

## **CURRICULUM VITAE (CV)**

**Name: Khushboo Agarwal**

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Date of Birth: 18th May 1987

### **Research positions**

2017- Till date: Indian Institute of Technology-Delhi, India

Worked as a postdoctoral fellow in a joint collaborative project between Bio-Nano Electronics Research Centre (BNERC), Toyo University Japan and Indian Institute of Technology-Delhi, India. Currently engaged in performing X-ray Photoelectron Microscopy (XPS) measurements and synthesis of metal nanoparticles for plasmonic applications.

### **Education**

2011-2017: Ph.D., Indian Institute of Technology Delhi, India

Ph.D. Supervisors- Prof B. R. Mehta (IIT-Delhi, India) & Prof. J. Brugger (EPFL, Laussane, Switzerland)

2009-2011: Research Associate, National Physical Lab, Delhi, India

2007-2009: MSc. Physics (Electronics), University of Delhi, India

2004-2007: BSc. (H) Physics, University of Delhi, India

### **Research Interest**

Synthesis of organic, inorganic and 2D thin films and nanocomposites, electrical and thermal characterizations, nanoscale measurements, p-n junctions, organic-inorganic hybrid structures, interfacial properties, grain structure, solar cells, thermoelectric measurements techniques, high resolution transmission electron microscopy, conductive atomic force microscopy, kelvin probe force microscopy, scanning thermal microscopy, X-ray photoelectron microscopy.

### **Technical Skills**

#### ***Deposition techniques***

Thermal evaporation, DC and RF magnetron sputtering, electrochemical deposition, solvothermal and chemical bath techniques.

#### ***Characterization techniques***

X-ray diffraction and X-ray photoelectron spectroscopy for structural analysis, Spectroscopic ellipsometry and UV-Vis-NIR for optical studies, two and four probe I-V using probe station for electrical studies, resistivity vs temperature, capacitance-voltage measurements, conductive atomic force microscope, kelvin probe force microscope and scanning thermal microscopy for nanoscale electrical and thermal studies, Seebeck effect measurement, photovoltaic response, frequency response analysis, cyclic voltammetry.

#### ***Device Testing***

Electrical and thermal measurement for thermoelectric and solar cell applications at macroscale and nanoscale level.

## ***Programming Languages***

C/C++ and labview programming for interfacing

## **Research Experience**

- Synthesis of thin film of polymers and various inorganic compounds using electrochemical deposition, RF magnetron sputtering and thermal evaporation systems.
- Synthesis of 2D thin films (graphene, MoS<sub>2</sub>, Bi<sub>2</sub>Te<sub>3</sub>) using CVD, MOCVD and solvothermal methods.
- Fabrication and electrical characterization Bi<sub>2</sub>Te<sub>3</sub> based nanocomposite structures with various 2-D as well as bulk materials for thermoelectric measurements.
- Understanding of the role of interface modification of nanocomposite structures and its charge transport on thermoelectric applications.
- Enhancement in figure of merit of Bi<sub>2</sub>Te<sub>3</sub> nanocomposites (ZT ~ 1.45) as compared to ZT for Bi<sub>2</sub>Te<sub>3</sub> (~ 0.40).
- Developed a new technique for measuring thermal conductivity of thin films based on modified Parker's method using commercial SThM.
- Understanding the reaction kinematics and equivalent circuits involved in electrochemical synthesis for doped polymers.
- Transport studies for disordered system on the basis of Mott's VRH model and Mott's parameters for polymer systems.

## **Honors & Awards**

- NET-UGC fellowship granted by Council for Scientific and Industrial Research (CSIR), Govt. of India for doctoral research work (2010-2015)
- Qualified Graduate Aptitude Test in Engineering (Physics) 2010 with a percentile of 98.4.
- Best oral presentation at Delhi Technical University (DTU) (2011)
- Best poster presentation at National Physical Laboratory (NPL), on science day (2011).

