[Article]

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一种在室温合成具有宽带隙CdS的简单方法

李 辉¹ 刘向鑫^{1,*} 张玉峰¹ 杜忠明¹ 杨 彪¹
韩俊峰^{2,3} BESLAND Marie-Paule³

(¹中国科学院电工研究所太阳能热利用及光伏系统重点实验室, 北京 100190; ²北京理工大学物理学院, 北京 100081; ³Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France)

摘要: 采用简单的磁控溅射方法, 在室温合成了CdS多晶薄膜. 在溅射CdS多晶薄膜过程中, 分别在Ar气中通入0%、0.88%、1.78%、2.58%和3.40% (体积分数, ϕ) 的O₂, 得到不同O含量的CdS多晶薄膜. 通过X射线衍射仪、拉曼光谱仪、扫描电子显微镜、X射线光电子能谱仪、紫外-可见光谱仪对得到的CdS多晶薄膜进行表征. 分析结果表明: O的掺入能得到结合更加致密, 晶粒尺寸更小的CdS多晶薄膜; 与溅射气体中没有O₂时制备的CdS多晶薄膜的光学带隙(2.48 eV)相比, 当溅射气体中O₂的含量为0.88%和1.78% (ϕ)时, 制备得到的CdS多晶薄膜具有更大的光学带隙, 分别为2.60和2.65 eV; 而当溅射气体中O₂的含量为2.58%和3.40% (ϕ)时, 得到的CdS光学带隙分别为2.50和2.49 eV, 与没有掺杂O的CdS的光学带隙(2.48 eV)相当; 当溅射气体中O₂的含量为0.88% (ϕ)时, 制备的CdS多晶薄膜具有最好的结晶质量. 通过磁控溅射方法, 在溅射气体中O₂含量为0.88% (ϕ)条件下制备的CdS多晶薄膜表面沉积了CdTe多晶薄膜并在CdCl₂气氛中进行了高温退火处理, 对退火前后的CdTe多晶薄膜进行了表征. 表征结果显示: CdS中掺入O能得到结合更紧密、退火后晶粒尺寸更大的CdTe多晶薄膜. 通过磁控溅射方法, 在CdS制备过程中于Ar中掺入O₂, 在室温就能得到具有更大光学带隙的CdS多晶薄膜, 该方法是一种简单和有效的方法, 非常适用于大规模工业化生产.

关键词: CdS; O掺杂; 磁控溅射; CdTe; 太阳能电池

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Synthesis of CdS with Large Band Gap Values by a Simple Route at Room Temperature

LI Hui¹ LIU Xiang-Xin^{1,*} ZHANG Yu-Feng¹ DU Zhong-Ming¹ YANG Biao¹
HAN Jun-Feng^{2,3} BESLAND Marie-Paule³

(¹The Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China; ²School of Physics, Beijing Institute of Technology, Beijing 100081, P. R. China;

³Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France)

Abstract: We report the synthesis of CdS polycrystalline thin films deposited with 0%, 0.88%, 1.78%, 2.58%, and 3.40% (volume fraction, ϕ) O₂ in sputtering Ar gas using a radio frequency magnetron sputtering method. The obtained CdS samples were characterized by X-ray diffraction, scanning electron microscope, Raman

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*Corresponding author. Email: shinelu@mail.ice.ac.cn; Tel: +86-10-82547044; Fax: +86-10-82547041.

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spectroscopy, ultraviolet-visible (UV-Vis) absorption spectroscopy, and X-ray photoelectron spectroscopy. O incorporation led to the formation of compact and small CdS grains. The band gap values of the CdS thin films deposited with 0.88% and 1.78% O₂ were 2.60 and 2.65 eV, respectively, and were larger than that of CdS (2.48 eV) deposited without O₂ gas in sputtering Ar gas. In contrast, the band gap values of the CdS thin films deposited with 2.58% and 3.40% O₂ (2.50 and 2.49 eV, respectively) were consistent with that of CdS (2.48 eV) deposited without O₂ gas in sputtering Ar+O₂ gas. The CdS thin film deposited with 0.88% O₂ displayed the highest crystalline quality. Subsequently, CdTe thin films were deposited by radio frequency magnetron sputtering method on the surface of the CdS thin films. The CdTe thin films were characterized before and after high-temperature anneal treatment in a CdCl₂ atmosphere. The results showed that O incorporation into CdS led to the formation of considerably more closely packed and larger CdTe grains. The synthesis of CdS with large band gap values at room temperature is facile and effective using the current method. Therefore, the method presented herein is very promising for large-scale industrial production.

