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# DEVELOPMENT OF $TiCoO_2$ SEMICONDUCTOR FILM

**M. N. Indro, A. Kartono, M. Kurniati and B. Safitri**
*Department of Physics, Institute of Agriculture Bogor*
*Kampus IPB Darmaga, Bogor*

## ABSTRACT

**DEVELOPMENT OF $TiCoO_2$ SEMICONDUCTOR FILM**. Good quality of $TiO_2$ and $TiCoO_2$ films may be developed using Metal Organic Chemical Vapor Deposition (MOCVD) technique at the temperature around 450 $^0$C on silicon substrate. The X-Rays Diffractometer (XRD) investigation on their crystals structure has shown that the samples resulted through this technique are almost as homogenously single crystals. Observation using Scanning Electron Microscope (SEM) technique on their surfaces has shown that the films have a constant thickness around 0.7mm and smooth surfaces. Further investigation on their magnetic behavior results in magnetic hysteresis at the coercive field around 80-150 Oe, with the largest remanent magnetization about 150-250 emu/cm$^3$.

***Key words*** : $TiCoO_2$, MOCVD, magnetic hysteresis

## ABSTRAK

**PENGEMBANGAN FILM SEMIKONDUKTOR $TiCoO_2$** . Film $TiO_2$ dan $TiCoO_2$ yang berkualitas tinggi dapat ditumbuhkan pada substrat siliKon dengan menggunakan teknik *Metal Organic Chemical Vapor Deposition* (*MOCVD*) pada suhu sekitar 450 $^0$C. Pengujian cuplikan dengan *X-Rays Diffractometer* (*XRD*) meperlihatkan bahwa film yang dihasilkan mempunyai struktur kristal yang homogen dan hampir berbentuk krital tunggal. Pengamatan permukaan film menggunakan *Scanning Electron Microscope* (*SEM*) memperlihatkan bahwa ketebalan film hampir konstan sekitar 0,7 mm, permukaannya halus dan rata. Pengamatan pada karakteristik magnetiknya menunjukkan bahwa film yang dihasilkan mengalami histerisis magnetik pada medan magnet *coercieve* antara 80 Oe sampai dengan 150 Oe dengan *magnetic remanent* antara 150 emu/cm$^3$ sampai dengan 250 emu/cm$^3$.

***Kata kunci*** : $TiCoO_2$, *MOCVD*, *magnetic hysteresis*

## INTRODUCTION

Investigations on ferromagnetic semiconductor materials has been an interesting topic for many scientists since the materials are suitable for composing spintronic devises such as spin transistor, LED, and a nonvolatile storage. [1,2]

Semiconductor thin film composed of GaAsMn has been the first ferromagnetic semiconductor material found, even though its ferromagnetism appears when the material cooled down to the temperature 110 K [3]. It is realized that this material is not recommended yet for practical applications since the operating temperature is far from the room temperature. Oxide ferromagnetic semiconductor $TiCoO_2$ has an opportunity to be a favorable material that satisfies the need. It has been found that a ferromagnetism phenomenon of $TiCoO_2$ crystals appears at room temperature [4]. Several techniques on developing the $TiCoO_2$ crystals have been carried out to produce good quality of the material. MOCVD is a good technique in developing $TiCoO_2$ thin film since the stability of the process will result in a high quality of material [5].

Following the technique suggested by Jones, this experiment was carried out to deposit $TiCoO_2$ thin films on Si(100) substrates. The temperature of deposition was varied between the values of 400 $^o$C to 550 $^o$C in oxygen ambient.

The crystal structures of the samples then were investigated using XRD. The surface of the films were observed using SEM and the ferromagnetism characteristic was observed using Vibrating Sample Magnetometer (VSM).

It is expected that the MOCVD processes at the temperatures between 400 $^o$C-550 $^o$C will produce good quality of $TiCoO_2$ crystals.

The magnetic properties and the smoothness of the $TiCoO_2$ film surfaces are influenced by the depositing temperatures.

