The Stannite Cu_2ZnSnS_4 Thin Films Prepared by Sulfurization of rf Magnetron Sputtered Metal Precursors

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Abstract: Cu_2ZnSnS_4 (CZTS) thin films for the absorber of thin film solar cells were successfully prepared by sulfurization of rf magnetron sputtered metal precursors on soda-lime glass substrate. The CZTS thin films having the single stannite-type phase structure with good crystalline quality were obtained as revealed in XRD analysis when the conditions of preparation and sulfurization of the precursors were optimized. Hall effect and UV-VIS measurements showed that sheet resistivity, absorption coefficient and optical band-gap energy for the films prepared under the optimized processing conditions are about 0.073 Ω·cm, 10^4 cm^{-1} and 1.53 eV, respectively, indicating that the CZTS films prepared by sulfurization of sputtered metal precursor are suitable for the thin film solar-cell absorber.

Key words: Cu_2ZnSnS_4; thin film; solar cell; rf magnetron sputtering

CLC number: TN304.2+1; TB43 Document code: A Article ID: 0529-6579 (2007) S1-0032-03

1 Introduction

Cu_2ZnSnS_4 (CZTS) thin film is a promising material for low-cost thin-film solar cells due to its promising optical properties (1.4~1.5 eV band gap energy, high absorption coefficient in the order of 10^4 cm^{-1}), as well as the abundant and nontoxic constituent elements[1-4]. In 2005, Katagiri attained the highest conversion efficiency of 5.45% of a solar cell with the device structure of ZnO: Al/CdS/CZTS/Mo/soda lime glass[5]. However, the efficiency is still lower than that of the competitive solar cells, such as Cu_2InSe_2. It is essential to investigate the basic properties of CZTS, e.g. the effect of the composition deviation from stoichiometry on electrical, optical, and structural properties. There are few reports on the basic properties of CZTS. The reason is probably the lack of the establishment of suitable fabrication technique for CZTS thin film. In our previous works, CZTS thin films were successfully prepared by using sulfurization of ion-beam sputtered metal precursors for the first time and a low sheet resistivity of about 0.156 Ω·cm, a high absorption coefficient 10^4 cm^{-1} and an optical band-gap energy of 1.51 eV were obtained[6]. However, these CZTS films sulfurized by ion-beam sputtered Cu/Sn/Zn precursors exhibited poor adhesion to substrate and grow rate of the metal precursor is too slow.

In the present work, rf magnetron sputtering technique was utilized for depositing stacked Cu/Sn/Zn layers precursors. This method is more suitable for large-scale production.

2 Experimental details

The studied samples were prepared by a two-step process. The Cu/Sn/Zn precursors were first deposited on soda lime glass substrates by rf magnetron sputtering technique. The metallic Cu, Sn and Zn (purity 99.99%) plates were used as the sputtering targets and pure argon as the sputtering gas. The RF Power was set at 20 W for Zn, 30 W for Sn, and 50 W for Cu, respectively. The deposition order of the stacked metal layers precursor was Zn, Sn, and Cu and the thickness of every layer were adjusted by altering deposition time. After the deposition, the precursors were immediately transferred to an electric furnace for sulfurization in the flux of S_2 (gas) and N_2 for obtaining CZTS film. The detail of the sulfurization process has been reported elsewhere[6]. The composition and crystallographic

①收稿日期: 2007-01-10
基金项目: 国家自然科学基金资助项目 (10574106).
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structure of samples were determined by energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD). The electrical and optical properties were analyzed by Hall effect measurements with Van der Pauw method, hot probe measurements and UV-VIS spectrophotometer.

3 Results and discussion

Tab.1 Thickness of each precursors and predicted atomic ratio

Precursor type	Thickness of each precursors/nm			Predicted atomic ratio	
	Cu	Zn	Sn	Cu/(Zn+Sn)	Zn/Sn
1	108	120	140	0.63	1.61
2	120	120	140	0.70	1.61
3	132	120	140	0.77	1.61
4	144	120	140	0.84	1.61
5	156	120	140	0.91	1.61

Table 1 shows the thickness of each layer of precursors and the predicted atomic ratios, the composition ratio of each element predicted by their density and atomic weigh. The composition ratios of each element after sulphurisation determined by EDS were shown in Tab.2.

It can be seen that after sulfurization the composition ratio of sulfur in all the films neared to about 50%, indicating the sufficient sulfurization was achieved. Meanwhile, the ratios of Cu/Zn/Sn in all precursors changed in evidence between different samples. Obviously thickness of Cu layer and content of Zn are very important factors for preparation of CZTS thin films with ideal stoichiometry.

