# CHAPTER 4

# RESULTS AND DISCUSSION

This chapter presents the process of preparating Ag-Sb-Te films, it is characterization, thermoelectric properties and fabrication thermoelectric generator prototype of Ag-Sb-Te films.

## THE RESULTES OF PHYSICAL PROPERTIES OF Ag-Sb-Te THIN FILMS

### Phase identification and crystallography of Ag-Sb-Te film

The phase identification of Ag-Sb-Te films was investigated by GIXRD technique as shown in Figure 22. The results show that the $Ag_2Te$ phase of films as-deposited on respective temperatures, the main of as-deposited films show that low crystallinity and not have sufficient energy to spread and coagulate at room temperature. For the films annealed at 300°C and 350°C, we observed crystallinity changes as well as quantity of phases additional when the annealing temperature increases up to 350 °C. The major diffraction peak appeared planes of $AgSbTe_2$ (Ref.00-015-0540), $Ag_2Te$ (Ref.00-021-1090) and $Sb_2Te_3$ (Ref.00-015-0874). The film annealed at 400 °C, a slow decomposition was to two phases between $Ag_2Te$ phase and $AgSbTe_2$ phase due to instability structural, the quantity of $Ag_2Te$ phases increases while remain as ever the $AgSbTe_2$ phase. The films annealed reached 450-500 °C, $Ag_2Te$ phases appeared while the $AgSbTe_2$ phase and the $Sb_2Te_3$ phase were invisible. The intensity of $Ag_2Te$ phases was gradually enhanced when the annealing temperature increased, which suggests that the crystal degree of films increase with the increasing annealing temperature. This implies that an antimony element loss to the annealing temperature process and the replacement of Ag in the Sb vacancy.

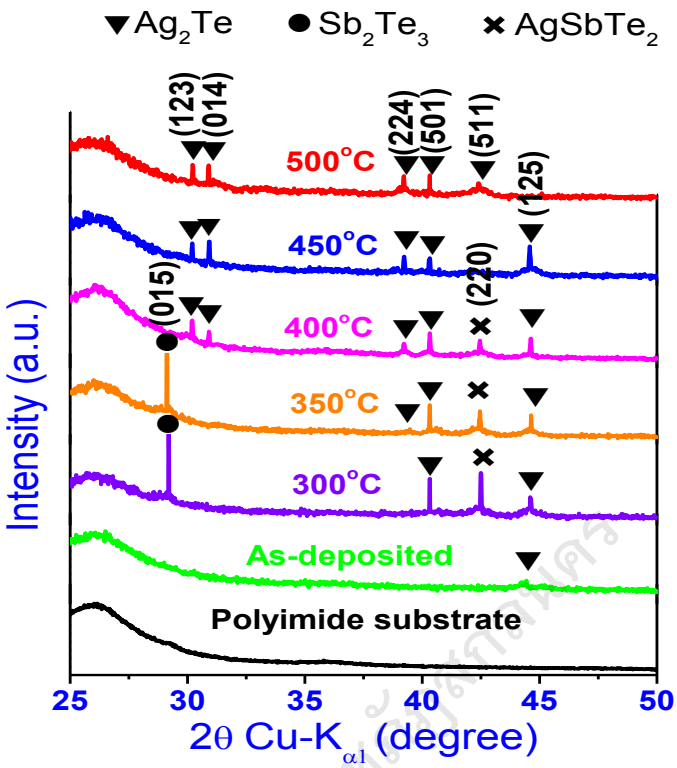


Figure 22 XRD patterns of the as-deposition and annealed Ag-Sb-Te films at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C, respectively.

**Morphology of Ag-Sb-Te film**

The surface images of Ag-Sb-Te film were observed by FE-SEM. Figure 23 (a), (b), (c), (d), (e) show the surface images of Ag-Sb-Te films annealed at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C. These images clearly reveal the effect of the annealing temperature on these characteristics. From Figure 23(a), it can be observed that the as-deposited film is smooth, dense, and strongly adherent. When the film is annealed at 300 °C (Figure 23(b)), the surface of the film appears unchanged from that of the as-deposited film. At an annealing temperature of 350 °C (Figure 23(c)), the surface becomes more grained and roughness. The surface of the film annealed at 400 °C (Figure 23(d)) shows a further increased porosity and crystals clusters.