## EXPERIMENTAL METHOD

Materials needed for depositing $TiCoO_2$ crystal on Si substrate are as the following ; plates of single crystal Silicon (100), precursor of organometalic titanium (IV) isopropoxide [Ti{OCH($CH_3$)$_2$}$_4$] 99.99 %, methanol, acetone, de-ionized water, tris (2,2,6,6-tetramethyl-3,5-heptanedionato) cobalt (III) 99 %, Co(TMHD)$_3$, tetrahydrofuran (THF, $C_4H_8O$), HF, Argon gas, and $O_2$ gas.

The equipments used in this experiment are; MOCVD reactor completed with vacuum pump and power supply, XRD (Philips PW 3710), SEM (Jeol JSM 6360LA), VSM (Oxford).

Several pieces of Si (100) substrate were carefully cleaned using methanol ($CH_2OH$) and acetone around 5 minutes. After that the substrates were cleaned again using a solution of 10 % HF and de-ionized water and finally were dried using nitrogen gas.

Before depositing $TiCoO_2$ films, we deposited $TiO_2$ on a Si substrate. This is a trial process done in order to check if the MOCVD procedure is working well or not. After knowing that the method is right we then deposited the $TiCoO_2$ films using the same method.

In order to deposit a $TiO_2$ film a clean Si substrate was mounted on the depositing vacuum chamber. The liquid of [Ti{OCH($CH_3$)$_2$}$_4$] was put into the bubbler and heated to its vaporizing temperature. Argon gas then flown to carry the Ti vapor to the depositing chamber. At the same time oxygen gas also flown to the depositing chamber. This process of deposition held around 120 minutes in a constant temperature and pressure. The $TiO_2$ film deposited then observed using XRD.

The trial process produced only one $TiO_2$ film. It was surprising that this film is in a good quality since the XRD observation showed that the film is almost homogenously $TiO_2$ structure as seen in the Figure 1. This means that MOCVD is a good method for developing $TiO_2$ film on Si substrate.

Since the method is convincingly correct then we have a strong confidence to deposit $TiCoO_2$ using the MOCVD technique. In order to deposit $TiCoO_2$ the process was repeated by adding solution of Co(TMHD)$_3$, 0.2 M into another bubbler. The Co(TMHD)$_3$, 0.2 M is also heated to its vaporizing temperature. Argon gas then flown to carry the Ti vapor and also Co vapor to the depositing chamber and mixed with the oxygen gas. The $TiCoO_2$ vapor then deposited on the Si substrate at a certain temperature.

The last process above then was repeated in different temperatures to produce four samples as shown in the Table 1 as the following. Each deposited $TiCoO_2$ sample was then investigated using XRD, SEM, and VSM.

**Table 1.** Depositing temperature of $TiCoO_2$ crystals done for around 2 hours, in a constant pressure.

| Sample ($TiCoO_2$) | Depositing Temperature |
|---|---|
| A | 400$^o$C |
| B | 450$^o$C |
| C | 500$^o$C |
| D | 550$^o$C |

## RESULTS AND DISCUSSION

The $TiO_2$ sample produced through this experiment is not being discussed here since the depositing $TiO_2$ sample is only to confirm if the method is right or not. Indeed the method is satisfying since the $TiO_2$ deposited on a Si substrate has been a good quality crystal as shown in the Figure 1.

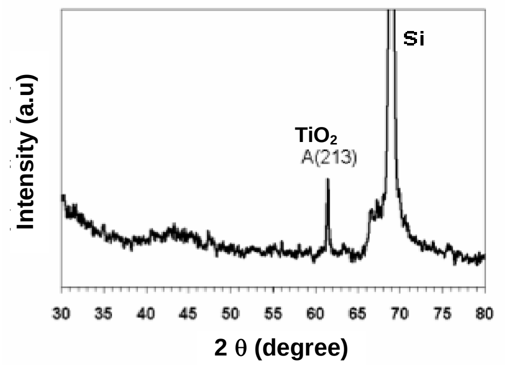


**Figure 1.** XRD pattern of $TiO_2$/Si film produced at 450 $^o$C showing anatase structure at around $2\theta = 62^o$

The samples resulted from the deposition of $TiCoO_2$ on the Si substrates are then been observed to know their crystal structures, their surfaces and their magnetization responses.

