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CHARACTERIZATION OF CdS:O THIN FILMS WITH DIFFERENT RATIO OF AMBIENT OXYGEN PREPARED BY RF MAGNETRON SPUTTERING AND ITS APPLICATION IN CdTe SOLAR CELLS

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CdS:O thin films with different ratio of ambient oxygen have been prepared by RF magnetron sputtering. CdTe solar cells with CdS:O thin films as window layer have also been prepared. In order to investigate the effects of oxygen on CdS:O thin films and CdTe solar cells, X-ray diffraction, UV-Vis, X-ray photoelectron spectroscopy, Raman spectroscopy, EQE and I-V curve have been measured. The result shows ambient oxygen can promote the transform from crystalline to amorphous, thus lead to the increase of transmission value and band gap, which can benefit the improvement of short wave response of CdTe solar cell. However, generation of sulfate in CdS:O thin films inhibits the growth of CdS_xTe_{1-x} heterojunction interface and decreases fill factor and open-circuit voltage. The final result shows CdTe solar cells with CdS:O thin film with 0.2% ratio of oxygen as window layer has best performance and the efficiency is 12.93% .

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Keywords: CdS:O, RF magnetron sputtering, XRD, Raman, XPS, CdTe solar cell

1. Introduction

With advantages of low cost, stable capacity, good performance in low light and low optical recession, CdTe solar cell develops rapidly and has become one of the most potential thin film solar cells. Currently, the conversion efficiency of a small area of CdTe solar cell device has reached 21.5%. In conventional structure of CdTe solar cell ---"TCO/CdS/CdTe/back contact/metal electrode", most shortwave photons of wavelengths less than 550nm does not contribute to the photocurrent due to the 2.42eV band gap and 550nm absorption edge of CdS. Therefore, studying new window layer of higher band gap to improve device's shortwave response has become one of the most concerns these days.

Oxygenated cadmium sulfide can alter the composition and characteristics of cadmium sulfide significantly and broaden the band gap without generating new lattice mismatch. Used as

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window layer, the shortwave response can be improved effectively and the conversion efficiency of CdTe solar cells can be enhanced. Therefore, the study of CdS:O thin films is of great significance. Compared with chemical vapor deposition, DC magnetron sputtering, vacuum evaporation and pulsed laser deposition, RF magnetron sputtering is an excellent deposition process with the advantage of good film quality, simple operation, repeatability and less toxicity. This work aims at the preparation of CdS:O thin films with different ratio of ambient oxygen by RF magnetron and the study of single layer's characteristics and the influence on performance of CdTe solar cell devices.

2. Experiment

CdS:O thin films were deposited on borosilicate glass by RF magnetron sputtering. The degree of vacuum is $5 \sim 6 \times 10^{-5}$Pa.During the process, the sputtering power is 35W and the chamber pressure was fixed to be 2Pa. The ratio of ambient oxygen was regulated to 0%-1% by flow controller. The thickness of thin films was fixed to 100~110nm.

The structure of CdTe solar cell in this work is "FTO/CdS:O/CdTe/ZnTe:Cu/Au". The process is as follows: CdS:O thin films with different ratio of ambient oxygen were deposited on SnO_2:F substrate, the thickness is 60nm. Then, CdTe thin films were deposited by VTD and the thickness is 3~5 μm (substrate temperature is 610℃, CdTe source temperature is 700℃); thereafter, the films were annealed in the presence of $CdCl_2$ in 385℃ for 35min. After corroded by bromine methanol for 10s, ~70nm ZnTe:Cu films were deposited as back contact. Finally, the films were annealed in 190℃ and ~100nm Au were vacuum deposited as electrode.

The crystallinity of thin films were measured by X-ray diffraction (XRD-DX-2600, Dandong, China) using Cu Kα radiation (λ = 1.5404 Å). The Raman spectroscopy (SR-303i-B, Andor Shamrock, EU) were measured using laser pulse wavelength of 532 nm as the excitation light. The transmission values of films were measured by UV/VIS/NIR Spectrophotometer (lambda 950, PerkinElmer, US). The I-V curves were measured by I-V test system (Zhongsen, Shaanxi, China); the EQE curves were measured by QE test system (QEX10, PV Measurements, US).

