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Conclusion and Scope of the Future Work

Continuously increasing global energy demands and the rapid deployment of fossil fuels compel the need of abundant, low cost energy resource. Solar energy being an ultimate resource is a viable option for this. Photovoltaic cells harness solar energy and convert it directly into the electricity. Extensive research has already been carried out to make photovoltaic a cost effective energy alternative with long term sustainability towards its' wider applications including distributed ones. Thin film solar cell technology has shown potential to replace existing costly wafer based solar cells with reasonably good efficiency achieved with CIGS and CdTe absorber solar cells. Cost competitiveness in terms of less material utilization and simpler fabrication techniques make thin film solar cell technology as the mainstream of photovoltaic research. However, the bottleneck in replacing the existing wafer based solar cell lies in the fact of comparatively low efficiency and utilization of scarce (In and Ga) and toxic (Cd) materials. In contrast, CZTS,Se is an environmentally benign substitute with a potential alternative but still a lot of work needs to be done to enhance the efficiency to an acceptable level for the real field applications.

In view of this, present thesis explores the growth of CZTS using low cost sol-gel spin coating technique. The complete CZTS solar cell structure is fabricated and the role of individual layer is discussed both experimentally and computationally. The fabricated solar cell is analyzed to understand the high efficiency barriers, associated with CZTS solar cell. An alternative absorber of same family CZGS/Se is also explored in terms of their structural, electronic and optical properties. The major thesis developments include:

1. Sol-gel spin coating technique is adopted because of its' simplicity and easy tunability of the composition in the prepared thin films by varying the composition of the constituents in the sol. We found that 2-methoxy ethanol is the suitable solvent, providing very stable sol. Nitrate and Chloride salt precursors are used to provide the constituent cations and thiourea is used for sulfur. The deposition of CZTS thin film is done in open environment at elevated temperature. We observed that nitrate salt based CZTS films consist of cracks and blisters on the surface. These low surface quality CZTS thin films lead to non-uniform resistivity and poor electrical response. In contrast, chloride salts based CZTS thin films showed smooth and dense morphology with uniform resistivity and good electrical properties. The flexibility of tailoring the property of the grown CZTS thin film by changing the composition of the sol or by changing the annealing conditions make this process attractive for making large area CZTS solar cell.

2. Al:ZnO/ZnO/CdS/CZTS/Mo/Glass heterostructure solar cells are fabricated and analyzed for further improvement. The spin coated CZTS absorber layer is subjected to the post sulfurization at elevated temperature of 550 ^{0}C under 5%H_2S+Ar gas environment to avoid any sulfur loss and also to restrict oxidation of metallic constituents. Post sulfurization of the spin coated films helped in grain growth and reduced the grain boundary barriers. The photovoltaic response of the prepared solar cell showed low efficiency, which is attributed to the high series resistance and low shunt resistance as observed from the Current-Voltage characteristics under illumination. High value of ideality factor suggests the presence of large recombination in these devices. Impedance spectroscopic analysis showed the presence of back contact barrier in the fabricated solar cells. The presence of back contact barrier and the

contribution of trap states near CdS/CZTS interface give rise to the inferior photovoltaic performance. The minority carrier life time from the impedance measurements is comparatively lower than that of measured from the OCVD measurements. The ambiguities in the measurement results may be due to the non-linear characteristics of the OCVD data, posing difficulties in estimating the accurate slope. In addition, the large current injection may also result in large values of minority carrier life time.

