Novel Solution Process for Fabricating Ultra-Thin-Film Absorber Layers in Fe_2SiS_4 and Fe_2GeS_4 Photovoltaics

Journal:	*2014 MRS Spring Meeting*
Manuscript ID:	MRSS14-1670-E02-04.R1
Manuscript Type:	Symposium E
Date Submitted by the Author:	12-May-2014
Complete List of Authors:	Orefuwa, Samuel; Delaware State University, Chemistry Lai, Cheng-Yu; Delaware State University, Chemistry Dobson, Kevin; Institute of Energy Conversion, University of Delaware, Ni, Chaoying; University of Delaware, Radu, Daniela; Delaware State University, Chemistry
Keywords:	photovoltaic, thin film, grain size

Novel Solution Process for Fabricating Ultra-Thin-Film Absorber Layers in Fe_2SiS_4 and Fe_2GeS_4 Photovoltaics

Samuel A. Orefuwa[1], Cheng-Yu Lai[1], Kevin Dobson[2], Chaoying Ni[3], Daniela Radu[1*]
[1]Department of Chemistry, Delaware State University, 1200 N. DuPont Highway,Dover, DE, U.S.A.
[2]Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, DE 19716, U.S.A.
[3]University of Delaware, Newark, DE 19716, U.S.A.
[*]Corresponding author

ABSTRACT

Fe_2SiS_4 and Fe_2GeS_4 crystalline materials posses direct bandgaps of ~1.55 and ~1.4 eV respectively and an absorption coefficient larger than 10^5 cm^{-1}; their theoretical potential as solar photovoltaic absorbers has been demonstrated. However, no solar devices that employ either Fe_2SiS_4 or Fe_2GeS_4 have been reported to date. In the presented work, nanoprecursors to Fe_2SiS_4 and Fe_2GeS_4 have been fabricated and employed to build ultra-thin-film layers via spray coating and rod coating methods. Temperature-dependent X-Ray diffraction analyses of nanoprecursors coatings show an unprecedented low temperature for forming crystalline Fe_2SiS_4 and Fe_2GeS_4. Fabricating of ultra-thin-film photovoltaic devices utilizing Fe_2SiS_4 and Fe_2GeS_4 as solar absorber material is presented.

INTRODUCTION

Three forms of thin-film solar panels have been developed and commercialized in the last decade by identifying materials that are both efficient absorbers of solar power and cost-effective for manufacturer and consumer; these are: amorphous silicon (a-Si), cadmium telluride (CdTe) and CIGS (copper indium gallium sulfo-selenide). Although they operate effectively in thin-film (1-3 microns), there are both environmental and economic concerns for the cost and sustainability of the materials and processes employed in these approaches.

An alternative solution was seen in pursuing sustainable PV materials composed of Earth-abundant elements such as $Cu_2ZnSn(S, Se)_4$ (copper zinc tin sulfide–CZTS or sulfo-selenide CZTSSe) or FeS_2 (iron sulfide) for the absorber layer. CZTSSe, benefiting from CIGS similarities, has already proved itself at efficiencies > 12%. [1] However, photovoltaic research using FeS_2 absorbers still reports very low efficiencies (~2%) despite material's potential comparable to a-Si, CdS and CIGS (>20%).

The use of Fe in PV was proposed more than 25 years ago in the form of FeS_2. FeS_2 (also called pyrite or "fool's gold") is an indirect band gap semiconductor with sustainable composition of abundant elements. Unfortunately, the performance problems associated to this material as PV absorber are not fully understood.[2]

The appeal of FeS_2, in addition to material's low cost and abundance, was that that exhibits a useful band gap ($E_g = 0.9$ eV) and an absorption coefficient above 10^5 at $E_g + 0.1$ eV. This high absorption coefficient makes FeS_2 unique among inorganic materials allowing downsizing the thickness of the absorber layer to lower than 0.1 µm in a solar cell able to capture most of the incident solar radiation. The attractiveness of this thickness is visible when compared to 1.5–3.0 µm for current thin-film technologies and > 200 µm for single-crystal Si cells. Such thin layers not only conserve material, but they also provide an avenue to high efficiency through efficient charge separation associated with a high internal electrical field. [2, 3] However, the FeS_2 promise as "golden" solution for PV has not come true.