Key Words: CdS; O incorporation; Magnetron sputtering; CdTe; Solar cell

1 Introduction

Cadmium sulfide (CdS) is an II-VI group semiconductor with a direct band gap of 2.4 eV (bulk CdS) at room temperature.¹ It has potential use in a wide range including photovoltaic cells,² thin-film transistors,³ light-emitting diodes,⁴ phosphors,⁵ biological labeling,⁶ etc. Due to its low electrical resistivity and high optical transmittance, CdS films are commonly used as a buffer layer material in thin film solar cells such as CdTe, CuInGaSe and so on.⁷⁻⁹ CdS thin films can be prepared by numerous methods such as chemical bath deposition (CBD),¹⁰ sputtering,⁷ laser ablation,¹¹ vacuum evaporation,¹² screen printing,¹³ and electro deposition.¹⁴ Among these methods, sputtering method is found to be suitable for the production of high purity, uniform, adherent, and reproducible large area CdS thin films.⁷ In addition, the optical properties of CdS are easily modified by changing the deposition parameters like deposition gas and substrate temperature. In thin film solar cells, reducing the optical absorption of the CdS is a critical issue to improve the efficiency in superstrate structure. CdS doped with O (CdS:O) is an effective way to reduce the optical absorption due to larger band gap of CdS:O than that of CdS.⁹ However, the comprehensive study of the oxygen incorporation into CdS is very limited, especially grown by sputtering method.

In order to clarify this issue, in this paper, CdS thin films were deposited by a radio-frequency (rf) magnetron sputtering method with various O₂ gas contents in the sputtering gas. The structure, morphology, optical properties and chemical information of CdS thin films with different O contents, and the effects on the CdTe absorb layer materials were studied.

2 Experimental

2.1 Fabrication of CdS and absorb layer materials

CdS thin films were deposited on 10 cm×10 cm SnO₂:F coated 3-mm-thick soda lime glass (NSG-Pilkington TEC15, from Pilkington North America Inc.) at room temperature by a rf magnetron sputtering method. The TEC15 glass was cleaned by micro-90, deionized water, and dried by high purity N₂ (99.999%,

5N). For CdS deposition, the sputter chamber was pumped to a base pressure of ~10⁻⁴ Pa. After that, the CdS was deposited at room temperature, 3 Pa, 0.88 W·cm⁻² rf power, 28.3 cm³·min⁻¹ Ar gas (high purity: 5N) together with 0 (0% (volume fraction, ϕ)), 0.25 (0.88% (ϕ)), 0.5 (1.78% (ϕ)), 0.75 (2.58% (ϕ)), and 1 (3.40% (ϕ)) cm³·min⁻¹ O₂ gas (high purity: 5N). The thickness of the CdS was 100 nm measured by an *in situ* optical transmission thickness apparatus.⁷ In order to study the influence of O incorporation into CdS on the absorb layer, we deposited CdTe on CdS by a rf magnetron sputtering method at 270 °C, 2 Pa, 1.32 W·cm⁻² rf power, and 28.3 cm³·min⁻¹ Ar gas. The thickness of the CdTe was 2.0–2.3 μ m measured by an *in situ* optical transmission thickness apparatus.⁷ High temperature anneal was carried out on CdS/CdTe films at 400 °C for 35 min in the atmosphere of CdCl₂ (99.998%, 4N, Alfa Aesar) and dry air. In this process, the CdS/CdTe thin films were proximately capped by a piece of CdCl₂ coated glass in a distance of 2 mm, with the CdTe layer facing to the CdCl₂ source, which is similar to the setup in our published paper.⁷ For Raman measurement, the CdS was deposited on the mica substrate.

2.2 Characterization of the films

The structure, morphology, and optical properties of the as-grown and annealed thin films were investigated by a Bruker D8 focus (Germany) for X-ray diffraction (XRD), a Zeiss SIGMA (Germany) scanning electron microscope (SEM). X-ray photoelectron spectra (XPS) was conducted in a PHI Quantera (Japan), which was calibrated by the C 1s peak at 284.8 eV. Raman measurement was carried out on a Renishaw system from inVia-Reflex (England), operating at a wavelength of 532 nm with a very low energy to obtain CdS Raman signal and to reduce the Raman intensity from the mica substrate. Optical properties of CdS thin films were measured in a Varian Cary 5000 ultraviolet visible absorption spectroscopy (UV-Vis) spectrometer (America). The thickness of CdS was further measured by a stylus profile (Dektak 150, Veeco).

