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Magnetic Properties of Co: TiO_2 Thin Films with Low Cobalt Concentration

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ABSTRACT

The magnetic properties of Co: TiO_2 thin film with low cobalt concentration was investigated. The Co: TiO_2 thin films were grown on n-type Si (100) substrate using metal organic chemical vapour deposition technique. The cobalt concentration in the Co: TiO_2 thin film was determined using energy dispersive X-ray spectrometer and the magnetic properties of the film was determined using a vibrating sample magnetometer. The energy dispersive X-ray spectrometer results show that the cobalt concentration in Co: TiO_2 thin films (denoted by x) are $x = 0$, $x = 0.2\%$, $x = 0.3\%$, $x = 0.7\%$, and $x = 1.1\%$. The vibrating sample magnetometer results indicate that each (exclude $x = 0$) after film exhibits ferromagnetic properties at room temperature. Saturation magnetisation of Co: TiO_2 thin film varies from 1,0 emu/cm^3 to 4,4 emu/cm^3 and increases as the cobalt concentration in Co: TiO_2 thin film increases. On the other hand, magnetic coercivity of Co: TiO_2 thin films varies from 4 mT to 12 mT and decreases as the concentration of cobalt in Co: TiO_2 thin film increases.

Keywords: Co: TiO_2, magnetic properties, metal organic chemical vapour deposition, thin film

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INTRODUCTION

Cobalt-doped TiO_2 (Co: TiO_2) thin film began to attract attention since Matsumoto et al., (2001) reported that it showed ferromagnetic properties above room temperature (Matsumoto et al., 2001). The film was grown using PLD (pulsed-layer deposition) methods on $LaAlO_3$(001) and $SrTiO_3$(001) single crystal substrate. The emergence of hysteresis in the magnetisation curve indicates ferromagnetic properties of film at room temperature. Matsumoto et al. obtained

METHODS

The growth of Co:TiO_2 thin film is divided into three stages: preparatory, growth, and cooling. The preparatory phase consists of preparing the precursor material and washing the substrate. The tube is filled with a mixture of 20 mL of TTIP and 20 mL of Co(TMHD)$_3$. Earlier, 900 mg powder Co(TMHD)$_3$ was dissolved in 20 mL of THF to obtain the precursor Co in liquid form. This is only done in the initial setup or if the precursor material in the evaporator tubes has been exhausted.

Washing substrate is a first stage towards the process of growing the film. The silicon substrate was washed using liquid acetone for 10 minutes, then with methanol for 10 minutes, and terminated by etching it with a mixed solution of HF de-ionised water for five minutes. Washing the substrate by acetone and methanol aims to remove organic materials that may be present on the substrate surface. Meanwhile, substrate is washed using HF solution mixed with de-ionised water aimed at etching the silicon oxide that may occur on the surface of the substrate. Subsequently, the substrate is dried by spraying N_2 gas with technical purity of 99.999%. After that, the substrate is inserted into the reactor chamber and placed on molybdenum heating plate using silver paste adhesive.

The second stage is the growth of thin films using MOCVD technique. In this experiment, the precursor material contained in an evaporator tube is heated to a temperature of 100°C for the growth of the Co: TiO_2 film. The vapour is then driven by argon gas at a rate of 70 sccm to the reactor chamber where the substrate is located. The substrate is heated at a constant temperature. Total reactor pressure is about 10^{-3} torr. The growth time is 120 minutes for each film.

The third or final stage is cooling. Cooling stage is after the film growing is completed. Cooling to the room temperature is done at a rate of 200°C/h.

Co Concentration and Magnetic Measurement

The concentration of Co atom in Co: TiO_2 was measured by energy dispersive X-ray spectrometer or EDS (JEOL tipe JSM-6510LA) while the magnetic properties of Co: TiO_2 thin films was measured using the vibrating sample magnetometer or VSM (Oxford 1.2 T). Magnetic properties were measured at room temperature of 300 K. In addition to Co: TiO_2 films, the magnetic properties of TiO_2 films were also measured.

RESULTS AND DISCUSSIONS

Five thin film samples were grown and the Co atom concentration in the film was measured using EDS. The results showed that the four samples had concentrations of Co atoms, each for $x = 0\%$ (pure TiO_2, without Co atoms) $x = 0.2\%$, $x = 0.3\%$, $x = 0.7\%$, and $x = 1.1\%$. Each sample was measured using VSM magnetic properties.