At the annealed at 450 °C (Figure 23(e)), the films exhibit a more porous with atomic agglomeration on display liquid-like behavior. The film annealed at 500 °C (Figure 23(f)) show increased agglomeration rendering a larger porosity.

The surface morphology of films annealed at 400 °C and 500°C show a noticeable difference in grain size. The result indicates that Sb is increasing replaced with Ag with annealing temperature and this was also in accordance with the result in the XRD patterns. Physically that seems highly unlikely but if it is true then that a surprising and significant result. One way or the other you have to change this statement or present scientific evidence to support this finding.

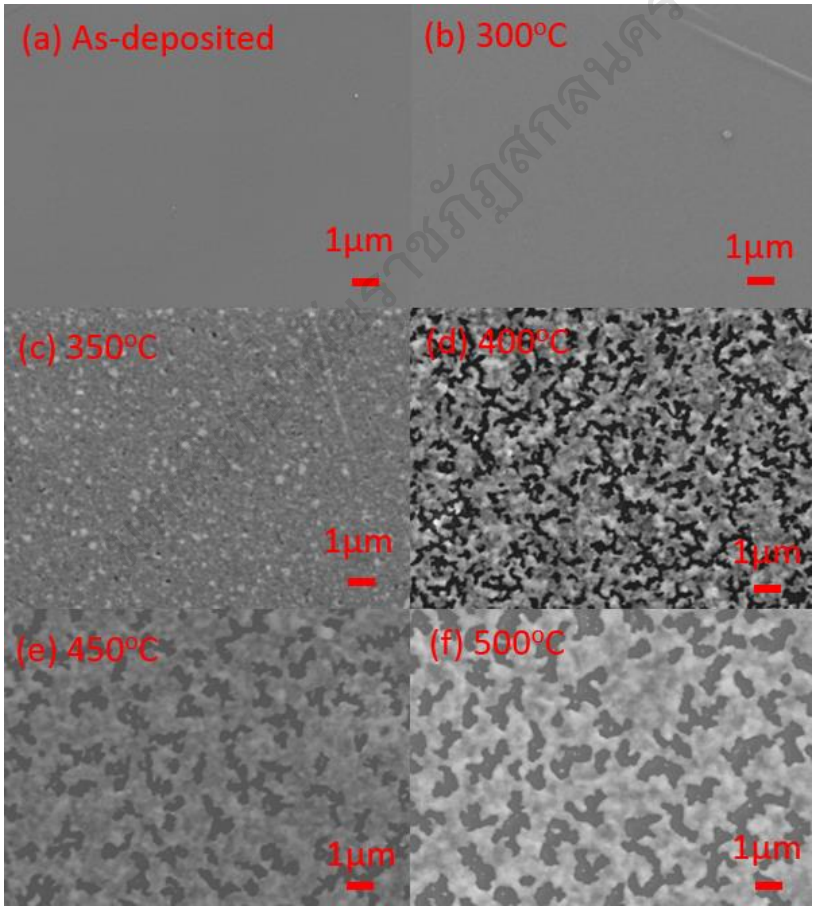


Figure 23 The surface images of Ag-Sb-Te films deposited on Polyimide substrate at various annealing temperatures.

**Atomic composition of Ag-Sb-Te film**

The atomic composition of the films are presented in Figure 24. The atomic composition of the film is Ag element, Sb element and Te element consistent with the XRD patterns (Figure 22). The Ag element in the film suddenly increased with annealing temperature ranging 400 °C concurrently a sudden decrease of the Sb element and Te element. After annealing temperature at 400 °C, the Sb element, Te element and Ag element in the films were rapidly varied in the opposite direction. Moreover, the XRD result show that at a temperature ranging 450-500 °C, the Sb element has disappeared, while the Ag portion doubled compared to the as-deposition films. This suggests that as the annealing temperature increases. The Sb element is replaced with the Ag element. Which is also consistent with the SEM and XRD patterns (see Figure 22 and Figure 23).