3. The different processing conditions are utilized to synthesize CZTS thin films and their impact on photovoltaic response. Low temperature processed film 'S1' exhibited Sn rich stoichiometry. This showed substantial Sn loss and changes into slightly Zn rich and Cu poor stoichiometry after annealing at high temperature under H_2S+Ar gaseous environment and named as 'S2'. Sn Mössbauer measurements showed only +4 Sn oxidation state for both S1 and S2 CZTS thin films. However, a large quadrupole splitting is observed in case of S1 and is attributed to the distortion at Sn sites. The excess Sn composition also facilitate the presence of Sn at Zn site which is acting as a compensating donor defect to the available acceptor defects with low formation energy such as Cu_{Zn} and V_{Cu}. Further, the lower carrier concentration observed from the Capacitance-Voltage measurements for cell using S1 absorber also validates this possibility. High temperature processing for S2 reduces Sn composition in the films due to Sn high volatility. Thus, the presence of less Sn in S2 reduces the possibility of Sn to occupy Cu or Zn sites. This is also reflected in Mössbauer measurements, where very low quadrupole splitting in Sn Mossbauer spectra for S2 absorber. High temperature processing also helped in grain growth reducing the grain boundary barriers and finally improved the electrical response. The result is also supported by the improved photovoltaic performance of the solar cell based on S2 absorber.

4. One dimensional solar cell simulation is carried out for CZTS/Se single junction with their possible tandem structure. In single junction CZTS/Se the efficiency increases with increasing the thickness of absorber layer due to enhanced absorption and ~ 2 μm thickness is found suitable for the maximum photon absorption. The absorber layer carrier concentration also plays a crucial role as the efficiency drastically decreases as we go beyond 5×10^{16} cm^{-3} for CZTS and 1×10^{17} cm^{-3} for CZTSe solar cells. The choice of optimum buffer layer material is also important for matched interface with absorber layer in solar cell. As the spike in the energy band at interface provides barrier to the current flow, causing reduction in the short circuit current density whereas cliff in the energy band results in lower open circuit voltage. A buffer layer material is also crucial as interface defects may increase in recombination speed of the photogenerated charge carriers at interface. CZTS defects reduce the minority carrier life time and defects at the absorber-buffer interface increases the interface recombination speed, which finally lowers the device performance. We also found that Mo may not be a suitable choice as the back contact material and the performance can be improved further with high work function metal back contact.
The tandem structure simulation is also simulated with CZTSe as a bottom cell absorber and CZTS as the top cell absorber. The current output of a tandem cell is limited by the minimum current from the individual sub cells while the maximum open circuit voltage of the tandem cell is the sum of open circuit voltages of the individual cells. An overall improvement in device performance is noticed with tandem cell as compared to the respective single junction cells by implementing a thin top cell on relatively thick bottom cell.

5. Density functional theoretical calculations are carried out on bulk $Cu_2ZnGe(S/Se)_4$ to understand their structural, electronic and optical properties towards their application for absorber. The mBJ exchange correlation functions are used to calculate the electronic and optical properties of the $Cu_2ZnGe(S/Se)_4$ in its tetragonal kesterite and stannite

phase. High absorption coefficient makes these materials a suitable choice for thin film photovoltaic single junction and as a top cell absorber material for the tandem cell structures.

Efforts are made to realize the cost effective and environmentally benign solution fir solar cell absorbers. The present work may be extended further to realize high efficiency solar device. These may include:

1. A double layer or graded architecture can be adopted for CZTS growth. A highly doped CZTS absorber layer at the back contact with shallow doping of bulk at the interface with n-type CdS buffer layer will result in a p-i-n device. Increasing carrier concentration will increase the open circuit voltage of the device in conjunction with increase in the minority carrier life time in bulk absorber in p-i-n structures.

2. The band gap tailoring with partial substitution of Sn with Ge for wide band dap absorber and substitution of S with Se for low bandgap absorber can be achieved and integrated in photovoltaic devices. A tandem structure or series connected solar cell structure can be fabricated for efficiency enhancement with a suitable combination of low and high bandgap absorbers.

3. Back contact engineering either by inserting an intermediate layer or by exfoliation and deposition of high work function material such as MoO_3/Au at the back can be used to reduce the Schottky back contact behavior present at the back contact of device.

4. Structures with similar elemental compositions with transition metals Fe, Mn, Ni in place of Zn can be explored further to realize the enhanced photovoltaic efficiency.

The new materials and defect engineering at different interfaces will play a crucial role in designing the environment friendly low cost photovoltaic materials with high efficiency. The detailed device understanding is required to pinpoint the issues and overcome these to realize the enhanced efficiencies.