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Mendeleev Commun., 2016, **26**, 443–445
Mendeleev Communications

Synthesis of $Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4$ thin films by the reactive magnetron sputtering of target components

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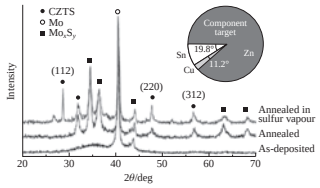
DOI: 10.1016/j.mencom.2016.09.027

The photosensitive thin kesterite films of $Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4$ were prepared by the reactive magnetron sputtering of composite targets followed by annealing with the formation of a kesterite phase.



Thin-film solar cells (TSCs) based on the quaternary copper compounds $Cu_{2-x}Zn_{2-y}Sn_yS_4$ with a kesterite structure are of considerable current interest.[1] However, the implementation of highly efficient TSCs faces problems due to specific phase diagrams and hardly controllable formation of impurity phases that requires a particularly accurate choice of synthetic conditions in order to obtain layers with predefined chemical, phase, and crystal composition and morphology.[2,3] Therefore, the synthesis of kesterite films by various methods has been intensively studied.[1,3–5] The best films in terms of applications as TSC absorbing layers were obtained by the magnetron sputtering of targets[3] with a maximum TSC performance of 8.4%.[6] These polycrystalline films were obtained by the simultaneous sputtering of Cu, ZnS and SnS targets followed by the annealing of precursor films in sulfur vapour[7] or by the successive layer-by-layer deposition of metallic Cu, Zn and Sn in sulfur vapour followed by annealing in a nitrogen atmosphere.[8] In these cases, annealing is required for film recrystallization and/or formation of a kesterite phase. An analysis of these data prompted us to search for the possibilities of two-stage sputtering of composite targets. The use of a multicomponent target makes it possible to adjust the film composition by fitting the Cu/Zn/Sn ratio that is technically easy. In particular, the preparation of thin films by the magnetron sputtering of Cu/In/Ga and Ni/Au composite targets or metal-carbon composite materials is well known.[9–11] As follows from published data,[3,6,8] the $Cu_{2-x}Zn_{2-y}Sn_yS_4$ absorbing layer should have $0.2 \leqslant x \leqslant 0.5$ and $0.7 \leqslant y \leqslant 0.9$ in order to achieve a high TSC performance. A performance above 5% was reached[4] for the composition $Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4$.

In view of this, we suggest a method for the preparation of thin kesterite films $Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4$ (CZTS) by the reactive magnetron sputtering[12] of Cu, Zn and Sn component targets with the subsequent annealing of samples to give a kesterite phase.

The synthesis of this compound from a composite target in an atmosphere of 15% H_2S + 85% Ar can be represented as follows:

$$0.75Cu_2S + 0.85SnS_2 + 1.15ZnS + 0.4S = Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4. \quad (1)$$

In order to determine the required ratio of the segment areas in the composite target, the growth rates of copper, zinc and tin sulfides were found. For this purpose, the reactive sputtering of metal targets was carried out followed by studies of the chemical composition of the resulting films. The thin films of kesterites and binary sulfides were obtained by the direct current magnetron sputtering of corresponding composite (Cu/Zn/Sn) and elementary metallic targets *in vacuo* in a VUP-5 vacuum device using the above gas mixture.[8] The working pressure in the chamber was $p = 4\times10^{-2}$ Torr, the distance between a target and a substrate was $L = 100$ mm, and the power was $P = 125$ W. Discs 105 mm in diameter made of high-purity (99.99%) Cu, Zn and Sn metal sectors were used as the targets. Glass and glass / 3 μm Mo were used as the substrates. The substrate temperature was 25 or 250 °C. CZTS films were annealed at $T = 550$ °C for 30 min in sulfur vapour in a sealed space of a three-zone furnace in a pre-evacuated ($p = 1\times10^{-2}$ Torr) quartz tube (volume, 150 cm^3). The final film thickness was ~1 μm. The phase composition of the resulting films was studied by X-ray powder diffraction analysis (XRD (DRON-4, CuKα) and Raman spectroscopy (Bruker Senterra micro-Raman system, 532 nm). The grain sizes in the films and the morphologies of film surfaces were estimated from the data of scanning electron microscopy [SEM (Zeiss SUPRA 25)]. The surface composition was analyzed by SEM with an adapter.

Since the fabrication of a transparent ohmic frontal electrode (typically, zinc oxide alloyed with aluminum) is time-consuming and requires complex techniques of alternate current magnetron sputtering or reactive sputtering, the procedure is accelerated using a photoelectrochemical cell (PEC[13]) with a photoactive electrolyte[14] of sodium polysulfide + NaOH and a 3 M silver/silver chloride reference electrode (Ag, AgCl/KCl). In this method, a photochemical reaction involving photo-generated current carriers occurs on the film surface. The photosensitivity of films manifests itself as a variation in the current amplitude upon the illumination of samples. This value is proportional to the photoconductivity of films. A sample was irradiated discontinuously, at intervals of about 10 s (power $P = 100$ mW cm^{-2}) under conditions close to AM1.5.

