# Enhancing the thermoelectric properties of CZTS thin films grown on multi-crystalline Si substrate by controlling the sulfurization time duration

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In this manuscript, we have reported the high value of the power factor for Copper Zinc Tin Sulfide (CZTS) thin films. CZTS samples used in this study were grown by a sol-gel method using spin coater on multi-crystalline Si (m-Si) substrate. After growth, effect of sulfurization time duration was tested by annealing the samples in the sulfur environment for different time durations (30-60 minutes) with a step of 10 minutes. The highest values of Seebeck (980 μV/$^0$C), electrical conductivity (830 S/m) and power factor ($7.88 \times 10^{-2}$ Wm$^{-1}$K$^{-2}$) were obtained for 60 minutes sulfurized sample. This enhancement in thermo-electric properties was related to the improvement of CZTS crystal structure due to increase by sulfurization time. The improvement in the crystal structure was supported by XRD and Raman spectroscopy measurements. XRD data demonstrated that a major CZTS (112) plane was observed at 2Ө=28.7° for all samples. Crystalline size of grown samples was found to be increased from 12.92 nm to 14.9 nm with increasing the sulfurization time duration. Raman spectroscopy data also suggested that intensity of CZTS related active modes increased and the number of secondary phases decreased by increasing sulfurization time duration.

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*Keywords:* CZTS thin film, Sol-gel method, Seebeck coefficient, XRD, Raman spectroscopy

## 1. Introduction

The demand of clean and cheap electrical energy is increasing day by day due to rapid industrialization. Energy production using conventional energy sources such as oil and gas is causing threat for environment due carbon emission [1]. Therefore the need of renewable energy sources for the production of environment friendly energy has fundamental importance. Different renewable energy sources such as photovoltaic, wind energy, bio gas and thermoelectricity are gaining the interest of research community. Among these energy sources, thermoelectricity is supposed to be the most cheap and pollution free energy source. The efficiency of any thermoelectric material can be quantified by a figure of merit (ZT) which is a dimensionless quantity defined as,

$$Z = S^2\boldsymbol{\sigma}/K$$

where Z is figure of merit, S is Seebeck coefficient, $\boldsymbol{\sigma}$ *is* electrical conductivity and *K* is thermal conductivity. It is clear from the above formula that the figure of merit depends on *S*, $\boldsymbol{\sigma}$, *T* and *K*. The materials with high Seebeck coefficient and electrical conductivity are highly recommended for thermoelectric power generation applications. The commercially used high efficiency reported thermo-electric materials include a wide class of materials such as Half-Heuslers, silicides, lead and bismuth telluride material. But such class of materials is highly toxic, expensive and rare earth elements [2-5]. Therefore, these materials are not efficient to be used at large scale in industrial process. TE materials are divided into three temperature ranges, classes such as low temperature range (200-400 K), middle temperature range (400-900 K) and high temperature range (> 900 K). The copper based chalcogenides (CZTS) are potential thermo-electric candidates due to high electrical conductivity and low thermal conductivity in mid-range temperature. Furthermore, CZTS material has quaternary elements which are non-toxic, earth abundant and cheaper than the other all materials which are used commercially for thermo-electric power generation. Therefore, in last few years CZTS attracted the attention of researchers due to its optimal band gap and complex structure. Generally, the complex structure reduces the thermal conductivity and large band gap further reduced the bipolar effect. One can find a few reports about the thermo-electric properties of copper based quaternary materials [6-9]. Our research group is also contributing to explore the potential of CZTS for thermo-electric power generation applications. For example, one of our manuscript demonstrated the modulation of thermoelectric properties of CZTS samples by varying the concentration Zn atoms ranging from 0.5-2.0 mM [10]. Our research group also successfully enhanced the different structural and thermoelectric properties by varying the concentration of Sn atoms during the synthesis process [11]. A. Ashfaq et al. have suggested that thermoelectric properties may be enhanced by controlling the number of secondary phases in the grown CZTS thin films. They have modulated the number of secondary phases by growing samples on various substrates [12]. All reported data suggested that type of substrate or different parameters associated with the growth of CZTS thin films may significantly enhanced the thermoelectric properties [10-12]. Therefore, a detailed study on controlling the sulfurization time duration may be an effective method to modulate the thermoelectric properties.

