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ساخت لایه جاذب چهارتایی Cu_2ZnSnS_4 (CZTS) به روش کند و پاش جریان مستقیم با هدف‌های فلزی و سولفوره کردن

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چکیده- Cu_2ZnSnS_4 یکی از لایه‌های جاذب مورد توجه در سلول‌های خورشیدی لایه نازک است. طی دهه گذشته سلول‌های خورشیدی مبتنی بر کستریت‌ها پیشرفت چشمگیری داشته‌اند. در این تحقیق، ساخت لایه نازک جاذب CZTS با استفاده از کند و پاش جریان مستقیم با هدف‌های فلزی مس، روی و قلع و یک مرحله سولفوره کردن را ارائه می‌کنیم. در لایه جاذب ساخته شده نسبت‌های اتمی به ترتیب ۱۷/۱۳، ۱۴/۲۱، ۱۲/۲۵ و ۵۶/۴۱ در صد برای مس، روی، قلع و گوگرد است که منجر به نسبت‌های ترکیبی Zn/Sn و Cu/(Zn+Sn) ۱/۱۶ و ۰/۶۵ می شود. گاف نوری این لایه ۱/۴۸ الکترون ولت است. این روش بسیار کارا و صنعتی بوده که کنترل خوبی بر استوکیومتری مواد در اختیار ما می‌گذارد. لایه CZTS ساخته شده در این مطالعه دارای ساختار تک فاز، همراه با خواص بلوری و ویژگی‌های نوری مطلوبی بوده که توسط آنالیزهای EDS، XRD، طیف رامان و UV-Vis تایید می‌شود.

کلید واژه- سلول خورشیدی لایه نازک؛ لایه جاذب؛ کند و پاش جریان مستقیم

Preparation of quaternary Cu_2ZnSnS_4 (CZTS) absorber Layer through DC sputtering of Cu, Zn, and Sn metallic targets and post-deposition sulfurization

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Abstract- Cu_2ZnSnS_4 is an intriguing absorber layer in thin-film photovoltaics. Solar cells based on kesterite have made considerable progress over the past few decades. In this work, we present the fabrication of bare Cu_2ZnSnS_4 absorber layer through DC sputtering of Cu, Zn and Sn metallic targets with a post-sulfurization step which reached atomic ratios of 17.13%, 14.21%, 12.25% and 56.41% for Cu, Zn, Sn, and S, respectively, leading to compositional ratios of 1.16 and 0.65, respectively for Zn/Sn and Cu/(Zn+Sn). The optical bandgap of the layer was 1.48 eV. This method is a versatile and industrial technique that provides good control over the material stoichiometry and is suitable for large scale production. The CZTS layer prepared in this work demonstrates high purity, good crystallographic and desirable optical features which are confirmed by EDS, XRD, Raman measurements and UV-Vis analysis.
Keywords: *Cu_2ZnSnS_4; Thin-film solar cells; DC magnetron sputtering*

1. Introduction

Over the past few decades, CIGS and CdTe thin-film absorbers have been studied comprehensively due to their excellent photovoltaic and photoreactive performances. Best devices attained 22.3%[1] and 22.1%[2] power conversion efficiencies (PCE), respectively. Except for Cu, all the elements are either toxic or expensive. Widespread applications of photovoltaics demand eco-benign, inexpensive and abundant constituents. CZTS(Se) photovoltaics encompasses all substantial features including above mentioned, high absorption coefficient and tuneable bandgap for long-term sustainability[3].

Lately, various paths have been developed to fabricate the CZTS(Se) layer. In essence, they are divided into the vacuum and non-vacuum-based methods. The safe route toward utilizing the application of CZTS(Se) thin-films is crucial. Due to applicability and maturity for large- scale production, sputtering has been extensively studied for preparing CZTS(Se) layers[3]. CZTS(Se) thin-films could be attained by depositing metallic or binary sulphide compounds multilayers[3] and co-sputtering of metallic or sulphide compound sources[4] followed by appropriate post-annealing treatments.

In this contribution, we present stack layers of Cu/Sn/Zn deposited on soda-lime glass (SLG) followed by sulfurization which results in a favorable CZTS absorber. This method has good tunability in stoichiometric ratios of the absorber which is due to control over the sputtering deposition parameters. This tunability along with the potential for industrial-scale fabrication makes our proposed method a promising technique for the preparation of CZTS solar cells.