3. Result and discuss

Fig. 1 shows the X-ray diffraction spectrum of CdS:O thin films. As shown in fig. 1, CdS thin film is polycrystalline of hexagonal phase with obvious (002) (101) (102) (103) diffraction peaks (PDF No.41-1049)

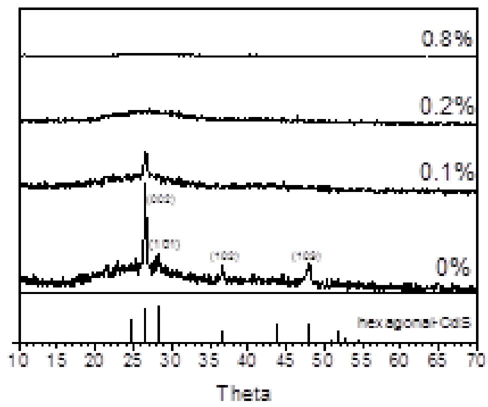

Fig1 X-ray diffraction spectrum of CdS:O thin films

The grain size can be calculated by Debye–Scherrer equation by the FWHM of the characteristic peak (002) as follow:

$$D = \frac{k\lambda}{\beta cos\theta}$$

where D is the coherence length, β is the full width at half maximum of peak, λ is the wavelength of X-ray radiation, k is the Scherrer constant and θ is the angle of diffraction for (002) plane. The average size is calculated as 34nm. When the ratio of ambient oxygen elevated to 0.1%, (101) (102) (103) planes all disappear and the (002) diffraction peak intensity decreases. The grain size can be calculated as 14.5nm. With the ratio of ambient oxygen continues to elevate, all diffraction peaks disappear and the grain size is nanoscale, which means the transform from polycrystalline to amorphous.

Figure 2 is the transmission value with different ratio of ambient oxygen. As can be seen, transmission value in shortwave region (250-500nm) increases with the ratio of ambient oxygen and the absorption edge has significant blue shift at the same time. This trend slows down when the oxygen ratio is above 0.4%.

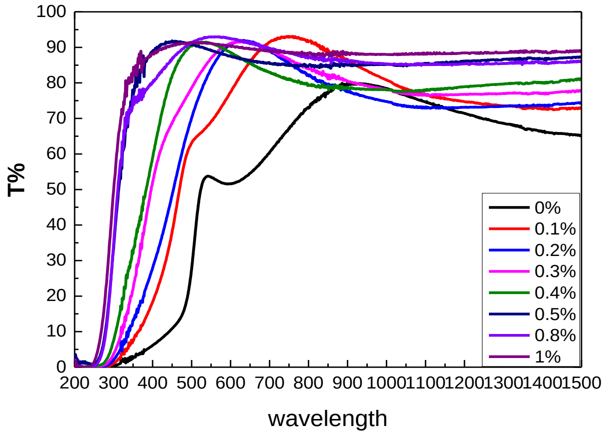

Fig. 2 The transmission value of CdS:O thin films

The band gap of thin films can be calculated by Tauc equation:

$$(\alpha h\nu)^2 = k^2(h\nu - E_g) \quad (2)$$

Where h is Planck constant, Eg is band gap of thin films, ν is light frequency, k is a constant and α is absorption coefficient.

The absorption coefficient α can be calculated by the following equation:

$$\alpha = -\ln T/d \quad (3)$$

Where d is the thickness of thin film and T is the transmission value.

The optical band gap of thin films can be obtained from the $(\alpha h\nu)^2$- $h\nu$ curve. As in Fig 3, by extrapolating the linear region of curves to the $h\nu$ axis, the intercept of $h\nu$ axis gives the direct optical band gap. Band gap of CdS thin film is 2.4eV and with the increase of oxygen ratio, the band gap increase to 2.9eV.

Increase of bandgap benefits the absorption of shortwave photons and more photons can be converted so that the shortwave response can be improved. The mechanism of increased band gap and the blue shift is the quantum size local effect caused by the nanoscale grain size, which is consistent with the X-ray diffraction results.

