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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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Experimental

Thin films of kesterites and binary sulfides (Cu_2S, ZnS and SnS_2) were obtained by direct-current magnetron sputtering of the corresponding composite (*Cu/Zn/Sn*) and elementary metallic targets *in vacuo* in a VUP-5 vacuum device, using a $15\%\ H_2S + 85\%\ Ar$ mixture[1] as the working gas. The working pressure in the chamber was p=4·10^{-2} Torr, distance between the target and the substrate L=100 mm, power P=125 W, target diameter D=105 mm. To ensure uniform film deposition, the substrate was rotated at a rate of ~60 rpm. Films were deposited for 60 min. Binary sulfides were sputter-deposited onto glass substrates at room temperature and at T=250°C. Kesterite films were synthesized without substrate heating (glass or glass/Mo). Discs consisting of high-purity (99.99%) metal sectors made of *Cu*, *Zn*, *Sn* were used as the targets. The *CuZnSnS CZTS* films obtained were annealed for 30 min at T=550°C in sulfur vapors in a sealed space of a three-zone furnace in pre-evacuated (p=1·10^{-2} Torr) quartz tubes (V_{tube} = 150 cm^3). The tube was pre-purged with pure nitrogen. The temperature maintained in the middle zone was T=550°C, while the temperature in the other two zones was T=800°C. Heating to the specified temperatures took 10 min. A precursor film was placed into the middle zone along with various amounts of sulfur (m=5–100 mg) and a small amount of tin (m~5 mg) in order to prevent the loss of tin in the film being synthesized.[2] Annealing was followed by fast (t~10 min) cooling to room temperature. 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, *Cu-K*α)) and Raman spectroscopy (Bruker Senterra micro-Raman system, radiation at 532 nm). The grain size in the films and the morphology of film surfaces were estimated from scanning electron microscopy data (SEM (Zeiss LEO SUPRA 25)).

The photosensitivity of the films was carried out in a photoelectrochemical cell (PEC).[3] Photosensitivity was determined as the change in the current density amplitude due to illumination of samples. This value is proportional to the photoconductivity of films. A sodium polysulfide + *NaOH* mixture[4] was used as the photoactive electrolyte. A 3*M* silver/silver chloride electrode was used as the reference electrode. A sample was irradiated by a pulse light source (τ_{pulse}=10 s, power P=100 mW/cm^2) under conditions close to AM1.5. A DRSh-250 lamp with a water filter and a SZS-23 light filter for decreasing light emission in IR and UV regions was used as the light source. An Elins P8-nano potentiostat/galvanostat with accessory software was used for voltammetric measurements. The potential sweep rate was 5 mV/s. The potential range was 1200−200 mV *versus* the silver/silver chloride electrode. The method is based on a study of changes in the voltammetric curve in an electrochemical cell where a semiconductor of interest on a conductive substrate exposed to light pulses is used as the working electrode.[4] This is an express test method that allows one to study the photovoltaic characteristics of layers without creating a solar cell.

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

Results and Discussion

A. Binary sulfides for the synthesis of kesterite films

The growth rate of binary sulfide films upon reactive sputtering of elementary metallic targets in a *15%* H_2S *+ 85% Ar* atmosphere was determined from the mass variation of the substrate. The data obtained are presented in Table 1.

In order to choose the required formulation of the composite target, we had to determine the composition of the films formed. The composition was studied using a combination of XRD and Raman spectroscopy. Figure S1 shows the X-ray diagrams of samples obtained by reactive magnetron sputtering of elementary targets at various temperatures of the substrate: at room temperature (T=25°C) and at T=250°C. The phase composition was analyzed using the PC-PDF2 electronic database.