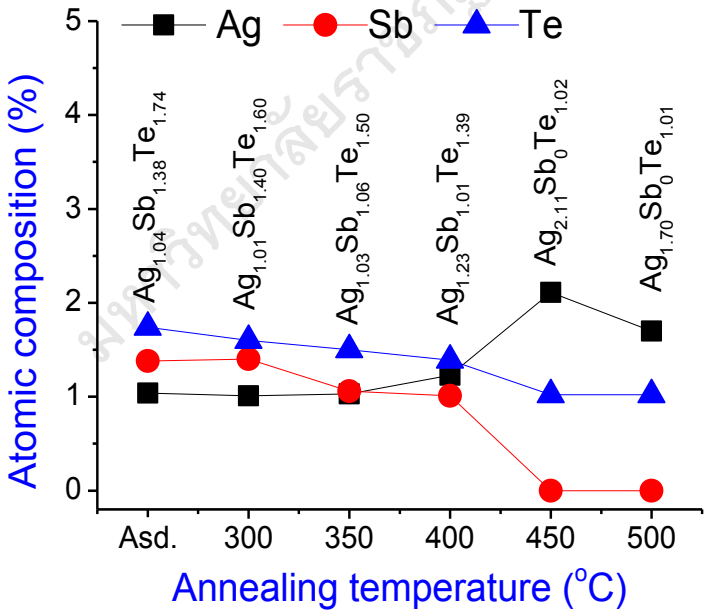


Figure 24 The atomic composition percentages of Ag-Sb-Te films.

**The roughness of Ag-Sb-Te film**

AFM 3D images of Ag-Sb-Te films shown in Figure 25(a) - (f) with all thin films in 1.5 × 1.5 $\mu m^2$. The analysis of these sample images revealed the roughness of these films is 0.69, 1.35, 2.82, 15.09, 16.08, and 17.57 nm, consistent with as-deposition and annealed temperature at 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C, respectively.

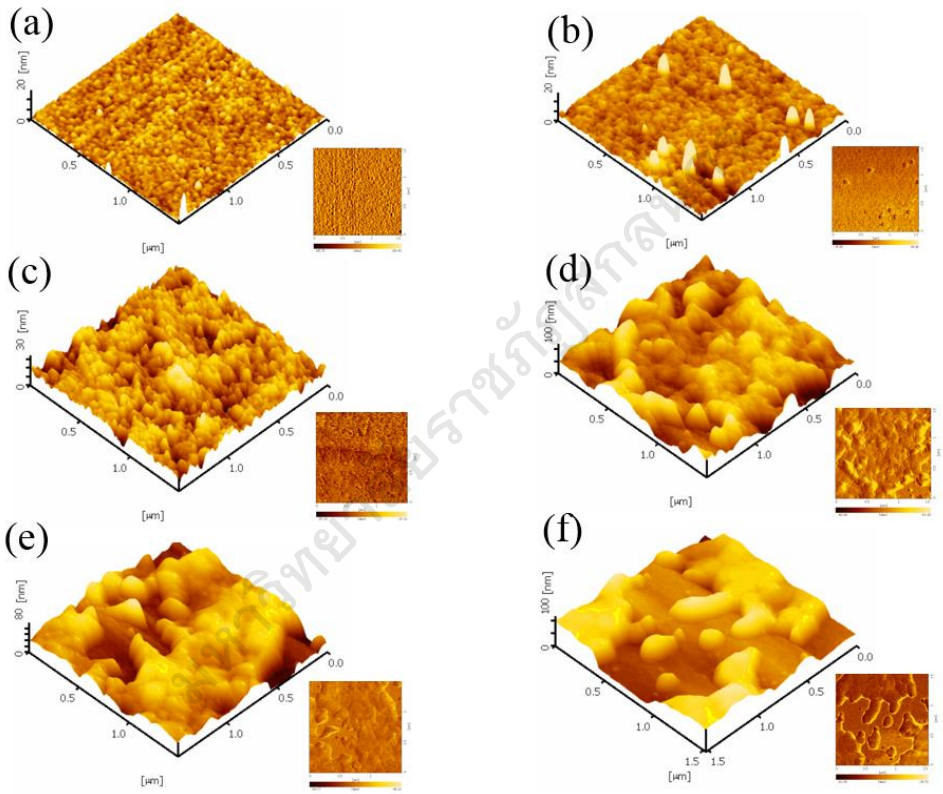


Figure 25 AFM 3D images of AST thin films surface morphology and roughness with Various annealing temperature: (a) As-deposited (b) 300 °C (c) 350 °C (d) 400 °C (e) 450 °C and (f) 500 °C.