Recently, a large team of scientists from NREL and Oregon State University[3] has investigated the phenomena related to lack of performance in FeS_2 and pointed to an intrinsic thermal instability of the material along with considerable challenges that must be surmounted for production of high-quality, single-phase FeS_2 films. To circumvent the problem, they have used the following design principle: "select systems that do not spontaneously phase-separate into sulfur (S) deficient conducting materials with small band-gaps". In order to provide a ligand-field splitting of sufficient magnitude for effective solar absorption the Fe^{2+} ion must be bound by at least six S atoms thus assuring a sufficiently large band gap. This generally requires Fe^{2+} in an octahedral site. Adding a third element with an electronegativity that favors strong covalent bonding with sulfur can stabilize such a site. From these considerations, Yu and co-workers have chosen Fe_2SiS_4 and Fe_2GeS_4 for investigation. The analytical evaluations (summary in Table 1) drove to the conclusion that the two materials are suitable to successfully deliver the performance originally expected from FeS_2.

Table 1. **Fe_2SiS_4 and Fe_2GeS_4 evaluation results (from Reference 3).**[3]

Material	**Calculated Direct Bandgap (eV)**	**Measured Direct Bandgap (eV)**	**Enthalpy of Decomposition in Binary Sulfides (eV)**	**TGA Mass Loss Starting Point (°C)**	**Calculated Absorption Coefficient (cm^{-1})**
Fe_2SiS_4	1.55	1.54	0.59	1000	$>10^5$
Fe_2GeS_4	1.4	1.36	0.64	725	$>10^5$

Thermal stability of the two materials along with their close to ideal bandgap for solar cell fabrication makes the two materials good candidates for achieving the initial FeS_2 promises.

Devices using Fe_2SiS_4 and Fe_2GeS_4, respectively, for the absorber layer using nano-scale precursors have been fabricated in our laboratory based on the process schematically showed in Figure 1.

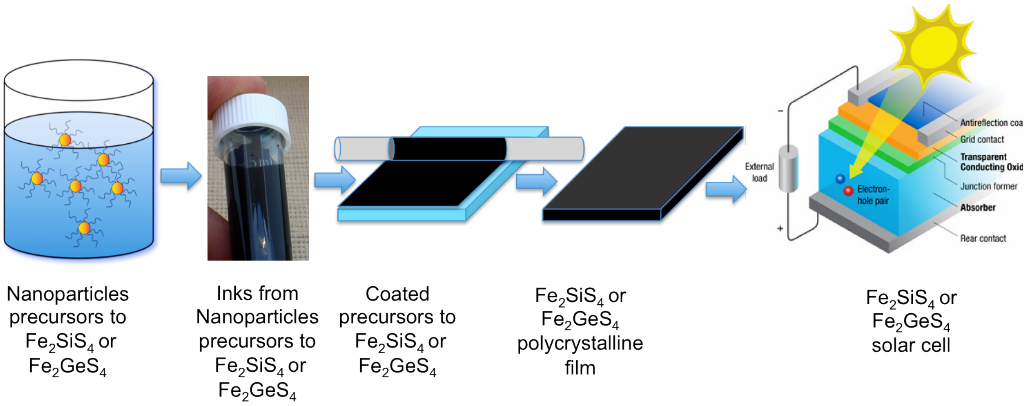

Figure 1. Schematic of workflow for fabricating Fe_2SiS_4 or Fe_2GeS_4-based solar devices

EXPERIMENTAL DETAILS

Nanoparticles Preparation

All reagents, except for $FeCl_2$ were purchased from Sigma Aldrich and used without further purification. Iron (II) chloride ($FeCl_2$, 99.5%) was purchased from Alfa Aesar. The nanoprecursors (NPs) mixture to Fe_2SiS_4 was obtained by combining 0.253 g of $FeCl_2$, 0.028g of Si nanopowder and 0.128g of S each dispersed by sonication in 10 mL of oleylamine at 104 ^oC. The dispersions were the combined and reacted at 220 ^oC. Similar procedure was used for the preparation of nanoprecursors mixture to Fe_2GeS_4, using 0.253 g of $FeCl_2$, 0.580g of GeI_4 and 0.128g of S.