## **Publications**

1. D. Sharma, N. Kamboj, **K. Agarwal** and B. R. Mehta. Structural, optical and photoelectrochemical properties of phase pure SnS and SnS<sub>2</sub> thin films prepared by vacuum evaporation method, Journal of Alloys and compounds, 822, 153653 (2020).
2. M. Vishwakarma, **K. Agrawal** and B. R. Mehta. Investigating the effect of sulphurization on volatility of compositions in Cu-poor and Sn-rich CZTS thin films, Applied Surface Science, 507, 145043 (2020).
3. N. Kodan, **K. Agarwal** and B. R. Mehta. All-Oxide  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub> Heterojunction Photoanode: A Platform for Stable and Enhanced Photoelectrochemical Performance through Favorable Band Edge Alignment, Journal of Physical Chemistry: C, 126, 3326 (2019).
4. **K. Agarwal**, D. Varandani and B. R. Mehta. Simultaneous Enhancement of Electron Transport and Phonon Scattering in Bi<sub>2</sub>Te<sub>3</sub>: Si Nanocomposites: Role of a Conducting Secondary Phase, Journal of Alloys and compounds, 698, 1058 (2017).
5. M. Ahmad, **K. Agarwal**, N. Kumari, B. R. Mehta. KPFM based investigation on the nature of Sb<sub>2</sub>Te<sub>3</sub>:MoS<sub>2</sub> and Bi<sub>2</sub>Te<sub>3</sub>:MoS<sub>2</sub> 2D interfaces and its effect on the electrical and thermoelectric applications, Applied Physics Letters, 111, 023904 (2017)

6. **K. Agarwal**, V. Kaushik, D. Varandani, A. Dhar and B. R. Mehta. Nanoscale Thermoelectric Properties of Bi<sub>2</sub>Te<sub>3</sub>- Graphene Nanocomposites: Conducting Atomic Force, Scanning Thermal and Kelvin Probe Microscopic Studies, Journal of Alloys and Compounds, 681, 394 (2016).
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9. **K. Agarwal** and B. R. Mehta, Structural, electrical, and thermoelectric properties of bismuth telluride: Silicon/carbon nanocomposites thin films, Journal of Applied Physics, 116, 083518 (2014).
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12. R. K. Singh, A. Kumar, **K. Agarwal**, D. Dwivedi, K. N. Sood and R. Singh. Influence of Binary Oxidant (FeCl<sub>3</sub>:APS) Ratio on the Spectroscopic and Microscopic Properties of Poly(2,5Dimethoxyaniline), Open Journal of Polymer Chemistry, 2, 105 (2012).

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1. **K. Agarwal** and B. R. Mehta, Synthesis and characterization of Bi<sub>2</sub>Te<sub>3</sub> nanocomposites for thermoelectric applications, Poster presented at ICONSAT (2014), Chandigarh, India
2. **K. Agarwal** and B. R. Mehta, Effect of silicon, carbon and tellurium on structural, electrical and thermoelectric properties of bismuth telluride nanocomposites thin films, Poster presented at MRS Fall Meeting & Exhibit (2014), Boston, MA.
3. **K. Agarwal** and B. R. Mehta, Nanocomposites thin films for improved thermoelectric properties, Poster presented at 2nd Indo-US workshop (2014), NPL, India
4. **K. Agarwal**, V. Kausik, D. Varandani and B. R. Mehta, Structural, electrical and thermoelectric transport of bulk Bi<sub>2</sub>Te<sub>3</sub> composite samples with graphene and carbon, Oral presentation at NCSMD (2016), IIT-Jodhpur, India
5. **K. Agarwal**, D. Varandani and B. R. Mehta, Nanoscopic and macroscopic study of the effect of carbon and silicon on structural, electrical and thermoelectric properties of bismuth telluride thin films, Poster presentation at NCSMD (2016), IIT-Jodhpur, India

## **References**

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# Nanoscale thermoelectric properties of Bi<sub>2</sub>Te<sub>3</sub> – Graphene nanocomposites: Conducting atomic force, scanning thermal and kelvin probe microscopy studies