## Crystal Structure

Observation using XRD on the structure of all the $TiCoO_2$ samples result in diffraction patterns as shown in the Figures 2, 3, 4, and 5. The Figure 2 shows that the peak of diffraction pattern of the A sample appears at the angle around $2\theta = 62^o$. It is believed that the peak is associated with the (213) anatase tetragonal structure as shown by previous researcher.[6] The appearance of single peak in the Figure 2 is also believed that the $TiCoO_2$ of the A sample is almost as a homogenous single crystal.

It is clearly shown in the Figure 3 that the diffraction pattern of the B sample is similar with that of the A pattern. This means that raising the depositing temperature from 400$^o$C to 450$^o$C did not result any significant change in its crystal structure even though the thickness of the sample has increased from 0.7 mm to be 0.8 mm. This means that the optimum depositing temperature is between 450$^o$C and 600$^o$C. [7]

Setting the depositing temperature at 500$^o$C for the C sample and 550$^o$C for the D sample result in different XRD pattern. The Figure 4 (for the C sample) shows two

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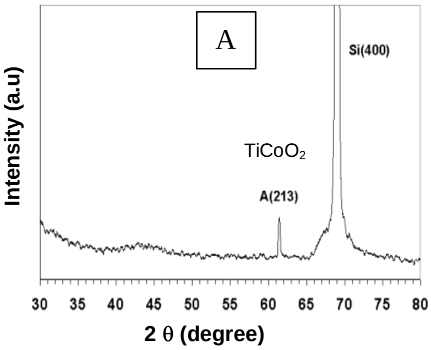


***Figure 2.*** XRD pattern of $TiCoO_2$/Si film (A sample) produced at 400 °C.

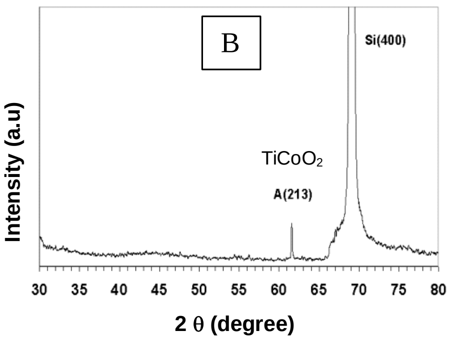


***Figure 3.*** XRD pattern of $TiCoO_2$/Si film (B sample) produced at 450 °C.

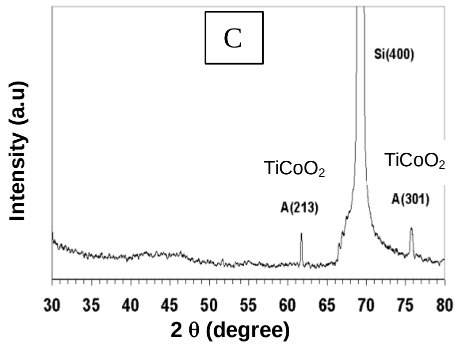


***Figure 4.*** XRD pattern of $TiCoO_2$/Si film (C sample) produced at 500 °C.

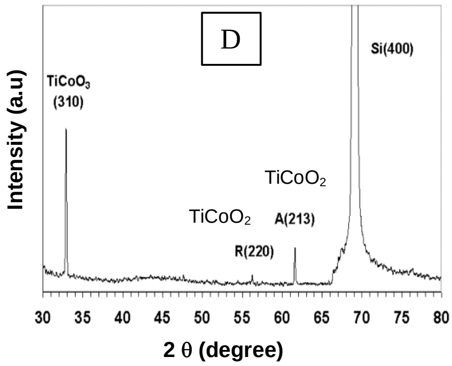


***Figure 5.*** XRD pattern of $TiCoO_2$/Si film (D sample) produced at 550 °C.

peaks in the XRD pattern, that are (213) at the value 2θ around 63 ° and (301) at the value 2θ around 76 °. It is seemed that the crystal structure of the C sample has been developed as a polycrystalline, at least there are two block of crystals with different orientation.