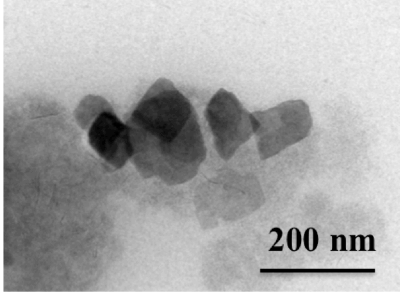

Figure 2. TEM image of Fe_2GeS_4 NPs

The mixtures were heated under reflux for 2 hours under inert atmosphere (argon). The particles were recovered by precipitation with anti-solvents followed by centrifugation. Several washing steps to remove residual organic groups were performed, by repeating the dispersion precipitation step.

Nanoparticles Ability to Form Crystalline Fe_2SiS_4 and Fe_2GeS_4

The precursors capability to generate crystalline Fe_2SiS_4 and Fe_2GeS_4 has been characterized by Temperature dependent X-Ray Powder Diffraction (TD-XRD). Formation of crystalline Fe_2SiS_4 and Fe_2GeS_4 was observed at temperatures as low as 500 °C (Figure 3)[4].

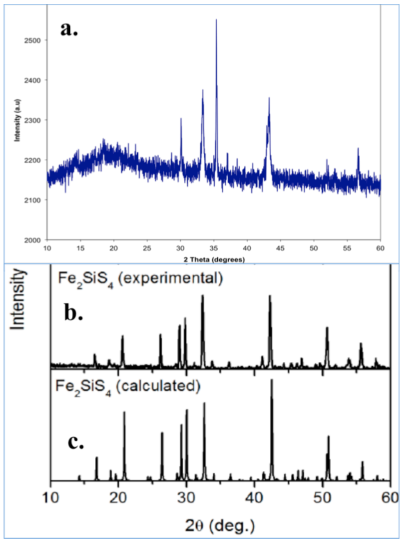

Figure 3. XRD of Fe_2SiS_4 : a. From our NPs; b. From micron size powder (Ref 4.) and c. calculated (Ref. 4)

Deposition of Nanoprecursors Layer

The nanoprecursors, prepared as dispersion in organic solvents with sulfur content, have been deposited by spin-coating and rod-coating, on Molybdenum-coated 1”x1” substrates. 3 to 5 layers of nanoparticle have been deposited for each sample.

Processing

The nanoprecursors films were subjected to a thermal treatment step. The annealing procedure was performed in a tube furnace, in Argon atmosphere and in the presence of sulfur, to preclude sulfur loss. Typical annealing temperature was 550 °C. The annealed films have been characterized by XPS. Both Fe_2SiS_4 and Fe_2GeS_4 films show the presence all elements in their composition. Despite air sensitivity indicated by the presence of oxygen (data not shown), the films composition was nearly stoichiometric (iron-poor $Fe_{1.5}GeS_4$ crystalline film). Furthermore, the presence of nitrogen and carbon in the films indicates that the annealing process did not lead to removal of capping groups on the nanoparticles surface.

Device fabrication and characterization.

Electrical characterization (exemplified Figure 4.b) of the fabricated devices was performed at IEC.

To determine the causes of poor performance, the devices were analyzed by SEM of thin samples milled by focused ion beam–FIB (Figure 4a.). The microstructure of the absorber layer shows that annealing at 550 °C did not promote grain growth. Dense organic material as well as voids were present in the film.

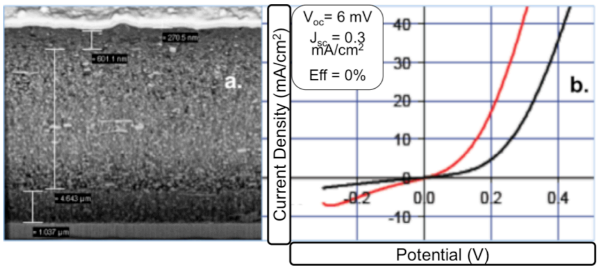

Figure 4. a. SEM image of a device cross-section; b. J-V characteristic of a device fabricated with Fe_2GeS_4 absorber