2. Experimental

In order to prepare the CZTS thin film, we required molybdenum coated glass as a substrate. For this purpose, we employed a high purity Mo target as the cathode in the DC sputtering process. The soda-lime glass substrates which were previously cleaned ultrasonically by successive use of soap, acetone, and ethanol were put in the target holder of the sputtering system. the sputtering chamber was vacuumed to the base pressure of 2×10^{-5} Torr and then increased to 1×10^{-1} Torr by the introduction of grade 5 Ar gas into the chamber so that the plasma can be started. For deposition of the Mo layer, a voltage of 440 V and a current of 250 mA giving a total power of 150 W was applied to the Mo target to initiate the plasma and then the pressure was reduced to 1.2×10^{-2} Torr to increase the deposition rate. The sputtering process was carried out for ~30 min to reach ~1 µm thickness. During the deposition, the substrate was rotated with a speed of 10 rpm to form a homogenous layer. After preparing the substrates, we used them to deposit CZT material. To this end, Cu, Zn, and Sn metallic targets were placed in the sputtering system and deposited using sequential DC sputtering. First, Zn with a thickness of 141 nm was deposited on Mo substrates and then it was coated by a 210 nm thick Sn layer. Cu was deposited on top of this stack with a thickness of 149 nm. All these steps were done in the same sputtering chamber to reduce any contamination and stress and all the samples were rotated with 10 rpm speed to achieve homogenous layers. The detailed sputtering parameters are illustrated in Table 1.

Table 1 Sputtering parameters

Target	Base Pressure (Torr)	Sputtering Pressure (Torr)	Applied Voltage (V)	Applied Current (A)	DC Power (W)	Thickness (nm)
Mo	2×10^{-5}	1.2×10^{-2}	440	0.25	110	~ 1000
Zn	2×10^{-5}	5.5×10^{-3}	410	0.08	32.8	~ 140
Sn	2×10^{-5}	7.8×10^{-3}	338	0.01	3.38	~ 210
Cu	2×10^{-5}	7.6×10^{-3}	550	0.08	44	~ 150

For the sulfurization process, the sample was put in the annealing furnace that contained 0.2 gr sulphur at one side of the furnace where the temperature is relatively low. The samples heated from room temperature to 350° c for 35 minutes (rate is $10^{\circ}c$ per minute), subsequently the samples heated from 300° c to 500° c during 18 min (rate is $8.3^{\circ}c$ per minute) and then marinated at 500° c for 30 min. the final thickness of the layer was 900 nm. This heat treatment in the presence of S causes the Sn, Zn and Cu layers diffuse into one another along with the sulfur which forms a final CZTS product.

3. Result and discussion

Fig. 1 shows the XRD pattern (Cu Kα radiation with λ = 1.54060 Å) of CZTS thin film grown by sulfurization of stacked layers deposited on Mo-coated SLG. we can clearly see the three most intensive peaks are at 2θ values of around 28.1, 47.11 and 55.38 which correspond to (112), (220) and (312) planes. This indicates the kesterite phase of CZTS according to the Joint Committee of Powder Diffraction Standard (JCPDS) file No.026-0575 is formed. In the XRD pattern, some small characteristic peaks of kesterite oriented along the (002), (101), (200), (008) and (332) were also observed. Additionally, the crystallite size of thin-film calculated by Debye-Scherrer formula is about 22 nm which is around the optimum value for desirable electrical properties in thin-film solar cells[5]. The peak at 2θ=40.5 is related to molybdenum back contact.