Meanwhile, the surfaces shown sample in Figure 25(a) - (c) show gradual atomic agglomeration change to clustered shape and shape spike which to be the result of oriented grains pushing out of thin films. On the other hand, the surfaces shown of sample in Figure 25(d) - (f) display a significant change the shape of thin films. We can observe the porosity increase, especially the samples in Figure 25(e) - (f) exhibit irregular shape of surface and that shown liquid-like behavior. We can be concluded that the surface of thin films varies with the annealing temperature. The film of annealing temperature at 450 $^{o}$C to 500 $^{o}$C has radically irregular shape which is a result of the loss of the Sb element. As mentioned above, it has a low electrical conductivity. The result of this direct observation is basically in accordance with the measurement by XRD and the atomic composition.

## THE RESULTS OF THERMOELECTRIC PROPERTIES OF Ag-Sb-Te THIN FILMS

### Carrier concentration and mobility of Ag-Sb-Te film

The concentration and mobility of the AST thin film were measured by Hall effect at room temperature as shown in Figure 26. The results show that an annealing temperature increasing, the concentration was gradually decreasing. In contrast, the mobility increases greatly up to an annealing temperature of 450 $^{o}$C and rapidly decreases when the annealed temperature approaches 500 $^{o}$C. The decrease of the concentration can be attributed to the decrease of Sb element leading to deterioration of the thin films and decrease of carrier scattering at the grain limits during the annealing process.

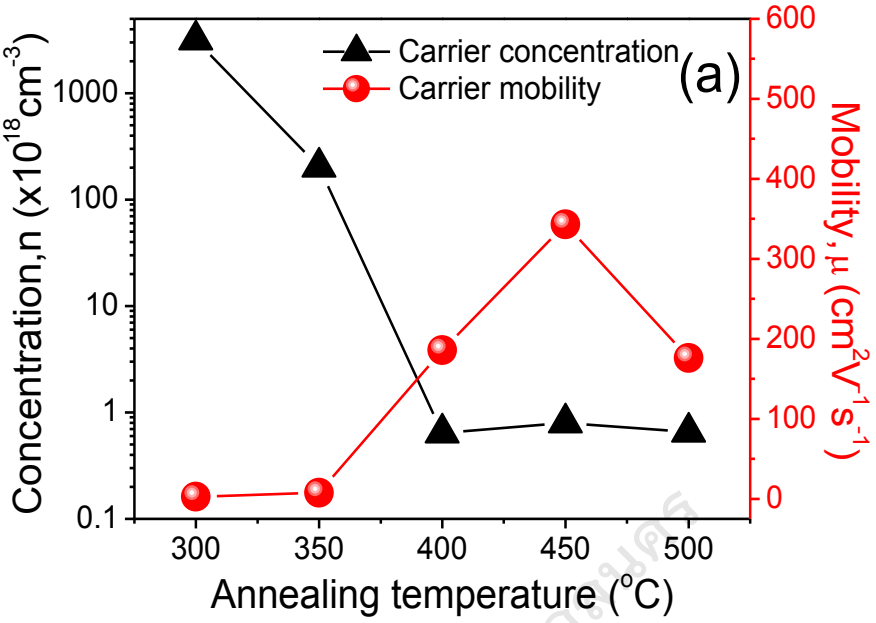


Figure 26 Measuments of carrier concentration and mobility of the Ag-Sb-Te film with various annealing temperatures.

**Electrical resistivity of Ag-Sb-Te film**

The electrical resistivity of the AST thin film is presented in Figure 27. The electrical resistivity of all the thin films increase with increasing annealing temperature. The electrical resistivity of films annealed at 350 °C is less than other films due to suitable the concentration and the mobility in all the thin films, these was approximately of $0.35 \times 10^{-4}$ Ω m and the electrical resistivity of annealed at 350°C is less than of the $Ag_6Sb_{53}Te_{41}$ thin films as reported to Jung et al. (2012, pp.219-224).

