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Preparation of Thin Films by a Bipolar Pulsed-DC Magnetron Sputtering System Using $Ca_3Co_4O_9$ and $CaMnO_3$ Targets

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ABSTRACT

The thin films were deposited on the glass substrates by an asymmetric bipolar pulsed-dc magnetron sputtering system using the $Ca_3Co_4O_9$ (p-type) and $CaMnO_3$ (n-type) targets of 60 mm diameter and 2.5 mm thickness. The targets were prepared from powder precursors, which obtained by a solid state reaction. Optical emissions from plasmas during sputter depositions of films were detected using a high resolution spectrometer. Thickness of thin film was estimated by Tolansky's Fizeau fringe method and ellipsometic measurement. Crystal structures were studied from X-ray diffraction. The thermoelectric properties were assessed from Seebeck coefficient and electrical resistivity measurements at room temperature. The power factors were calculated. It was found that the optical emission spectrums showed that the Ca, Mn, Co and O atoms were sputtered from the targets onto glass substrates. As-deposited Ca-Co-O and Ca-Mn-O films thickness values were 0.435 μm and 0.449 μm, respectively. The X-ray diffraction patterns clearly showed amorphous nature of the as-deposited films. Determining thermoelectric properties of Ca-Co-O film gave Seebeck coefficient of 0.146 mV/K, electrical resistivity of 0.473 Ω·cm, and power factor of 4.531 μW/m·K at room temperature. Ca-Mn-O film baring a high resistance was not the experimental determination of thermoelectric properties.

Keywords: Thermoelectric Thin Film; $Ca_3Co_4O_9$; $CaMnO_3$; Bipolar Pulsed-DC Magnetron Sputtering System

1. Introduction

In the past, the metal coating in form of thin films to improve the quality of material was done by electroplating process which is often also called electro-deposition. The disadvantage of electroplating was harmful to the environment. Subsequently, the vacuum depositions were developed in chemical vapor deposition (CVD) and physical vapor deposition (PVD). CVD is a technique whereby gaseous reactants can be deposited onto a substrate. However, often dangerous by-products are removed by gas flow. PVD is a clean coating technology that involves evaporation and deposition of a material. Material vaporizes are removed from a source by physical processes such as evaporation sputtering and it is transported in the form of a vapor atomic beam through a vacuum to the substrate. Magnetron sputtering is one of PVD methods, which are widely used in thin film technology. The various types of magnetron sputtering technique are direct current (DC), alternating current (AC), radio frequency (RF), and pulsed-dc [1]. Pulsed-dc magnetron sputtering is one of the latest developments of sputtering technology for thin films deposition, which has many advantages over others. Namely, it is versatile and provides the ability to deposit thin films of oxide compounds at high deposition rate and to eliminate arcing problems of poisoned targets [2]. This is interested to apply the deposition technology. It may be possible to customize the deposition conditions so that the thin films of highly preferred orientation can be grown.

In this work, the depositions of thin films have been carried out by a bipolar pulsed-dc magnetron sputtering system using the $Ca_3Co_4O_9$ and $CaMnO_3$ targets, which were made from powder precursors obtained from the solid state reaction (SSR) route. Optical emissions from plasmas during sputter deposition of thin films were measured using a high resolution spectrometer. Crystal structures of the as-deposited films were studied from X-ray diffraction (XRD). The thickness of thin films and thermoelectric properties were investigated.

2. Experimentation

The preparation of thin films by a pulsed-dc magnetron sputtering system is shown in **Figure 1** [3]. The details of

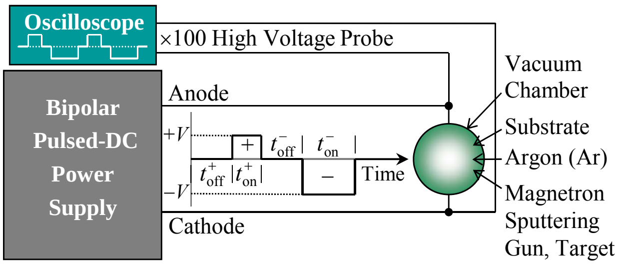

Figure 1. Experimental setup of a bipolar pulsed-dc magnetron sputtering system.

deposition conditions, plasma and characterizations, and thermoelectric properties measurements are given below.

