CZTS fabrication via a non-vacuum deposition method

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Introduction

CZTS absorber layer is a class of quarternary compound that had gained much interest in recent years as an alternative to CIGS[1]. The appeal towards this class of device is furthered favored as a result of non-toxic elements and abundance of source materials used. This had therefore produced much impetus towards the study of the engineering of this material. Conventionally, CZTS is produced by high thermal treatment of the film to obtain the correct phase in the film[2]. However, the efficacy of the film remained low in many of these thermal techniques. This is partly due to the fact that the chemistry of the fabrication had been overlooked in most cases. Interestingly, the highest efficiency reported for CZTS at 11% had been achieved by modulating the complexation chemistry during the fabrication step[3]. Yet, much of the chemistry underlining the formation of CZTS remains highly speculative.

In this report, we present a simple dip-coating approach based on the principles of metal-ligand coordination to control the formation of a highly condensed thin-film CZTS[4]. The thin film were examined by EDX, XRD, RAMAN and IR and the data is as shown below.

Methodology

The precursor solution was prepared by dissolving copper (II) acetate (0.05 M), zinc acetate (0.025 M), tin (II) chloride (0.025 M) in methanol. Thiourea (0.25 M) was then added to form the colourless metal-ligand complex. The solution was then dip-coated on soda-lime glasses with a layer of sputtered molybdenum. Between each deposition, the layers were treated at 220˚C in air for 10 minutes, resulting in a grayish film. A total of 20 layers was built on the molybdenum surface. The films were finally annealed in argon flux at 450˚C for 4 hours to remove any organic residual. The thin film was subsequently analyzed before and after thermal annealing with EDX, RAMAN, XRD, FTIR and SEM.

Complexation Chemistry

$$Cu^{2+} + nSCN_2H_4 \longrightarrow [Cu(SCN_2H_4)_n]^{+}$$

$$Zn^{2+} + nSCN_2H_4 \longrightarrow [Zn(SCN_2H_4)_n]^{2+}$$

$$Sn^{4+} + nSCN_2H_4 \longrightarrow [Sn(SCN_2H_4)_n]^{4+}$$

$$[Cu(SCN_2H_4)_n]^{+} + [Zn(SCN_2H_4)_n]^{2+} + [Sn(SCN_2H_4)_n]^{4+} \longrightarrow CuZnSn(SCN_2H_4)_n]^{m+}$$

