Seebeck coefficient of synthesized Titanium Dioxide thin film on FTO glass substrate

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Abstract. In order to fabricate a thermoelectric device on glass substrate for harvesting waste heat energy through house appliances, the Seebeck coefficient of translucent TiO₂ thin film was investigated. The TiO₂ thin film was synthesized by using hydrothermal method with F-SnO₂ coated glass as substrate. From scanning electron microscopy analysis, the synthesized TiO₂ thin film was found to be in nanometer-scale rod structure with a thickness of 4 µm. The Seebeck coefficient was measured in the temperature range of 300 – 400 K. The Seebeck coefficient is found to be in negative value which shows that synthesized film is an n-type semiconductor material, and is lower than the value of bulk-size material. This reduction in Seebeck coefficient of TiO₂ thin film is likely due to the low dimensional effect and the difference of carrier concentration.

1. Introduction

Global warming issues such as greenhouse gas emission have been a concern among researchers which encourage them to reuse waste heat as an alternative power generation resource [1, 2]. The ability of thermoelectric devices to directly convert waste heat energy into electrical energy without any moving parts, with high durability, and without maintenance has attracted the significant interest of researchers [3-5]. The thermoelectric conversion efficiency is determined by the figure-of-merit Z, which is proportional to the square of Seebeck coefficient S and electrical conductivity σ and inversely proportional to the thermal conductivity κ [6, 7]. High S and σ are needed to produce a large voltage with a small temperature difference and low κ is needed to reduce heat leakage and maintain temperature difference [8]. Moreover, the enhancement of Z is a difficult task since S, σ and κ are strongly dependent on the carrier concentration and not independent with each other which results a difficulty to find an optimum value [9, 10]. The introduction of nanostructure is theoretically predicted to enhance the S and reduce the κ simultaneously, and this approach has been shown to be one effective way of improving the Z [10, 11].
Moreover, current thermoelectric material of high performance thermoelectric device is costly and hazardous [12-14]. Thus, material which is less expensive, chemically stable, and non-toxic is considered as an ideal substitution to be used for fabricating the thermoelectric device. In addition, for harvesting waste heat energy through glass based house appliances such as house window, a transparent and manufacturable material on glass substrate is needed. TiO$_2$ is one of the excellent candidate to fulfill the requirement as it provides the desired features [15, 16]. However, its Z is comparatively low with other established thermoelectric materials [17]. It has been reported that the Z of TiO$_2$ can be enhanced by increasing the $\sigma$ through impurity doping and by reducing the $\kappa$ through nanostructuring [17-21]. However, there is no report regarding the enhancement of Z by increasing the S through nanostructuring. Therefore, in this study, we synthesized a translucent nanostructured TiO$_2$ thin film on F-SnO$_2$ coated (FTO) glass substrate and its S was measured in order to observe the enhancement of S in nanostructured TiO$_2$ thin film.

2. Experiment

The TiO$_2$ thin films discussed in this study was synthesized using the same method as used in our previous investigation and the synthesized procedures is shown in Figure 1 [22]. FTO glass was used as a substrate with a dimension of 10 × 20 mm$^2$. 120 ml of concentrated Hydrochloric (HCl) acid was dissolved in 120 ml of deionized (DI) water. The mixture was stirred for five minutes until a homogenous solution was obtained. An amount of 5 ml of C$_{16}$H$_{36}$O$_4$Ti (TBOT) was then carefully dripped into the solution by pipette. The solution was inserted into a steel-made autoclave after it was stirred for ten minutes, together with the FTO glass substrate which was placed in the autoclave with the conducting FTO layer surface facing upward. The hydrothermal process was performed at 150 °C for ten hours.

The surface morphology of the samples was investigated by using field-emission scanning electron microscopy (FESEM). The thickness of the sample was estimated from the FESEM image. In this study, the crystallinity of the sample was not analyzed since the sample was synthesized in the same manner as in previous study [22]. The thermo electromotive force and temperature difference of the sample were measured by using conventional S measurement system (ULVAC ZEM-3) in the temperature range of 300 – 400 K. The S was evaluated from the gradient of the linear relation between the thermo electromotive force and temperature difference which were measured simultaneously.

3. Results and Discussion

Figure 2 a) and b) show the FESEM images of the cross section and the top of sample, respectively. From this figure, it is revealed that the sample is composed with dense TiO$_2$ nanorod layer which are uniformly deposited on FTO layer. It is also found that the nanorod TiO$_2$ layer has a thickness of 4 µm. From the inset in Figure 2 b), it is observed that the grown nanorods is in square shape with average

![Figure 1. Schematic diagram of synthesis process flow.](image)
width approximately 30 nm. Moreover, from the XRD pattern analysis in previous study, it is confirmed that the synthesized nanorod TiO2 thin film is rutile since only peaks of the rutile phase were observed [22]. Thus, it is suggested that a uniform and well vertically oriented nanorod TiO2 thin film can be reproducible by using this synthesis method.

The evaluated S is shown in Figure 3 as a function of average temperature. The filled diamonds represent the reported values of S of bulk TiO2 and filled triangles represent the evaluated S of FTO glass substrate. From Figure 3, the evaluated S is found to be in negative value which indicates that the synthesized sample is an n-type semiconductor and in good agreement with the polarity of reported bulk TiO2 [23, 24]. This n-type behaviour of the sample is considered due to the electrons that originating from the Ti and the oxygen vacancies [25]. The evaluated S is also found to be higher than the evaluated S of FTO glass substrate which confirms that the measured S is contributed by nanorod TiO2 layer. Moreover, the S of the sample is observed to be almost constant in the temperature range of 300 – 370 K and then slightly increases with increasing the temperature. This fact shows that the synthesized TiO2 thin film on FTO glass substrate is stable for application near room temperature and further investigation is needed for clarifying the increase in S at higher temperature.

However, by comparing the S of synthesized sample and the reported values, it is found that the difference is large compared with the reported value by Kitagawa et al. and small compared with the reported value by Mikami et al. [23, 24]. In addition, the value of S of synthesized sample is close to
Figure 3. Evaluated S as a function of average temperature. The filled triangle and diamonds represent the evaluated S of FTO glass and reported S of bulk TiO$_2$, respectively [23, 24].

the calculated value of bulk rutile TiO$_2$ with carrier concentration of 5x10$^{20}$ cm$^{-3}$ by Bayerl et al. using Boltzmann transport formalism which is around -200 µV/K [26]. That is, one of the reasons of the difference in S between the synthesized sample and reported values is likely due to the difference of carrier concentration in the sample. On the other point of views, the dimension of the sample is also different between the samples which is likely influenced the S of the sample. Salleh et al. has reported that by decreasing the cross section of a Si thin film, the contribution of phonon system to S will be eliminated which results a decrease in total S of the sample even at room temperature [27]. Therefore, there is a possibility that the decrease in S of nanorod TiO$_2$ film is likely due to elimination of phonon contribution part in total S through decreasing the sample dimension, and further investigation is needed.

4. Conclusion
S of nanorod TiO$_2$ thin films deposited on FTO glass substrate by using hydrothermal method has been investigated. The S is found to be in negative value which shows an n-type semiconductor behaviour and in a good agreement with reported bulk TiO$_2$. However, the value of S of synthesized sample is found to be much lower than the reported values. This is likely due to the difference in carrier concentration or the elimination of phonon system contribution in S through low dimensional affect, and further investigation is needed. Moreover, the S of the sample is found to be nearly constant around room temperature. Consequently, the TiO$_2$ thin film deposited on FTO glass substrate is possible to be utilised in near room temperature applications.

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