Characterization of Co:TiO₂ Thin Film Grown by MOCVD Technique

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Abstract. The Co:TiO₂ thin film was grown on n-type Si(100) by metal organic chemical vapor deposition (MOCVD) technique. The film’s growth parameters are as follow: substrate temperature of 450°C, bubbler temperature of 70°C, reactor chamber pressure of 2 militorr, and growth time of 2 hours. We characterized the structure of film by X-ray Difractometer (XRD), the morphology was characterized by Scanning Electron Microscope (SEM), and the fraction of Co atoms in TiO₂ was characterized by Energy Dispersive x-ray Spectroscopy (EDS). The XRD result shows that the Co:TiO₂ thin film is a anatase phase crystal dominated by A(213) orientation. Using Warren-Scherrer’s formula, the average grain size of Co:TiO₂ is 169 nm. The SEM result shows that the Co:TiO₂ film surface is quite coarse with relatively homogeneous grain shape. the average growth rate of Co:TiO₂ film is 0.78 μm/h. In addition, the EDS result shows that Co atoms have been incorporated into the film replacing a portion of the Ti atoms by 0.085%.

1. Introduction
Titanium dioxide, TiO₂, is one of semiconductor materials that studied for many purposes. Because of its properties, TiO₂ can be applied in various fields [1]. TiO₂ have been applied in optical components [2] and photocatalysis [3] and have a high potential application in as a nonlinear optic material, sensitive solar cell, and dynamic random access memory [4]. TiO₂ also have an interesting properties for spintronic application. TiO₂ doped by Co atoms shows the ferromagnetic properties at room temperature [5].

TiO₂ can be grown on a substrate by various methods such as molecular beam epitaxy (MBE) [5], DC and RF Sputtering [6], atomic layer deposition (ALD) [7], pulsed laser deposition (PLD) [8], and metal organic chemical vapor deposition (MOCVD) [1], [9], [10]. Compared to other methods, MOCVD has many advantages, i. e., film can be grown epitaxial, film can be deposited selectively, and film can be grown by simple growth parameter [10].

In this paper, we focused on a structural a morphology characterization of TiO₂ doped by Co atoms (Co:TiO₂).

2. Experimental Details
The Co:TiO₂ was grown on n-type Si(100) by MOCVD technique. Materials used in this experiment are Ti(C₃H₇O)₄ (titanium (IV) isopropoxide or TTIP), Co(C₁₁H₁₉O₂)₃ (Cobalt tris 2,2,6,6-tetramethyl -
3,5-heptanedionato or Co(TMHD)$_3$, and C$_4$H$_3$O (tetrahydrofuran or THF). TTIP 99.99% from Sigma Aldrich Chemical Co., Inc. was used as TiO$_2$ precursor, Co(TMHD)$_3$ from Strem Chemical Inc. was used as Co precursor, and THF 99.99% from Sigma Aldrich Chemical Co., Inc., was used as Co solvent.

The process of the film growth was done in the following way. The vaporized tube containing the 20 mL TTIP and 900 mg Co(TMHD)$_2$ (in 20 mL THF) were heated to a constant temperature of 70°C. TTIP and Co(TMHD)$_2$ vapor pressurized 20 kPa was driven by argon gas at a rate of 70 sccm to the reactor chamber through a connecting pipe. In the reactor chamber, n-type Si(100) substrate has been pasted at molybdenum disk for the film growth process at temperature of 450°C. The total reactor pressure was 2 millitorr. The growth time was 2 hours.

Characterization of Co:TiO$_2$ thin films was done using XRD, SEM, and EDS. XRD was used to find out the structure and orientation of the Co:TiO$_2$ film. In this case, XRD uses Cu K$_\alpha$ radiation at a wavelength of 1.54060 angstrom (Philips PW3710). SEM (JEOL type JSM-6510LA) was used to characterize the surface morphology and the thickness of Co:TiO$_2$ film. Meanwhile, EDS was used to measure the fraction of Co atoms in TiO$_2$.

3. Results and Discussion

3.1. XRD

Figure 1 shows the XRD result of Co:TiO$_2$ thin film. There are two diffraction peaks that appear at $2\theta =$ 55.00 degree and $2\theta =$ 61.70 degree. These peaks belongs to anatase phase, i.e., A(211) and A(213), respectively. Intensity of A(213) is more higher than A(211). Therefore, it can be revealed that the Co:TiO$_2$ thin film is an anatase phase crystal dominated by A(213) orientation.

Referring to the standard diffraction peak for TiO$_2$, the peak of A(213) is present at $2\theta =$ 62.119° and A(211) at $2\theta =$ 55.060°. This means that there is a diffraction peak shift for Co:TiO$_2$. Such a shift may occur because the bit doping of Co atoms in TiO$_2$ films change the film lattice constants.

The size (diameter) of the crystals was obtained by using the following Warren-Scherer equations [11]:

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

where D is the diameter of the crystal, $\lambda$ is X-ray wavelength, $\theta$ is the angle of Bragg diffraction, B is half of FWHM (full-width at half-maximum) of the selected peak, and K is the constant. Generally, the value of K chosen is 0.89.
By substituting the value of $K = 0.89, \lambda = 1.5046$ angstrom, $B = 0.000955$ rad (for $2\theta = 61.70$ degree), and $\theta = 0.53804066$ rad into the Warren-Scherrer equation, the obtained crystalline diameter is 169 nm. The size of this crystal diameter indicates that the MOCVD method has successfully grown film by grain size in the order of nanometers.

3.2. SEM
The surface morphology and cross section of the film was characterized by SEM. Figure 2(a) shows the SEM image of the Co:TiO$_2$ film surface. It can be seen that, in general, all surfaces of the film appear to be quite coarse with relatively homogeneous grain shape.

The SEM cross-sectional image of the film is shown in Figure 2(b). The film is composed of crystal-like grains of crystal. In the substrate-film interface, the crystal grains appear irregular. This is because the growth of crystals is competitive so that the grains formed depend on the diffusion process of the surfaces of the precursor atoms. This competitive crystal growth is due to the diverse orientation of crystal grains that are bound to the surface of the substrate [12].

For 2 hours growth of the Co:TiO$_2$ film, the average thickness of the film is 1.56 um. This shows that the average growth rate of the Co:TiO$_2$ film is 0.78 $\mu$m/h.

Figure 2. SEM image of Co:TiO$_2$ thin film: (a) surface and (b) cross-section.

3.3. EDS
EDS characterization was performed to determine the composition of the atoms of the film. Figure 3 shows the EDS graph of the Co:TiO$_2$ film. Based on the tabulation of the percentage of atoms, it is obtained that O: Ti: Co = 64.84: 35.13: 0.03. Referring to this comparison, the fraction of Co atoms to Ti is $0.03 : 35.13 \times 100\% = 0.085\%$. Thus, the Co atoms have been incorporated into the film replacing a portion of the Ti atoms by 0.085%.

4. Conclusion
The Co:TiO$_2$ thin film have been successfully grown by MOCVD technique. XRD result show that the Co:TiO$_2$ thin film is an anatase phase crystal dominated by A(213) orientation. From the SEM image, in general, all surfaces of the film appear to be quite coarse with relatively homogeneous grain shape, the film is composed of crystal-like grains of crystal, and the average growth rate of Co:TiO$_2$ film is 0.78 $\mu$m/h. EDS results show that Co atoms have been incorporated into TiO$_2$ film.
Figure 3. EDS Result of Co:TiO\textsubscript{2} thin film

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