$$[CuZnSn(SCN_2H_4)_n]^{m+} \xrightarrow{\text{thermal annealing}} CZTS$$

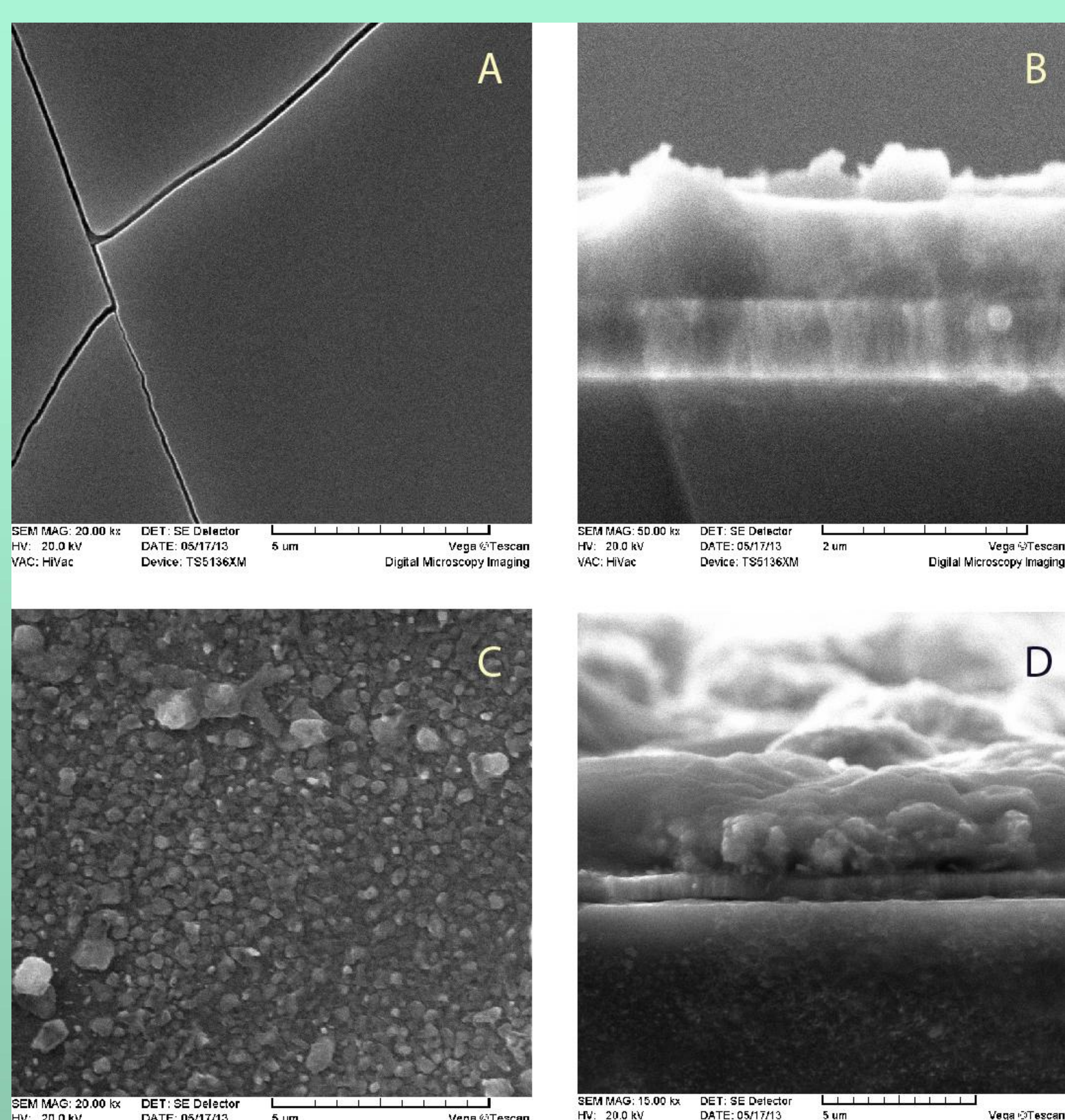


Figure 1. Top view of Scanning electron micrograph on the thin film for (A) before thermal annealing and (C) after 450˚C annealing. The cross section as shown for (B) before thermal annealing illustrates an average film thickness of 1 microns while film expansion was observed after themal treatment (D), averaging a thickness of 3 microns.

EDX analysis of the CZTS film

	Atomic percentage				Atomic ratio		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/metals
Before annealing	24.45	12.07	11.62	51.85	1.03	1.04	1.08
After annealing	23.60	13.58	14.96	47.86	0.83	0.91	0.92

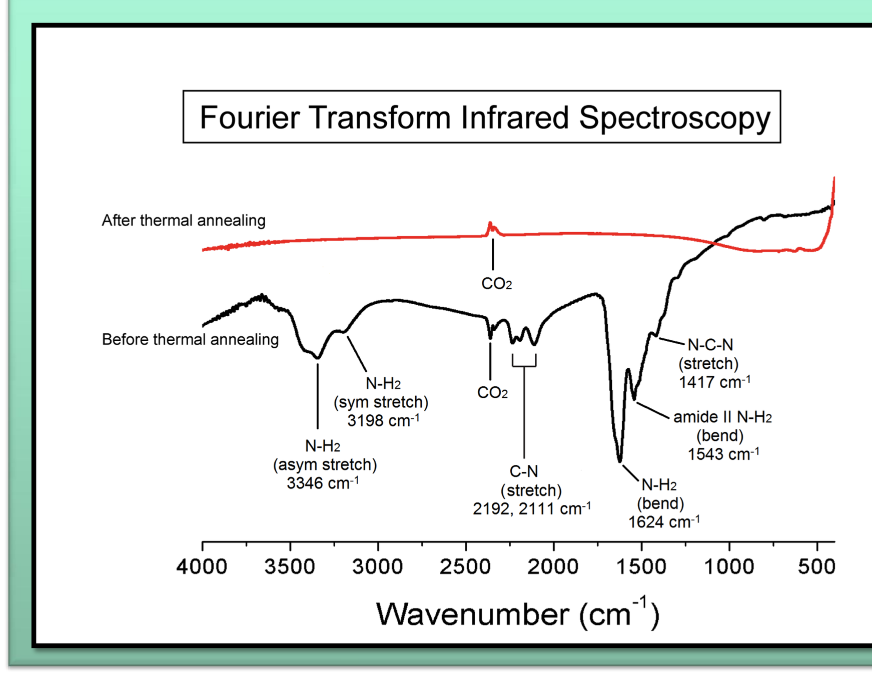
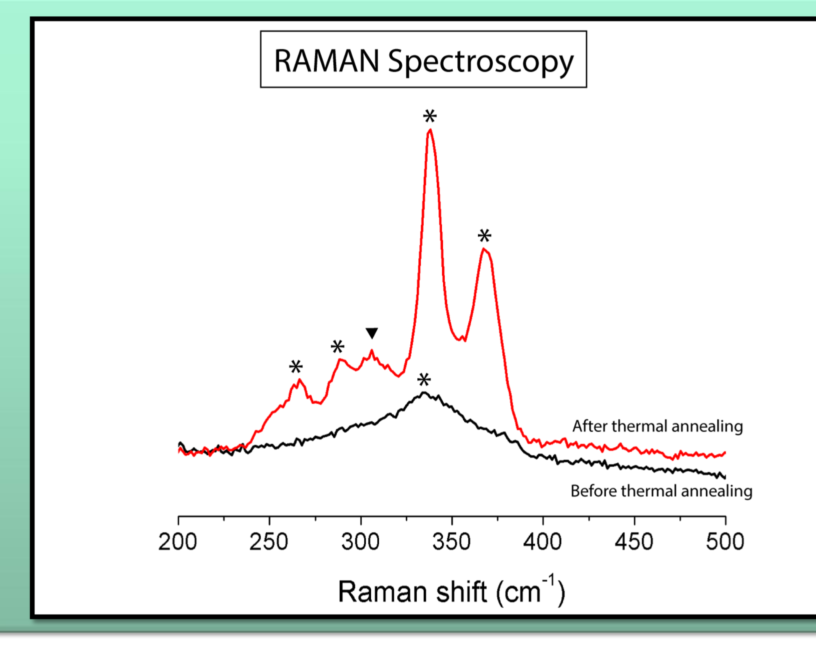


