Electrodeposition of zinc antimony alloy thermoelectric materials

A L N Hairin¹, M N Romainor¹, R Othman², F D M Daud¹

¹Department of Manufacturing and Materials Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia
²Department of Science in Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia

Email: assaidatul_laila@iium.edu.my

Abstract. Zinc antimonite, Zn₄Sb₃, is a promising thermoelectric material because of its high thermoelectric performance and abundance of Zn and Sb in nature. Thus, in this study, samples of Zn-Sb alloy were prepared using electrodeposition method because of its simple experimental set-up, which also carried out in the room temperature. From the XRD results, all samples deposited exhibit Zn-Sb alloy compositions. The best results were S1 and S3 as they had dominant peaks that showed the crystal lattice of Zn₄Sb₃. From the SEM images, the surface morphology of Zn-Sb alloy deposited samples showed were all irregular, course and rough structures. While, the atoms arrangement of the deposited samples were all flowery-like. Based on physical properties characterization, the best samples; S1 (0.1M ZnCl₂-0.1M SbCl₃, 100mA, 120min) and S3 (0.1M ZnCl₂-0.1M SbCl₃, 50mA, 120min), were selected and investigated their thermoelectric performances; electrical conductivity and Seebeck coefficient, to determine their power factor, PF. Heat capacity of the samples was also examined to relate it with thermal conductivity of Zn-Sb deposited samples. For thermoelectric performance, S1 obtained power factor of 1.37x10⁻⁷ V/K. Ω.cm at 102°C with the Seebeck coefficient of 181μV/K. While as for S3, the power factor was 1.58x10⁻⁷ V/K. Ω.cm with Seebeck coefficient of 113μV/K at 101°C. From DSC analysis, it showed that S3 obtained higher C_p than S1. C_p for S3 was 46.8093mJ/°C while S1 was 38.3722mJ/°C.

1. Introduction

Studies of thermoelectricity were rather active at the time of world wars. Even after the world wars era end, the studies still carried out for use in valuable technologies, which mainly based on cooling and power generation for application in the military and civilian uses. However, due to the beneficial of some individual in the political and economic, the development of thermoelectric devices were very secretive and made it very difficult to advance to another stage of studies. This was because of slow publication and information sharing especially between Eastern European and Western countries. Despite the difficulties of information sharing, the development of thermoelectricity had significant achievement by the 1950’s when cooling application demonstrates the ability to cooling from ambient temperature to the temperature below 0°C and the efficiencies of power generator had achieved 5%. These successes in the development of thermoelectricity ultimately lead to some feasible industries.
There were many speculations that assumed thermoelectricity capable of replacing refrigeration and conventional heat engines, which lead to big interest in these technologies.

A good thermoelectric material is the one that has a high Seebeck coefficient, a good electrical conductivity and a low thermal conductivity. These parameters then are related into the dimensionless figure of merit, \( ZT=S^2\sigma T/\kappa \) where \( \sigma \) is electrical conductivity, \( S \) is Seebeck coefficient, \( \kappa \) is thermal conductivity and \( T \) is absolute temperature of the materials. For thermal conductivity, it is the sum of lattice thermal conductivity, \( \kappa_l \) and electronic thermal conductivity, \( \kappa_e \) \((\kappa_l + \kappa_e)\). In addition to \( ZT \), the performance of thermoelectric materials can also be characterized by power factor, \( PF=S^2\sigma \). Thus, high quality thermoelectric materials will have higher \( PF \) and \( ZT \) [1–8]. Based on these two factors, among the materials that known as thermoelectric materials; bismuth telluride (Bi\(_2\)Te\(_3\)), bismuth antimony (Bi\(_{1-x}\)Sb\(_x\)), lead telluride (PbTe), silicon-germanium alloy, skutterudites, clathrates, boron carbide and oxides, bismuth telluride and lead telluride are regarded as high class of thermoelectric materials all the time. Despite their high dimensionless figure of merit, these two materials are toxicity, which are very harmful to the user if have direct contact and regarded as expensive materials [6-7].