Tab.2 Chemical compositions of CZTS films with various precursors

Precursor Type	Chemical compositions analyzed by EDX(at%)				atomic ratio of composition		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
1	18.9	14.2	13.9	53	0.68	1.02	1.12
2	20.5	14.0	13.5	52	0.75	1.04	1.09
3	23.1	13.5	12.4	51	0.89	1.09	1.04
4	26.1	13.4	12.0	48.5	1.03	1.11	0.92
5	26.3	12.8	11.4	49.5	1.09	1.13	0.98

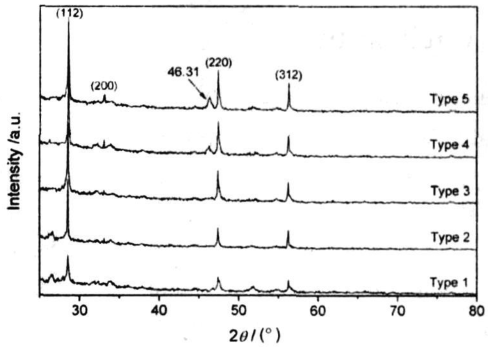

Fig.1 The XRD patterns of CZTS films with various thicknesses of Cu layers

Tab.3 Results of the Hall Effect measurements of the CZTS films with various precursors

Precursor type	Resistance /(Ω·cm)	Mobility (cm^{-2}·V^{-1}·s^{-1})	Carrier concentration /cm^{-3}	Conductivity type
1	6.973	6.0	+1.7438E+18	p
2	4.169	5.6	+6.4947E+18	p
3	0.073	8.3	+7.2010E+19	p
4	0.089	7.4	+6.2010E+19	p
5	0.053	8.9	+9.2010E+19	p

Figure 1 shows the XRD patterns of the CZTS films with various thicknesses of Cu layers. For all the thin films there are strong peaks appeared at $2\theta=28.55°$, $33.05°$, $47.35°$ and $56.25°$, which can be attributed to the diffraction of (112), (200), (220) and (312) orientation of stannite structure CZTS. Meanwhile, other peak at $2\theta=46.31°$ could also be seen in type 4 and 5 films, which are the diffraction peak of Cu_xS. The results indicate that in the copper-poor condition besides the stannite structure CZTS no other second phase compound appeared, but with the increase of thickness of Cu layer, a new phase, Cu_xS begin to appear.

The hot-probe and Hall Effect measurements indicated that all the films exhibited p-type conductivity, and the results were shown in Tab.3. The optical properties of the fabricated CZTS samples were evaluated by measuring the transmittance spectra in the wavelength range of 550~1100 nm. It was found that all the samples in this study had a large absorption coefficient in the order of 10^4 cm^{-1} near a fundamental absorption edge. Meanwhile, the band gap of films decreased from 1.53 eV to 1.45 eV as the thickness of Cu layer increased. This value is apparently an appropriate energy band gap for the solar cell absorber with high conversion.

4 Conclusions

Stannite Cu_2ZnSnS_4 thin films with high crystallinity quality were successfully fabricated by using rf magnetron sputtered metal precursor together with sulfurization of the precursor. The electrical and optical properties of the prepared samples have a strong dependence on the atomic ratio of the constituents in the thin films. The thickness of Cu layer and the content of Zn are important influence factors on the preparation of the CZTS films with high crystalline quality. Furthermore, a low sheet resistivity as about 0.073 Ω · cm and a high absorption coefficient as 10^4 cm^{-1} were achieved. The optical band-gap energy of the CZTS sample is about 1.53 eV, which is very close to the optimum value for a solar cell absorber. These properties indicate that the CZTS film fabricated by this technique is suitable for the use as the absorber of the low-cost and environment friendly thin film solar cell.

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射频溅射金属前驱体硫化法制备的 Cu_2ZnSnS_4 薄膜

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摘 要：采用射频溅射技术沉积 Cu/Sn/Zn金属前驱体叠层结合硫化技术在玻璃衬底上成功制备了 Cu_2ZnSnS_4 薄膜。X-射线衍射分析表明, 通过优化制备条件可以获得单一黝锡矿结构且具有 (221) 择优取向的 Cu_2ZnSnS_4 薄膜。霍尔效应和紫外可见透过谱测量表明, 样品的薄膜电阻、吸收系数和光学带隙分别达到 0.073 Ω · cm, 10^4 cm^{-1}和 1.53 eV, 具有适合作为薄膜太阳电池吸收层应用的可能性。

关键词：Cu_2ZnSnS_4 薄膜；太阳电池；射频磁控溅射

中图分类号：TN304.2+1; TB43