Optical absorption spectra were obtained on a Shimadzu UV-3101PC spectrophotometer.

The growth rate of binary sulfide films during the reactive sputtering of elementary metallic targets in a reactive atmosphere

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Table 1 Growth rates and molar sputtering factors in the reactive sputtering of elementary targets.

$T_{substrate}$/°C, target material	V_{growth}[a]/g cm^{-2} h^{-1}	Film[b]	ν_M[c]/mmol cm^{-2} h^{-1}
25, Cu	6.63×10^{-4}	Cu_2S	6.942×10^{-6}
25, Zn	7.59×10^{-5}	ZnS	7.79×10^{-7}
25, Sn	7.992×10^{-4}	SnS_2	4.374×10^{-6}
250, Cu	6.981×10^{-4}		
250, Zn	2.98×10^{-5}		
250, Sn	8.925×10^{-4}		

[a] Film growth rate in case of sputtering of the corresponding elementary target. [b] Film composition determined by XRD and Raman spectroscopy. [c] Molar coefficient (rate) of sputter deposition of binary sulfides.

was determined from substrate mass variations (Table 1). In order to choose the required formulation of a composite target, we had to determine the composition of the films formed by a combination of XRD and Raman spectroscopy. The reactive sputtering in an atmosphere of 15% H_2S + 85% Ar gave the sulfides Cu_2S, ZnS and SnS_2. The heating of the substrate to 250 °C resulted in the decomposition of copper sulfide and tin sulfide. The XRD patterns of the films obtained by the sputtering of tin targets contained the lines of metallic tin in addition to the lines of hexagonal SnS_2 (PC PDF2 C83-1307 or C21-1231). The films obtained at T = 250 °C consisted of copper [preferential orientation (111)]. The samples synthesized at room temperature consisted of monoclinic modification $Cu_{2-x}S$ (PC-PDF2 C83-1463). Therefore, we concluded that the synthesis of kesterite films from a segmented target is better to perform without substrate heating. Taking the films formed into account, the molar coefficients of sputtering of binary sulfides, ν_M, were calculated (see Table 1).

With consideration for the data in Table 1 and the assumed final composition of $Cu_{1.5}Zn_{1.15}Sn_{0.85}S_4$ for a target consisting of circular sectors, the calculated angles of elementary metallic segments were 11.2°, 329°, and 19.8° for Cu, Zn, and Sn segments, respectively. The sputtering target was fabricated using these data. The film growth rate was 4.546×10^{-4} g cm^{-2} h^{-1}.

The XRD data indicated that the films obtained by this method are amorphous: the XRD pattern contained only lines characteristic of molybdenum (Figure 1, curve *1*). Narrow lines appeared upon annealing of these films in evacuated glass tubes at T = = 550 °C for 60 min (Figure 1, curve *2*). However, XRD data showed no kesterite phase in the sample. It was assumed that the sulfur content of the starting film before annealing was insufficient. Apparently, reaction (1) did not go to completion in our experiments.

To check this assumption, we annealed the starting films in sulfur vapour in a sealed space using a three-zone furnace. Figure 1 (curve *3*) shows the XRD pattern of a sample obtained in this

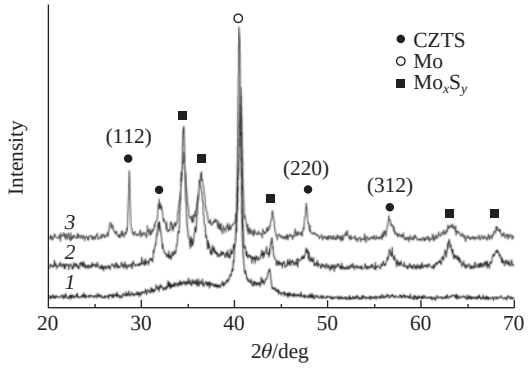

Figure 1 XRD data for (*1*) the starting sample and the samples annealed in an evacuated tube (*2*) without sulfur and (*3*) in sulfur vapour.

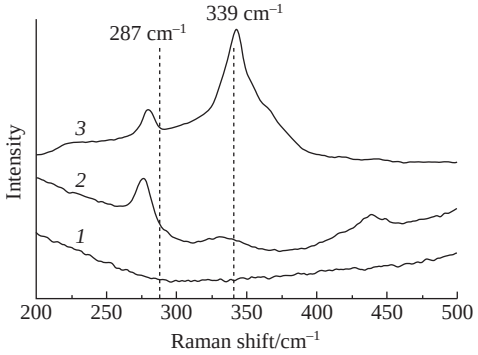

Figure 2 Raman spectra for (*1*) the starting sample and the samples annealed in an evacuated tube (*2*) without sulfur and (*3*) in sulfur vapour.

way. The film contained a kesterite phase [the main peaks of this phase belong to the (112), (220) and (312)] planes, whereas the other lines belong to molybdenum and, probably, molybdenum sulfides. The refined lattice parameters were a = 5.417(10), C = = 10.74(5), V = 315.2(20); tetragonal syngony, I-42m.