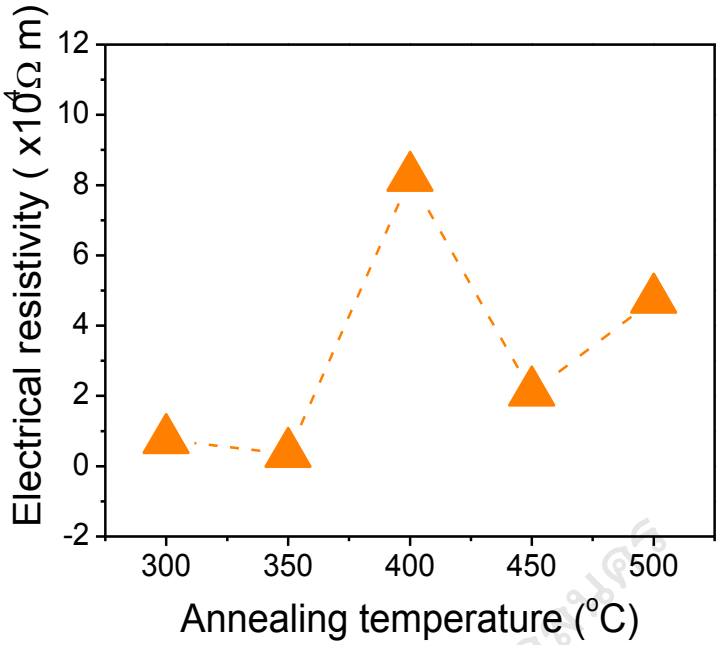


Figure 27 Measuments of electrical resistivity of the Ag-Sb-Te film with various annealing temperatures.

**Seebeck coefficient of Ag-Sb-Te film**

Figure 28 shows the Seebeck coefficient of five samples. The Seebeck coefficient measurement was conducted on these sample at room temperature and determined from the slope of the thermoelectric electromotive force versus the temperature difference between the hot and the cold ends of the films. The samples annealed at 400 °C to 500 °C have negative of Seebeck coefficient values, indicating that the film was on an n - type semiconductor. On the other hand, the samples annealed at 300 °C to 350 °C have positive Seebeck coefficient, indicating that the film was on p-type semiconductor in which holes act as the major carrier. The Seebeck coefficient decreased with decreasing Sb - Te ratio and this is due to the evaporated Sb element, the defects of thin films greatly increase consistent with the relative change of the electrical resistivity which relates to the phase change as discussed above (Zhang et al, 2012, pp.4160-4169). The maximum Seebeck coefficient of 186 μ V $K^{-1}$ were fond for

films annealed at 350 °C which is higher than that of the $Ag_6Sb_{53}Te_{41}$ thin films as reported by Jung et al. (2012, pp.219-224).

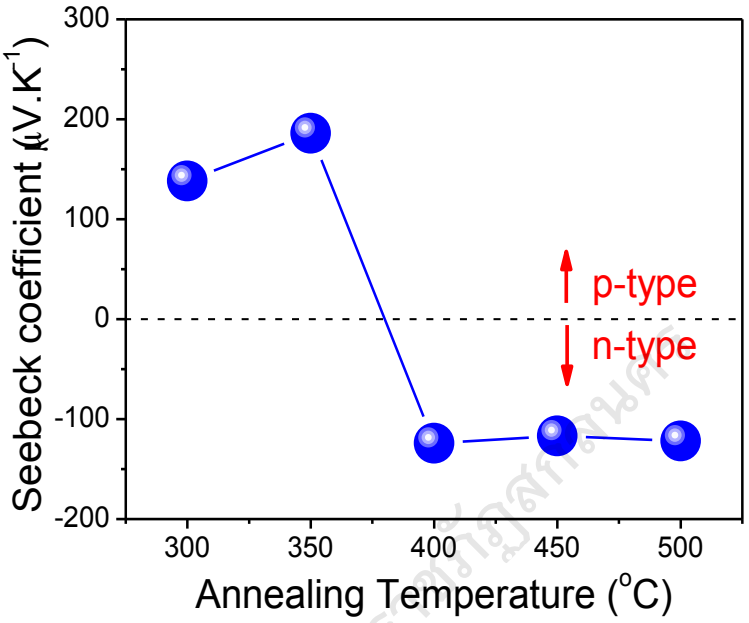


Figure 28 Measuments of Seebeck coefficient of the Ag-Sb-Te film with various annealing temperatures.