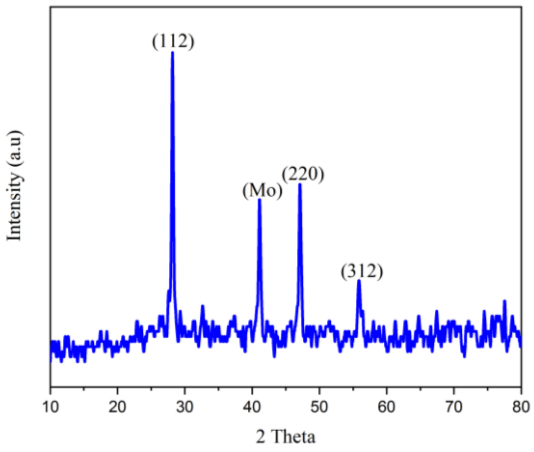

Figure 2 The XRD pattern of CZTS

Although there are no peaks related to other crystalline compounds in the XRD pattern, it should be mentioned that the main peaks of CZTS, ZnS, and Cu_2SnS_3 are so close and may overlap in XRD pattern due to their similar crystal structure. Therefore, their diffraction peaks cannot clearly be distinguished by the XRD result. In order to certainly identify the kesterite-CZTS from other secondary phases, Raman measurement can be useful. Raman measurement with the 532 nm excitation wavelength was carried out at room temperature. From Fig. 2 It can be observed that the main peaks are 280 cm^{-1} and 336 cm^{-1}, which are in good agreement with the kesterite-CZTS phases[3]. The high intensity of these peaks demonstrates a suitable formation of CZTS absorber structure[6].
The elemental compositional ratios of the CZTS layer subjected to 500° c for 1-hour sulfurization

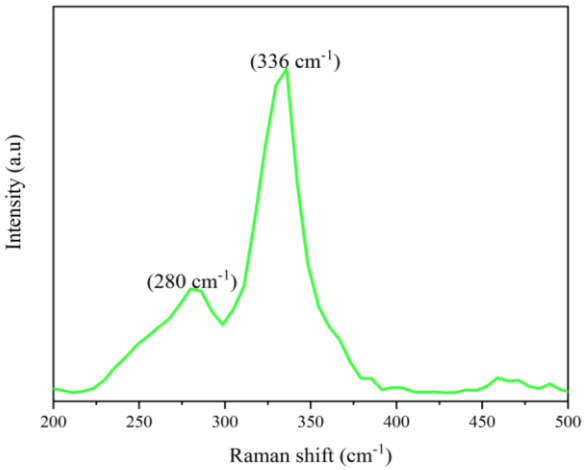

Figure 1 Raman spectra in the range of 200- 500 cm

treatment were performed using an X-ray energy dispersive spectrometer (EDS), which is shown in Fig 3 and Table 2. Previous studies indicate that Cu-poor and Zn-rich qualities are essential for accomplishing high-efficiency CZTS thin-film solar cells[3]. The EDS analysis reveals the chemical composition of the Cu_2ZnSnS_4 layer is non-stoichiometric and the atomic ratios are Zn/Sn=1.16 and Cu/Zn+Sn=0.65, which were in good agreement with optimum ratios of high-efficiency CZTS solar cells[3].

Table 2 Atomic percentages and the compositional ratios of the elements in the films deposited on SLG

Sample	Atomic ratio				Compositional ratio	
	Cu	Zn	Sn	S	Cu/ Zn+Sn	Zn/ Sn
Sulfurized	17.13	14.21	12.25	56.41	0.65	1.16

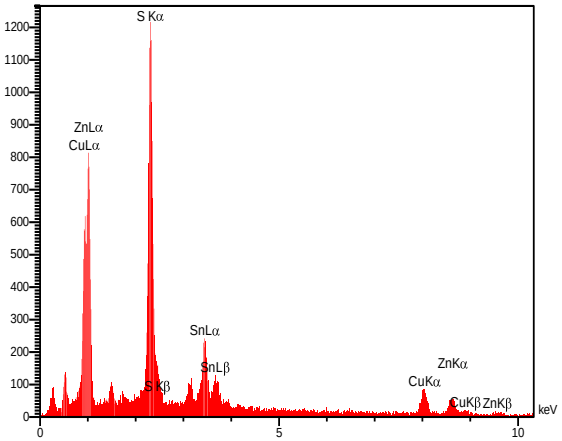

Figure 3 EDS spectrum of sulfurized CZTS

We have also studied the optical properties of the vacuum-annealed CZTS absorber layer. Fig. 4 shows $(\alpha h\nu)^n$ versus $h\nu$. Considering the direct bandgap nature of the structure, the