The formation of a kesterite phase was also confirmed by Raman spectroscopy (Figure 2). The films before annealing contained no kesterite phase (Figure 2, curve *1*). After annealing in an evacuated tube, Raman spectra (Figure 2, curve *2*) contained kesterite lines near 287 and 339 cm^{-1}, which are characteristic of CZTS.[15,16] However, the most intense line at 339 cm^{-1} becomes distinct only after annealing in sulfur vapour (Figure 2, curve *3*). Note that the lines in the spectrum are shifted in comparison with the reference ones. This can be explained by possible CZTS alloying with molybdenum sulfide whose lines were probably observed in the XRD patterns (Figure 1, curve *3*).

The annealing of CZTS films in sulfur vapour at 550 °C resulted in a considerable enlargement of grains and a change in their crystal structure. The estimation of mean grain sizes in the films based on SEM data showed a size of about 5 nm, whereas one can see grains, presumably with a columnar structure (with diameters from 10 to 120 nm), on the film surface annealed in sulfur vapour (Figure 3).

It was important[17] to estimate the nonuniformity of the surface composition and, accordingly, to assess the necessity of chemical or physical etching of the absorbing layer surface. The etching should precede the formation of the heterojunction since the microstructure of films can determine the conductivity type and characteristics (Singh *et al.*[8] assumed that the surface structure of CZTS films can also affect the performance of TSCs based on them). Therefore, we carried out the elemental analysis of various surface fragments using SEM with an adapter (accelerating voltage, 13.00 kV) and presented the results in Table 2 as an example. Thus, the surface formed in the synthesis is nonuniform and requires physical or chemical etching.

To analyze the optical absorption spectra, we determined the shape of the absorption spectrum near the long-wave limit using

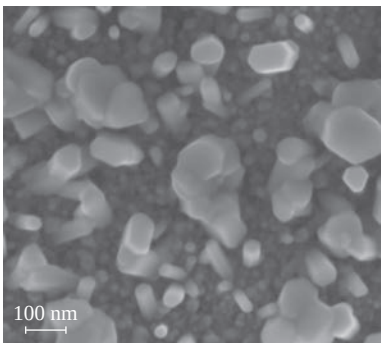

Figure 3 SEM data for a CZTS film after annealing in sulfur vapour.

Table 2 Atomic % of elements in the test points on the surface of a CZTS film and the calculated compositions.

Test point	Cu L	Zn L	Sn L	S K	Composition
1	4.05	48.08	4.45	43.42	$Cu_{1.5}Zn_{17.8}Sn_{1.65}S_{16}$
2	3.20	52.66	3.83	40.30	$Cu_{1.5}Zn_{24.7}Sn_{1.78}S_{18.9}$

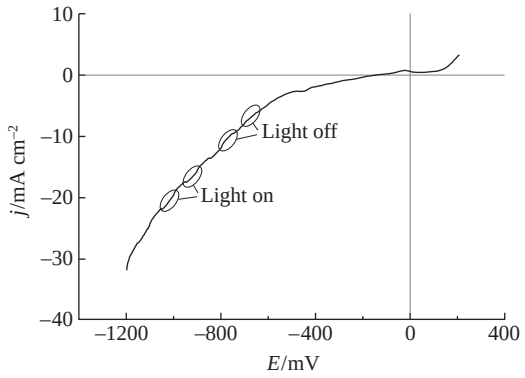

Figure 4 PEC data for a CZTS film after annealing in sulfur vapour.

a conventional method. The law of absorption gain in our samples as a function of light quantum energy in this energy range corresponded to direct optical transitions. The extrapolation of these plots to the energy axis gave E_g = 1.53 eV. The value thus obtained was close to that known from the literature.[8]

The photosensitivity of the films is presented in Figure 4. The sample was photosensitive, but the photochemical reaction occurred rather slowly. The photoresponse had a small fast component poorly observable on this scale, as well as a slow component related to the reaction. The increase in the photocurrent amplitude on shifting to the negative potential range indicates that the dark conductivity of the sample is of the *p*-type.

Thus, we proposed a method for synthesizing thin CZTS films based on the reactive magnetron sputtering of component targets followed by the annealing of films in sulfur vapour. Photosensitive CZTS films with *p*-type dark conductivity were obtained. The formation of a kesterite phase was confirmed by Raman spectroscopy and XRD analysis.

This study was supported by the Russian Foundation for Basic Research (grant nos. 14-08-31753 and 16-08-01234).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.09.027.

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Received: 12th February 2016; Com. 16/4845