Investigation of $CuIn_{1-x}Al_xSe_2$ Thin Film for Solar Cells Prepared by a Selenization Process

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Abstract: CuInAl (CIA) films as precursors for CIAS were prepared using middle frequency A. C. magnetron sputtering and CIAS absorbers were obtained by selenization. SEM and XRD were used to observe and analyze the compositions, microstructures, and surface morphologies of the films. The results show that the CIAS absorber films with a Cu/(In+Al) atomic ratio of approaching 1 and an adjustable Al/(In+Al) ratio could be obtained by adjusting Al concentration in CIA precursors. CIAS obtained in the work is composed of $Cu(In_{1-x}Al_x)Se_2$ phase. Al exists mainly in solid solution by substituting In.

Key words: solar cell; CIAS; magnetron sputtering; precursor film; selenization
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Solar cells based on $CuInSe_2$ thin films have received considerable attention as promising potential candidates for thin film and low-cost photovoltaic devices[3]. $CuIn_{1-x}Al_xSe_2$ single junction solar cell exhibited an efficiency of 16.9%[4]. In this work CIAS absorber films were obtained. Compositions, microstructures, surface morphologies of the films were analyzed.

1 Experiments

CIA precursor films were deposited using middle frequency A. C. magnetron sputtering by sputtering CuIn alloy target and CuAl composite target alternately. A rotary drive mechanism was used to rotate the substrates to ensure uniformity. The CIA precursors were then selenized in selenium vapor for 15 min at 610℃. CIAS samples obtained are numbered as B1, B2, B3, and B4 corresponding to the CIA samples A1, A2, A3, and A4. The CIA precursors and CIAS films were characterized by SEM, EDS, and XRD.

2 Results and discussion

2.1 Compositions of CIA precursors and CIAS absorbers

Tab. 1 and Tab. 2 show the compositions for the films before and after selenization. Cu/(In+Al) atomic ratios of the CIA samples could be stabilized around 1∶1 with a little lack of Cu. Al/(In+Al) atomic ratios increased from 0.22∶1 to 0.39∶1. Cu/(In+Al) atomic ratios of the CIAS film could also be stabilized around 1∶1 and Al/(In+Al) ratio increase along with the increase of Al concentration of precursors. The results show that selenization process can keep a Cu/(In+Al) atomic ratio of approaching 1 and adjusting Al/(In+Al) ratio.

Tab. 1 Compositions for CIA films

No.	A1	A2	A3	A4
n_{Cu}/%	44.29	42.95	47.00	46.95
n_{In}/%	43.38	41.79	36.82	32.12
n_{Al}/%	12.33	15.26	16.17	20.92
$n_{Cu}/(n_{In}+n_{Al})$	0.80	0.75	0.89	0.89
$n_{Al}/(n_{In}+n_{Al})$	0.22	0.27	0.31	0.39

Tab. 2 Compositions for corresponding CIAS films

No.	B1	B2	B3	B4
n_{Cu}/%	26.86	23.95	27.65	24.84
n_{In}/%	25.69	25.45	22.67	20.55
n_{Al}/%	0.41	3.94	4.28	5.12
n_{Se}/%	47.03	46.66	45.40	49.49
$n_{Cu}/(n_{In}+n_{Al})$	1.03	0.81	1.03	0.97
$n_{Al}/(n_{In}+n_{Al})$	0.02	0.13	0.16	0.20

2.2 Microstructure of the films

Fig. 1 shows that all selenized samples consist of CIAS with chalcopyrite phase. Peak positions, espe-

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cially the 2θ for (312) crystal plane, increase along with the increase of Al concentration of precursors, due to a decrease in lattice parameters. It may be attributed to the fact that Al substitutes partly for In in crystal lattice.

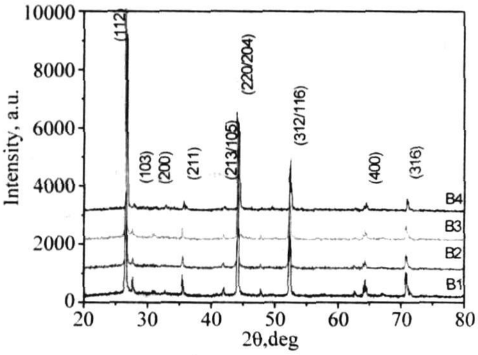

Fig.1 XRD spectrum of CIAS films

2.3 Surface morphologies

Surface morphologies of CIAS films (Fig.2) are mainly composed of smooth grey area and white protuberant area. The results of EDS micro-analysis show that white area are Al-poor and Cu-rich phase while grey area are of Al-rich and Cu-poor phase. With the increase of Al concentration in precursor films the size of Cu — rich grains decreases and distribution get sparse. The phenomena may be attributed the reason that because of Al lower diffusion and shorter diffusion length it is favorable for the sample of high Al concentration to form small crystal grains during selenization.

3 Summaries

The selenization process could be efficient to prepare CIAS absorber films with an adjustable Al/(In+

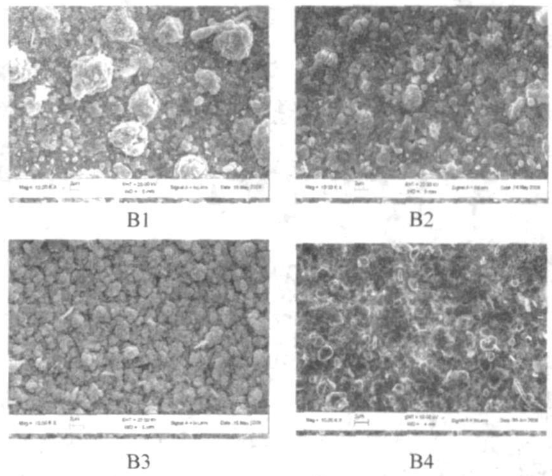

Fig.2 SEM images of the CIAS film surface

Al) ratio and with good structural properties. The properties of solar cells based on CIAS thin films will be studied.

References

[1] GREEN M A. Recent development in photovoltaics[J]. Solar Energy, 76 (2004): 3－8.

[2] MIGUEL A C, et al. Diode characteristics in state-of-the-art ZnO/CdS/Cu($In_{1-x}Ga_x$) Se_2 solar cells[J]. Progress in Photovoltaics: Research and Applications, 2005, 13: 209－216.

[3] ZHUANG Daming, ZHANG Gong. State-of arts and application prospect of thin film solar cells based on Cu(In, Ga) Se_2[J]. Vacuum, 2004, 41: 1－7.

[4] MARSILLAC S, PAULSON P D, HAIMBODI M W, et al. High-efficiency solar cells based on Cu(InAl) Se_2 thin films[J]. Applied Physics Letters, 2002, 81(7): 1350－1352.

硒化法制备铜铟铝硒薄膜及其性能研究

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摘　要: 采用中频交流磁控溅射方法制备了 CIA前驱膜, 并采用固态硒化法进行处理, 获得了 CIAS吸收层薄膜。采用 SEM和 XRD观察和分析了薄膜的成分、组织结构和表面形貌。结果表明, 通过调节 CIA前驱膜的 Al含量可制备得到 Cu/(In+Al)原子比接近 1, 且 Al/(In+Al)比例可调的 CIAS薄膜。CIAS薄膜由 Cu($In_{1-x}Al_x$) Se_2 固溶体相组成, Al主要是以替代 In的固溶形式存在。

关键词: 太阳能电池; CIAS; 磁控溅射; 前驱膜; 硒化
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