Figure 1 shows the relationship between magnetisation and external magnetic field (M-H curve) of the Si substrate (Figure 1(a)) and TiO_2 thin films (Figure 1(b)). In Figure 1(a), the greater the value of H, the smaller the value of M. This shows that Si substrate has the negative magnetic susceptibility (χ = gradient of the curve is negative) and hence, the Si substrate has diamagnetic properties. This is due to the non-cooperative behaviour of the electron orbit when there is an external magnetic field. Diamagnetic materials are composed of atoms that do not have a net magnetic moment, i.e., all orbits are filled and there are no unpaired electrons.

On the other hand, in Figure 1(b), the greater the value of H, the greater the value of M. This shows that TiO_2 thin film has positive magnetic susceptibility (χ = gradient of the curve is positive). In other words, the TiO_2 thin film has paramagnetic properties. This shows that each TiO_2 atom has a permanent dipole moment generated by a mutually exclusive process and which is not perfect from an orbital magnetic moment and/or electron spin. When there is no external magnetic field, the magnetic moments of atoms are randomly oriented. When an external magnetic field is given, the magnetic moments of the atoms are parallel, by means of rotating, so the relative permeability is increased to greater than 1. Thus, the total magnetic moment continues to increase linearly with increasing external magnetic field. The paramagnetic properties of TiO_2 films can be derived from the sub-stoichiometric oxygen generating paramagnetic ions Ti^{3+} and/or the presence of undesirable impurities (Sangaletti et al., 2006).

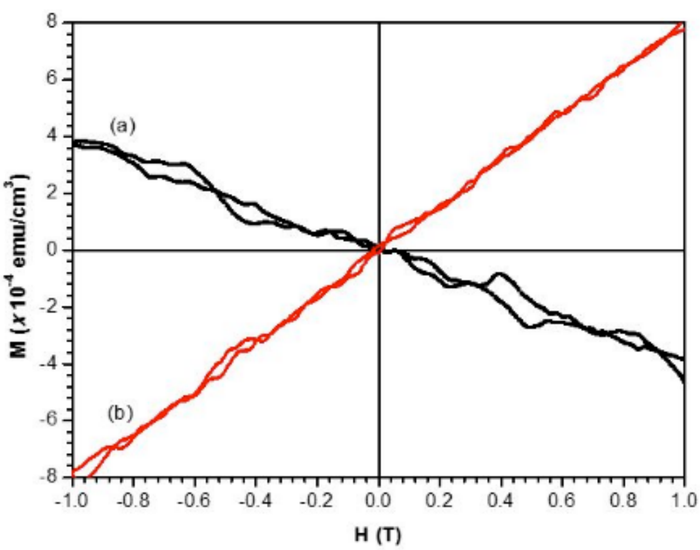

Figure 1. M-H curve for: (a) Si substrate and (b) TiO_2

M-H curves of Co: TiO_2 thin films for Co atom concentrations of x = 0.3% and x = 1.1% is shown in Figure 2. The curve does not show the existence of saturation magnetisation. Instead, magnetisation actually appears to increase almost linearly when the external magnetic field increases. This occurs due to the paramagnetic properties effect of TiO_2 which is not shown on the graph.

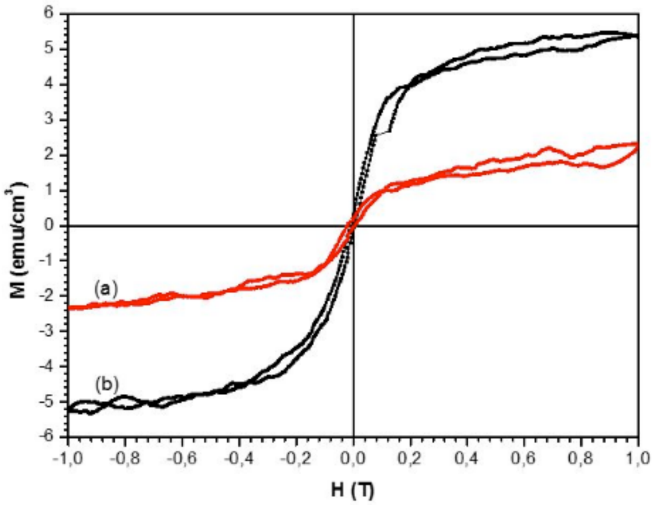

Figure 2. M-H curves of Co: TiO_2 thin films for (a) x = 0,3 % and (b) *x* = 1,1 %

Referring to the Zajac theory, the emergence of the M-H curve as shown in Figure 2 shows the contribution of the paramagnetic effect of TiO_2. Measurable magnetisation is a combination of effects from the ferromagnetic properties of Co and paramagnetic properties of TiO_2. Therefore, the M-H curve is then decomposed into two components, i.e., ferromagnetic, FM, and paramagnetic PM (Zajac et al., 2003).

