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## Metal Chalcogenide Thin Film based Solar Cells and Supercapacitor: A review

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Abstract: Semiconductor and semiconductor manufacturing devices have been the fundamental basis of progress for several decades in each industry and nation's scientific and technological growth. Thin films are promising materials for optoelectronic device applications. Thin films could be used for supercapacitors due to low cost, high power density, good specific capacitance, fast charging and discharging. Generally, supercapacitors are used in many applications requiring rapid charge and discharge cycles rather than long-term compact energy storage. Thin films solar cells such as amorphous silicon, cadmium telluride and copper indium gallium selenide are currently being developed worldwide. Because of these films rising power conversion efficiencies, minimum material usage, and lower production cost. In the recent years, there are several methods have been implemented, studied and tested in order to improve power conversion efficiency of solar cells. In this review, the main focus has been on materials such as thin films (metal telluride and metal sulfide) and discuss the up-to-date progress achieved in the field of supercapacitor. We expected that these materials are promising candidate for next generation energy-related applications. On the other hand, we also discuss recent thin film solar cells designs and how to improve the performance of solar cell as well. The photovoltaic parameters such as fill factor, open circuit voltage, short circuit current, and power conversion efficiency, were highlighted for the solar cell prepared under different conditions.

Keywords: Thin film, supercapacitors, semiconductor, solar cell, power conversion efficiency.

#### **1** Introduction

The success of any new technology is only possible through success in the rapidly increasing technical environment. Semiconductor and semiconductor manufacturing devices have been the fundamental basis of progress for several decades in each industry and nation's scientific and technological growth [1]. The development of semiconductor technologies involves manufacturing and creating new processing techniques for bulk and film crystals for new semiconductor materials [2]. One of the most critical areas has been described as semiconductor technology in broad fields, particularly the solar photovoltaic and supercapacitor sectors, that needs excellent emphasis in light of the ever-expanding future demands. Those focusing on thin-film energy semiconductors have made it possible for cost-effective solar cell devices to satisfy the ever-increasing power

demand of specific photovoltaic devices [3]. The main focus of today's work in this sector is the understanding and advancement of movie technology for the low-cost, effective, and high-efficiency production of solar cells and super capacitors. With the continued development of optoelectronic applications, high demand is being placed on semiconductor materials with unique properties [4]. Semiconductors are also valuable materials for solar cells [5-7], photo catalysis [8,9], super capacitors, electrochemical sensors, and sensor applications [10-12]. The accomplishment of modern and high-performance semiconductor products is significant for the solid-state electronic industry's potential growth [13]. Thin film is of significant importance in particular real-life matters as a two-dimensional device. It means a solid material layer, not only a thin film but also a liquid and a gas phase. A 'thin film' may be described as a layer of solid or liquid with a thickness of between a few Å and 10 µm [14].



Thin films are also classified into three categories based on the thickness, such as ultra-thin (few to 100 Å), thin films (100 to 1000 Å) and comparatively thicker (greater than 1000 Å). Mathematically, a thin film may be considered any solid or liquid substance with one (z) dimension far below the other two (x, y) dimensions [14]. The dimension (z) is referred to as the thickness of the film (t). The magnitude varies from Å to 10  $\mu$ m. Thin film technology is considered to be the foundation of three, namely manufacture, characterization and application [15].

Various physical and chemical methods exist for depositing thin films made of different metals, insulators, and dielectric materials. In this computer world, several characterization methods can thoroughly investigate and apply the material properties. Because of its reduced diameter, high volume-to-surface ratio, and unique physical structure, thin films differ from bulk materials in terms of their properties. The thin film properties depend primarily on the testing process, material for the substrate, the temperature of the substrate, and the rate of deposition [16]. The deposits of Faraday were most likely the first thin films that evaporated when inert atmospheric metal wires exploded in 1857. The possibility of vacuuming thin metal films via platinum wire heating with joules was discovered by Nahrword (1887) to gage the index refractive of metal films. Thin solid films have been extensively explored for over a century and a half due to their potential value and scientific curiosity. The fact that the physics behind it isn't really known is challenging for thin-film engineering. Therefore, the advancement of emerging technologies can be used for potential uses and experience and commitment to design, function, and new features of thin films.

