Journal of Physics: Theories and Applications E-ISSN: 2549-7324 / P-ISSN: 2549-7316
J. Phys.: Theor. Appl. Vol. 7 No. 1 (2023) 36-44 doi: 10.20961/jphystheor-appl.v7i1.66951

Fabrication of p-type (MCCO) thin film using DC magnetron sputtering as a preparator for thermoelectric module

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Received 11 November 2022, Revised 25 Feb 2023, Published 27 March 2023

Abstract: Based on existing research, thermoelectric efficiency can be improved through material selection. In this study, the material used is $CaCO_3$ doped with Mn and Co_2O_3 to form $CaCo_{3.5}Mn_{0.5}O_9$ material as a p-type thermoelectric material. The substrate used is glass. The stages in this research are material synthesis, sputtering process using DC Magnetron Sputtering machine to form thin films, and testing. The synthesis process includes grinding, calcination, and sintering. Grinding is done using a Ball Mill machine with a rotation speed of 250 rpm for 5 hours. Furthermore, the calcination step was carried out by heating the sample into a furnace at a temperature of 800°C for 10 hours. Then the sintering process was carried out at a temperature of 850°C for 12 hours. After the synthesis process is complete, enter the sputtering process using a DC Magnetron Sputtering machine for approximately 10 minutes. The gas used in this research is Argon (Ar). After the sputtering process was carried out, several tests appeared, such as the XRD test to determine the type of crystal, the ZEM-3 test to determine the Seebeck coefficient and resistivity, the thickness of the thin film formed, and the power factor test to determine the maximum voltage and power generated by the module formed. Several power factor test results were obtained, consisting of 107 $\mu W/mK^2$ at 100°C, 108 $\mu W/mK^2$ at 200°C, and 332 $\mu W/mK^2$ at 300°C and a thickness of 90.34 nm.

Keywords: DC magnetron sputtering, MCCO, thermoelectric, thin film.

1. Introduction

The recent study finds the number of new materials used as thermoelectric module. Starting from inorganic materials to thermoelectric with organic materials (Jo et al., 2017; Zheng et al., 2017). Eco-friendly thermoelectric has attracted so much attention in recent years (Mikami et al., 2005). Y. Miyazaki et al. and S. Li et al. have been reported a compound exhibiting large thermoelectric power as well as low resistivity and low thermal conductivity in Ca-Co-O system (S. Li et al., 1999; Miyazaki et al., 2000).

The potential of a material for thermoelectric applications is determined in large part to a measure of the material's dimensionless figure of merit:

$$ZT = \frac{\alpha^2 \sigma T}{k} = \frac{\alpha^2 T}{\rho k} \quad (1)$$

Where, α is the Seebeck Coefficient, σ the electrical conductivity, ρ the electrical resistivity, and k the total thermal conductivity, respectively (Alam, 2013). In general, for a good TE material with a high value of ZT, a high thermopower S, a high electrical conductivity σ and a low thermal conductivity κ are required.

However, in semiconductor materials the σ and the S are generally related to the carrier concentration and the mobility in opposite ways, and hence it is hard to optimize them simultaneously (Kaur et al., 2021). An exception is the coexistence of a high S and a relatively high σ in single-crystal $Ca_3Co_4O_9$, makes it a promising p-type TE material (Wang et al., 2010a; Pinitsoontorn et al., 2010; Shikano & Funahashi, 2003). D. Li et all. had been investigated that Mn doped $Ca_3Co_4O_9$ would be a promising thermoelectric material at high temperature (D. Li et al., 2005b). For practical applications, the ZT value must be greater than one. Sigiura K., et al. (Sugiura et al., 2007) have reported that the ZT value of $Ca_3Co_4O_9$ (CCO) single crystal exceeds 0.8 at 1000 K. This value is very near the level required for practical application.