Figure 3 shows the decomposition results of the M-H curve of the Co: TiO_2. thin film for *x* = 1.1% (decomposed from Figure 2(b)). Figure 3(a) is the total magnetisation, a combination of ferromagnetic contributions of Co and TiO_2. paramagnetic contribution. After deducting the paramagnetic effect of TiO_2. (Figure 3(b)), a hysteresis curve was obtained which shows the ferromagnetic properties of Co: TiO_2. thin film (Figure 3(c)). Thus, it appears that the M-H curve indicates saturation.

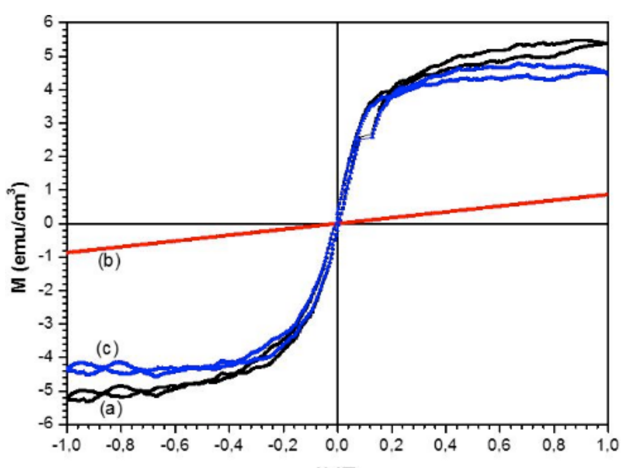

Figure 3. Decomposition results of the M-H curve of Co: TiO_2 thin films for *x* = 1,1 %: (a) before decomposition, (b) TiO_2 paramagnetic effect, and (c) after decomposition

Figure 4 shows the M-H curve of the Co: TiO_2 thin films for *x* = 0.2% and *x* = 0.7%. It is clear there is diamagnetic effect of the substrate on the Co: TiO_2 thin films. Diamagnetic si substrate effect on M-H curve is common, readable by the results of VSM on the thin film. Therefore, to get the curve M-H thin film that actually, the results of a VSM test reading corrected (reduced) in advance by the effect.

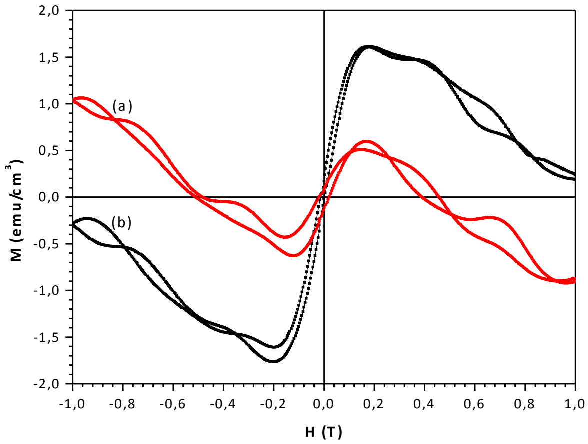

Figure 4. M-H curves of Co: TiO_2 thin films for (a) *x* = 0,2 % and (b) *x* = 0,7 %.

Figure 5 shows the M-H curves of Co: TiO_2 thin films for *x* = 0.7%, before (Figure 5(a)) and after being corrected (Figure 5(c)) by the diamagnetic effect of the substrate (Figure 5(b)). In the figures, it appears that M-H curve of the film form a ferromagnetic hysteresis as in general.