In this work, preparation of thin films (metal telluride and metal sulfide) has been reported by using various vacuum and non-vacuum deposition methods. The paper described that the obtained films were used in solar cell application and super capacitors. The photovoltaic parameters of solar cell were studied.

#### 2 Literature Survey

#### 2.1 Thin Film based Supercapacitors

The thin film has become very useful in energy applications due to numerous advantageous features, including adjustable electrical properties, flexibility, and high processability of the solution. So, the thin-film electrodes, composed of a layer of active material varying from few nanometers to several micrometers, are extensively investigated in supercapacitors, particularly thin-film supercapacitors, flexible-supercapacitors, and microsupercapacitors. Although considerable efforts have been made to manufacture thin film-based supercapacitors, many scientific and technical problems remain unresolved [17]. Moreover, one of the essential properties of a supercapacitor is that the electrodes are submerged in the electrolyte, which is achieved via a combination of two electrodes, electrolyte and separator. Supercapacitors may be classified into two kinds based on the difference in the storing method used, namely electrochemical double-layer capacitors and pseudo-capacitors [18]. They have gotten a lot of attention because of their unique characteristics like high specific capacitance, high power density, extended cycle life, and their ability to be used in an environmentally responsible manner [19]. Supercapacitors have emerged as superior candidates for various applications in recent decades, owing to their apparent advantages over batteries. This is due to the ultra-high-rate performance of supercapacitors, which allows them to maintain fast charging and discharging processes while discharging at a high current. As a result, the energy from supercapacitors can be supplied in a short period of time, on the scale of seconds or less. Moreover, the supercapacitors electrodes with a layer of active material varying in thickness from a few nanometers to several hundred micrometers are known as thin-film electrodes, and they are one smart form of supercapacitors electrode (Fig 1).

The researcher focuses on designing thin films supercapacitor electrodes using metal oxides complex to help them reach maximum performance. Su and co-workers [20] have prepared MnO<sub>2</sub>-PEDOT:PSS composite by a coelectrodeposition strategy which exhibits an aerial Cs of 1670mF cm<sup>-2</sup> at 0.5 mAcm<sup>-2</sup> and excellent mechanical robustness. Figure 2 depicts the fabrication process of MnO<sub>2</sub>-PEDOT: PSS composite and its SEM images. Also, an ultra-thin (< 200 µm) asymmetric supercapacitor is fabricated with high Ed, Pd, and rate capability. Immanuel and co-workers [21] reported the Cr/Mn<sub>3</sub>O<sub>4</sub> thin films electrode electrochemical properties, and the 3% Cr doped Mn<sub>3</sub>O<sub>4</sub> thin film electrode has an excellent specific capacitance of 181 Fg-1. In order to increase electrochemical characteristics, Yue and co-workers [22] reported that a daily-used nylon lycra fabric coated with PPy was utilized as the electrode for flexible supercapacitors. Xu and co-workers [23] designed a coresheath structured polypyrrole/bacterial cellulose membrane for flexible supercapacitors, reaching a high capacitance of 459.5 F g<sup>-1</sup> at 0.16 A g<sup>-1</sup> current density.

A flexible paper electrode employing layered 2D  $Ti_3C_2Tx$  was developed by Fu and co-workers [24] and, after the stability test, obtained the high volumetric rating of 892 F cm<sup>-3</sup> and with outstanding cycling performance. MXenes and PEDOT-PSS-enhanced Yarn SCs are manufactured to resist twisting and bending, with exceptional device performance [25]. Shah and co-workers [26] proved that when  $Ti_3C_2T_x$  nanosheets are soaked, they expand, flex, and become wrinkled, reversing the shape change. For stretchable SCs, Wang and co-workers [27]



Fig. 1: The overview of the thin-film electrodes-based supercapacitors (TFE-SCs) [17].



Fig. 2: The schematic diagram of MnO<sub>2</sub>-PEDOT:PSS composite preparation process and electrode SEM images [20].

