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Ảnh hưởng của HCl lên hiệu suất của pin mặt trời màng mỏng Cu_2ZnSnS_4 chế tạo bằng phương pháp phun nóng

Influence of HCl on the performance of spray-deposited Cu_2ZnSnS_4 thin film solar cells

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Abstract

Keterite Cu_2ZnSnS_4 (CZTS) thin films were fabricated by spray pyrolysis deposition using aqueous precursor solutions with and without the addition of HCl. The effects of HCl on the crystallinity, morphology and photovoltaic properties of CZTS thin films were investigated. The results showed that the presence of HCl had significant effects on the crystal growth, grain size, and surface morphology of the fabricated CZTS thin films resulting in the improvement of the photovoltaic properties of the solar cell.

Keywords: Cu_2ZnSnS_4; thin-film solar cells; effects of HCl; spray pyrolysis technique.

Tóm tắt

Màng mỏng kesterite Cu_2ZnSnS_4 được chế tạo bằng phương pháp phun nóng từ các dung dịch tiền chất không chứa và có chứa HCl. Ảnh hưởng của HCl lên cấu trúc tinh thể, hình thái học và tính chất quang điện của màng mỏng CZTS được phân tích. Kết quả chỉ ra rằng sự có mặt của HCl có ảnh hưởng lớn đến sự phát triển tinh thể, kích thước hạt, hình thái học bề mặt của màng mỏng CZTS chế tạo được dẫn đến sự cải thiện tính chất quang điện của pin mặt trời.

Từ khóa: Cu_2ZnSnS_4; pin mặt trời màng mỏng; ảnh hưởng của HCl; công nghệ phun nóng.

1. Introduction

Thin film photovoltaic solar cells are promising alternatives to the commonly used silicon-based solar cells due to their high conversion efficiency and low manufacturing cost. Among the choices of compound semiconductors for the absorber layer of the thin-film solar cells, kesterite Cu_2ZnSnS_4

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(CZTS), $Cu_2ZnSnSe_4$ (CZTSe), and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) have attracted much attention.[1, 2] These kesterite materials consist of abundant and low-cost metallic elements with optimum band gap energies ranging from 1.0-1.5 eV and high absorption coefficients of more than 10^4 cm^{-1}, they can achieve high absorption of photons from sunlight within a few hundred nanometers of thickness.[3, 4] However, the reported power conversion efficiency (PCE) of the kesterite solar cells has not yet reached the expected values for commercial applications, therefore further studies for improvement of PCE are necessary.[5]

In view of the toxicity issue, pure sulfide (CZTS) would be preferable. Various synthesis methods for CZTS thin films have been proposed, including vacuum processes such as sputtering, evaporation, pulse laser deposition, and non-vacuum processes such as sol-gel deposition, spray pyrolysis, and electrochemical deposition.[6, 7] Among them, spray pyrolysis is an attractive non-vacuum method for low-cost deposition of solution-processed thin films because its advantages are easier thickness control in a large area, the capability of deposition on non-flat surfaces, and lower material loss during deposition, which are of great value for industrial applications.

In our previous study, we found that the presence of HCl helps to prevent precipitation in the spray solution for the deposition of CZTS thin films.[8] However, the effect of HCl on the properties of fabricated thin films remains unclear and needs to be clarified. Therefore, in this work, we fabricated CZTS thin films by spray pyrolysis method using different spray solutions without and with the addition of HCl and investigated the effects of HCl on the crystallinity, phase purity, and morphology using X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. Complete solar cells with Al/ITO/ZnO/CdS/CZTS/Mo/glass structure derived from fabricated films were used to determine photovoltaic properties. The results showed that the presence of HCl in the precursor spray solution had significant effects on the crystal growth, grain size, and surface morphology of the CZTS films resulting in the improvement of photovoltaic performance with an increase in power conversion efficiency of CZTS solar cell up to 5.7 %.

2. Experimental

Two aqueous precursor solutions were prepared from 0.019 M copper nitrate ($Cu(NO_3)_2$), 0.009 M zinc nitrate ($Zn(NO_3)_2$), 0.0125 M tin methanesulfonate ($Sn(CH_3SO_3)_2$) and 0.06 M thiourea ($SC(NH_2)_2$). A few drops of concentrated HCl acid were added to one aqueous solution. Deposition of CZTS thin films was carried out by spraying these precursor solutions on Mo-coated glass substrates heated at 380 °C. The thus obtained films were annealed in an evacuated borosilicate glass ampoule together with 20 mg S powder at 600 °C for 30 min and labeled CZTS_w/o and CZTS_HCl for the film fabricated from precursor solution without and with the addition of HCl, respectively. For the fabrication of CZTS solar cells, a CdS buffer layer was deposited on CZTS films by chemical bath deposition. An ITO/ZnO bilayer was then deposited on top of the CdS layer by radio frequency (RF) magnetron sputtering and Al top contact was deposited by thermal evaporation to form a device with a structure of Al/ITO/ZnO/CdS/CZTS/Mo/glass.