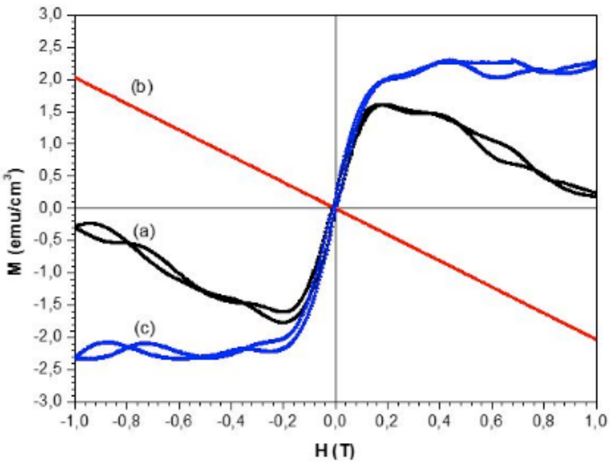

Figure 5. M-H curves of Co: TiO_2 with *x* = 0,7 %: (a) before corrected, (b) diamagnetic effect of substrate, and (c) after corrected

After paramagnetic or diamagnetic effect is subtracted from the M-H curves, overall, the hysteresis curve of Co: TiO_2 thin films are shown in Figure 6. The films are measured at room temperature. The existence of hysteresis at room temperature shows that the films Co: TiO_2 grown are ferromagnetic at room temperature.

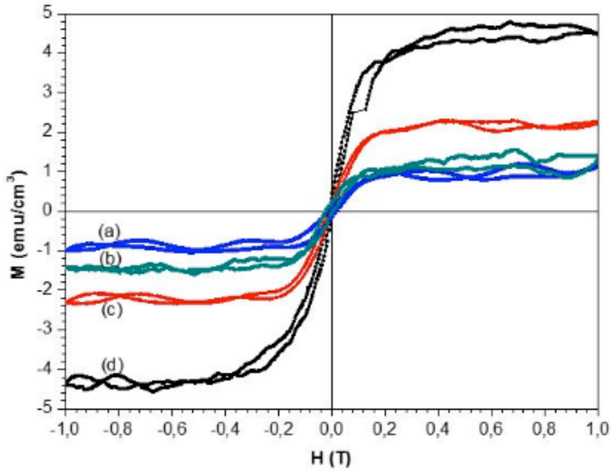

Figure 6. Ferromagnetic properties of Co: TiO_2 thin films for (a) $x = 0.2$ %, (b) $x = 0.3$ %, (c) $x = 0.7$ %, and (d) $x = 1.1$ %

From the M-H curve, mathematically, the magnetic coercivity value is the value of H when M = 0, denoted by H_c. Therefore, based on Figure 6, magnetic coercivity values of Co: TiO_2 thin films produced in this study ranged from 4 mT (40 Oe) to 14 mT (140 Oe). This magnetic coercivity value is low, less than 1000 Oe. Materials with H_c <1000 Oe include those with soft magnetic response (Awschalom et al., 2013). A magnetic polarisation film with soft magnetic response is to be reversed so that the energy consumption is low. Thus, the Co: TiO_2 thin films produced in this study had a soft magnetic response that its magnetic polarisation is reversed.

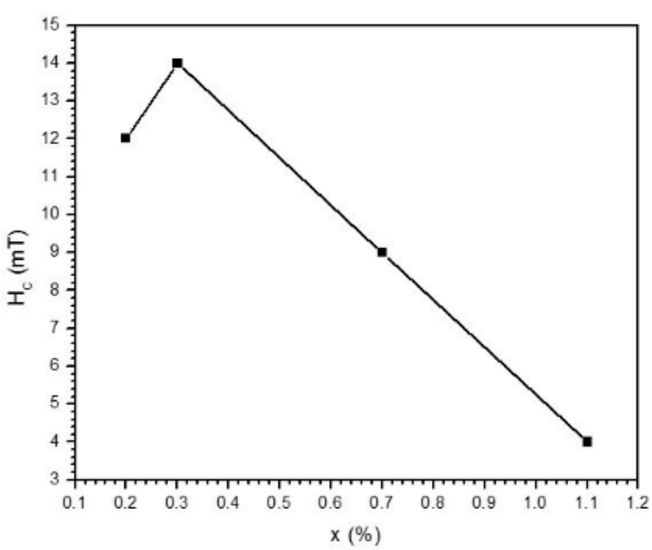

Figure 7. Magnetic coercivity, H_c, versus concentration of Co atom, x

A graph of magnetic coercivity versus concentration of Co atom is shown in Figure 7. The magnetic coercivity increased from 12 mT to 14 mT when the concentration of Co atom increased from 0.2% to 0.4% and vice versa. From the graph, it can be said that the value of the magnetic coercivity decreases when Co atom concentrations increase. A similar situation was observed by Seong et al. (2002). The decline is related to the tendency of atoms that form $Co_{1-x}T_{ix}$ clusters at a high concentration of Co atom. The $Co_{1-x}T_{ix}$ clusters have soft magnetic properties that depress the magnetic coercivity value (Seong et al., 2002).