Considering those factors of Bi\(_2\)Te\(_3\) and PbTe, in this study, zinc antimony was chosen as the thermoelectric materials. Zinc antimony is greatly intoxicated and abundance than Bi\(_2\)Te\(_3\) and PbTe. Zinc also has significantly lower in price compared to bismuth and lead [4-8]. In term of thermoelectric properties; dimensionless figure of merit and power factor, zinc antimony has a high performance in the temperature range of 450 – 650 K. Zinc antimony usually exist in two phase; β-\(\text{Zn}_2\text{Sb}\) and \(\text{ZnSb}\). β-\(\text{Zn}_2\text{Sb}\); with a complex hexagonal crystal structure has been discovered to be one of the promising candidates for thermoelectric power generation applications. The figure of merit, \( Z \) of β-\(\text{Zn}_2\text{Sb}\) is in the range of 450 – 650 K is comparable to both bismuth telluride and lead telluride [4-8]. In this work, zinc antimony was prepared by using electrodeposition method and the effect of deposition parameters; current, time, electrolytic bath formulation, on \(\text{Zn-Sb}\) alloy composition, and thermoelectric properties; electrical conductivity, Seebeck coefficient and thermal conductivity, of \(\text{Zn-Sb}\) alloy were identified and investigated.

2. Experimental procedures

2.1 Materials and apparatus

In the early period of this study, a design of copper substrate which in form of flame retardant 4 (FR4) or also known as printed circuit board (PCB) was fabricated by photolithography process. For holding the substrate at fix distance with the working electrode, Zn plate (99.99% purity), a holder from acrylic board was constructed. To fit Zn plate to the holder, it cut to rectangular form with dimension of 20mm X 50mm. The center of the holder then drilled to form specific depositing area. Electrolytic bath that had been used in this study were 0.1M and 0.2M of zinc chloride, \(\text{ZnCl}_2\) (EMSURE grade) and antimony chloride, \(\text{SbCl}_3\) (Merck KgaA grade). \(\text{ZnCl}_2\) were prepared by dissolving the weighted salt with distilled water. While for \(\text{SbCl}_3\), the weighted salt was dissolved with citric acid, \(\text{C}_6\text{H}_5\text{O}_7\) (HmbG grade) and sodium citrate, \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\) (Bendosen grade) with ratio of 16:49.35 in distilled water. The electrodeposition process was done using AUTOLAB PGSTAT128N machine.

2.2 Electrodeposition process of \(\text{Zn-Sb}\) alloy

The electrolytic cell consisted of zinc plate as the working electrode and copper substrate as the counter electrode. The copper substrate and Zn plate clamped to acrylic holder. The distance between the two electrodes and deposition area fixed to standardize the process for all experiments. The displacement, \(D\) between two electrodes was 20 mm and the diameter, \(d\) of the holder’s windows was 11.5 mm. For this work, the electrolytic baths used were the mixture of 0.1M \(\text{ZnCl}_2\)-0.1M \(\text{SbCl}_3\) and 0.2M \(\text{ZnCl}_2\)-0.2M \(\text{SbCl}_3\). The deposition time varied from 30min to 120min and the current density varied from 50 mA to 100 mA as listed in table 1. The electrolyte volume maintained at 60 ml. The negative terminal of the machine connected to copper substrate and positive terminal connected to Zn plate.
Table 1. Parameters of electrodeposition of Zn-Sb in ZnCl$_2$-SbCl$_3$.

| Sample | Concentration ZnCl$_2$ (M) | Concentration SbCl$_3$ (M) | Deposition time, min | Working electrode | Current, (mA) |
|--------|---------------------------|---------------------------|----------------------|-------------------|---------------|
| 1      | 0.1                       | 0.1                       | 120                  | Zn                | 100           |
| 2      | 0.1                       | 0.1                       | 60                   | Zn                | 100           |
| 3      | 0.1                       | 0.1                       | 120                  | Zn                | 50            |
| 4      | 0.1                       | 0.1                       | 60                   | Zn                | 50            |
| 5      | 0.2                       | 0.2                       | 30                   | Zn                | 100           |