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## ABSTRACT

In the present study, the effect of the presence of monolayer graphene (G) on the nanoscale electrical and thermal conductivities of Bi<sub>2</sub>Te<sub>3</sub> has been investigated. Atomic force and conducting atomic force microscopic studies show that G incorporation results in lower electrical conductivity at Bi<sub>2</sub>Te<sub>3</sub>:Graphene (Bi<sub>2</sub>Te<sub>3</sub>:G) interfaces. The Kelvin probe and scanning thermal images show that Bi<sub>2</sub>Te<sub>3</sub> composites have different work function and thermal conductivity values compared to Bi<sub>2</sub>Te<sub>3</sub> sample. The decrease in the value of thermal conductivity was further confirmed by measuring the thermoelectric properties of Bi<sub>2</sub>Te<sub>3</sub> and its composites in the temperature range 300–480 K. The simultaneous increase in the value of power factor and decrease in the value of thermal conductivity of the Bi<sub>2</sub>Te<sub>3</sub>/G composite sample led to enhanced value of ZT = 0.92. This increase in the value of ZT is attributed to increased phonon scattering, and limited effect on the electron transport due to large interface area and 2D nature of G. The present study provides an insight into a new path for direct nanoscale measurements of topographical, electrical and thermally conducting characteristics of nanocomposite samples which is important for establishing the role of 2D materials for improving thermoelectric properties.

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## 1. Introduction

Recent research on thermoelectric (TE) materials is mainly focussed on nanoscale modification of existing TE materials and the search for new materials offering enhanced TE performance [1–4]. The main challenge in enhancing the TE performance is the inter-related terms in the figure of merit (ZT) of TE material. ZT is defined as  $\sigma S^2 T / \kappa$ , where  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity,  $S$  is the Seebeck coefficient and  $T$  is the temperature [5]. As the value of  $\sigma$  increases, the electronic contribution to the thermal conductivity increases and  $S$  tends to decrease, which in turn has a negative effect on ZT [6]. Thus, to enhance ZT, it is necessary to decouple these parameters. The most effective and promising approach for enhancing ZT is to introduce scattering centres which can scatter phonons, while leaving electron transport unhampered. Moreover, as  $S$  is inversely

proportional to the value of carrier concentration, therefore, an increase in the value of electrical conductivity due to the increased mobility of carriers is more favourable alternative than on account of increased carrier concentration [7]. Bismuth Telluride (Bi<sub>2</sub>Te<sub>3</sub>) is a V<sub>2</sub>–VI<sub>3</sub> compound semiconductor material with the hexagonal crystal structure and a band gap of ~0.11 eV [8]. It is best suited for the TE application due to large carrier effective mass, good electrical performance and low value of thermal conductivity [9,10].

Literature on the composite materials for TE application comprises of a large number of reports related to the different material systems with varying dimensions [5,10,11]. Nanocomposite approach is one of the methods which has been employed to enhance the values of ZT in different systems [7]. An efficient strategy to increase the value of ZT is to develop a composite material that can combine high value of electrical conductivity of the base material with low value of thermal conductivity of the composite structure. The central idea of this approach is to decrease the thermal conductivity of the composite without affecting the electrical properties. Kongli Xu et al. have recently reported greatly enhanced TE performance in poly(3,4-ethylenedioxythiophene)–

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# Simultaneous improvement in electron transport and phonon scattering properties in Bi<sub>2</sub>Te<sub>3</sub>:Si nanocomposite thin films: Role of a conducting secondary phase



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## ABSTRACT

In the present study, thin films of Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub>:Si nanocomposites, with varying concentration of Si, have been synthesized using co-sputtering technique. The effect of concentration of Si secondary phase segregated along Bi<sub>2</sub>Te<sub>3</sub> crystallite boundaries on electrical and thermal properties of Bi<sub>2</sub>Te<sub>3</sub>:Si nanocomposite thin films has been investigated. Structural and morphological studies were carried out using X-ray diffraction and scanning electron microscopy. X-ray diffraction revealed the effect of Si incorporation on orientation and structural changes of the deposited composite thin films. Hall measurements were carried out in the temperature range 100–300 K and value of ZT was determined at room temperature using Harman's four probe technique. The obtained values of ZT were correlated with the changes in the carrier concentration and mobility of the deposited samples. The effect of Si concentration on the thermal conductivity of Bi<sub>2</sub>Te<sub>3</sub>:Si nanocomposites at nanoscale level was investigated using scanning thermal microscopic studies. Incorporation of optimized concentration of Si (4%) results in change in electronic properties due to modification in crystallite orientation, and the presence of a secondary conducting phase along Bi<sub>2</sub>Te<sub>3</sub> crystallites, which results in higher electron transport and increased phonon scattering.