The Figure 5 (for the D sample) shows three peaks in the XRD pattern, that are (213) at the value 2θ around 62 °, (220) at the value 2θ around 56 ° and (310) at the value 2θ around 33 °. This is more surprising that the further increment in depositing temperature result in reducing the homogeneity of the deposited structure. It is seen that there are more structures and crystalline orientations appear on the XRD pattern. The peak at around 56 ° is belonging to a rutile structure. This may be predicted that the rutile structure grows in a temperature higher than 500 °C.

## Surface Photograph

The observation using SEM was carried out on the surface of all samples. The photographs of the samples are magnified 30000 times as shown in the Figures 6, 7, 8 and 9.

The Figure 6 shows the SEM photograph of the A sample. It is clearly shown that the Si surface has been covered by $TiCoO_2$ film with the thickness of around 0.7 μm. The orientation of the surface structure is almost as a homogenous as a bulk and this confirmed by the

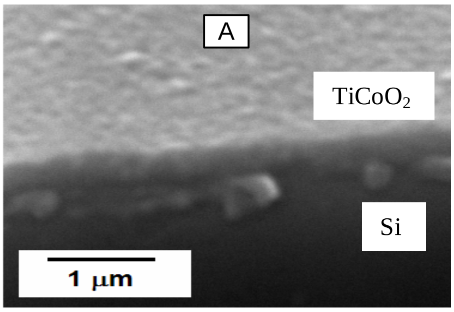


***Figure 6.*** A surface photograph of $TiCoO_2$/Si film (A sample) deposited at 400 °C (produced using SEM, magnified 30000 times).

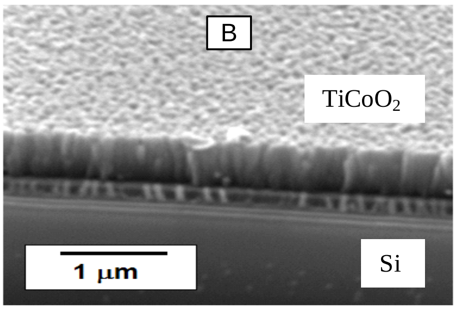


***Figure 7.*** A surface photograph of $TiCoO_2$/Si film (B sample) deposited at 450 °C (produced using SEM, magnified 30000 times).

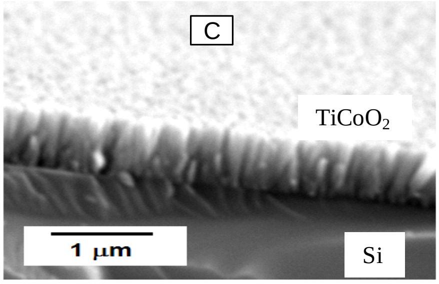


***Figure 8.*** A surface photograph of $TiCoO_2$/Si film (C sample) deposited at 500 °C (produced using SEM, magnified 30000 times).

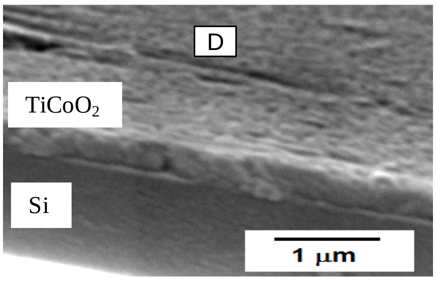


***Figure 9.*** A surface photograph of $TiCoO_2$/Si film (D sample) deposited at 550 °C (produced using SEM, magnified 30000 times).