This specific study reported the influence of post growth sulfurization time duration on the various thermo-power parameters for CZTS thin films grown Silicon substrate via a chemical solution method. The reported results have demonstrated that TE properties were increased significantly by increasing the sulfurization time duration because the crystallinity was improved.

## 2. Experimental section

CZTS thin films were grown via a chemical solution method on the multi-crystalline Si substrate. The solution was prepared using precursors of Copper, Zinc, Tin and Sulfur. 1.9 mM of Copper Acetate Monohydrate (99 %, Merck), 1.02 mM of Zinc Acetate (99 %, Merck) and 0.99 mM of Stannous chloride (98 %, Merck) were dissolved in 4 ml of propylene glycol for 60 min at 60 $^{o}$C. After dissolving of these precursors, the color of the solution was transformed to transparent greenish. Finally, 8.01 mM of $CH_4N_2S$ was added in greenish solution and stirred for 10 min. At the end the light transparent yellow sol-gel of CZTS was prepared.

The prepared sol-gel was coated on m-Si substrate by a spin coating technique which is already reported in our previous manuscript [13]. The multiple coating was performed to obtain the required thickness. The thickness of samples was 0,5 micro-meter which was measured by filmtronics thickness monitor. The grown samples were sulfurized at different time durations of 30, 40, 50 and 60 minutes in a tube furnace by fixing other parameters like temperature (500 $^{o}$C), vacuum (0.1 torr), source quantity (1 mg) and source to substrate distance (12 cm) constant.

The XRD crystallographic structures were recorded using BRUKER D8 ADVANCED machine. Surface morphology was studied by Scanning electron microscope (SEM) by EmCraft Cube 1100. Confocal Micro Raman Mapping (MN STEX-PRI 100) was used to measure Raman spectra and thermoelectric parameters were recorded using in-house developed Seebeck system. Further detail can be found in references [10-12].

## 3. Results and discussion

Fig. 1 depicts the sulfurization time and measurement temperature dependent Seebeck coefficient of CZTS thin films grown on multi-crystalline Silicon (m-Si) substrate in the measurement temperature range 25-100 $^{o}$C. The data indicated that the value of Seebeck coefficient was increased from 338-980 μV/$^{o}$C as the sulfurization time increased from 30 min to 60 min. This increasing trend of Seebeck coefficient with sulfurization time duration is may be linked with the improvement of crystalline structure. Similar behavior of crystalline structure with sulfurization time of CZTS samples was already investigated by our research group [11]. The high value of Seebeck coefficient for all samples may be due the lattice mismatch between the substrate (m-Si) and CZTS thin films which cause dangling bond effect. Due to this lattice mismatch, various energy trap states developed in the grown the CZTS thin films. These trap states acted as extra/secondary phases in the host crystal of synthesized thin films. Such secondary phases can act as energy barrier for slow moving carriers at the interface of two secondary phases and only high mobile carriers are able to reach at the cold end of sample. Therefore, high mobile carriers enhanced thermo-motive force [14]. To strengthen our argument, we have measured the mobility of carriers using Hall measurements and it was found that carrier mobility was increased from 1.7-12.3 cm$^2$/V-S when time duration increased to 60 minutes. Measured data also suggested that electromotive force also strongly depend upon the measurement temperature. This increment of Seebeck value with increasingly measurement temperature was expected because the charge carriers obtained more thermal energy at a higher measurement temperature which cause to improve the Seebeck coefficient.