3. Results and Discussion

3.1 XRD analysis of deposited samples

Figure 1 shows the XRD patterns for prepared samples with different molarity, current applied and deposition time during electrodeposition process. The patterns shows that, there are two group of patterns from S1 to S5. The patterns for S1 and S3 show the dominant peaks are located in the range of 36°-44° which indexing plane (223) to (006) of Zn$_4$Sb$_3$. Other than that, there is also a peak observed at 54° define the (244) Zn$_4$Sb$_3$ plane. There are also significant diffraction peak located at 70°-71° that related to Zn$_4$Sb$_3$ (360) to (238) planes as shown in figure 1. As for S2, S4 and S5, the patterns of these three samples show almost identical pattern with the major diffraction peak located around 29° which indexing the reflection from (220) planes of Zn$_4$Sb$_3$. Other than that, the peaks are all very weak, thus cannot used for evaluation. The lack of the diffraction intensity produced from these three samples may because of the samples thickness, which are very thin. Besides, scan rate of the XRD machine also may contribute to the lack of the diffraction intensity. Thus from the diffraction patterns of these five samples, it can be seen that samples prepare for 30-60min deposition time have very weak peaks which can also be related to worst crystal quality. However as the deposition time increase, the samples shows a good patterns with several dominant peaks that indicate the lattice atom of the samples start to crystallize and form Zn$_4$Sb$_3$.

![Figure 1. XRD patterns of Zn-Sb deposited at different parameters.](image-url)
3.2 Surface morphology from SEM

Figure 2 shows the surface morphology of the samples prepared with different deposition parameters, S1 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 100mA, 120min), S2 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 100mA, 60min), S3 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 50mA, 120min), S4 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 50mA, 60min) and S5 (0.2M ZnCl$_2$-0.2M SbCl$_3$, 100mA, 30min) in different magnification. From the figure 3.2, samples S1, S2, S3 and S4 microstructures were very irregular, sparse and flowery-like. Crystalline grain of the samples are fuzzy and surface morphology also very rough. The roughness of the surfaces make crystalline grain almost invisible which indicate the poor crystallization. Figure 2 also indicates that as the current applied during electrodeposition process decrease, the quality of the deposited Zn-Sb alloy also increase. Thus, making S3 and S4 look denser than S1 and S2. However, when the deposition time increase from 60min to 120min, the quantity of deposited ions increase, thus, make the samples become rougher and thicker. The adhesion of the samples also decrease as the Zn-Sb deposited easily wear off from the deposited area.

Based on figure 2, as the molarity of electrolytic bath increase, the structure of Zn-Sb deposited change significantly. Although the surface morphology of S5 is also sparse and rough but flowery-like arrangement of this sample, become significant. The figures also show that the atoms arrange themselves in stacking manner, which then form the flowery-like arrangement. For all the samples, they are to be expected that the surface morphology of Zn-Sb alloy to be course and rough but the flowery-like arrangement is not expected [9]. The complex hexagonal crystal structure of Zn$_4$Sb$_3$ as reported also unable to be verified [4-8].

3.3 Seebeck coefficient, $S$ of Zn-Sb deposited

The Seebeck coefficient of the Zn-Sb alloy deposited of S1 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 100mA, 120min) and S3 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 50mA, 120min) were measured in temperature range of 30°C to 300°C. As shown in figure 3, Seebeck coefficient of S1 has both negative values and positive values. The values started around zero and then drastically decreased to approximately -100μV/K before up back to be around zero. Then the values showed slight increased and then peaked to approximately 181μV/K at 102°C. The values then drop back and fluctuating in the range of 0μV/K to 44μV/K throughout the rest of temperature range. As for S3, the pattern of the graph was almost identical to S1 but the different it only had positive values. The graph started to have peaks at 38.1°C with Seebeck value of 15.5μV/K and at 46.6°C with Seebeck value of 16.5μV/K. The values then drop
to almost zero and the speeded to 113μV/K at 101°C. The graph then had sharp declined and fluctuated in a range of 0μV/K to 27μV/K. When comparing graphs pattern of S1 and S3 with the previous work and Bismuth Telluride thin film, it can be said that approximately at 100°C, the $S$ for both samples were higher. However, as the temperature increase, the $S$ values of the samples decrease and fluctuate which differed from the result that has been expected [10, 12].