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## 1. Introduction

Direct conversion of heat energy into electrical energy by thermoelectric (TE) effect is quite advantageous as, in addition to providing a clean source of energy it also offers optimum utilization of waste heat [1,2]. The efficiency of a TE material is related to a dimensionless quantity, ZT, defined as the figure of merit of a TE material, which depends on  $\sigma$ , the electrical conductivity,  $S$ , the Seebeck coefficient,  $\kappa$ , the thermal conductivity and  $T$ , the absolute temperature, by the relation  $ZT = \frac{S^2\sigma T}{\kappa}$ . According to the above relation, a high value of electrical conductivity, large Seebeck coefficient and low value of thermal conductivity is required for realization of a high performance TE material [3,4]. High value of electrical conductivity ensures low joule heating, and large Seebeck coefficient implies high potential difference, whereas, large temperature difference can be attained due to low thermal conductivity of the material. The main challenge in increasing the efficiency of a

TE material is the complex inter-dependence of the different quantities in the expression for ZT. As electrical conductivity increases, Seebeck coefficient tends to decrease and electronic component of thermal conductivity tends to increase which in turn has negative effect on the value of ZT [5]. To enhance the value of ZT the material should possess high value of carrier mobility and optimized carrier concentration so that significantly high values of electrical conductivity and Seebeck coefficient can be attained simultaneously [3,6]. Moreover, to decrease the value of thermal conductivity phonon scattering should be enhanced.

Various approaches have been employed to realize higher electrical conductivity and lower thermal conductivity, such as, superlattice structure, nanostructures, alloying, composite structures, doping, etc. [7–12]. In general, doping is accomplished by adding different types of impurity atoms within the parent lattice to increase the carrier concentration. However, these impurity atoms tend to decrease the mobility of carriers due to enhanced scattering, thereby, having a negative effect on Seebeck coefficient. In the above context, superlattice structures are very promising as they offer the possibility of good electrical conductivity along with reduction in thermal conductivity. The practical realization of

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# KPFM based investigation on the nature of $\text{Sb}_2\text{Te}_3\text{:MoS}_2$ and $\text{Bi}_2\text{Te}_3\text{:MoS}_2$ 2D interfaces and its effect on the electrical and thermoelectric properties

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In this study, the effect of incorporation of 2D nanoflakes on an n type and a p type thermoelectric matrixes,  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$ , respectively, has been studied.  $\text{MoS}_2$  has been used to prepare nanocomposite bulk samples having n-n or n-p 2D interfaces. Kelvin probe force microscopy based measurements were used to characterize nanocomposite samples which revealed a difference in potentials barrier at the 2D interface for  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$  and  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$  samples, respectively. The electrical conductivity of  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$  was observed to be lower as compared to the pristine  $\text{Bi}_2\text{Te}_3$  due to increased electron scattering at 2D interfaces, whereas in the case of  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$ , the incorporation of  $\text{MoS}_2$  led to the increase in the value of electrical conductivity due to higher carrier mobility. In  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$ , a large decrease in thermal conductivity due to reduced electronic contribution is observed in contrast to no change in the case of the  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$  nanocomposite sample. The Seebeck coefficient is observed to increase in both the types of nanocomposite samples but owing to different mechanisms. The presence of potential barrier for electrons restricts the flow of majority carriers in the  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$  nanocomposite, whereas in the case of  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$  nanocomposite samples, the increased potential barrier helps in assisting the flow of holes, thereby increasing the mobility of carriers in the case of  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$ . *Published by AIP Publishing.*

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The Thermoelectric (TE) energy conversion is a method for producing electrical power from a variety of heat sources, which makes it useful for energy saving and energy harvesting applications. The performance of a thermoelectric material is determined by a dimensionless quantity, defined as figure of merit,  $ZT = \frac{\sigma S^2 T}{\kappa}$ , where  $\sigma$ ,  $\kappa$ ,  $S$ , and  $T$  are the electrical conductivity, thermal conductivity, Seebeck coefficient, and absolute temperature, respectively.<sup>1,2</sup> According to the relation mentioned earlier, for higher  $ZT$  values, a material should exhibit high power factor ( $\sigma S^2$ ) and low values of thermal conductivity simultaneously. In the literature, several techniques have been used to reduce the value of thermal conductivity by introducing scattering centres resulting in increased phonon scattering at the interface and grain boundaries by making nanocomposite,<sup>3</sup> alloying,<sup>4</sup> doping,<sup>5</sup> nanostructure,<sup>6</sup> quantum dot, and superlattice structures.<sup>7,8</sup>