2.1. Deposition Conditions

The sputtering targets were the p-$Ca_3Co_4O_9$ and n-$CaMnO_3$ pellets of 60 mm diameter, 2.5 mm thickness, 3.218 and 2.862 g/cm^3 densities, respectively. The glass slide substrates of 1.0 mm thick in dimension 25.0 × 50.0 mm^2 were used. The substrates were placed at a distance of 5.0 cm above the targets and no additional heating was applied. To generate the pulsed-dc plasma and initiate the thin film deposition, the vacuum chamber was pumped down to a base pressure of 2.00 N/m^2 and flushed with high purity argon (Ar 99.999%) gas flow rate of 15.0 ± 0.1 sccm the total working pressures was 5.33 N/m^2 for sputtering from the $Ca_3Co_4O_9$ and $CaMnO_3$ targets. The pulse off time was kept constant at 14 µs (t_{off}^{+} and t_{off}^{-}). The reverse positive and cathode negative pulse widths of the power supply were fixed at 10 µs (t_{on}^{+}) and 20 µs (t_{on}^{-}), respectively. These values of timings give the corresponding pulse frequency of 17.24 kHz. The anode positive power was set to be the same current-voltage of 20 mA and 100 V. The cathode negative current fixed at 120 mA, the output voltage were about 260 - 280 V with deposition time of 60 minutes. Here are the optimal conditions for the deposition, which are summarized in **Table 1**.

2.2. Plasma and Characterizations

Optical emissions from plasma during sputter deposition of films were observed in the wavelength range of 360 - 800 nm using a high resolution spectrometer (the getSpec-2048 spectrometer, Sentronic GmbH) as shown in **Figure 2**. The spectral lines were indexed to the ASD data information of National Institute of Standards and Technology [4]. Crystal structures of as-deposited films were investigated by X-ray diffractometer (PW3043 Philips X-ray diffractometer of the Netherlands) at room temperature using CuKα radiation, λ = 0.15406 nm. Each film was measured in the 2-theta angle range of $10^\circ \le 2\theta \le 70^\circ$ with scanning rate of 0.02˚/s. Thin film thickness can be estimated from the optical interference using Tolansky's Fizeau fringe method which is now accepted [5]. The thickness (t) of the

Table 1. Deposition conditions of thin films.

Ar Flow Rate	Frequency	Positive Pulse	Negative Pulse
15.0 ± 0.1 sccm	17.24 kHz	20 mA 100V	120 mA 260 - 280 V

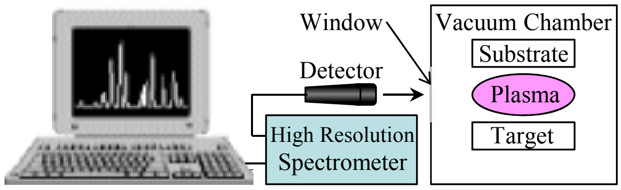

Figure 2. Observation of optical emission from plasma during sputter deposition.

film is given by Equation (1) [6],

$$t = \left[\frac{\Delta x}{x}\right]\left[\frac{\lambda}{2}\right] \tag{1}$$

where Δx is the displacement of fringes at step, x is the distance between consecutive fringes, and λ is the wavelength of monochromatic light. The experimental arrangement and fringe pattern is shown in **Figure 3**. The film thickness was measured by the Ellipsometer (Model L 115 S 300, Gaertner Scientific Corporation, USA) for comparison of the calculated values of thickness.