The value of saturation magnetisation is the value of *M* when the curve has been flat or not depending on increasing *H*. From Figure 6, saturation magnetisation of Co: TiO_2 films in this study were in the range of 1.0 to 4.4 emu/cm^3. This is much lower compared with findings of earlier studies in the range 20-70 emu/cm^3 (Seong et al., 2002) and 20-50 emu/cm^3 (Stampe, Kennedy, Xin, & Parker, 2002).

Saturation magnetisation increased with increasing Co atom concentrations, as shown in Figure 8. The results of this study are similar with that of Seong et al., (2002). They showed the effect of the Co concentration 3% to 12% on the saturation magnetisation. When comparing the Co concentration ratio in this study (0.2% - 1.1%) and Seong et al., (2002) (3% - 12%), it is believed that the low value is related to the low concentrations of Co atoms in the Co: TiO_2 thin film.

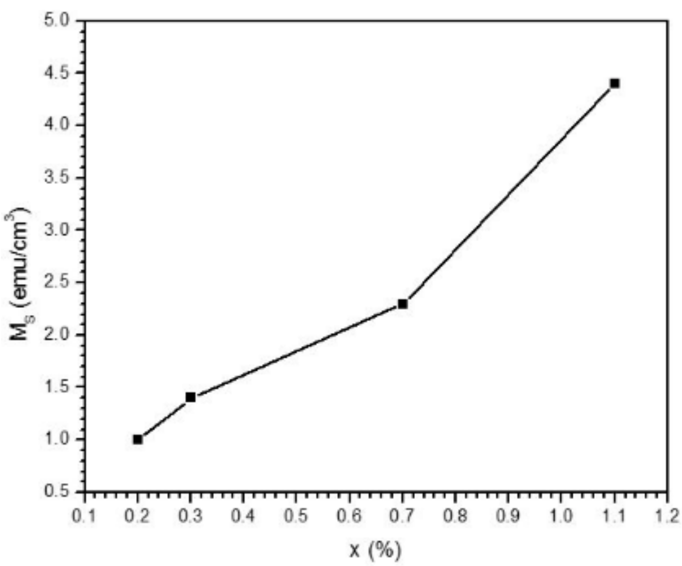

Figure 8. Saturation magnetisation, M_S, versus concentration of Co atom, *x*

The value of saturation magnetisation rises with increased concentration of Co atoms in the Co: TiO_2 thin film which indicated that Co atoms entered into the TiO_2 lattice and contributed to ferromagnetic properties of the film. The increase in saturation magnetisation shows that Co atoms have replaced Ti atoms randomly in the matrix lattice of TiO_2.

The magnetic moment of the Co: TiO_2 thin film produced in this study was in the range 1.2 to 1.6 μB/Co. The value of the magnetic moment is within the range that is commonly produced by other researchers. Generally, the value of saturation magnetic moment of the Co: TiO_2 thin film obtained were in the range of 0.03 to 1.7 μB/Co (Matsumoto et al., 2001; Chambers et al., 2001; Stampe et al., 2002; Shinde et al., 2003; Jeong, Heo, Norton, & Hebard, 2005; Griffin, Pakhomov, Wang, Heald, & Krishnan, 2005; Lee, Kumar, Marún, de Jong & Jansen, 2010; Singh et al., 2012). Some researchers have produced saturation magnetic moment higher than 1.7 μB/Co (Seong et al., 2002).

For the same film growth method, the MOCVD, the magnetic moment of the film Co: TiO_2 produced in this study is higher than McClure, et al.'s, i.e., 0.35 μB/Co (McClure et al., 2008). Although not explicitly stated, the results of Seong, et al.'s research (2002), indicate that the magnetic moment of the Co: TiO_2 thin film is in the range of 2.0 - 2.8 μB/Co for Co concentrations in the range of 3-12%. Thus, the magnetic moment of the Co: TiO_2 thin film in the current study is lower. The difference in the magnetic moment and content of Co may be due to differences in the film growth conditions.

CONCLUSION

This study investigated the magnetic properties of Co: TiO_2 thin films with low cobalt concentration. It was shown that even with low cobalt concentration, the Co: TiO_2 thin films exhibit ferromagnetic properties at room temperature. Saturation magnetisation of film increases as the concentration of cobalt ion in TiO_2 builds.

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