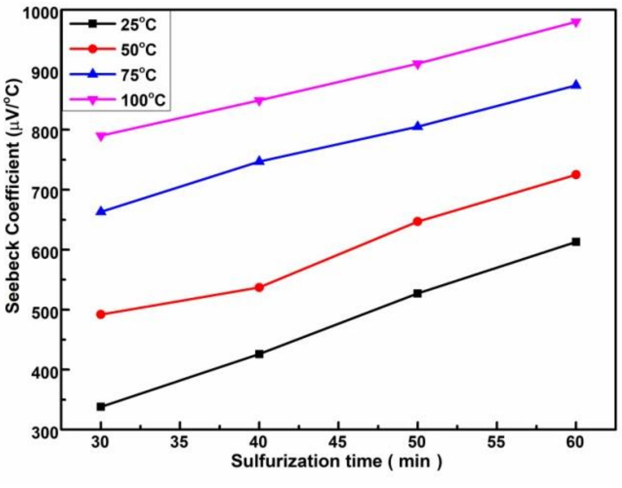

*Fig. 1. Graph of Seebeck Coefficient versus sulfurized time duration of CZTS/m-Si thin films (color online)*

Fig. 2 depicts the effect of sulfurization time on the conduction of CZTS/m-Si thin films measured at various measurement temperatures. The increased in carrier conduction from 340-830 S/cm was observed with increasing the duration of sulfurization time (30-60 minutes). The enhancement in the electrical conductivity with sulfurization time is due to the fact that increasing sulfurization time significantly improved the crystal structure of CZTS (explained by XRD measurements later) which causes the production of only high mobile carriers. As the electrical conductivity has strong dependence on mobility, therefore increase in the electrical conductivity is obvious.

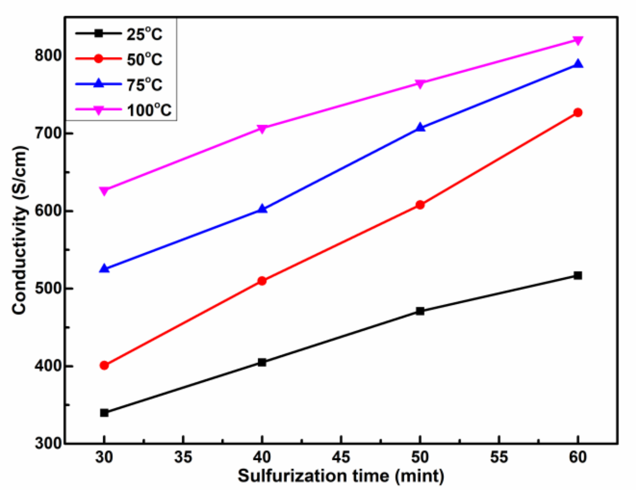

*Fig. 2. Relationship between electrical Conductivity and sulfurization time duration of CZTS/m-Si thin films (color online)*

The power factor is highly based on Seebeck coefficient and electrical conductivity using formula below and illustrated in Fig. 3.

$$PF = S^2\alpha$$

where PF is power factor, S is Seebeck coefficient and $\alpha$ is electrical conductivity. We have reported the highest values of thermoelectric performance parameters for bulk CZTS as compared to previous reported values of 26 S/m and 355 µV/$^0$C respectively [15]. As followings the results of Seebeck coefficient and electrical conductivity, the highest value of power factor for 60 minutes sulfurization time duration is expected [16, 17].

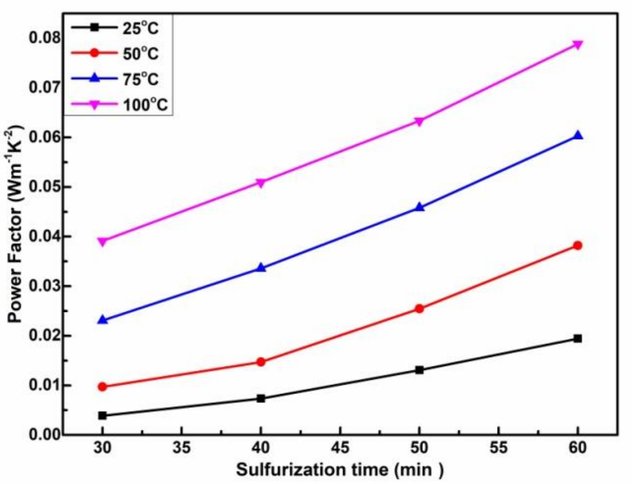

*Fig. 3. Variation of thermo-power factor with the sulfurization time duration for CZTS/m-Si thin films (color online)*