XRD pattern (the Figure 2). In the Figure 7 shown that the surface of the B sample is also as a homogenous bulk, even though the surface seemed concise of smaller grains compare with the surface of the A sample.

Further temperature increments from 450 °C to 500 °C and 550 °C result in less homogenous surfaces as shown in the Figure 8 and Figure 9. These diagrams show also several cracks in the surface the C and D samples. The inhomogeneous surfaces have also been proved by the XRD data show the appearance of more than one crystalline orientation on those structures.

## Hysteresis Curve

Observation using VSM was carried out in order to see the ferromagnetism characteristic of the samples. The results were shown in the Figure 10, 11, 12 and 13 respectively for the A, B, C and D samples. All of the samples show their magnetization response when an external magnetic field in order of $10^3$ Oe was applied. The lowest response is shown by the A sample, while the highest response is shown by the B sample even though the C and D samples showing similar response with the B sample.

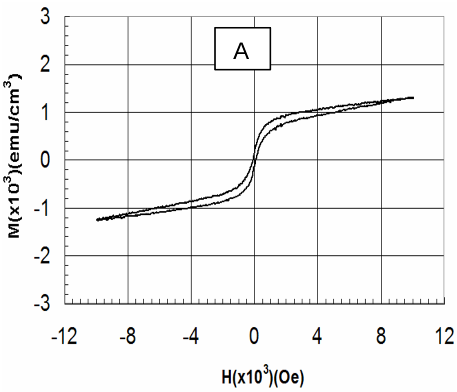


***Figure 10.*** Hysteresis curve of $TiCoO_2$/Si film deposited at 400 °C (produced using VSM).

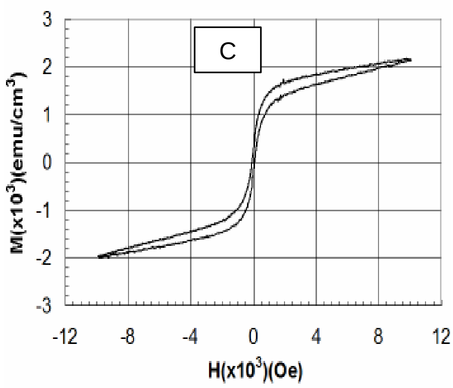


***Figure 12.*** Hysteresis curve of $TiCoO_2$/Si film deposited at 500 °C (produced using VSM).

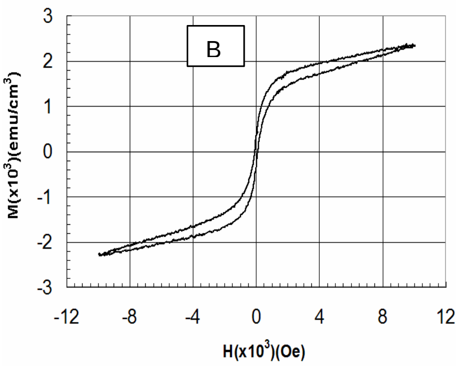


***Figure 11.*** Hysteresis curve of $TiCoO_2$/Si film deposited at 450 °C (produced using VSM).

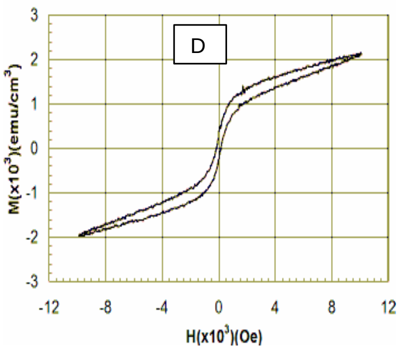


***Figure 13.*** Hysteresis curve of $TiCoO_2$/Si film deposited at 450 °C (produced using VSM).

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The magnetic characteristics observed (demagnetizing factor, remanent magnetization and coercive field) of the samples shown in the Table 2.