2.3. Thermoelectric Properties Measurements

The measurement of thermoelectric properties at room temperature in air by the Keithley instruments included the charge carrier, Seebeck coefficient, and electrical resistivity. The experimental setups can be elucidated as follows.

Firstly, the charge carrier and Seebeck coefficient were determined by hot probe method [7,8] as shown in **Figure 4**. The hot and cold junctions between across two ends of a film were connected to the digital voltmeter (Keithley 617 Programmable electrometer). The temperatures T_H and T_C were sensed using the type K thermocouples, which were connected to the digital thermometers (7563 Digital thermometer, Yokogawa). The silicone thermal insulator pads were placed between junctions and thermocouples. The resistor of 10 W 5 Ω was used to heat at hot junction by applying currents to a resistor placed on hot side. Seebeck coefficient (S) was measured by the relation between thermoelectric voltage (ΔV) and temperature difference (ΔT). The S is defined as [8]:

$$S = \frac{\Delta V}{\Delta T} \tag{2}$$

Secondly, the electrical resistivity was measured by four-point probe method, which can be conveniently determined by the Van der Pauw resistivity measurement technique [9] as shown in **Figure 5**. All contacts were made by silver paste, which showed ohmic characteristics over a wide range of currents. The current-voltage characteristics for

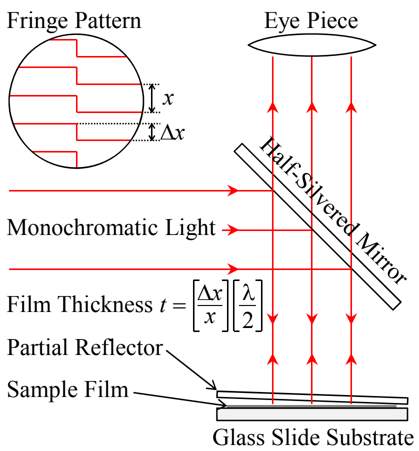

Figure 3. Experimental arrangement for Tolansky's Fizeau fringe method.

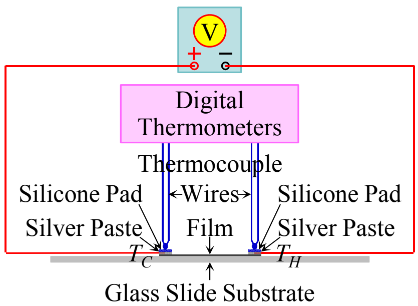

Figure 4. Side view (vertical cross section) of charge carrier and Seebeck coefficient measurement.

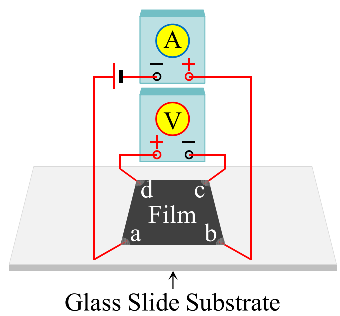

Figure 5. Three-dimensional top view of electrical resistivity measurement.

measurement of resistivity (ρ) are measured. The ρ can be estimated from [9]

$$\rho = \frac{\pi t}{\ln 2}\left[\frac{R_{ab,dc} + R_{bc,ad}}{2}\right] F \left[\frac{R_{ab,dc}}{R_{bc,ad}}\right] \quad (3)$$

where t is the film thickness, $R_{ab,dc} = \Delta V_{dc}/I_{ab}$, $R_{bc,ad} = \Delta V_{ad}/I_{bc}$, and F is correction function which can be calculated from $\left(R_{ab,dc} - R_{bc,ad}\right)/\left(R_{ab,dc} + R_{bc,ad}\right) = \left(F/\ln 2\right)$ arccos$h$ $\left[\exp\left(\ln 2/F\right)/2\right]$.

Finally, the thermoelectric efficiency can be examined from power factor (P), which was calculated from the S and ρ in Equation (4) [7,10].

