INVESTIGATING SPUTTERED $Cu_2Si_{1-x}Sn_xS_3$ [CSTS] FOR EARTH ABUNDANT THIN FILM PHOTOVOLTAICS

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ABSTRACT

This study investigates the synthesis of chalcopyrite $Cu_2Si_{1-x}Sn_xS_3$ (CSTS) thin films for photovoltaic solar cell absorber layers. Preliminary results indicate that layered sputtering of Cu, Sn, and Si followed by annealing in a sulfur atmosphere at 500ºC does not provide adequate mixing or sulfur incorporation. Annealing/sulfurizing a homogeneous co-sputtered film of Cu, Sn, and Si may lead to CSTS formation, although low sulfur incorporation and undesired copper sulfide phase formation need to be resolved. Sputtering from sulfide targets may lead to formation of CSTS.

INTRODUCTION

CSTS is a potential earth abundant alternative to CIGS and CdTe thin films, replacing In, Ga, Cd, and Se with inexpensive and benign elements potentially enabling scalability to >GW power production levels. CSTS has not previously been reported in thin film form, and its ability to perform similarly to CIGS and CdTe must still be determined. CSTS formed by solid-state reaction of pressed powders of Cu_2S, Si, Sn, and S is *p*-type and exhibits significant photoconductivity. In addition, compositions with $0.4<x<0.6$ result in near-optimal bandgaps from 1.25 to 1.45 eV [1]. High defect tolerance in CIGS allows long minority carrier lifetimes, which enables its use in thin film cells [2]. Recent computational results also predict similar behavior in the related compound Cu_2ZnSnS_4 (CZTS) [3]. The similar bonding and bandstructure of CSTS to these materials suggest it might also achieve useful lifetimes [2,4].

EXPERIMENTAL

3 Thin Film Deposition Methods

Samples were deposited in a Sputtered Films Inc (SFI) sputtering chamber with 3 magnetron heads. The substrate, sodalime glass with about 1 μm of sputtered Mo on the surface, was plasma etched before deposition. Base pressure achieved in the chamber was $2x10^{-7}$ Torr vacuum and sputtering pressure was $5x10^{-3}$ Torr Ar. Three different deposition regimes are examined: RF sputtering from a single CSTS target, consecutively DC sputtering layers of Cu, Sn, and Si, and DC co-sputtering a homogenous layer containing Cu, Sn, Si.

Sulfurization and Annealing

After deposition, samples are exposed to a sulfur environment above atmospheric pressure in a 3" diameter tube furnace with 2 heat zones (see figure 1). The temperature profile is shown in figure 2.

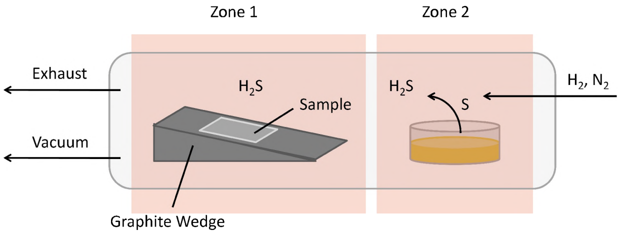

Figure 1 Diagram of 2-zone annealing oven.

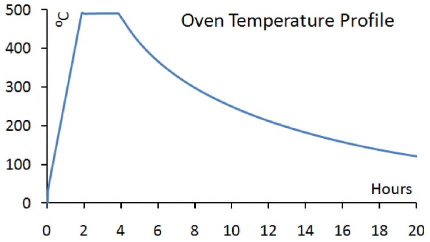

Figure 2 Oven temperature profile for the sample heat zone.

RESULTS

Single CSTS Target

Sputtering and annealing of CSTS increases S and decreases Cu content (see figure 3). Oxidation is also evident.

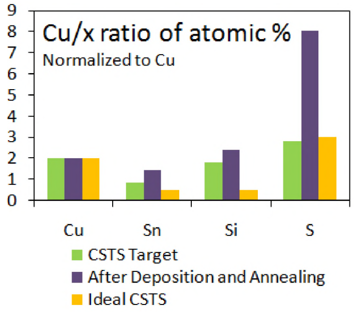

Figure 3 XRF compositional analysis of the CSTS target is compared to EDS compositional analysis of the deposited thin film after annealing.

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Layered depositions of Cu, Sn, Si

Layers in consecutively sputtered depositions are not adequately mixed during annealing and sulfur content is low. Two different layering schemes, shown in figure 4, both demonstrate this effect.

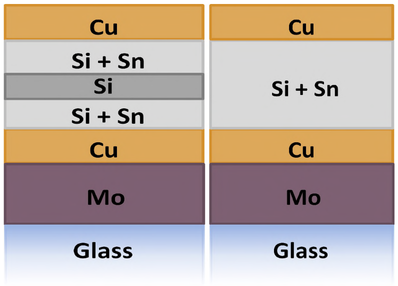

Figure 4 a,b Layered depositions. Si and Sn, shown in the light gray layers, were co-sputtered.