Fig. 4 showed the XRD spectrum of CZTS TFs synthesized on the multi-crystalline Silicon substrate with different ramping of sulfurization time (30-60 min). The major phase of CZTS TF was observed at 2theta 28.7$^{o}$C with (112) plane of Kesterite structure (JPCDS-26-0575). The secondary phases of CZTS were also observed at 2 theta 23.1$^{o}$, 32.9$^{o}$, 47.3$^{o}$ and 57.6$^{o}$ corresponding to (110), (200), (220) and (312) planes respectively (JPCDS-26-0575). The binary secondary phases of CuS were also observed at 2theta 29.4$^{o}$ and 31.8$^{o}$ with planes of (102) and (103) respectively (JPCD-01-1281). CuS phase with plane (103) was present in all samples but the (102) plane of CuS was emerged with as the time duration was increased. It is further noted that few other extra/secondary phases were also observed at 2theta 26.0$^{o}$ and 27.0$^{o}$ with planes (012) and (100) respectively. (JPCD 01-0984, 01-0677). These extra planes are assigned due to SnO and ZnO based phases. SnS phase with plane (012) was observed in all samples but ZnS phase with plane (100) was disappeared with ramping of sulfurization time. Weak XRD peaks suggested that m-Si substrate was not well supported the growth of CZTS TFs due to the lattice mismatch between grown film and substrate [18]. It is also evident from XRD data that sulfurization time was also affected on the crystal structure of CZTS TFs. At the low sulfurization time of 30 min, XRD peak intensity of CZTS phases is quite low as well high number of extra/secondary phases. But as the sulfurization time increased, the intensity of XRD peaks improved and secondary phases were also reduced. We have also calculated the values of crystalline size, micro-stain and dislocation density. Similar results were also reported by Ashfaq et al. that crystalline structure of CZTS/ITO TFs was improved with increasing the sulfurization time [13].

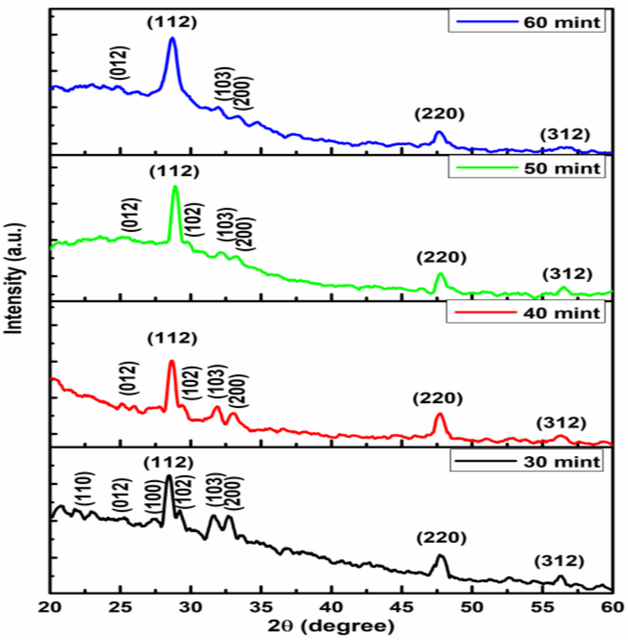

*Fig. 4. X-Ray Diffraction spectrum of CZTS/m-Si thin films sulfurized at different time durations (color online)*