Doping is one of the most important methods for improving the performance of semiconductors through modifying the carrier concentration (Pei, 2022). For n-type thermoelectric materials, (Cahyaningsih, 2020) found that Ag, WO_3, and Al_2O_3 can reduce the resistivity of ZnO. As a p-type TE material, the carrier concentration of CCO can also be changed by doping with metallic elements (Moualhi et al., 2020). Wang et all. have reported that Ag, Fe, Mn, and Cu doping can improve the thermoelectric properties of CCO (Lee et al., 2010; Yin et al., 2017). The crystal structure of $Ca_3Co_4O_9$ has been described as two sub systems, CoO_2 and Ca_2CoO_3 (Masset et al., 2000). The CoO_2 sheets are believed to be conduction planes. Ca_2CoO_3 subsystem consists of two Ca–O planes and one Co–O plane, with the Ca–O planes playing a role of donors to the CoO_2 metallic layers (Rebola et al., 2012). The studies showed that the substitutions at Ca and Co-sites with transition metals have different effects for TE properties (Huang et al., 2012).

In general, doping on Ca-sites only changes the carrier concentration of the system and has less influence on the band structure (Yan et al., 2016). In contrast, doping on Co-sites, especially in the CoO_2 layer, can cause a large change in the physical properties because the band structure and the transport mechanism are affected (Asahi et al., 2002; Wang et al., 2010b). For the substitutions at the Co-site mostly various transitional elements (Ti, Mn, Ni, Pt, Cu, Zn) were considered (Constantinescu et al., 2015; Fu et al., 2011; Huang, Zhao, Lin, Ang, Song, et al., 2014; Huang, Zhao, Lin, Ang, & Sun, 2014; D. Li et al., 2005a; Xu et al., 2010). In order to improve the ZT of CCO compound this study is done.

2. Methodology

The stages in conducting this research include material synthesis, fabrication, and testing.

2.1. Synthesis

Thin films having Mn-doped $Ca_3Co_4O_9$ targets were prepared by DC magnetron sputtering method from a mixture of stoichiometric $CaCO_3$ (18.0893 grams), Co_2O_3 (1.6589 grams), and Mn (17.487 grams). The mixture was homogenized in a planetary ball mill for 2 hours, then calcined for 5 hours at 500°C. After that, the mixture was pressed using a pressure of 250 kPa into pellets with a diameter of 60 mm and a thickness of 3 mm, then sintered at 850°C for 12 hours in air.

2.2. Fabrication

The DC magnetron sputtering system having a base pressure of 3×10^{-5} torr is used for thin film deposition. The target is placed on the cathode and the substrate is placed on the anode. Argon gas is used during the sputtering process, to make a plasma. Using 20 mm x 20 mm Glass which serves as the substrate.

2.3. Measurement

Thin films are prepared to perform measurements such as crystal structure, thickness, and thermoelectric properties. The phase (target) and crystal (thin film) structures of the samples obtained were determined using an X-ray diffractometer (XRD-6100 Shimadzu) with Cu-Kα radiation. The Seebeck coefficient and electrical resistivity were determined using ZEM-3 (ULVAC-RIKO). Thin film thickness was determined using the Fizeau fringe Tolansky method.

3. Results and Discussions

In this study, the following results were obtained.

3.1. Thin Film Thickness

After the thin film is formed, it is necessary to know the thickness of the thin film formed. This test is performed using a device called the Tolansky Apparatus. This tool consists of a set of microscopes and halogen lamps. The resulting thin film was taken using a manual camera to calculate its thickness. Thickness measurements were carried out using Tolansky's formula as follows:

$$t = \frac{\Delta x}{x}\left(\frac{\lambda}{2}\right) \tag{2}$$

Based on the test results formed, this thin p-type film has a very thin size. The thickness of the film formed depends on the length of the sputtering process. Observation photos taken using the Tolansky Apparatus method can be seen in Figure 1.

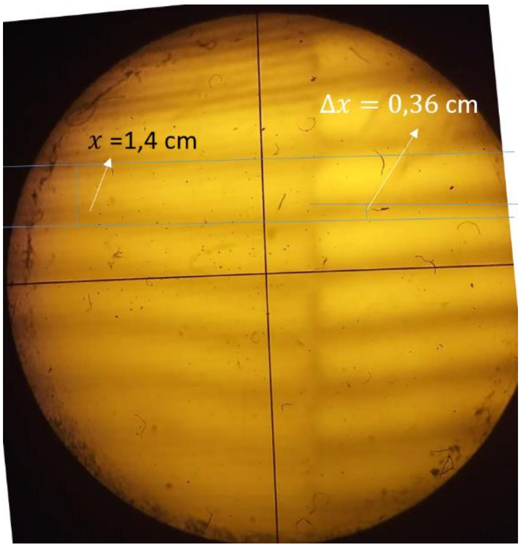

Figure 1. Thickness Measurement

After obtaining images from observations using Tolansky Apparatus, manual calculations are performed to determine the thickness of the thin film formed. The wavelength used in this measurement is 589 nm. So the thickness of the thin film measured is:

$$t = \frac{\Delta x}{x}\left(\frac{\lambda}{2}\right) = \frac{0.36}{1.4}\left(\frac{589}{2}\right) = 75.73nm \quad (3)$$