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produced rGO-based spring electrodes that retained 82.4 % of Cs after nearly 100 % stretch and 54.2 % after the third healing cycle. Moreover, Maitra and co-workers [28] reported fabricating a bio-piezoelectric run self-charging ASC consisting of NiCoOH-CuO@Cu foil as a +ve electrode and rGO@Cu foil as a -ve electrode with a porous fish swim bladder electrolyte dipped in PVA-KOH gel electrolyte as a bio-piezoelectric separator. This SC can be charged up to 281.3 mV in about 80 seconds. There are tremendous difficulties in processing and manufacturing devices using thin films electrodes. Laboratory circumstances are often not considered in basic research, and they don't address industrial and environmental concerns. Future research should include using cheaper and more environmentally friendly raw materials to develop thin films electrodes for practical application. The utilization of extreme temperature and pressure conditions be avoided while conducting should large-scale manufacturing, whereas gentler settings are recommended. In-plane micro supercapacitor manufacturing may be sped up, made less expensive, and produced in more significant quantities using ink-jet and 3D printing, which enables the direct creation of patterns on prototypes (both electrode and electrolyte). We may expect advances in industrial-scale thin films electrode processing and device manufacturing to be realized owing to ongoing development in this area.

#### 2.2 Thin Film based Solar Cells

The thin films solar cells such as amorphous silicon, cadmium telluride and copper indium gallium selenide are currently being developed worldwide. Because of these films rising power conversion efficiencies, minimum material usage, and lower production cost [29]. Researchers observed that the consumer confidence and greater investments should be established [30], so that, thin films solar cells were expected to continue growing quickly annually.

Development of amorphous silicon solar cells has been highlighted by many researchers. In 1981, amorphous silicon carbide was made using plasma decomposition of  $[SiH_4(1-x)+CH_4(X)]$ , under PH3 dopant gas [31]. The photovoltaic parameters of a-SiC:H/a-Si:H heterojunction solar cell such as Voc (0.887 V), Jsc (12.33 mA/cm<sup>2</sup>), fill factor (0.653) and power conversion efficiency (7.14%) were reported. In 1986, performance of amorphous silicon p-i-n solar cell was successfully improved, and the fill factor was 0.771 [32]. The synthesis of mixed stacked a-Si:H/µc-Si:H tandem cell [33] was highlighted. The power conversion efficacy reached 9.1%. Experimental results indicated no degradation of the cell performance under intense light soaking. The power conversion of a-Si:H/poly-Si/poly-Si cell was 12%. Experimental findings showed that active poly-Si layer was made from plasma chemical capor deposition, using low temperature [34]. The front transparent conductive oxide (TCO) was fabricated by using low pressure chemical vapor deposition ZnO. The power conversion efficiency values are 9.47% (amorphous silicon single junction p-i-n cell) and 12.3% (tandem solar cells), respectively [35]. The hydrogenated amorphous silicon (a-Si:H) films were prepared under different deposition rates via diode and triode plasma enhanced chemical vapor deposition method. The best result could be observed when deposition rate was 1-3x10-2 nm/s by triode PECVD method, indicating low amount of metastable defect and high band gap. Researchers confirmed that power conversion efficacy were 10.22% and 12.69% for single junction and a-Si:H/hydrogenated microcrystalline silicon tandem solar cells [36]. The triple junction solar cell (a-Si:H/µc-Si:H/µc-Si:H) has been fabricated and power conversion efficiencies about 13.6% [37]. Experimental results pointed out that high short circuit current density (32.9 mA/cm<sup>2</sup>) was observed in single junction µc-Si:H solar cells.