DISCUSSION

The development of solution-processed thin-film $Cu_2ZnSn(S,Se)_4$, (called CZTS, CZTSe or CZTSSe, based on the chalcogenide: S, Se or both) using nano-precursors to build the absorber layer has seen exponential growth upon introduction of various processing steps.[5-10]

Temperature dependent X-Ray diffraction data indicate that nanoparticles precursors to Fe_2SiS_4 and Fe_2GeS_4 lead to polycrystalline Fe_2SiS_4 and Fe_2GeS_4 at temperatures below 600 °C. Synthesis of Fe_2SiS_4 from elemental, commercially-available micron-size powder precursors, require temperatures ~1000 °C to generate pure Fe_2SiS_4.[11] In addition, based on X-ray photoelectron spectroscopy (XPS), films fabricated to date exhibit a composition close to stoichiometry, with a most successful preparation to date being an iron-poor $Fe_{1.5}GeS_4$ crystalline film.

CONCLUSIONS

The work presented herein shows the promise for building crystalline layers of Fe_2SiS_4 and Fe_2GeS_4 starting from nanoprecursors. The annealing temperature of nanoprecursors films obtained by typical coating methods was in the range of 500–500 °C and crystalline films have been formed (confirmed by XRD). Devices have been fabricated, however, no photovoltaic behavior was observed to date. The poor electrical characteristics of the cell (exemplified in Figure 3) could be easily correlated with the large thickness of the absorber layer at current time. The rationale behind building thick layers is to compensate avoid pinholes. However, the thermal treatment did not result in large crystal growth in the absorber layer. Current focus is on two processing aspects: a). Improving nanoparticles deposition methods to achieve sub-micron thickness of the nanoprecursors layer and b). Optimizing the annealing step to achieve crystal growth.

ACKNOWLEDGEMENTS

This work was funded by DOE SunShot DISTANCE Solar program, award number DE-EE-0006322.

REFERENCES

1. T. K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu and D. B. Mitzi, Advanced Energy Materials **3** (1), 34-38 (2013).
2. C. Steinhagen, T. B. Harvey, C. J. Stolle, J. Harris and B. A. Korgel, The Journal of Physical Chemistry Letters **3** (17), 2352-2356 (2012).
3. L. Yu, S. Lany, R. Kykyneshi, V. Jieratum, R. Ravichandran, B. Pelatt, E. Altschul, H. A. S. Platt, J. F. Wager, D. A. Keszler and A. Zunger, Advanced Energy Materials **1** (5), 748-753 (2011).
4. V. Jieratum, Oregon State University (2012).
5. L. K. Johnson, D. R. Radu, C.-Y. Lai, M. Lu and I. Malajovich, Patent No. WO2011066205A1 (2011).
6. Y. Cao, M. S. Denny, J. V. Caspar, W. E. Farneth, Q. Guo, A. S. Ionkin, L. K. Johnson, M. Lu, I. Malajovich, D. Radu, H. D. Rosenfeld, K. R. Choudhury and W. Wu, Journal of the American Chemical Society **134** (38), 15644-15647 (2012).
7. D. R. Radu, J. V. Caspar, M. Lu, L. K. Johnson, Y. Cao, A. S. Ionkin, I. Malajovich, H. D. Rosenfeld, F. Sun and N. G. Tassi, Prepr. Symp. - Am. Chem. Soc., Div. Fuel Chem. **56** (Copyright (C) 2013 American Chemical Society (ACS). All Rights Reserved.), 179 (2011).
8. D. R. Radu, J. V. Caspar, M. Lu, L. K. Johnson, Y. Cao, A. S. Ionkin, I. Malajovich, H. D. Rosenfeld, F. Sun and N. G. Tassi, 2011 (unpublished).
9. D. R. Radu, J. V. Caspar, L. K. Johnson, H. D. Rosenfeld, I. Malajovich and M. Lu, Patent No. WO2010135622A1 (2010).
10. C. H. Leidholm, Charlie ; Breeze Alison; Sunderland Chris; and W. Z. Ki, Don NREL report **NREL/SR-5200-56501** (2012).
11. H. Vincent, E. F. Bertaut, W. H. Baur and R. D. Shannon, Acta Crystallogr., Sect. B **B32** (6), 1749-1755 (1976).