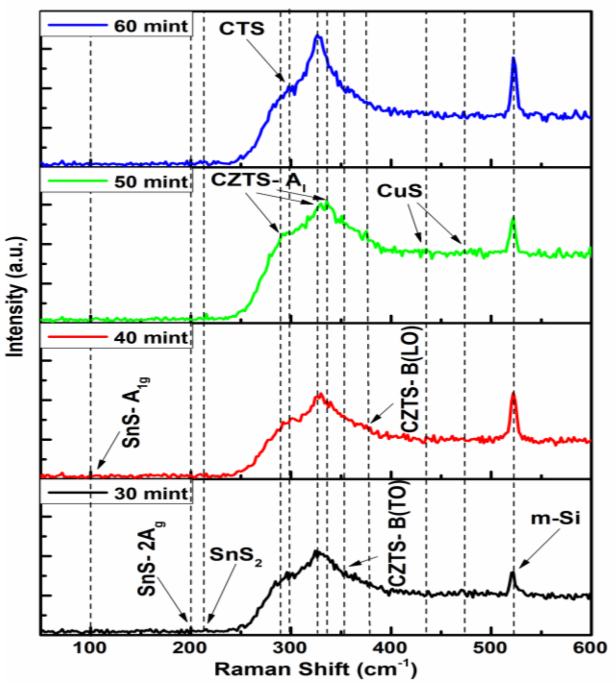

*Fig. 5. Raman spectrum of CZTS/m-Si thin films taken after various sulfurization time durations (color online)*

Fig. 5 demonstrated some strong vibration modes of CZTS structure at 288, 329 and 336 $cm^{-1}$ and assigned as $A_1$ modes. In addition to basic modes, we have also observed a couple of secondary vibrations at 354 and 374 $cm^{-1}$ with Transverse Optical (TO) and Longitudinal Optical (LO) modes respectively [13]. A small vibration due to secondary phases ($Cu_2SnS_3$, CuS, SnS and $SnS_2$) was observed at different positions and is illustrated in Fig. 5 [11-13]. The vibration mode of multi-crystalline silicon (substrate) was detected in all samples at 522 $cm^{-1}$. Raman data suggest that the intensity of major active vibrations of CZTS TFs were improved by increasing the sulfurization time at a constant temperature. XRD data also backed the observed Raman results.

Fig. 6 represents the SEM images of CZTS samples sulfurized for different times. As lower sulfurization time, SEM micrograph is revealed the small grain size of copper sulfide. It is clearly seen from images that as we have increased the time duration, large grain size of ($Cu_2S$, $Cu_xS$) at the top of the CZTS surface which may act as secondary phases.

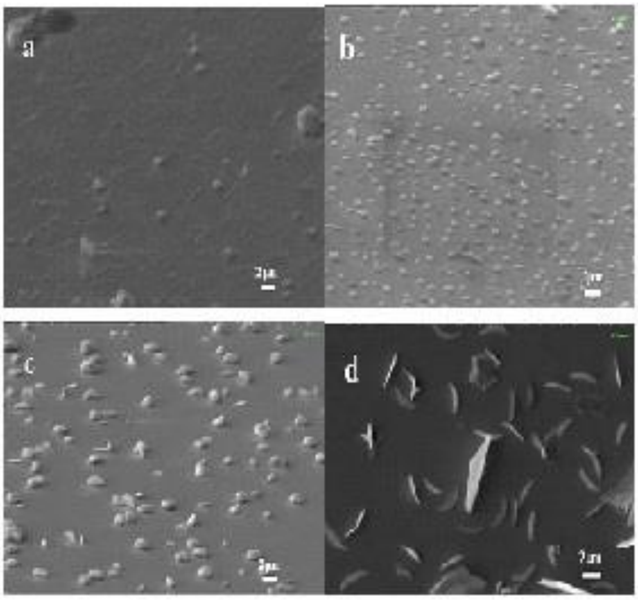

*Fig. 6. SEM images of CZTS thin films annealed for different sulfurization time durations*

## 4. Conclusion

We have reported an enhancement in various thermoelectric parameters of solution grown CZTS samples by increasing the post growth sulfurization time duration. Time duration effect was demonstrated by annealing the grown samples in the sulfur environment for different time durations (20-60 minutes) using the vacuum tube furnace. We have observed a significant enhancement in various thermoelectric with sulfurization time, this enhancement in thermoelectric properties was due to the fact structure of grown CZTS improved with increasing the sulfurization time duration. In order to support this argument, we have performed a number of additional measurements.