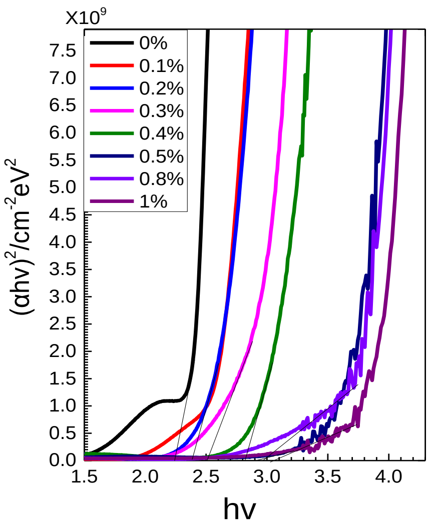

Fig. 3. Scheme of $(\alpha h\nu)^2$ *vs* $h\nu$

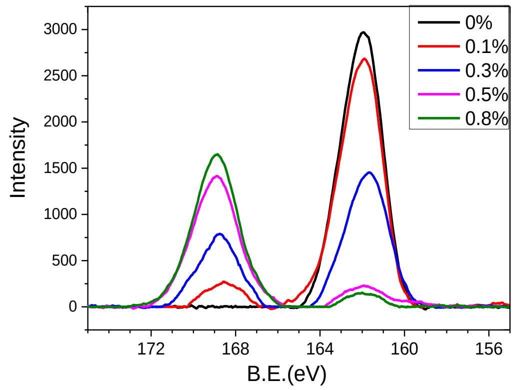

Fig. 4 X-ray photoelectron spectrum of S_{2p} tunnel in CdS:O thin films

Figure 4 is the X-ray photoelectron spectrum of S_{2p} tunnel in CdS:O thin films. Binding energy of 161.7eV and 168.6eV correspond to sulfide and sulfate. As shown in figure, CdS film has only one peak at 161.7eV corresponding to sulfide. Peak at 168.6eV appears when oxygen was added and it means the generation of sulfate. The content of sulfate increases gradually with the increase of ambient oxygen while the sulfide is the opposite. The generation of sulfate can seriously affect the growth of CdS/CdTe heterojunction interface.

Raman spectrum of thin films can be seen in Fig 5. 1LO and 2LO Raman peaks of CdS at 300nm and 602nm can be observed in CdS thin films. 2LO Raman peak disappears when oxygen is added. The intensity of 1LO peak decreases with the increase of ambient oxygen and it disappears when the ratio of ambient oxygen reaches to 0.4%. The disappearance of 1LO Raman peak due to the reduction of CdS content and the amorphous phenomenon caused by the grain size becoming nanoscale. Besides, the appearance of broad peak at 470nm may be associated with the generation of cadmium sulfate.

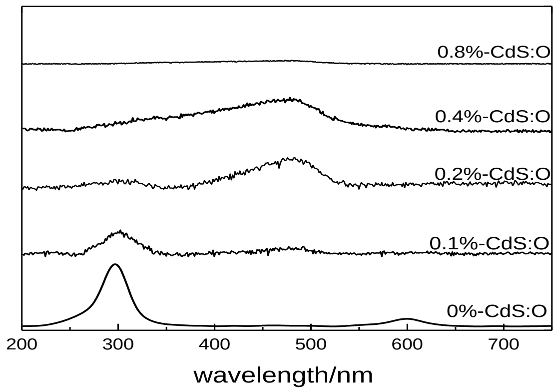

Fig. 5 Raman spectrum of CdS:O thin films.

Fig 6 is the EQE curve of CdTe solar cells. As shown in figure6, the shortwave response (300-500nm) improves rapidly with the increase of ambient oxygen. It is caused by the increase of shortwave absorption. However, the longwave response attenuates with the increase of ambient oxygen, especially when the ratio reached to 0.4%. Long wave response reflects the CdS/CdTe heterojunction properties directly. And this decline is caused by the generation of cadmium sulfate.

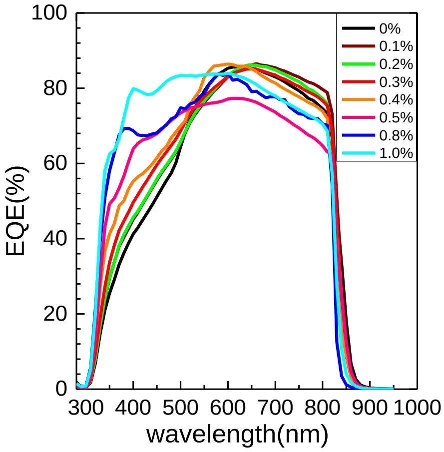

Fig. 6 EQE spectrum of CdTe solar cells

Fig. 7 (a) (b) (c) (d) show the change of short-circuit current density, open-circuit voltage, fill factor and conversion efficiency with the increase of ambient oxygen. With the increase of oxygen from 0% to 0.2%, all parameters improve in varying degree, in which, improvement of short- circuit current density is the most obvious. Combined with Fig6, we can know the improvement mainly due to the increase of short wave response. Device performance declines greatly with the ratio of ambient oxygen increases to more than 0.4%, which due to the very poor junction properties caused by the increasing content of cadmium sulfate.