**Power factor of Ag-Sb-Te film**

The power factor is one of the important thermoelectric parameters which is defined as $PF = S^2 / \rho$. The power factor and Seebeck coefficient show a similar trend insofar that both trends show an initial increases followed by a decline in the 350-400°C range. The power factor of thin film annealed at 500 °C exhibited lower the power factor than other films and the maximum power factor value of 971.1 μ W $m^{-1}$ $K^{-2}$ as annealed at 350 °C which above than of the $Ag_6Sb_{53}Te_{41}$ thin films and $Ag_{12}$ $Sb_{41}Te_{47}$ thin films as reported to Jung et al. (2012, pp.219-224).

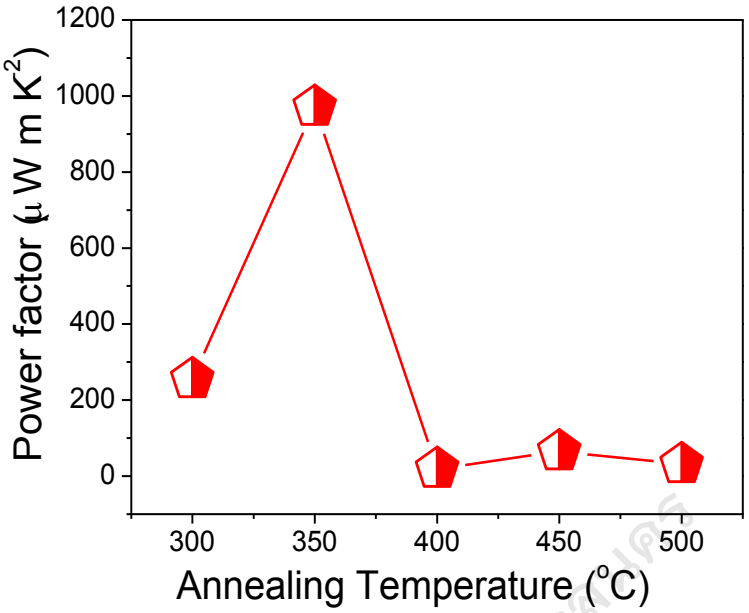


Figure 29 Measuments of and power factor of the Ag-Sb-Te film with various annealing temperatures.

## THE RESULTS OF THERMOELECTRIC GENERATOR PROTOTYPE OF Ag-Sb-Te THIN FILMS

To maeasure the performance of the thermoelectric generator, a temperature difference was applied between the ends of the generator. The temperatures on both sides were investigate using the thermocouples attached to the generator. When heat flows from the hot surface to the cold surface through the thermoelectric material, free charges (electrons and holes) of the semiconductors are also in movement. This charge movement converts the thermal energy into DC electrical energy. The output circuit voltage ($V_{oc}$) was measured using a digital multi-meter. The linearity was observed in all $V_{oc}$ versus $\Delta T$ pots, The $V_{oc}$ value for all films increased with increasing temperature difference. The maximum $V_{oc}$ of 22.11 mV was obtained at $\Delta T$ = 20 °C for film annealed at 350 °C which corresponds to the Figure 30.

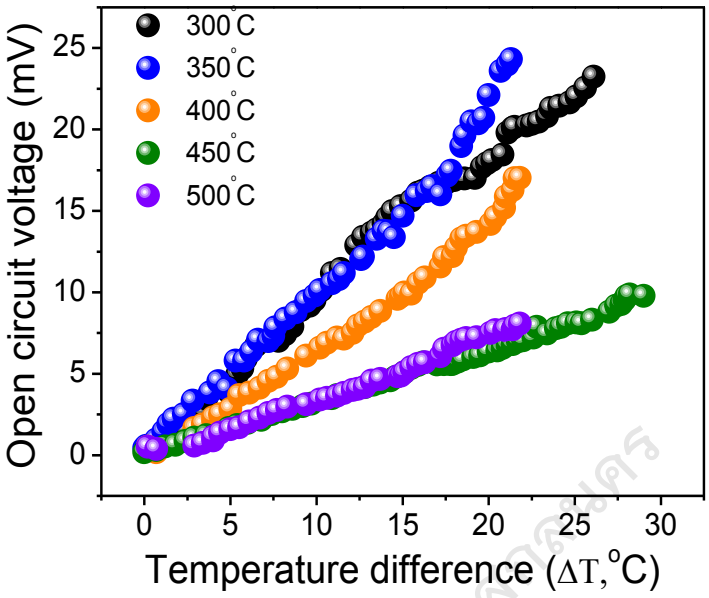


Figure 30 the thin film thermoelectric generator open circuit output voltage versus difference temperature gradients.