3. Results and Discussion

The results and discussion of plasma, characterizations, and thermoelectric properties are given below.

3.1. Plasma and Characterizations

The cathode voltage waveforms, photographs of stable glow discharges, and optical emission spectrums of the bipolar pulsed-dc magnetron argon discharge during the sputtering of the $Ca_3Co_4O_9$ and $CaMnO_3$ targets are shown in **Figure 6**. These results indicated the good pulsed-dc plasma characteristics. The spectral lines were indexed to the ASD data information of NIST [4]. It was found that the emission lines of Ar (422.57, 656.34, 696.66, 706.83, 738.55, 750.50, 751.57, 763.63, 772.51, 794.94 and 797.25 nm), Ca (370.26, 393.36 and 396.85 nm), Co (361.46 and 399.43 nm), and Mn (361.06 and 403.11 nm) were prominent features. The emission line of O (777.41 nm) was detected, but it is not intense due to the strong line of this species is not in measured range. The optical emission spectrums showed that Ca, Co, Mn, and O atoms were sputtered from the targets. Hence, it can be expected that

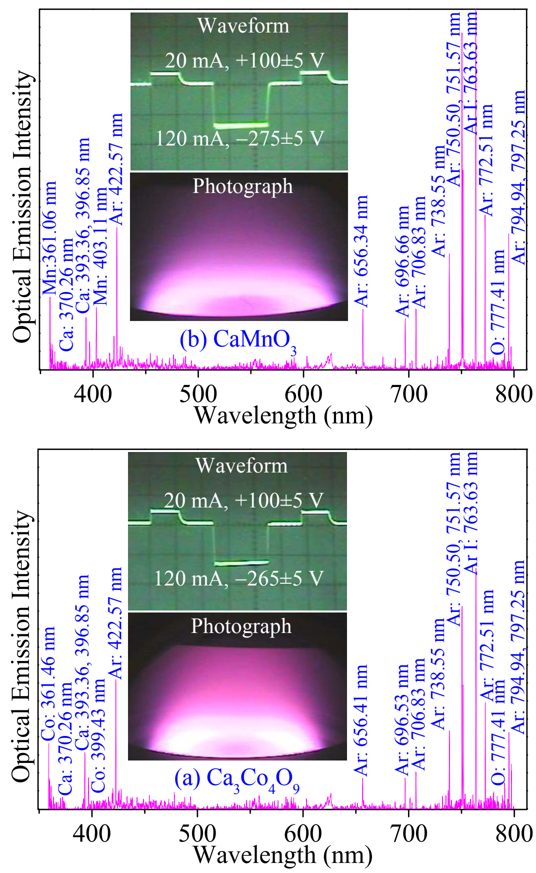

Figure 6. Waveforms, photographs, and spectral lines during the sputtering of (a) $Ca_3Co_4O_9$ and (b) $CaMnO_4$.

the deposited films will contain these atomic species. From this point onward, the deposited films will be referred to as Ca-Co-O and Ca-Mn-O containing. The as-deposited films of 1.60 × 1.60 cm^2 and XRD patterns are shown in **Figure 7**. From this figure clearly indicated amorphous nature of the as-deposited films. This was expected since the substrates were not heated during the deposition process. Therefore, the kinetic energy of atomic species at the substrate surface was not enough to promote the growth of a crystal. Each film thickness was initially estimated using optical interference method (yellow sodium light, λ = 589.3 nm) and was obtained from ellipsometic measurement (red laser light, λ = 632.8 nm). The results are given in **Table 2**. The results of measurement gave the thickness of 435.31 nm and 449.35 nm for as-deposited Ca-Co-O and Ca-Mn-O films, respectively.

3.2. Thermoelectric Properties

The results of investigations on thermoelectric properties of Ca-Co-O and Ca-Mn-O films such as the types of charge carrier, Seebeck coefficient, electrical resistivity, and power factor are presented and discussed.