3 Results and discussion

The as-grown CdS thin films were first characterized by XRD to determine the structure of the obtained thin films. Fig.1(A) shows the XRD patterns of as-grown CdS deposited with 0% (sample a), 0.88% (sample b), 1.78% (sample c), 2.58% (sample d), 3.40% (sample e) (φ) O_2 gas in the $Ar+O_2$ gas. As shown in Fig.1 (A), except for the diffraction peaks of SnO_2 (ICDD:PDF #46-1088) coming from TEC15 substrate, all the diffraction peaks of samples a–d are well indexed based on hexagonal CdS (ICDD: PDF #41-1049), which can be more clearly seen from Fig.1(B). That result indicates that the O incorporation has little effect on the structure of CdS at the present growth condition. However, no diffraction peaks are observed in the XRD pattern for sample e (Fig.1(A)), indicating amorphous structure of sample e. Therefore, the O_2 content in the $Ar+O_2$ sputtering gas should be less than 3.40% (φ) at the present deposition condition to obtain CdS thin films with high crystalline quality. The properties of samples a–e were further studied by Raman measurements. Fig.2 shows Raman spectra of mica substrate and samples a–e grown on mica substrate. Three peaks located at about 262.0, 409.5, and 703.5 cm^{-1} , corresponding to Raman modes of mica substrate, are observed in the Raman spectra (Fig.2(A)) of mica substrate and samples a–e. In the Raman spectra for samples a–e, two peaks located at about 300 and 600 cm^{-1} are also observed (Fig.2(A)). In the Raman spectrum for sample a, the peaks located at about 297.5 and 601.2 cm^{-1} are corresponding to 1 longitudinal (1LO) and 2LO vibration modes of CdS, respectively.^{15,16} However, in the Raman spectra for samples b–d, the 1LO Raman peak intensity

Fig.1 XRD patterns of (A) samples a–e and (B) samples a and b

Fig.2 (A) Raman spectra of mica substrate and samples a–e, (B) Raman spectra of mica substrate and samples a–e in the 200–400 cm^{-1} wavenumber range

decreases with the increase of O_2 content in the sputtering gas due to the reduction in volume of the crystalline CdS.¹⁶ The 1LO Raman peak is not observed in the Raman spectrum of sample e, which is due to the amorphous structure of sample e. 1LO Raman peak of samples b–d shifts to higher wavenumber compared with that of sample a (297.5 cm^{-1} , clearly seen in Fig.2(B)) due to the incorporation of oxygen into the CdS films.^{15,16} For example, the 1LO vibrational mode of sample b shifts to 299.8 cm^{-1} , as shown in Fig.2(A, B).

The morphologies of the CdS films were examined by SEM. Fig.3(A–D) shows the SEM images of samples a–d. To clarify the morphologies of CdS and FTO, the SEM image of TEC15 glass is also shown in Fig.3(E). The sample e shows amorphous structure and blurred grain boundaries, which makes it be difficult to observe the morphology *via* SEM may be due to high resistivity of CdS. Thus, it is seen that the CdS properties such as structural and electrical properties were deteriorated with 3.40% (φ) O_2 in the sputtering gas. The morphologies of the other CdS thin films are clear observed by SEM. The morphologies (Fig.3(A–D)) of samples a–d are quite different from that of FTO (Fig.3(E)). As shown in Fig.3(A), some black contaminants dotted by the circle are observed on the surface of sample a, which may come from contaminants on TEC15 substrate. Such contaminants could come from surface adsorption of air pollutants, such as hydrocarbons. No black contaminants are observed on the surfaces of samples b–d (Fig.3(B–D)), implying that O_2 in the sputtering gas is effective in removing the surface contaminants on the TEC15 substrates.¹⁷

The grain size of sample a is in the range of tens to hundreds nanometers (Fig.3(A)). The samples b and c (Fig.3(B, C)) have

Fig.3 SEM images of (A) sample a, (B) sample b, (C) sample c, (D) sample d, and (E) SEM image of TEC15 substrate

much more uniform, compact, and smaller grains than sample a (Fig.3(A)). However, the sample d (Fig.3(D)) has the most compact, and the largest size grains among all the obtained films. Our results indicate that oxygen is helpful to obtain clean, compact and small CdS grains, which is similar to the reported results.^{17,18} CdS thin films with much more clean, compact and smaller grains are helpful to reduce the possibility of shunting path formation in the CdTe solar cells.¹⁷