Crystalline structures of the films were analyzed by X-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer and Raman spectroscopy using a JASCO NRC

3100 laser Raman spectrophotometer. Morphologies of the films were examined by using a Hitachi S-5000 field emission scanning electron microscope (SEM). Current density-voltage (J-V) characteristics of solar cell devices were determined with a Bunhoh-Keiki CEP-015 photovoltaic measurement system under a simulated amplitude modulation of AM1.5G irradiation.

3. Results and Discussion

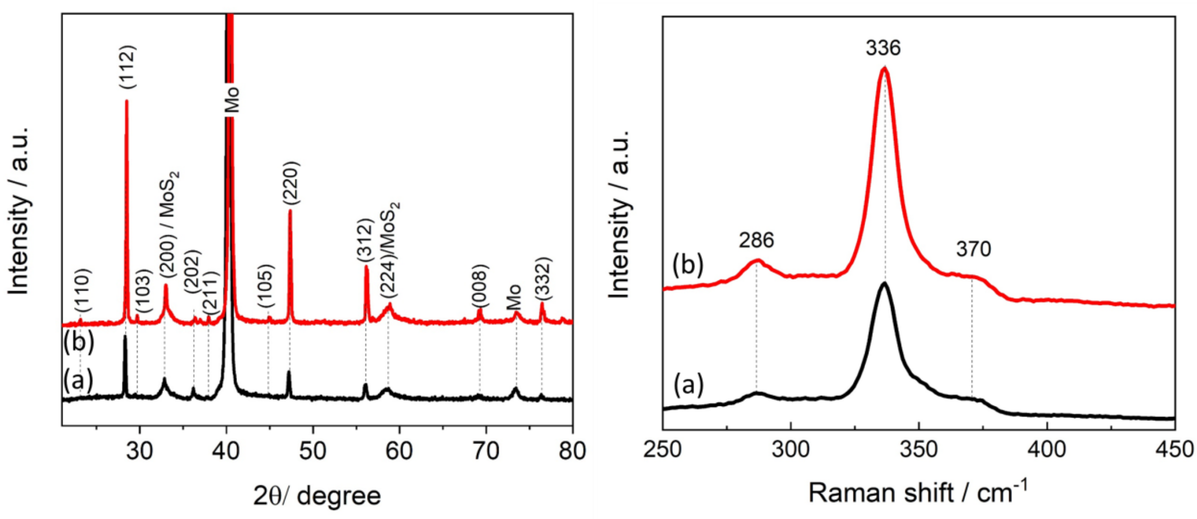

Figure 1. (Left) XRD patterns and (right) Raman spectra of CZTS films obtained from precursor solutions (a) without and (b) with the addition of HCl after annealing at 600 °C for 30 min.

Figure 1 shows XRD patterns and Raman spectra of CZTS films obtained from precursor solutions without and with the addition of HCl after annealing at 600 °C in an evacuated glass ampoule containing sulfur powder for 30 min. XRD patterns of these samples showed typical diffraction peaks corresponding to the (110), (112), (103), (200), (202), (211), (105), (220), (312), (224), (008), and (332) plans of reflections derived from the kesterite CZTS structure.[9, 10] The peaks derived from the Mo substrate and its sulfurized form MoS_2 were also observed due to the partial sulfurization during annealing. It should also be noted that the main peaks of the CZTS sample fabricated from the precursor solution containing HCl are more intense than those of the sample fabricated from the precursor solution without the addition of HCl, this may be due to the better crystallinity of this CZTS_HCl sample. Raman spectra of the films showed main peaks at 286, 336, and 370 cm^{-1} assignable to the kesterite CZTS crystal, and there are no secondary peaks observed.[11, 12] Hence, the fabricated films obtained in this study were confirmed to form the kesterite CZTS crystal structure.