Firstly, the types of charge carriers were determined by hot probe method (see **Figure 4**). The result of measurement on Ca-Co-O film, the cold junction showed higher voltage than the hot junction, indicating that the holes conduction dominated transport property (p-type). The measurement results of relation between Seebeck emf (ΔV) and temperature difference (ΔT) are shown in **Figure 8**. Ca-Co-O film indicated linear dependence between ΔV and

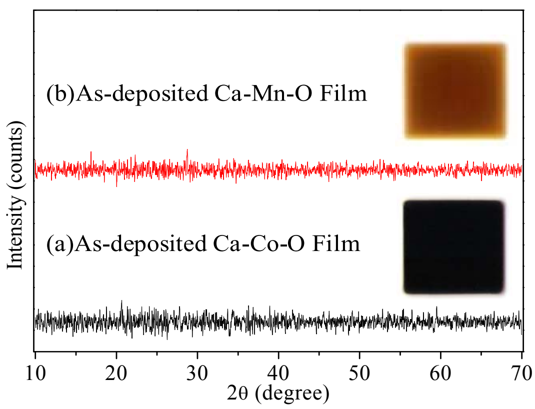

Figure 7. As-deposited Ca-Co-O and Ca-Mn-O films of 1.60 × 1.60 cm^2 and XRD patterns.

Table 2. Thickness of the as-deposited Ca-Co-O and Ca-Mn-O films.

Samples	Calculation (nm)	Measurement (nm)	Refractive Index
$Ca_3Co_4O_9$	~441.98	435.31 ± 3.37	2.22 ± 0.01
$CaMnO_3$	~452.50	449.35 ± 1.27	2.06 ± 0.01

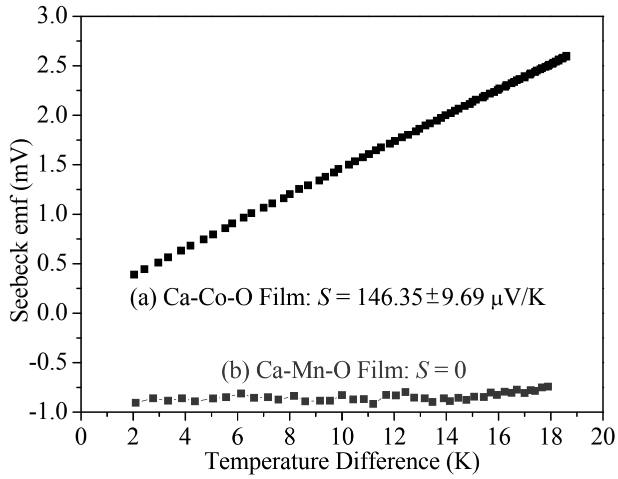

Figure 8. Seebeck emf of thin films as a function of temperature difference (a) Ca-Co-O film and (b) Ca-Mn-O film.

ΔT, the S of 146.35 μV/K is obtained. Ca-Mn-O film baring a high resistance was not the experimental determination of charge carrier and Seebeck coefficient.

Secondly, the current-voltage characteristics were obtained by the Van der Pauw four-probe measurement (see **Figure 5**). The experimental result of Ca-Co-O film is shown in **Figure 9**. The plot exhibited good ohmic I-V characteristics. The ρ value obtained from this I-V plot, it is 0.473 Ω·cm. For the experimental measurement of Ca-Mn-O film could not be determined.

Finally, the power factor was calculated from S and ρ in Equation: $P = S^2/\rho$. The result of Ca-Co-O film gave value of 4.53 μW/m·K.