Thus, the thickness of the thin film formed is 75.73nm. The amount is so small that it can be said that the layer formed is very thin. In general, good thin films have a thickness of the micrometer type.

3.2. XRD Caracterization

To verify the crystal structure and phase purity of the sample, XRD analysis was performed. XRD analysis was performed using XRD-6100 Shimadzu with Cu-Kα radiation. Figure 2 shows the results of the XRD analysis for the three samples, namely reference films, targets, and thin films.

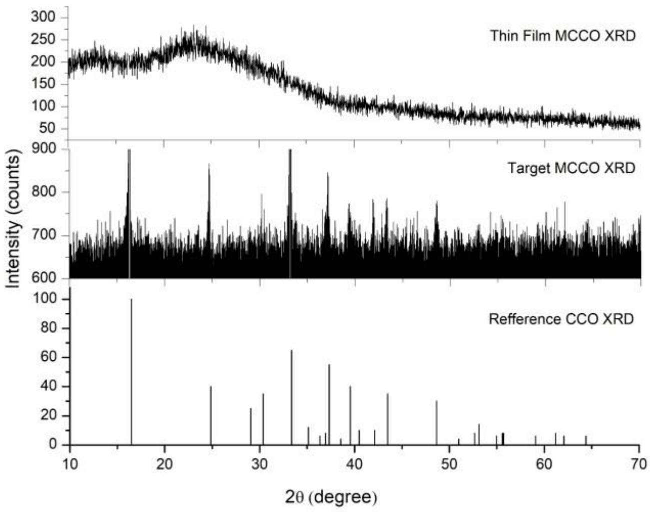

Figure 2. XRD Test Result

The Figure 2 shows that the target have relation with the reference. From the XRD test results, it can be seen that the phase formed is crystalline because there are many extreme peaks. To ensure that the phase formed corresponds to the reference, XRD peak matching is carried out between the sample made with the reference. The peaks formed have the same angle between this study and the reference so that the sample phase corresponds to the reference phase. However, the results of the thin film process did not show a significant peak, from this fact we suspect that the thin film consists of amorphous crystals which are glassy properties.

3.3. Thermoelectric Properties

Measurements of thermoelectric properties include:

3.3.1. Resistivity

The temperature dependence of the resistivity for Mn-doped CCO thin films on glass substrates is between 373–573 K as shown in Figure 3.

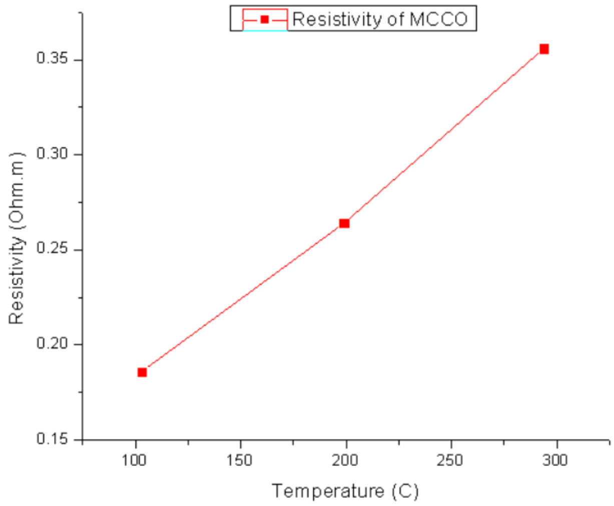

Figure 3. Resistivity Measurement

Resistivity exhibits metal-like behavior. For metals in general, the electrical resistivity increases with temperature. At high temperatures, the resistance of the metal increases linearly with temperature. As with previous studies for this type of material, the charge transport process in the semiconductor regime is determined by the mechanism by which the thermally activated hole jumps from Co_4^+ to Co_3^+ whereas in the metallic regime, the charge carriers are excited from the valence to the conduction band.