The cadmium telluride (CdTe) films were used as thin film solar cell materials [38] due to high value of absorption coefficient (more than 10<sup>3</sup>cm<sup>-1</sup>). Low values of saturation current (10<sup>-13</sup> to 10<sup>-10</sup> A/cm<sup>2</sup>) and power conversion efficiency reached 8% from CdTe pn junction solar cell [39]. The CdTe shallow homo-junction was made via close spaced vapor transport method. The photovoltaic parameters including Voc (0.85V), Isc (20 mA/cm<sup>2</sup>), fill factor (70%) and power conversion efficiency (11%) were investigated [40]. The CdS/CdTe heterojunction solar cells were fabricated and showed power conversion efficiency about 15.8% [41]. The CdS and CdTe films have been produced by using chemical bath deposition and close spaced sublimation technique, respectively. Researchers have designed CTO/ZTO/CdS/CdTe solar cell indicated efficiency of 16.5%, and achieved fill factor of 77.34% [42]. The zinc telluride was used as the back layer material during the experiment. The obtained results showed that 1µm CdTe showed efficiency about 19.5% if compared to thicker (10 µm) CdTe films [43]. The polycrystalline zinc blended CdTe films were reported [44]. The poor electrical properties caused by the presence of the buried wurtzite layers. Post deposition processing was described for improving the performance of solar cell. Results showed that power conversion efficiency of CdS/CdTe solar cell achieved 14.5% with an optimized CdCl<sub>2</sub> activation process [45]. The flexible glass was used to replace rigid glass substrates, in order to make CdTe solar cell. The obtained results showed the power conversion efficiency about 14.05%, and tolerate bending without a reduce in solar cell performance [46]. Researchers reported that very high power conversion efficiency could be reached by using soda lime glass as substrate (the presence of sodium in soda lime glass caused decrease of the fill factor). Magnetron sputtering deposition technique was used to produce CdS films with controlled sodium content [47]. Sb<sub>2</sub>Te<sub>3</sub> was used as back contact which is low gap p-type semiconductor and high conductivity. The influence of CdTe thickness in the performance of solar cell was studied. Experimental results revealed that slightly reduces happened in open circuit voltage, short circuit current and fill factor when the thickness was decreased from 3  $\mu$ m to 1  $\mu$ m [48]. The best power conversion was 10% with 1 µm CdTe. However, all photovoltaic parameters were reduced rapidly, when the film thickness below 1 µm.

The quaternary semiconductor of Cu<sub>2</sub>ZnSnS<sub>4</sub> films showed attractive (CZTS) an low-cost. environmentally benign and stable photovoltaic materials. These materials were synthesized via atom beam sputtering [49]. These p-type materials showed band gap of 1.45 eV [50], absorption coefficient about  $1 \times 10^4$  cm<sup>-1</sup> and the resistivity about 104 Ocm The Al/ZnO/CdS/CZTS/Mo/soda lime glass was designed, and indicated open circuit voltage up to 400 mV [51]. The inline type vacuum apparatus was used to produce CZTS films. The power conversion efficiency about 5.74% by optimizing the material composition [52]. The CZTS films have been prepared by using rf sources co-sputtering followed by annealing under sulfurized conditions. The power conversion efficiency reached 6.7% as reported [53]. Researchers have described that 11% efficiency CZTS solar cell and high open circuit voltage (730 mV) by using heat treatment [54]. They explain that heat treatment facilitates elemental inter-diffusion, directly inducing Cd atoms to occupy Zn or Cu lattice sites, and promotes Na accumulation accompanied by local Cu deficiency within the heterojunction region. The CZTS films (film thickness= 600 nm) have been prepared using vacuum process, and compositional analysis showed copper poor and zinc rich. Experimental results indicated good short circuit current, power conversion efficiency reached 8.4% [55]. The enhancement of the conversion efficiency of solar cell through the introduction of p-MoS<sub>2</sub> into the interface between the CZTS/Mo layers and tuning of its band gap increased the open circuit voltage  $(V_{oc})$ . Experimental results revealed that increase in absorption coefficient of the CZTS films, increased the short circuit current  $(J_{sc})$ ,

provided conversion efficiency of 18.05% [56]. Researchers reported that the performance of solar cell could be improved by low pressure sulfurization. The solar cell efficiency was increased from 4.1% (atmosphere pressure sulfurization) to 5.7% (low pressure sulfurization) through the boost of open circuit and fill factor [57]. The annealing process for CZTS films was studied. The obtained results indicated that annealing time gas a minor effect on the open circuit voltage (until 10 minutes of dwell time). The reduction of performance of solar cell and open circuit voltage could be observed for longer anneals, due to loss of sulfur from the reaction zone [58].