4. Conclusion

The preparation of Ca-Co-O and Ca-Mn-O thin films using a bipolar pulsed-dc magnetron sputtering system were successfully deposited on glass substrates from the $Ca_3Co_4O_9$ and $CaMnO_3$ targets, respectively. The XRD patterns clearly indicated amorphous nature of the as-deposited films. Determining thermoelectric properties of Ca-Co-O film showed the low Seebeck coefficient and high electrical resistivity, which leaded to a low power factor. Ca-Mn-O film baring a high resistance was not an experiment. The post deposition annealing and doped metals have been expected candidates for good thermoelectric properties. This will be further investigated.

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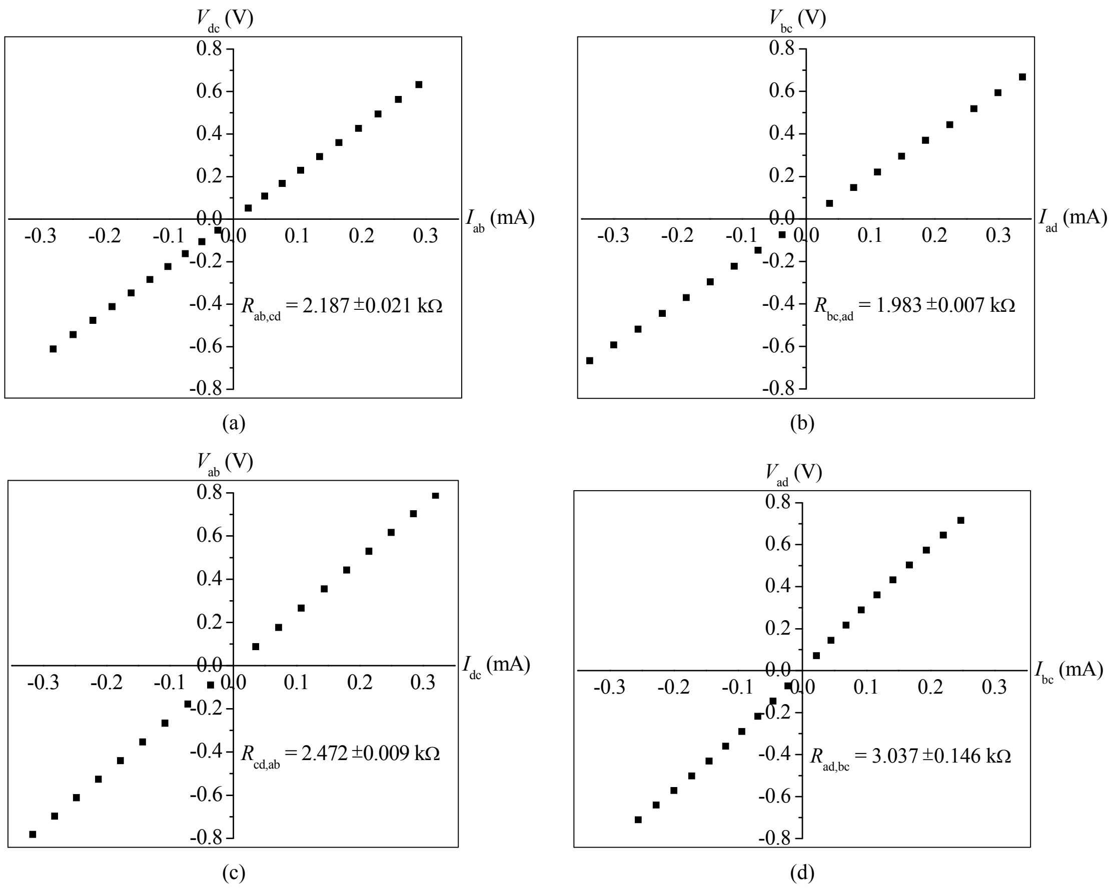

Figure 9. Plot of the current-voltage characteristics for the electrical resistivity measurement of Ca-Co-O film (a) I_{ab}-V_{dc}; (b) I_{ad}-V_{bc}; (c) I_{dc}-V_{ab} and (d) I_{bc}-V_{ad}.

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