One can see from the figure that the half-widths of lines for samples obtained from tin targets at 250°C and at room temperature (curves 1 and 2, respectively) differ: the lines at the lower temperature of the substrate are broad, which indicates that the film contains nanosized grains. The grains obtained at the higher temperature are larger (the line width in the X-ray diagram is smaller). Grain enlargement was confirmed by SEM data. The mean size of nanoparticles in the film obtained at room temperature of the substrate was about 15-20 nm. The films obtained at the higher temperature of the substrate had disordered petal surface structure and consisted of conglomerates (2 to 4 μm) of nanoparticles of about the same size, *i.e.*, 15-20 nm. At the same time, the X-ray diffraction patterns contained, in addition to the lines of hexagonal SnS_2 modification (PC PDF2 C83-1307 or C21-1231), also lines of metallic tin (Figure S1, curve 1). Apparently, heating of SnS_2 in a vacuum results in its partial destruction. Formation of the SnS_2 phase was also confirmed by data of Raman spectroscopy (characteristic lines at 160 and 194 cm^{-1} were recorded).

The lines in the X-ray diffraction patterns of the films obtained from zinc targets (Figure S1, curves 3 and 4) were found to have a considerable width, which makes them hard to interpret. Presumably, this is due to the amorphousness of the films or their small thickness. However, the Raman spectra of these films were found to contain lines characteristic of ZnS (352 and 275 cm^{-1}). Based on SEM data, the size of grains obtained at 25°C was found to be 20 nm and that at 250°C was found to be 40 nm. In the former case, at least two different phases were observed (the film surface contained grains of two different shapes). The film obtained with heating apparently consisted of zinc grains.

Figure S1 (curves 5 and 6) demonstrates the X-ray diffraction patterns of samples obtained by reactive magnetron sputtering of copper targets. As follows from the figure, the films obtained at T=250°C consist of copper with preferred orientation (111). The samples synthesized at room temperature consist of the monoclinic modification of $Cu_{2-x}S$ (PC-PDF2 C83-1463). Furthermore, a considerable half-width of the lines is observed, suggesting that the grains in the film are nano-sized. Furthermore, the spectrum contains lines corresponding to metallic copper (in small amounts since the corresponding peaks have very low intensity). Apparently, *in vacuo* heating results in decomposition of the copper sulfide formed.

B. Kesterite films

Thus, reactive sputtering in a $15\%\ H_2S + 85\%\ Ar$ environment gave sulfides Cu_2S, ZnS and SnS_2. If the substrate was heated in our experiments, copper and tin sulfides decomposed. It was therefore concluded that synthesis of kesterite films from a segmented target is better to perform without heating of the substrate.

The rest of the text is provided in the main paper.

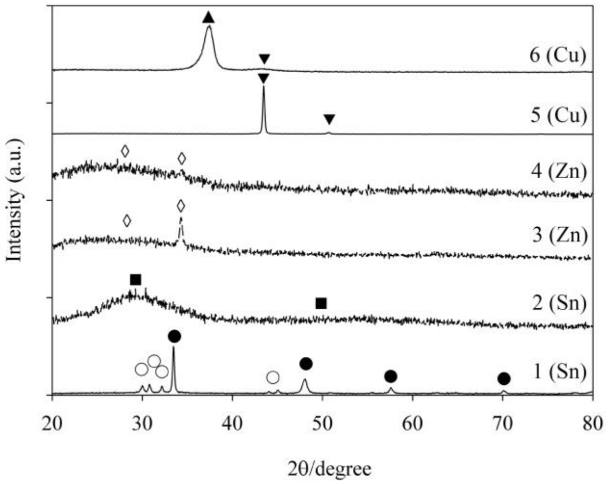

Figure S1 XRD data for films obtained by reactive magnetron sputtering of targets (Sn, Zn, Cu) at various temperatures T of the substrate: curves 1, 3, 5 – at T=250°C; 2, 4, 6 – ct T=25°C. The signs designate the phases: ■ – SnS_2 (Berndtite-4H, 21-1231), ● – SnS_2 (H, 83-1307), ○ – Sn, ◊ – ZnS (10H,72-162),▼– Cu, ▲ – $Cu_{2-x}S$ (M).

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