3.3.2. Seebeck Coefficient

The results of the Seebeck coefficient measurement using ZEM-3 have been successfully carried out on MCCO thin films. Seebeck coefficient measurement using three temperature variations, 100°C, 200°C and 300°C. Positive values of the Seebeck Coefficient (S) confirm the P-type of the MCCO sample determined that, the main charge carriers in MCCO are holes. In general, samples with higher electrical resistivity show a higher Seebeck S Coefficient. As we can see from Figure 4 it is determined that, the Seebeck coefficient increases with increasing temperature.

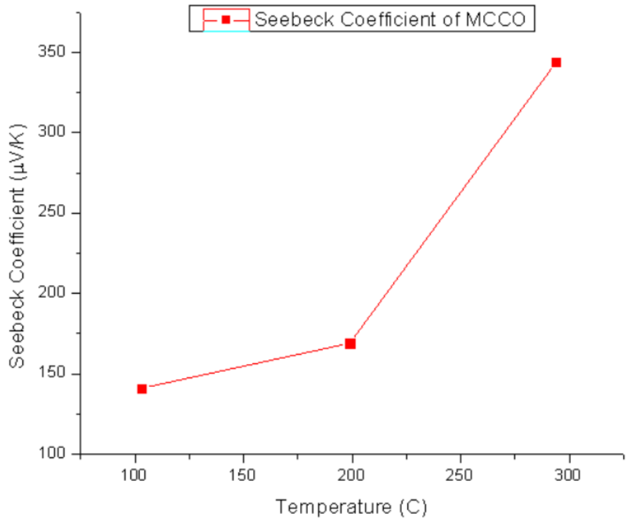

Figure 4. Seebeck Coefficient

The highest seebeck coefficient value was obtained at a temperature of 300°C with a value of 344 µV/K.

3.3.3. Power Factor

Figure 5 shows the temperature dependence of the power factor for MCCO thin films in the temperature range of 373–573 K. As we can see from Figure 5, when the temperatures are 373, 473 and 573 K, the MCCO thin films produce power factors of 107, 108, 322 µW/mK, respectively.

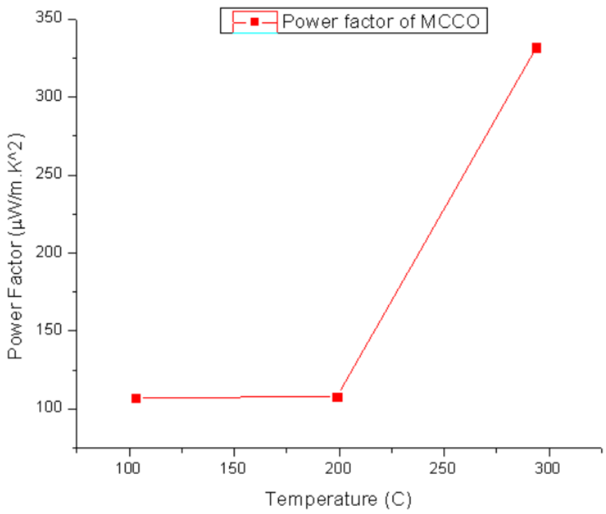

Figure 5. Power Factor Measurement

Power Factor describes the ability of a material to be a good thermoelectric module. From the results of the tests that have been carried out, the MCCO material is good for use as a thermoelectric module at high temperatures.

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4. Conclusion

The conclusion from these results, the thickness of the thin layer is 75.73 nm. The highest seebeck coefficient value was obtained at a temperature of 300°C with a value of 344 μV/K. The results showed that the resistivity value decreased with increasing temperature, while the Seebeck coefficient and power factor increased with increasing temperature. So it can be concluded that the MCCO thin film material is good for use as a thermoelectric at high temperatures.

Acknowledgements

The author would like to thank the Sepuluh Nopember Institute of Technology (ITS) and the Center of Excellence on Alternative Energy (CEAE) for conducting research collaborations in the thermoelectric field. The author would also like to thank the Department of Mechatronics and Artificial Intelligence, Universitas Pendidikan Indonesia, which has provided the facility to submit this article. Hopefully this article can have a big impact on the development of science and technology today and in the future.

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