Transmission spectra of samples a–e are present in Fig.4(A). It can be seen that the oxygen has great effect on the optical properties of CdS. The sample c shows the highest optical transmission in the 400–1000 nm wavelength range. The absorption edges of samples b and c shift to shorter wavelength compared with that of sample a, indicating larger band gap of samples b and c than that of sample a. The sample b shows the sharpest absorption edge, indicating the best crystalline quality. However, the absorption edges of samples d and e show the similar character with that of sample a, indicating the similar band gap with that of sample a. In some wavelength range, sample e shows above 100% optical transmission, further confirming the effect of O plasma on the FTO surface.¹⁷

The band gap of the CdS thin films were calculated based on following equations:

$$T(\lambda) = I(\lambda)/I_0(\lambda) \quad (1)$$

$$I(\lambda) = I_0(\lambda) \cdot [1 - R_1(\lambda)] \cdot [(1 - R_2(\lambda))e^{-\alpha(\lambda)d}] \quad (2)$$

$$(ah\nu)^n = A(h\nu - E_g) \quad (3)$$

where d is the film thickness measured by a stylus profiler from

Fig.4 (A) Transmission spectra of samples a–e, (B) plots of $(ah\nu)^2$ versus $h\nu$ of samples a and b, (C) plots of $(ah\nu)^2$ versus $h\nu$ of samples c–e, and (D) band gap values of samples a–e

Dektak150 Veeco, $T(\lambda)$ is transmittance of the film, $\alpha(\lambda)$ is absorption coefficient, R is reflectivity, R_1 and R_2 are the reflectivities of front and back surfaces of CdS, respectively. I_0 and I are the intensities of incident and emergent light, respectively. A is a constant. And n is also a constant related to the material, which is 2 for direct band gap material. From the curve of the relationship between $(\alpha h\nu)^2$ and $h\nu$, the band gap of CdS is the intercept point with X axis extrapolated from the linear part of the curve. The calculated band gap of sample a is 2.48 eV, while the calculated band gaps of samples b, c, d, and e are 2.60, 2.65, 2.50, and 2.49 eV (as shown in the Fig.4(B–D)), respectively. Therefore, the band gap values of samples b and c are enlarged compared with that of sample a. The band gap increase may be due to the quantum confinement effect, which has been reported before.¹⁹ The decrease of the grain size of samples b and c, characterized by SEM, leads to the quantum confinement effect of samples b and c.¹⁹ Samples d and e show similar band gap with that of sample a if we considering the calculated error. The size of sample d is larger than that of sample a, further confirming the enlarged band gap of CdS doped with O coming from quantum confinement effect. Higher optical transmittance, higher crystalline quality, and larger band gap CdS thin film can reduce the absorption of short wavelength photons and contribute to a higher photon-current. A higher O₂ content in the sputtering gas such as 2.58% (φ) and 3.40% (φ) leads to an unchanged band gap and a worse crystalline quality of CdS thin films. However, a smaller O₂ content in the sputtering gas such as 0.88% (φ) or 1.78% (φ) results in a larger band gap of CdS. Thus, the proper O₂ gas content

in the present growth condition is in the range of 0.88%–1.78% (φ). Moreover, 0.88% (φ) O₂ content in the sputtering gas results in the highest crystalline quality of CdS.

It is well known that XPS can provide important information on surface electronic state, chemical state, composition, and oxidation of CdS.²⁰ No O related peaks are observed in the XPS spectra of sample a. However, the O related peaks are found in the survey XPS spectra of samples b–e. Fig.5(A) shows the XPS spectrum of sample b. As evident in Fig.5(A), the Cd, S, O peaks are present in the XPS survey spectra of sample b. In addition, a considerable amount of carbon is observed, which is characteristic of unclear surfaces. High resolution scans were performed on the areas around the peaks of Cd 3d, S 2p, and O 1s. In the high resolution XPS spectrum of Cd 3d (Fig.5(B)), the peak located at 412.0 and 405.3 eV is corresponding to the Cd 3d_{3/2} and Cd 3d_{5/2}, respectively. The energy splitting between the Cd 3d_{3/2} and Cd 3d_{5/2} states is 6.7 eV, corresponding to the Cd²⁺ cations in CdS.²¹ The peak located at 531.9 eV (Fig.5(C)) is corresponding to O 1s binding energy of O²⁻ anion,²¹ indicating the O incorporation into the CdS thin films. In the high resolution XPS spectrum of S as shown in Fig.5(D), the peaks located at 161.4 and 162.4 eV are corresponding to the S 2p of S²⁻ anion in CdS.²¹ However, the binding energies of S 2p at 169.5 and 168.3 eV correspond to S⁶⁺ in SO₄²⁻ states,²¹ implying the coexistence of CdSO₄ in sample b. The enlarged optical band gap of CdS incorporated with O could also be caused by formation of other oxidized species except for the quantum confinement effect.²² The oxygen contents were calculated based on the XPS results. The oxygen contents in the

