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Thio-olivine Mn_2SiS_4 thin films by reactive magnetron sputtering: Structural and optical properties with insights from first principles calculations

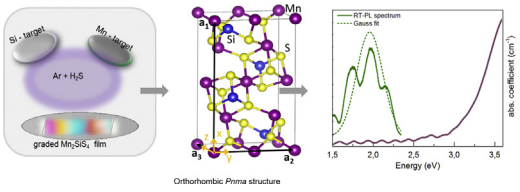
A. Davydova [a,*], J. Eriksson [a], R. Chen [a], K. Rudisch [a], C. Persson [b,c], J.J.S. Scragg [a]

[a] Ångström Solar Center, Solid State Electronics, Department of Engineering Sciences, Uppsala University, Box 534, SE-75121 Uppsala, Sweden
[b] Centre for Materials Science and Nanotechnology, Department of Physics, University of Oslo, P.O. Box 1048, Blindern, NO-0316 Oslo, Norway
[c] Department of Materials Science and Engineering, KTH Royal Institute of Technology, 10044, Sweden

HIGHLIGHTS

- Manufacturing of graded Mn_2SiS_4 thin films is performed (Mn/Si ratio 1.2–2.1).
- Precursor instability due to reactive SiS_2 sub-phase is noted after deposition (Mn/Si ratio <1.6).
- The best structural properties were found on the film with Mn/Si of about 1.4.
- Absorption coefficient rise to 10^4 cm^{-1} 0.9 eV above the estimated band gap which is ~1.9 eV.
- Mn_2SiS_4 films are suspected to be unsuited to photovoltaic applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Thio-olivines such as $(Fe,Mn)_2(Si,Ge)S_4$ have been proposed as candidate earth-abundant materials for single and multi-junction solar cells. In this work we present the first investigation of Mn_2SiS_4thin films prepared by reactive magnetron sputtering deposition, using a composition grading approach. Precursor instability in ambient conditions is observed, revealing the oxidation/hydrolysis of Si—S bonds from the as-deposited film as a blocking mechanism for the ternary compound formation. Structural, morphological and optical properties of the annealed Mn_2SiS_4 films are reported for the first time. Resulting Mn_2SiS_4 films have orthorhombic *Pnma* structure and are polycrystalline. Raman active modes at 325 nm excitation are observed at 262, 320, 400 and 464 cm^{-1}. From room temperature photoluminescence at 532 nm excitation the band gap is estimated to be about 1.9 eV, but a high optical absorption coefficient of $>10^4$ cm^{-1} was only obtained at E > 2.8 eV. First principles calculations are used for better understanding of opto-electronic properties. From the calculations, Mn_2SiS_4 is suggested to have a band gap of about 1.73–1.86 eV depending on the magnetic configuration of Mn and slight indirect nature. The slow absorption onset is interpreted by strong anisotropy due to one of the components of the dielectric function.

1. Introduction

Recent activities in solar photovoltaics (PV) research focus on the demand of manufacturing new "absorber layer" materials, which are essential components in solar cell structures [1]. There are a few

* Corresponding author.
E-mail address: alexandra.davydova@angstrom.uu.se (A. Davydova).

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requirements applied to these photo-active layers. Besides appropriate opto-electronic properties, it is nowadays important to consider earth-abundance, embodied energy, cost-effectiveness, low toxicity and long-term stability. Moreover, suitable materials with band gaps of about 1.6–1.8 eV are sought for producing next generation, multi-junction solar cells [2]. In order to fulfill these needs, researchers have broadened their search away from traditional solar cell materials such as crystalline Si [3,4], Cu(In, Ga)Se_2 [5–7] and CdTe [8–10] towards alternative, earth-abundant materials. It can require a considerable investment to develop a successful synthesis of a new material with sufficient quality to provide final conclusions on its suitability for PV. To assist in the search for new compounds, guidance from computational predictions can be extremely valuable too. Basic information that can be calculated for a prospective PV material includes the size and nature of the fundamental band gap and the magnitude of the absorption coefficient, but, as our computational abilities improve, it is natural to shift more of the burden of screening and evaluation of new compounds into the computational domain. In this work, we use experimental and theoretical approaches to study a new group of compounds recently predicted to have merit for PV. We find implications for both their practical application as well as for PV materials design efforts in the future.

Group of the compounds which is poorly investigated but might be promising for future PV technologies - the ternary metal chalcogenides with olivine structure. These compounds are related to the mineral "olivine" or magnesium iron silicate $(Mg, Fe)_2SiO_4$, which has an orthorhombic crystal structure and can be extensively found in the Earth's mantle. Earth-abundant metal chalcogenides with chemical formula $M_2T(S, Se)_4$, where M = Mg, Mn, Fe and T = Si, Sn, also exhibit the olivine structure, but are less studied in comparison with the namesake oxides.