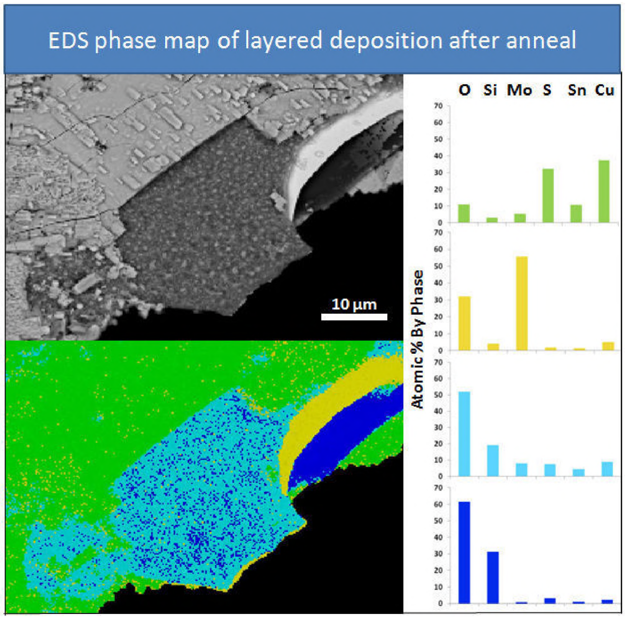

Figure 5 EDS phase map of deposition scheme shown in figure 4a with atomic compositions of each phase.

The Si rich layer above (cyan color) indicates that the sputtered Si layer might be responsible for inadequate mixing during annealing. However, co-sputtering Sn and Si still results in a layered film as can be seen in figure 6.

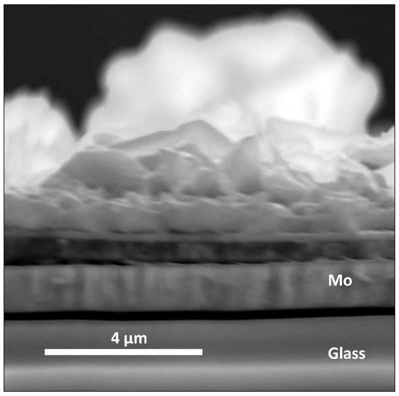

Figure 6 SEM cross-sectional image of deposition scheme in figure 4b.

Co-Sputtering Cu, Si, Sn

Annealing and sulfurizing a homogenous co-sputtered Cu, Sn, Si film with a Cu:Si:Sn ratio of 2:0.55:0.47 still results in some phase separation, The predominant surface phase resembles copper sulfide. But the phase underneath contains a Cu:Si:Sn ratio very close to CSTS.

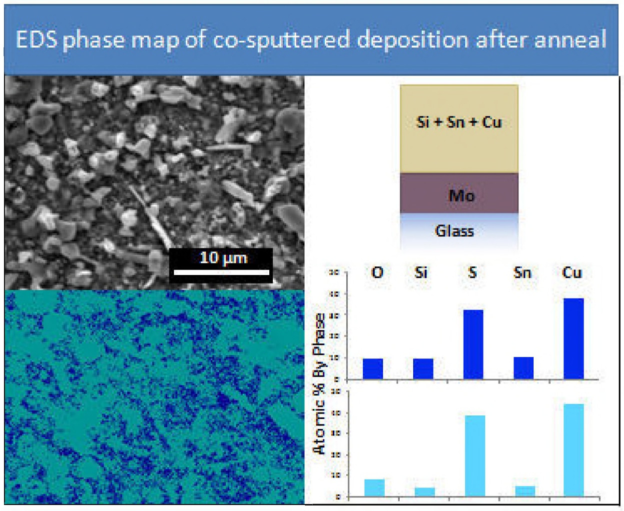

Figure 7 EDS phase map of co-sputtered Cu, Sn, and Si with atomic compositions of each phase.

CONCLUSIONS

Sputtering from a single target of CSTS and then annealing/sulfurizing results in compositional variation from the target to the deposited film. Compensating for this shift requires independently tuning deposition rates of Cu, Sn, and Si. When metals Cu, Sn, and Si are sputtered consecutively and then annealed in a sulfur atmosphere, layered, nonhomogeneous films with undesired phase formation and low sulfur content result. Co-sputtering Cu, Si, and then annealing/sulfurizing still results in undesired phase formation and low sulfur content. However, the ratio of Cu:Si:Sn is closer to desired stoichiometry. Adjusting deposition and annealing parameters may lead to CSTS formation. Sputtering from sulfur-containing targets (i.e. Cu_2S, SnS_2) may lead to sufficient incorporation of sulfur during the annealing procedure as demonstrated by excess sulfur content after annealing a film sputtered from a CSTS target.

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