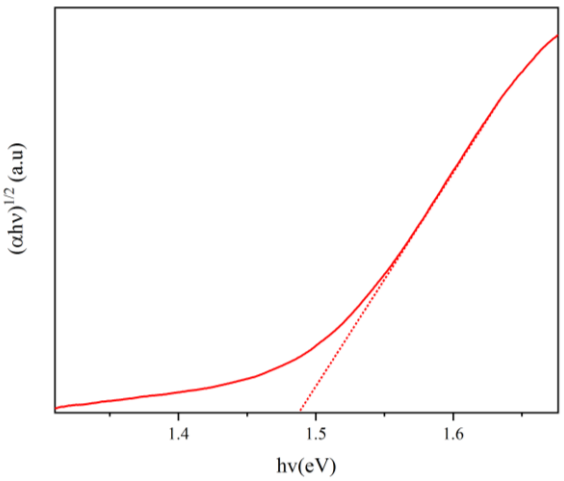

Figure 4 Plot of (αhn)1/2 as function of energy for CZTS absorber layer

value of n would be ½. The optical bandgap of the layer is obtained by extrapolating the linear part of the curve to the horizontal axis. The spectrum reveals that the optical bandgap is around 1.48 eV which is desirable for solar cell energy conversion application in a single-bandgap device[7]. This also confirms the absence of ZnS and Cu_2SnS_3 secondary phases whose bandgaps are 3.7 and 0.93 eV, respectively[8].

4. Conclusions

In this study, we prepared a quaternary CZTS absorber using a two-stage sputtering sulfurization process. In the first stage we deposited Zn/Sn/Cu layers by the sputtering method, sulfurization of stacked layers at 500 c for 1 hour was the second step. The XRD and Raman measurements confirmed the formation of the kesterite phase of CZTS without any undesirable secondary phases. According to the EDS analyses, the stoichiometry of the CZTS thin film was Cu-poor and Zn-rich, which is the optimum condition of high-performance devices. The optical bandgap of 1.48 eV was obtained from UV-Vis.

References

1. Kamada R, Yagioka T, Adachi S, et al. New world record Cu(In,Ga)(Se,S)$_2$ thin film solar cell efficiency beyond 22%. *2017 IEEE 44th Photovolt SpecConfPVSC2017*.2017:1-5. doi:10.1109/PVSC.2017.8366261
2. Hayes KJ. CdTe Solar Cell Optimization by Planar and Transmission EBSD. *Microsc Microanaylsis*. 2016;2:2-3. https://www.microscopy.org/MandM/2016/program/abstracts/PDP-22.pdf.
3. Lin YP, Chi YF, Hsieh TE, Chen YC, Huang KP. Preparation of Cu_2ZnSnS_4 (CZTS) sputtering target and its application to the fabrication of CZTS thin-film solar cells. *J Alloys Compd*. 2016;654:498-508. doi:10.1016/j.jallcom.2015.09.111
4. Yan C, Sun K, Liu F, Huang J, Zhou F, Hao X. Boost Voc of pure sulfide kesterite solar cell via a double CZTS layer stacks. *Sol Energy Mater Sol Cells*.2017;160(August2016):7-11. doi:10.1016/j.solmat.2016.09.027
5. Isah KU, Yabagi JA, Ahmadu U, et al. Effect of different copper precursor layer thickness on properties of Cu_2ZnSnS_4 (CZTS) thin films prepared by sulfurization of thermally deposited stacked metallic layers. 2013;2(6):14-19.
6. Scragg JJS, Choubrac L, Lafond A, et al. A low-temperature order-disorder transition in Cu_2ZnSnS_4 thin films A low-temperature order-disorder transition in Cu $_2$ ZnSnS $_4$ thin films. 2014;041911:1-5. doi:10.1063/1.4863685
7. Cui Y, Zuo S, Jiang J, Yuan S, Chu J. Synthesis and characterization of co-electroplated Cu_2ZnSnS_4 thin films as potential photovoltaic material. *Sol Energy Mater Sol Cells*. 2011;95(8):2136-2140. doi:10.1016/j.solmat.2011.03.013
8. Wei M, Du Q, Wang D, Liu W, Jiang G, Zhu C. Synthesis of spindle-like kesterite Cu_2ZnSnS_4 nanoparticles using thiorea as sulfur source. *Mater Lett*. 2012;79:177-179. doi:10.1016/j.matlet.2012.03.080