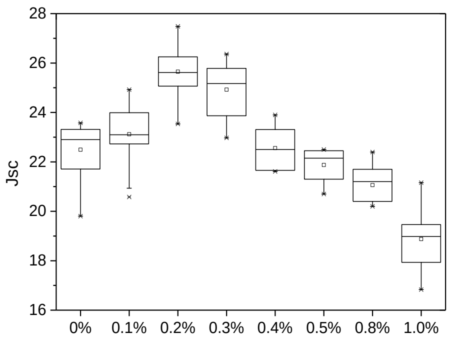

Fig7(a)Short-circuit current density vs ratio of ambient oxygen

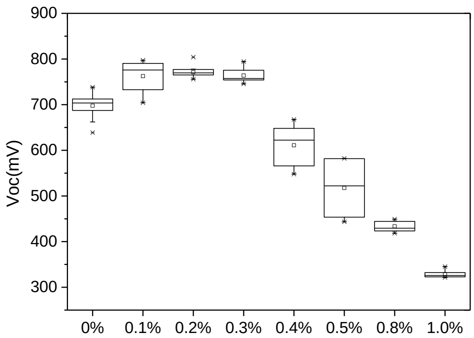

Fig7(b) Open-circuit voltage vs ratio of ambient oxygen

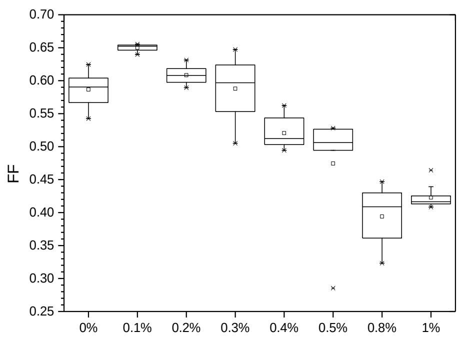

Fig7(c)Fill factor of CdTe solar cells vs vs ratio of ambient oxygen

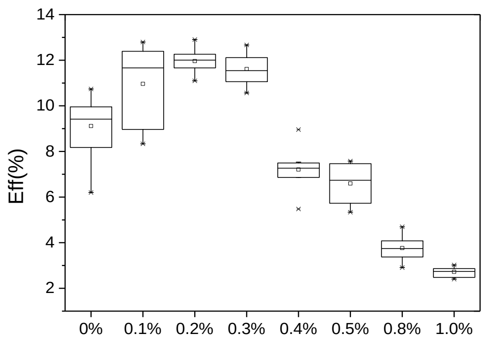

Fig7(d) Conversion efficiency of CdTe solar cells vs ratio of ambient oxygen

In summary, though CdS:O thin films can improve the short wave response, it interferes the growth of CdS/CdTe interface also. And the interface is of great significance to reducing the mismatch of CdS/CdTe and promoting the growth of CdTe thin film. In this work, it can help improve the short wave response without affecting the properties of interface obviously when the ratio of ambient oxygen is 0.1%-0.3%., which leads to the increase of device conversion efficiency. And the highest conversion efficiency is 12.93% with 0.2% ratio of ambient oxygen.

4. Conclusion

In this work, CdS:O thin films with different ratio of ambient oxygen and related CdTe solar cells were prepared. With the increase of ambient oxygen, X-ray diffraction spectrum show the grain size changes from 34nm to 14.5nm and then to nanoscale; UV-Vis spectrum show the increase of transmission value and the blue shift of absorption edge caused by quantum size local effect; X-ray photoelectron spectrum and Raman spectrum show the generation and increase of cadmium sulfate content and the decrease of cadmium sulfide content. EQE curves and device parameters show the effects of ambient oxygen on device performance. CdS:O thin films can improve the short wave response and interfere the properties of CdS/CdTe interface at the same time. The ratio of ambient oxygen from 0.1% to 0.3% can improve the device performance and the highest conversion efficiency is 12.93% with 0.2% ratio of ambient oxygen.

Acknowledgements

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References

[1] Geisthardt, R. M, Topic, Marko, Sites, et al. IEEE Journal of photovoltaics **5**, 4 (2015).
[2] Functional Material Information **12**, 1 (2015).
[3] See http://investor.firstsolar.com/releasedetail.cfm?ReleaseID=828273 for First Solar press release.
[4] K.A.M.H.Siddiquee, M.A.K.Pathan, S.Alama, et al. Optik - International Journal for Light and Electron Optics **124**, 20 (2013).
[5] W.WG, S.R, Horn,K. Journal of Vacuum Science & Technology B **7**, 4 (1989).
[6] S.N.A, S.R.R, M.W. Journal of Alloys and Compounds **512**, 1 (2012).
[7] E.A. Sanchez-Ramirez, M.A. Hernandez-Perez , J.R. Aguilar-Hernandezb. Applied Surface Science **347**, 30 (2015).
[8] W.X., Y.Y., D,R.G. Physica Status Solidi C 4 (2004).
[9] K.P.M., L.F., A.A., 2014 IEEE 40th Photovoltaic Specialists Conference (PVSC), (2014).
[10] N. E, Gorji. Optical and Quantum Electronics **47**, 8 (2015).

[11] C.V, R.N, S.G, et al. Journal of Vacuum Science & Technology A-Vacuumm Surfaces and Films **2**, 1 (2015)
[12] U.H, I.S, S.H. Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Reviews Papers **29**, 1 (1990).
[13] R.J.McIntyre. Solar Energy Materials **7**, 1 (1982).
[14] M.KW, F.AL, B.RH. Journal of Applied Physics **48**, 10 (1977).
[15] N.Hernandez-Como, V.Martinez-LanderosI. Mejia, et al. Thin Solid Films 550 (2014).