$\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  are best suited TE materials for room temperature applications as they exhibit highest  $ZT$  at room temperature.<sup>9,10</sup> Nanoengineering techniques have significantly improved the  $ZT$  value of these alloys.<sup>11,12</sup>  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  are n-type and p-type narrow band gap semiconductors, respectively, with hexagonal structures. Both materials possess intrinsically high values of electrical conductivity and low values of thermal conductivity.<sup>13,14</sup> The main motivation for choosing 2D  $\text{MoS}_2$  nanoflakes does not only rely solely on the high mobility of  $\text{MoS}_2$  but also the ability to tune its electronic properties which can be tailored by controlling the number of layers.<sup>15–17</sup> Bulk  $\text{MoS}_2$  has an indirect bandgap of 1.2 eV whereas single layer  $\text{MoS}_2$  shows a direct band gap of 1.8 eV.<sup>18</sup> The TE properties of single layer, few layer, and bulk  $\text{MoS}_2$  have previously been studied theoretically.<sup>19,20</sup> A few theoretical studies have predicted that the electrical

conductivity and the Seebeck coefficient may vary with the number of layers. The experimental values of Seebeck coefficients obtained for single layer and bulk  $\text{MoS}_2$  also validate the postulates laid by theoretical studies and are reported to be 10 mV/K and 7 mV/K, respectively.<sup>21</sup>

By introducing 2D nanoscale interfaces by incorporating n type  $\text{MoS}_2$  nanoflakes in the  $\text{Bi}_2\text{Te}_3$  (n-type) matrix, or the  $\text{Sb}_2\text{Te}_3$  (p-type) matrix, electron and phonon scattering can be controlled, and TE properties can be improved.<sup>22</sup> The central objective of the present work is to study the effect of the difference in the nature (n-n or n-p) of 2D interfaces in  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$  and  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$  on the electrical and thermoelectric properties of nanocomposite samples. A Kelvin probe force microscopy (KPFM) based study has been carried out to investigate the nature of interface in the  $\text{Bi}_2\text{Te}_3$  (or  $\text{Sb}_2\text{Te}_3$ ): $\text{MoS}_2$  nanocomposite.

$\text{Sb}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_3$  (99.98%) nanopowder were purchased from Sigma Aldrich Chemical Co. For  $\text{MoS}_2$  synthesis, 2.42 g Sodium Molybdate ( $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ ), 1.21 g Thiourea, and 0.28 g polyethylene glycol (EG) were mixed with 60 ml deionized water (DI). The prepared solution was stirred for 30 min at room temperature. The resultant solution was then poured into a Teflon lined stainless steel autoclave which was further kept in an oven at 240 °C for 24 h. The  $\text{MoS}_2$  powder obtained was rinsed and centrifuged several times with DI water and ethanol. The final  $\text{MoS}_2$  powder was dried at 60 °C for 12 h. The nanocomposite  $\text{Bi}_2\text{Te}_3\text{:MoS}_2$  and  $\text{Sb}_2\text{Te}_3\text{:MoS}_2$  samples were prepared by mixing 0.05% of  $\text{MoS}_2$  as prepared  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  powders, respectively. For preparing the pellets, the powder mixture was transferred into a stainless steel die (diameter 13 mm) at a 2 MPa pressure applied on the die using a hydraulic pressure machine for



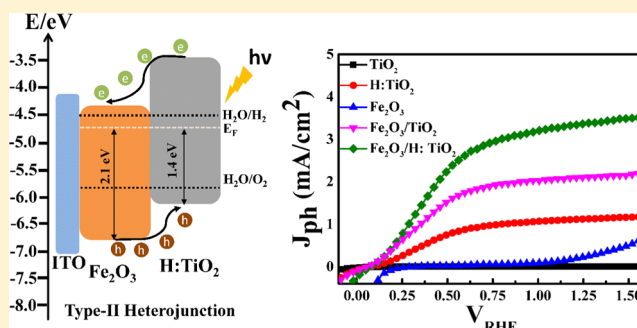
# All-Oxide $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub> Heterojunction Photoanode: A Platform for Stable and Enhanced Photoelectrochemical Performance through Favorable Band Edge Alignment