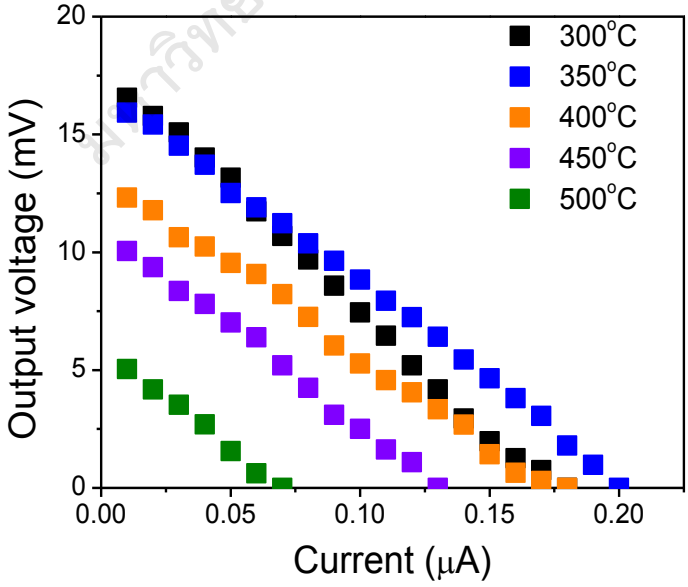


Figure 31 Output voltage of thermoelectric generator versus output current of Ag-Sb-Te film with different temperature at 20 °C.

Figure 31 shows the output voltage of all prototypes plotted as a function of the output current. The plot shows a nearly linear tread for the output voltage at a temperature difference at 20 °C. Moreover, the plot shows that output voltage of film annealed at temperature of 350 °C is higher than the other film due to optimal thermoelectric properties and higher internal resistance. Internal resistance is affected by the porosity and roughness on surface morphology.

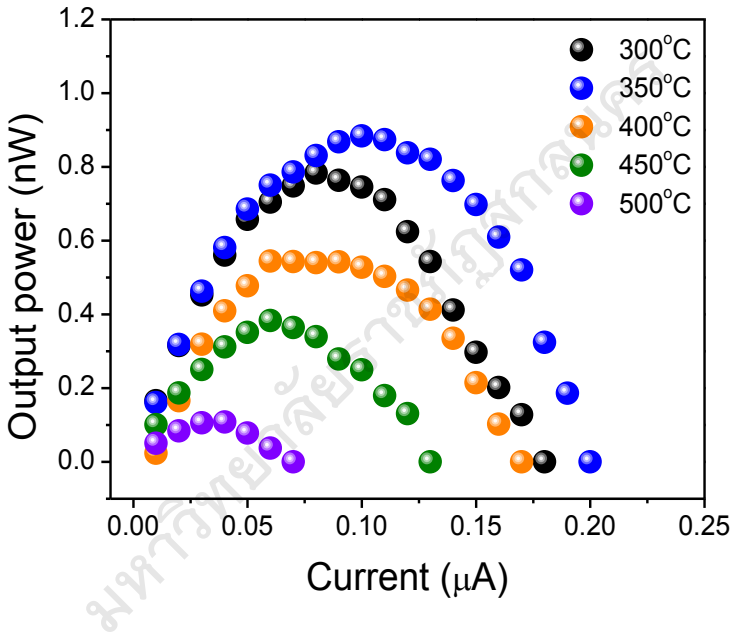


Figure 32 Output power of thermoelectric generator versus output current of Ag-Sb-Te film with different temperature at 20 °C.

Figure 32 shows the output current and power output as function of current when the temperature difference is 20 °C. The power output curve shows the wake in output power with the wake in electric current. However, after a certain wake in electric current, power output decreases due to the thermal saturation point. The magnitude of power output depends on the applied electric current. Therefore, power generation is zero when current is zero.

This optimum value of current depends on $S$, $R_{in}$ and $\Delta T$. Any current larger than this optimum value causes a reduced of the net power output.

Meanwhile, the performance of thermoelectric generator can be improved to reduce the contact resistance sufficiently to operate potential applications. However, We demonstrated successful fabrication of thermoelectric generator of Ag-Sb-Te film using dc-magnetron sputtering on flexible polyimide.