![Figure 3](image_url)  
**Figure 3.** Seebeck coefficient of S1 and S3 deposited sample.

### 3.4 Electrical conductivity, $\sigma$ of Zn-Sb deposited

The electrical conductivity of S1 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 100mA, 120min) and S3 (0.1M ZnCl$_2$-0.1M SbCl$_3$, 50mA, 120min) are seen to be constant throughout the temperature range. It can be said that both samples have semiconductors electrical conductivity (around $10^{-6}$ to $10^{-4}$Ω·cm$^{-1}$) which are less then metals’ electrical conductivity (around $10^{7}$ Ω$^{-1}$·cm$^{-1}$) [11]. For S1, the $\sigma$ is 4.06Ω$^{-1}$·cm$^{-1}$ and for S3, it has the value of 12.2Ω$^{-1}$·cm$^{-1}$ as shown in the figure 4. These values considered as very low because from previous work, the $\sigma$ for Zn-Sb alloy deposited around 100Ω$^{-1}$·cm$^{-1}$ if the Zn content more than 50% and around 600Ω$^{-1}$·cm$^{-1}$ if the Zn content around 40%. The reasons as the $\sigma$ for both samples are very low may because of the poor crystalline structure of the deposited Zn-Sb as shown in the figure 2.

![Figure 4](image_url)  
**Figure 4.** Electrical conductivity of S1 and S3 deposited samples.
3.5 Power factor, PF of Zn-Sb deposited
From Seebeck coefficient, S and electrical conductivity, \( \sigma \), power factor, PF have been calculated. As shown in Figure 3.5, S1 (0.1M ZnCl\(_2\)-0.1M SbCl\(_3\), 100mA, 120min) has a significant power factor at 102°C with value 1.37x10\(^{-7}\) V/K. \( \Omega \).cm. Then the values plummet significantly to be around 0x10\(^{-9}\) V/K. \( \Omega \).cm. The peak value of power factor of S3 (0.1M ZnCl\(_2\)-0.1M SbCl\(_3\), 50mA, 120min) is just above 1.5x10\(^{-7}\) V/K. \( \Omega \).cm which is at 101°C. The rest of the graph for S3 was basically having the same pattern as S1. The reason for a power factor of S3 higher than S1 was expected due to the compactness of the sample. As the S3 is prepared with less current that is 50mA, the ions deposited on the substrate at a slower rate that eventually give enough time to the ions to construct themselves better as shown in Figure 5. Due to this, S3 becomes smoother which contributed to the higher electrical conductivity value. On the other hand, because of the rough surface of the samples, the power factor of both samples become inconsistent that in the end reduce the thermoelectric performance of Zn-Sb deposited. These results are not as expected as the previous work [10].

![Figure 5. Power factor of S1 and S3 deposited samples.](image)

3.6 Heat capacity, \( C_p \) of Zn-Sb deposited
To compensate the thermal conductivity, heat capacity, \( C_p \) of S1 (0.1M ZnCl\(_2\)-0.1M SbCl\(_3\), 100mA, 120min) and S3 (0.1M ZnCl\(_2\)-0.1M SbCl\(_3\), 50mA, 120min) have been investigated using DSC. The data from the DSC have been recorded in Table 2. Based on Table 2, it shows that S3 has a higher \( C_p \) than S1. \textit{Chip} for S3 is 46.8093mJ/°C while S1 is 38.3722mJ/°C with the difference of 8.4371m J/°C between the two samples. This difference could be related to the compactness of S3 compare to S1, which allow the samples to store more heat energy. When the samples have the ability to store more heat energy, it can be concluded that the thermal diffusivity of the samples are low. Thus, according to thermal conductivity equation, when the thermal diffusivity low, the thermal conductivity also low.