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## S Supporting Information

**ABSTRACT:** To improve the photoelectrochemical (PEC) performance of hematite thin-film photoanode, we report a novel heterostructure based on Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and hydrogenated Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub>) for faster charge transfer owing to passivation of surface states in Fe<sub>2</sub>O<sub>3</sub> via TiO<sub>2</sub> overlayer and favorable band alignment using hydrogen annealing of TiO<sub>2</sub> overlayer. The valence band offset, band gap and work function values have been measured using X-ray photoelectron spectroscopy, optical absorption, and Kelvin probe force microscopy to construct the energy band diagram of the heterostructure photoanodes. The results confirm the upshift in the valence band edge of TiO<sub>2</sub> over Fe<sub>2</sub>O<sub>3</sub> after hydrogen treatment of TiO<sub>2</sub> overlayer, which leads to the formation of type II band edge alignment in Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub> heterojunction and improved PEC performance compared to Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, pristine Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> thin-film photoelectrodes. The well-straddled and improved band alignment in Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub> heterostructure gives rise to substantial enhancement in photocurrent density, up to 3.36 mA/cm<sup>2</sup> at 1.23 V (vs reversible hydrogen electrode (RHE)) with a low onset potential of 0.1 V (vs RHE), under AM1.5 illumination condition. The observed photocurrent density in Fe<sub>2</sub>O<sub>3</sub>/H:TiO<sub>2</sub> heterostructure is 15-fold higher than bare Fe<sub>2</sub>O<sub>3</sub> (0.22 mA/cm<sup>2</sup>) photoanode. This work shows how a simple bilayer junction and its hydrogen treatment can be used to enhance the PEC response of heterojunctions and offers valuable insights into the further development of all-oxide heterojunctions.



## 1. INTRODUCTION

Generation of clean solar hydrogen by photoelectrochemical (PEC) water splitting for harnessing solar energy represents a promising but challenging route to attain sustainable energy production.<sup>1</sup> The PEC water splitting for generation of solar hydrogen is a viable method for the practical application of the most abundant renewable energy source.<sup>2</sup> It can be recognized as a reasonably good solution to the ever-growing energy challenge with negligible impact on the environment. The reformation of solar energy into the elementary form of fuel (H<sub>2</sub>) can be perceived by means of semiconductor materials as working electrodes in a PEC water splitting cell.<sup>3,4</sup> A crucial criterion for PEC water splitting is to look for a suitable photoelectrode material that satisfies the challenging requirements of band edge (conduction band (CB) and valence band (VB)) alignment, high visible light absorption, and better charge generation and separation, for solar hydrogen production along with stability against photocorrosion. Among the various metal oxide candidates, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a most promising n-type semiconductor photoanode owing to large abundance of its constituent elements, good stability in chemical environment, nontoxicity, cost-effective and appropriate energy level for water oxidation, and high visible light absorption.<sup>5</sup> In spite of these advantages, the

efficiency of hematite decreases due to a number of factors such as slow hole kinetics of the oxygen evolution reaction, short diffusion length, high probability of charge trapping in surface states, and positive conduction band edge to the hydrogen redox potential.<sup>6,7</sup> In addition, surface recombination is also a serious issue that limits water oxidation efficiencies.<sup>8–10</sup> Therefore, to enhance light absorption, suppress charge carrier recombination, and improve charge transport, the most commonly used strategies are nanostructure engineering,<sup>11–14</sup> elemental doping,<sup>15–18</sup> and formation of nano-heterostructure.<sup>19–24,8,25</sup> Additionally, the involvement of catalysts (oxygen evolution catalysts), e.g., Ni-, Ir-, Co-, and Ru-based ones,<sup>19,26,27,16,9,28</sup> for surface treatment of the hematite layer has been utilized to improve the photocurrent and reduce the overpotential. Among the various material modification strategies, formation of heterojunction photoelectrodes helps in upgrading the system efficiency, by creating potential gradients in the photoelectrode, which facilitates charge separation to improve the carrier transfer rate at the semiconductor–liquid interface.<sup>29,30</sup> There have been several