***Table 2.*** Magnetic characteristics.

| Sample | Td ($^{o}$C) | N | Mr (emu/cm$^{3}$) | Hc (Oe) |
|---|---|---|---|---|
| A | 400 | 0,718 | 150 | 80 |
| B | 450 | 0,394 | 250 | 100 |
| C | 500 | 0,410 | 220 | 80 |
| D | 550 | 0,722 | 250 | 148 |

Td = depositing temperature
N = demagnetizing factor
Mr = remanent magnetization
Hc = coercive field

The hysteresis curves and the data in the Table 2 have confirmed that all of the samples are indeed ferromagnetic materials. In the Table 2 is also shown that the B and C samples have smaller demagnetizing factor than the A and D samples. This means that B and C samples are easier to be magnetized than the A and D samples, and of course the ferromagnetic quality of the B and C samples should be better than that of the A and D samples. It may be suggested that in order to develop $TiCoO_2$ ferromagnetic films the optimum depositing temperature is between 450$^{o}$C to 500$^{o}$C.

However if the intention is developing a permanently magnetic material, it is suggested that sample D is the best among the four samples. The D sample has big value of remanent magnetization and the biggest value of coercive magnetic field. A Material that has big values of Mr and Hc (as the D sample) is called as hard magnetic material, while that has small values of Mr and Hc (as the A sample) is called as a soft magnetic material.

## CONCLUSIONS

It has been proofed that the MOCVD is a good technique in developing $TiO_2$ and $TiCoO_2$ crystals. Investigation on the crystal structure of the samples using XRD technique have shown that the $TiO_2$ and $TiCoO_2$ exhibit good quality crystals. The appearance of only one peak in around $2\theta = 62\,^{0}$ is associated that the crystals are almost homogenously structure as single crystals. However increasing of the depositing temperature to 550 $^{0}$C results in less homogenous structure of the crystals.

Investigation using SEM technique on the surface of the samples showing that the thickness and the smoothness of the surfaces. It is shown that the depositing temperature between 400 $^{0}$C-500 $^{0}$C results smooth surfaces with similar thickness around 0.7 mm. And increasing of the depositing temperature to 550 $^{0}$C results in less smooth surfaces of the crystals.

The magnetization curves resulted from VSM investigations have shown that all of the sample showing magnetism hysteresis at room temperature. The appearance of magnetism hysteresis means that the $TiCoO_2$ material has an opportunity to be used as magnetic data storage though their storage capacity are not quite high. The highest remanent magnetization of the hysteresis curve found when the depositing temperature is set up to 450 $^{0}$C and 550 $^{0}$C.

## REFERENCES

[1]. H. OHNO and T. DIETL., *MRS Bulletin*, **28** (2003)

[2]. S.A. CHAMBER and Y.K. YOO, *MRS Bulletin*, **28** (2003)

[3]. H. OHNO, M. FUMIHIRO and O.YUZO, *Semiconductor Spin Electronics*. JSAP International No.5, (2002)

[4]. Y. MATSUMOTO, M. MAKOTO, S. TOMOJI, H. TETSUYA, F. TOMOTERU, K. MASASHI, A. PARHAT, C. TOYOHIRO, K. SHIN-YA, and K. HIDEOMI, *Room-Temperature Ferromagnetism in Transparent Transition Metal-Doped Titanium Dioxide*. **291** (5505), (2001) 854-546

[5]. A.C. JONES and P. O'BRIEN, *CVD of Compound Semiconductors: Precursors Synthesis, Development and Applications*, VCH Verlagsgesellschaft mbH, Germany, (1997)

[6]. J. GUNLAZUARDI, Photo Catalysis on $TiO_2$ Surface, *Prosiding of 2$^{nd}$ National Seminar on Physical Chemistry*, Serpong, (2001)

[7]. Z. LU, J. K. TRUMAN, M. E. JOHANSSON, D. ZHANG, C. F. SHIH and G. C. LIANG, *Appl. Phys. Lett.* **67**, (1995) 71