Two specific thio-olivine materials reported in recent studies are the iron containing sulfides Fe_2SiS_4 (FSS) and Fe_2GeS_4 (FGS). Yu et al. [11] theoretically predicted both these compounds to be suitable for the absorber layer in solar cell structures and estimated band gap values of 1.40–1.55 eV (for the Ge and Si containing compounds respectively) and high absorption coefficients $>10^5$ cm^{-1}, by using density-functional theory calculations. Both FSS and FGS were prepared by Vincent et al. [12] as a single crystal and reported to have orthorhombic symmetry with *Pnma* space group. Baron et al. [13] provided neutron powder diffraction investigations of the structural and magnetic properties of Fe_2SiS_4. After the recent theoretical prediction [11], several experimental papers reported manufacturing of Fe_2GeS_4 colloidal nanostructures via solution synthesis [14] and solvent-free mechanochemical processes [15]. The authors demonstrated XRD pattern of nanocrystals, as well as X-ray photoelectron spectroscopy and TEM imaging. Bo-In Park et al. [15] also provided diffuse reflectance spectra and room temperature photoluminescence measurements and measured the band gap of FGS to be about 1.41–1.43 eV which is quite similar to the predicted values from Yu et al. [11]. FGS nanoparticles reported to be rather stable after the synthesis [14,15]. No thin film synthesis for FSS or device manufacturing for both FSS and FGS compounds was performed so far. However, a brief remark about the necessity to protect FSS precursors from oxygen contamination during the synthesis was made by Vincent [12], due to hydrolysis of SiS_2 in ambient air.

In comparison with iron–based thio-olivines, the manganese-based compound Mn_2SiS_4 (MSS) is much less investigated. However, as well as containing only earth-abundant elements, Mn-based thio-olivines have the same crystal structure and therefore are expected to have comparable optical properties, including a high absorption and a band gap suitable for solar cell structures. In particular, the band gap is expected to be somewhat larger than FSS and FGS, due to the smaller unit cell, which would be interesting for multi-junction solar cells. Due to magnetic nature of Mn, the MSS compound was primary investigated for its magnetic properties [16–19]. Fuhrmann and Pickard in 1989 reported MSS single crystal growth by using I_2 transport with MnS, Si and S_8 as reactants in sealed quartz ampoules at around 900 K. As a result, an olivine structured crystal with *Pnma* group was investigated by XRD measurements – the first report about this compound [20]. Church et al. prepared a MSS single crystal for magnetic property investigations [19]. For $(Mn,Fe)_2SiS_4$, no thin film synthesis or optical property investigations were performed so far. However, if we propose the integration of Fe- or Mn- based thio-olivines in thin film solar cells, it is highly important to develop a thin film synthesis. Moreover, the demand of extensive experimental information about optical and structural properties of FSS or MSS films should be fulfilled prior to any promises about PV applications.

In this work, we aim to shed light on one of the less investigated olivine structured compounds, Mn_2SiS_4, in thin-film form. Synthesis is made via magnetron sputtering deposition of precursors, followed by thermal treatment. A compositional grading approach helps to identify the chemical origin of instabilities of the precursor. Crystalline structure, morphology, Raman spectroscopy and optical properties are acquired for Mn_2SiS_4 thin films for the first time. In the last section we present analysis of the electronic and optical properties by ab-initio calculations which are of great help for understanding of the unusual optoelectronic properties of Mn_2SiS_4, and the potential role of thio-olivine compounds in PV applications.

2. Experimental

2.1. Synthesis and characterization

Thin film preparation with compositional variation across the sample was done by magnetron sputtering deposition in Von Ardenne CS 600 chamber. Pure Mn (99.95% purity, Kurt J. Lesker) and Si targets (99.9999% purity Si, undoped, Kurt J. Lesker) were connected to DC and RF sources respectively and reactively co-sputtered in H_2S + Ar atmosphere. The base pressure of the system was below $1 \cdot 10^{-6}$ mbar. A working pressure of $2 \cdot 10^{-2}$ mbar was reached by introducing H_2S and Ar mixture in the chamber with 1:1 ratio and mass flow rate of 25 sccm for both sources giving the total mass flow of 50 sccm. Co-sputtering was performed with power set to 200 W and 250 W on the Si and Mn target respectively. The substrate was heated to 300 °C and the rotation of the substrate holder was switched off to create compositionally graded films with variation in stoichiometry from Si to Mn-rich sides. Before the actual thin film deposition, pre-sputtering of Mn and Si targets was done in Ar atmosphere for 20 min. Film thicknesses of 500 nm and 1500 nm were produced with sputtering time of 1.5 and 4 h respectively. In all cases, deposition was performed on both soda lime glass (SLG) and molybdenum-coated soda lime glass substrates with size of 50 × 10 mm^2 for 500 nm and 70 × 15 mm^2 for 1500 nm films respectively.

The resulting precursors were then directly transferred from the sputtering chamber to a tube furnace for the following annealing procedure. For annealing, as-deposited films were located in coated graphite box together with 14 mg of elemental sulfur (99.999% Alfa Aesar). The tube furnace was filled with static argon pressure of 350 Torrand preheated to a set temperature of 640 °C. The graphite box was then inserted into the heated zone and left there for 10 min. The estimated sample temperature, from a thermocouple embedded in the sample holder, rose quickly to around 600 °C during this process. The annealed samples then were moved to a cold zone and consequently cooled down to room temperature within 40 min.

Compositional analysis of the precursors and annealed Mn_2SiS_4 films was performed by energy dispersive X-ray spectroscopy (EDS) by Zeiss Leo 1550 electron microscope and morphology of the films were examined by scanning electron microscope (SEM) on the same instrument. EDS data was collected at 12 keV accelerating voltage and Mn/Si, S/(2Si + Mn) and O/(Si + Mn + S) ratios were quantified statistically across the graded film surface. From chemical formula of Mn_2SiS_4 compound, the Mn/Si ratio should be equal 2 at stoichiometric composition