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## Full Length Article

## Investigating the effect of sulphurization on volatility of compositions in Cu-poor and Sn-rich CZTS thin films

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## ABSTRACT

In the present work, the Cu-poor and Sn-rich CZTS thin films were prepared in order to study the volatility of Sn with respect to other components. Thin film compositions were kept intentionally Sn-rich to understand the behaviour of loss and segregation of Sn during sulphurization. The homogeneous composition distribution in precursor thin films turns heterogeneous with a change in morphology after sulphurization. The inability of identifying nanoscale secondary phases in CZTS thin film by conventional analytical techniques such as XRD and Raman, can be fulfilled by employing HAADF-STEM analysis. XPS and HAADF-STEM analyses provide the quantification of nanoscale secondary phases across the thin film and surface, respectively. The volatility of Sn was revealed in the form of segregation in the middle layer of CZTS cross-sectional lamella rather than loss to annealing atmosphere. It was observed that among the cations of CZTS, Sn segregates more than Cu, while Zn segregates least. The nanoscale spurious phases were observed to vary across different regions in the sulphurized CZTS sample. The reactive annealing lead to grain growth and formation of grain boundary features in the CZTS thin films, where annealing significantly modifies the potential difference and band bending at grain boundaries with respect to intra-grains.

## 1. Introduction

Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) based thin films with suitable optoelectronic properties ( $\alpha \geq 10^4 \text{ cm}^{-1}$  and  $E_g \sim 1.4\text{--}1.5 \text{ eV}$ ) are potential absorbers for photovoltaic applications [1]. CZTS is a suitable alternative material to CIGS because of earth abundant and non-toxic constituent [1]. Various physical and chemical techniques have extensively been used for the synthesis of kesterite-type films. Shin et al. have prepared the CZTS thin film by thermal evaporation and observed a solar cell efficiency  $\sim 8.4\%$  [2]. In comparison, a CZTSSe thin film solar cell prepared by pure hydrazine solution method achieved the highest efficiency of 12.6% [3]. However, further improvement in the efficiency of kesterite solar cells is limited by the high open circuit voltage deficit,  $E_g/q - V_{oc} \geq 0.6 \text{ Volts}$ , where  $V_{oc}$  is the highest open circuit voltage reported in the CZTS solar cells [3]. Several interdependent factors are responsible for the lower  $V_{oc}$  in the kesterite solar cells in comparison to the CIGS system [4]. Predominantly, the increase in photovoltaic efficiency is hindered due to the complex phase diagram of the CZTS [5]. Synthesizing a defect free, single phase kesterite appears to be challenging because the stability of this quaternary compound is limited to a very narrow region in between the secondary phases Cu<sub>2-x</sub>S,

ZnS, SnS, SnS<sub>2</sub>, Sn<sub>2</sub>S<sub>3</sub> and Cu<sub>2</sub>SnS<sub>3</sub> in the phase diagram [5]. Another important issue in obtaining homogenous Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films with stoichiometric composition ratio,  $\text{Cu}/(\text{Zn} + \text{Sn}) \sim 0.8$ ,  $\text{Zn}/\text{Sn} \sim 1.2$ , is the loss of Sn due to the high volatility of SnS above 400°C [6–8]. To maintain the stoichiometry of the CZTS thin film, a slightly higher Sn concentration is desirable to compensate the loss of Sn in precursor Cu-Zn-Sn-S thin film during sulphurization [9]. However, an excess amount of Sn may again lead to the presence of secondary phases in the CZTS thin film because of the close relation between the compositional ratio and surface secondary phases [10]. Minor deviations from the stoichiometry can also lead to parallel growth of secondary phases in the kesterite system [11]. In the sulphide system (CZTS), three secondary phases Cu<sub>x</sub>S, Cu<sub>2</sub>SnS<sub>3</sub>, SnS having a lower band gap than CZTS are supposed to co-exist, which are highly detrimental to the photovoltaic performance [12]. The presence of such phases in the surface region of the CZTS thin film results in narrowing the band gap at the junction of CZTS/CdS solar cell devices [13]. Controlling the composition allows to change the density of defects present in the band gap of the photoactive material [14]. CZTS may also react with the Mo contact [15] generating Cu<sub>2</sub>S, ZnS, SnS and MoS<sub>2</sub> during the sulphurization process, which can promote the formation of SnS<sub>2</sub> via condensation of

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