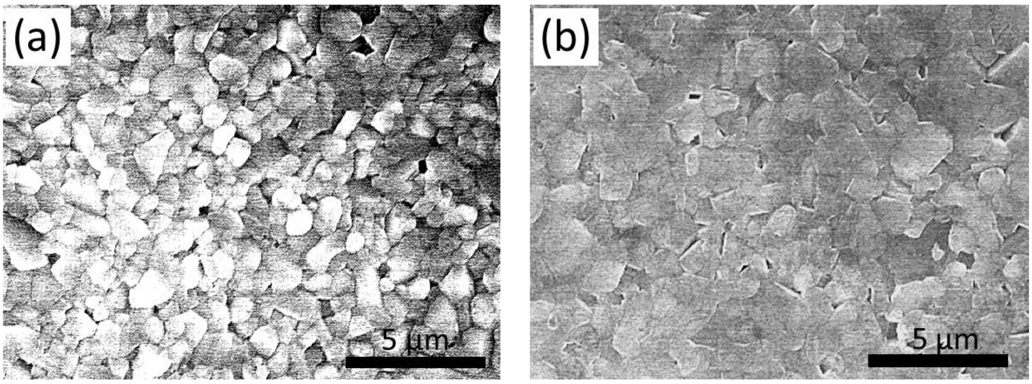

Figure 2. Surface SEM images of CZTS films obtained from precursor solutions (a) without and (b) with the addition of HCl after annealing at 600 °C for 30 min.

Figure 2 shows surface SEM images of the CZTS films after annealing at 600 °C for 30 min. The films were composed of densely packed submicron-sized crystal grains. For the CZTS sample derived from the precursor solution containing HCl, the film morphology became more compact and the surface was smoother and less appreciable pinhole. In addition, based on the analyses of grain-size distributions obtained by measuring major axes of several tens grains in these films, the grains in the CZTS_HCl were larger than those in the CZTS_w/o sample. This result is consistent with intense and sharp peaks in the XRD pattern of this sample. Thus, it can be observed that the presence of HCl is effective for the crystallinity and grain growth of CZTS film fabricated by the spray pyrolysis method.

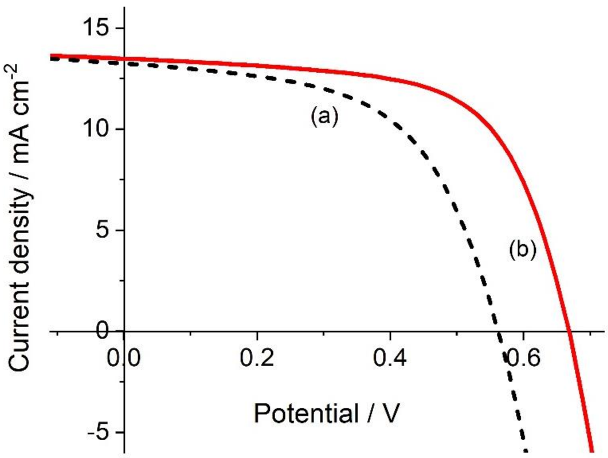

Figure 3. J-V characteristics of Al/ITO/ZnO/CdS/CZTS/Mo/glass solar cells made from (a) CZTS_w/o and (b) CZTS_HCl films.

Solar cells with a device structure of Al/ITO/ZnO/CdS/CZTS/Mo/glass were prepared by deposition of CdS, ZnO, and ITO layers and an Al top contact onto CZTS_w/o and CZTS_HCl films. Figure 3 shows the J-V curves of these devices under irradiation of simulated sunlight (AM 1.5 G). Short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE) of these cells were determined from illuminated J-V curves, these cell parameters are summarized in Table 1. As can be expected from crystalline and morphological properties, compared to the J-V characteristic of the device made from the CZTS_w/o film with a PCE of 4.2 %, the CZTS_HCl film exhibited a higher PCE of 5.7 %. This higher PCE is mainly from the improvement of V_{OC}

and FF, it is due to the larger grain size and smoother surface supported for carrier transport in the bulk and at the interface of CZTS and CdS layers of the solar cell.

Table 1: Solar cell parameters of solar cells made from CZTS_w/o and CZTS_HCl films

Sample	J_{SC} /mA cm^{-2}	V_{OC}/mV	FF	PCE (%)
CZTS_w/o	13.2	562	0.56	4.2
CZTS_HCl	13.5	668	0.63	5.7

4. Conclusion

In summary, we have investigated the effects of HCl in the precursor solutions on the performance of CZTS thin films through a low-cost spray pyrolysis method. It was found that the presence of HCl in the precursor solution had significant effects on the fabrication of CZTS thin film; the crystal growth, grain size, and surface morphology of the CZTS film were improved, leading to the improvement of photovoltaic properties. Compared to the device made from the CZTS_w/o sample, the solar cell with Al/ITO/ZnO/CdS/CZTS/Mo/glass structure derived from the CZTS_HCl sample was shown to have good performance with an increase in PCE up to 5.7 %. The result of this work may provide a perspective for the further development of high-efficiency CZTS thin film solar cells.

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