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## References

[1] Y. Zhao, C. Burda, Energy & Envir. Sci. **5**, 5564 (2012).

[2] B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, Z. Ren, Sci. **320**, 634 (2008).

[3] R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'quinn, Nature **413**, 597 (2001).

[4] C. Yang, D. Souchay, M. Kneiß, M. Bogner, H. M. Wei, M. Lorenz, O. Oeckler, G. Benstetter, Y. Q. Fu, M. Grundmann, Nature Communications **8**, 16076 (2017).

[5] Z. H. Ge, L. D. Zhao, D. Wu, X. Liu, B. P. Zhang, J. F. Li, J. He, Mater. Today **19**, 227 (2016).

[6] A. Rehman, J. Jacob, R. Zahra, K. Mahmood, A. Ali, U. Rehaman, Y. Ali, A. Ashfaq, W. Ahmad, S. Ikram, N. Amin, S. Hussian, Ceramics International **45**(13), 16275 (2019).

[7] J. Jacob, R. Wahid, A. Ali, R. Zahra, S. Ikram, N. Amin, A. Ashfa, U. Rehman, S. Hussain, D. S. Al-Othmany, S. Z. Ilyas, K. Mahmood, Physica B: Condensed Matter. **562**, 59 (2019).

[8] K. Mahmood, J. Jacob, A. Rehman, A. Ali, U Rehman, N. Amin, S. Ikram, A. Ashfaq, S. Hussain, Ceramics International **45**(15), 18701 (2019).

[9] R. Zahra, J. Jacob, N. Bano, A. Ali, K. Mahmood, S. Ikram, M. I. Arshad, A. Ashfaq, U. Rehman, S. Hussain, Physica B: Condensed Matter. **564**, 143 (2019).

[10] A. Ali, J. Jacob, A. Ashfaq, M. Tamseel, K. Mahmood, N. Amin, S. Hussain, W. Ahmad, U. Rehman, S. Ikram, Dheya Shjaa Al-Othmany, Ceram. Internat. **45**, 12820 (2019).

[11] A. Ali, J. Jacob, A. Ashfaq, K. Mahmood, S. Ahmad, U. Rehman, W. Ahmad, N. Amin, S. Ikram, S. Hussain, N. Ali, M. A. Khan, Ceramics Internat. **45**, 22513 (2019).

[12] A. Ashfaq, J. Jacob, N. Bano, A. Ali, W. Ahmad, K. Mahmood, M. I. Arshad, S. Ikram, U. Rehman, S. Hussain, Physica B: Condensed Matter. **558**, 86 (2019).

[13] A. Ashfaq, J. Jacob, N. Bano, M. Ajaz Un Nabi, A. Ali, W. Ahmad, K. Mahmood, M. I. Arshad, S. Ikram, U. Rehman, N. Amin, S. Hussain, Ceramics Internat. **45**, 10876 (2019).

[14] R. People, J. C. Bean, Appl. Phys. Letter **47**, 322 (1985).

[15] M. L. Liu, F. Q. Huang, L. D. Chen, I. W. Chen, Appl. Phys. Lett. **94**, 202103 (2009).

[16] L. D. Hicks, M. S. Dresselhaus, MRS Online Proceedings Library Archive **326**, 47366 (1993).

[17] H. Yang, L. A. Jauregui, G. Zhang, Y. P. Chen, Y. Wu, Nano Lett. **12**, 540 (2012).

[18] A. Houimi, S. Y. Gezgin, B. Mercimek, H. Ş. Kılıç, Optical Materials **121**, 111544 (2021).

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