Figure 2. FTIR spectra of CZTS film before and after thermal annealing. After thermal annealing, all organic traces in the films had been removed.

Figure 3. RAMAN spectra of the dip-coated CZTS thin film before and after themal annealing. The peak in asterisk at 266 cm-1, 288 cm-1, 338 cm-1 and 374 cm-1 are characteristic peaks indicative of fully formed CZTS phase. The peak as denoted by the triangle at 305 cm-1 is attributed to CTS phase pertaining to minimal loss of the zinc during the thermal annealing step. CZTS indicative peak at 338 cm-1 was also observed for the film before thermal annealing as shown.



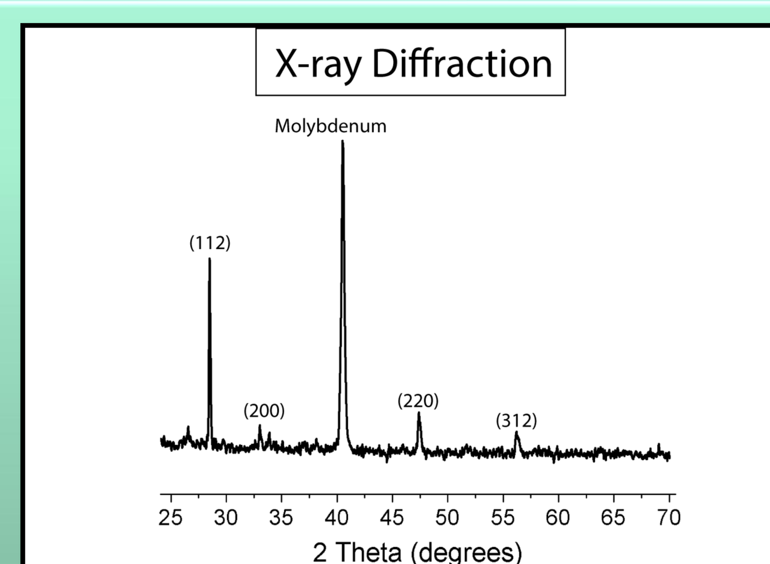


Figure 4. XRD of thermally treated film as shown had exhibited characteristic 2 theta peaks at 28.8˚ (112), 33.0˚ (200), 47.4˚ (220) and 56.2˚ (312). This fully correspond with the kesterite CZTS as reported in JCPDS data file number 26-0575.

Conclusion

Herein, CZTS thin films had been successfully fabricated and examined with a range of different analytical tools. The absorber film produced after thermal annealing had exhibited characterizations much in agreement with the kesterite CZTS used in many solar devices. Hence, the future work would involve the production of a viable solar device using this current methodological approach.

References

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