The quaternary semiconductor such as CIGS could be used for thin film materials solar cell due to low cost, high conversion efficiency, tunable band gap [59], high stability and high absorption coefficient of about  $10^7 \text{ m}^{-1}$ . The power conversion efficiency of 3C-SiC/Copper Indium Gallium Selenide solar cell reached 25.5% when 50 nm thick cubic silicon carbide (3C-SiC) film was used. The cubic silicon carbide is non-toxic nature and showed wide band gap. Researcher concluded that the reduction of short circuit current density when the buffer layer thickness was increased from 50 nm to 150 nm, because of loss of quantum efficiency especially in the blue region [60]. Barman and Kalita [61] reported efficiency of Al/ITO/Al-ZnO/i-ZnO/CIGS (3 µm layer)/Mo/Substrate about 22.67%, after adding back surface field (PbS) layer, improved the efficiency of solar cell reached 24.2%. The copper indium gallium selenide/tungsten disulphide solar cell was fabricated and the photovoltaic parameters such as open circuit voltage (1.026 V), short-circuit current (29.57  $mA/cm^2$ ), fill factor (86.96%), and conversion efficiency (26.4%) were highlighted [62]. The influence of the gallium absorber concentration of the layer on the Mo/Si/CuInGaSe<sub>2</sub>/ZnS/ZnO solar cell was studied [63]. Power conversion efficiency was increased from 20.74% (10% gallium) to 21.08% (20% gallium), then, reduced from 20.17% (30% gallium) to 19.07% (40% gallium). Ajay and co-workers described that copper indium gallium selenide solar cell by using ITO (front gate) showed power conversion efficiency of 23.074%, indicating very high photo generation rate and excellent photo absorption rate as well [64]. Nour and Patane [65] pointed out the performance of CuInSe/Copper Indium Gallium Selenide/CdS solar cell. Photovoltaic parameters including Voc (751 mV), Jsc (41.44 mA/cm<sup>2</sup>), fill factor (78.63%) and efficiency (24.5%) were reported. There are several researchers investigated the performance of CIGS thin film solar cells as indicated in Table 1. The photovoltaic parameters were reported in research findings.



Highlighted experimental results	References
• The 1.6 µm thick (CuIn <sub>0.5</sub> Ga <sub>0.5</sub> Se) absorber layer with band gap (1.3 eV) was produced.	Li and co-workers [66]
• The power conversion efficiency (16.3%) and short circuit current density (31.4 mA/cm <sup>2</sup> ) were reported.	
<ul> <li>Nickel oxide could be used as the front surface field due to wide band gap, p-type materials, low electron affinity and stable cubic structure.</li> <li>The power conversion efficiency of CuInGaSe<sub>2</sub> solar cell with the NiO layer (16.35%) and without the layer (15.81%) was investigated.</li> </ul>	Youn and co-workers [67]
• The Mo/PI/Mo/Cu(In,Ga)Se <sub>2</sub> /CdS/i-ZnO/ITO/(Ni)Al/MgF <sub>2</sub> solar cell was designed.	Kihwan and co-workers [68]
• The Voc (0.696 V), Jsc (35.4 mA/cm <sup>2</sup> ), fill factor (75.3%) and power conversion efficiency (18.6%) were studied.	
<ul> <li>The solar cell consisted of Mo(0.5 μm)/p-Cu(In,Ga)Se<sub>2</sub>(2μm)/n-CdS(0.05 μm)/n-ZnO(0.2 μm).</li> </ul>	Bouabdelli and co-workers [69]
• The power conversion efficiency was increased about 0.8% per 10K, and 2 mV/K in open circuit voltage (240 K to 400 K). The highest conversion efficiency reached 32.45% when the temperature was 240K.	
<ul> <li>The solar cell made from ZnO/n-CdS/p-copper indium gallium diselenide/ZnO/n-CdS/p-CIGS/Mo.</li> <li>The conversion efficiency was improved from 25.35% to 27% in optimization conditions.</li> </ul>	Bouanani and co-workers [70]

Table 1: The performance of the CIGS solar cells.

#### **3** Conclusions

The thin film technologies made a remarkable advent in solar cell industry and supercapacitor applications. We briefly describe the recent research progress in this field. These progressive efforts, can have shown an excellent property with the advanced methods and under different experimental conditions. Experimental results showed that thin film based supercapacitors have high power density, good specific capacitance, fast charging and discharging. Development of amorphous silicon, cadmium telluride and copper indium gallium selenide has been highlighted by many researchers. These films are considered as promising absorber because of appropriate band gap high absorption coefficient. The power and conversion efficiency of solar cell has been reported.

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