2$:Au film deposited at 400 °C showed rutile (002) (R (002)) and anatase (211) (A (211)) crystal planes, whereas the 450 ºC films showed rutile (200) (R (200)), A (211), and R (002) planes, the 500 ºC films showed only R (002) planes (indicating that it grew epitaxially), and the 550 ºC films showed R (200) and R (002) planes. The crystalline domain sizes were around 27.32, 20.38, and 32.86 nm for the 450 ºC, 500 ºC, and 550 ºC films, respectively. The 500 ºC films thus had the smallest crystalline domain size and hence the highest porosity. The band gaps were 3.2, 3.4, 3.5, and 3.8 eV for the 400 ºC, 450 ºC, 500 ºC, and 550 ºC films, respectively. The film's linear I–V characteristics indicated ohmic behavior for Ag. EDS characterizations indicated that the Au contents were 0.08%, 0.03%, and 0.01% for the 450 ºC, 500 ºC, and 550 ºC films, respectively. The surface morphologies showed that they were composed of nanometer-scale granules. Based on this research results, TiO$_2$: Au thin film grown at a temperature of 500 °C is very potential to be used as a primary material for making CO gas sensors.

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