| \( S_1 \)      | Heat Flow (mW) | Heat Capacity (mJ/°C) | \( S_3 \) | Heat Flow (mW) | Heat Capacity (mJ/°C) |
|--------------|----------------|-----------------------|----------|----------------|-----------------------|
| a            | 0.2597         | 1.5577                | a        | 0.2650         | 1.5898                |
|              | n/a            | n/a                   |          | 1.5429         | 9.2558                |
|              | 0.2501         | 1.5005                | b        | 17.9410        | 107.6244              |
|              | 4.9225         | 29.5294               |          | n/a            | n/a                   |
4. Conclusion

In summary, it can be demonstrated that Zn-Sb alloy was successfully fabricated by using electrodeposition method. Two types of electrolytic bath formulation; the mixture of 0.1M ZnCl₂-0.1M SbCl₃ and 0.2M ZnCl₂-0.2M SbCl₃ were prepared for Zn-Sb deposited. From the XRD results, all the samples deposited to form thin films samples exhibit Zn-Sb alloy compositions. The obvious results were S1 and S3 as they had significant peaks that shows the crystal lattice of Zn₄Sb₃. S2, S3 and S5 exhibited the alloy needed, but had a lot of noise in the spectra. The noise was assumed caused by the thickness and roughness of the samples. SEM images showed that the surface morphology of all samples were rough and coarse. When the current lower, the samples become denser. However, when the deposition time increased, quantity of deposited ions increased, thus, made the samples become rougher and thicker. The compactness of the samples affected the thermoelectric performances of the samples significantly. Due to that S3 had higher power factor compared to S1. Although the Seebeck coefficient of S3 (113μV/K) was not as high as S1 (181μV/K), but because of its atomic arrangement that made the sample denser, the electrical conductivity of the S3 surpasses the value of S1. Thus because of this difference only, S3 had produced Zn-Sb alloy with better power factor (1.58x10⁻⁷V/K. Ω.cm at 101°C) which indicated its efficiency in converting thermal energy to electricity compared to S1 (1.37x10⁻⁷V/K. Ω.cm at 102°C).

Acknowledgement

This work was financially supported by RIGS16-073-0237, International Islamic University Malaysia (IIUM).

References

[1] Budak S, Guner S, Muntele C. I, and Ila D 2015 Phys. Procedia 66 pp 329–335
[2] Carlini R, Marré D, Pallecchi I, Ricciardi R and Zanichetti G 2014 Intermetallics 45 pp 60–64
[3] Bjerg L, Iversen B. B, and Madsen G. K. H 2014 Phys. Rev. B - Condens. Matter Mater. Phys. 89 (2) pp 024304
[4] Li J, Li J, Zhang Q, Zhang Z, Yang G, Ma H, Lu Z, Fang W, Xie H, Liang C and Yin F 2016 Comput. Mater. Sci. 125 pp 183–7
[5] Okamura C, Ueda T and Hasezaki K 2010 Materials Transactions 51(5) pp 860-862
[6] Pothin R, Ayral R M, Berche A, Granier D, Rouessac F and Jund P 2016 Chem. Eng. J. 299 pp 126-134
[7] Rouessac F and Ayral R M 2012 J. Alloys Compd. 530 pp. 56-62
[8] Wrona A, Bilewska K, Mazur J, Lis M and Staszewski M 2014 J. Alloys Compd. 616 pp 350-355
[9] Fan P, Fan W F, Zheng Z H, Zhang Y, Luo J T, Liang G X and Zhang D P 2014 Journal of Materials Science: Materials in Electronics 25 pp 5060-5065
[10] Zheng Z H, Fan P, Liu P J, Luo J T, Liang G X and Zhang D P 2014 Journal of Alloys and Compounds 594 pp 122-126
[11] Quirk M and Serda J 2001 Semiconductor manufacturing technology. Upper Saddle River, NJ: Prentice Hall, 1
[12] Kim D H, Byon E, Lee G H and Cho S 2006 Thin Solid Films 510 pp 148-153