Fig.5 (A) XPS spectra of sample b; high-resolution XPS spectra of (B) Cd 3d, (C) O 1s, and (D) S 2p of sample b

CdS thin films deposited with 0.88%, 1.78%, 2.58%, and 3.40% (ϕ) O_2 in the sputtering gas are 17.3%, 19.5%, 25.1%, and 32.8% (atomic fraction), respectively. In CdS, Cd atoms are coordinated by S nearest neighboring atoms. During CdS growth with O_2 in the sputtering gas, part of the S atoms combined with O to form SO_4 complexes while other S atoms formed CdS with Cd atoms.¹⁹ As the O_2 content in the sputtering gas increases, the Cd—S bond decreases and the SO_4 complex increases. The coordination number of the nearest S shell around Cd decreases and the local disorder increases.¹⁹ Thus, with higher O_2 content in the sputtering gas during the CdS growth, CdS shows amorphous structure which has been characterized by XRD, Raman, and SEM results. Higher disorder in the CdS thin films leads to higher resistivity (well consistent with the SEM results) of sample e and reduction of the energy gaps of samples d and e.²³ Low resistivity, high crystalline quality, and high transmittance are needed for the window layer in the solar cell. In addition, the O_2 in the sputtering gas has great effect on the CdS growth rate. The growth rate decreased with the O_2 content increase in the sputtering gas. The growth rates of CdS on mica substrate are 6.25, 4.54, 2.94, 0.77, and 0.00035 $nm \cdot min^{-1}$ with 0%, 0.88%, 1.78%, 2.58%, and 3.40% (ϕ) O_2 gas in the Ar+ O_2 gas, respectively. Therefore, the CdS thin film deposited with 0.88% (ϕ) O_2 in the sputtering gas may be the best thin film used as a window layer in the solar cell such as CdTe and CuInGaSe considering the growth rate, resistivity, crystalline quality, and transmittance.

In order to study the influence of O incorporation into the CdS on the related thin films such as CdTe and CuInGaSe, we deposited CdTe thin films on the top of samples a and b. Our results

indicate that the O incorporation has effect on the morphology and grain size of CdTe. Fig.6 shows the typical SEM images of as-grown CdTe thin film grown on the top of samples a and b. The CdTe grown on the top of sample b has compact grains (Fig.6(B)). Gaps are barely seen between CdTe grains (Fig.6(B)), which may be due to the much more uniform nucleation of CdTe on the CdS:O surface with much more uniform and smaller grain size. By contrary, the as-grown CdTe film grown on the surface of sample a shows clear grain gaps between CdTe grains (Fig.6(A)), indicating that the O incorporation into the CdS leads to closely packed CdTe grains. It is well known that Cl treatment is quite important to obtain high performance of CdTe solar cells.^{7,24,25} So, we conducted Cl treatment on the CdTe/CdS thin films. After Cl treatment, the CdTe films grown on the top of samples a and b also show greatly different (Fig.7). The Cl-treated CdTe film grown on the top of sample a shows clear gaps between CdTe grains (Fig.7(A)). It could lead to shunting paths in the CdTe solar cell devices.⁷ In addition, the CdTe film is composed of small grains (500 nm) and large grains (about 3–4 μm). After Cl treatment, the CdTe thin film grown on the top of sample b shows closely packed CdTe grains (Fig.7(B)). Moreover, the CdTe thin film shows much narrower inter-grain gaps (Fig.7(B)). The CdTe film is also composed of CdTe grains with a smaller size (about 500 nm) and larger size (about 3–4 μm). However, the CdTe grains with a larger size (larger than 1 μm) are about 80% (Fig.7(B)). The biggest grain size is about 4 μm (Fig.7(B)). Therefore, the O incorporation into the CdS leads to a more compacted CdTe films with smaller grain gap size and larger grain size. The as-grown and Cl-treated CdTe thin films grown on top of sample b

Fig.6 SEM images of as-grown CdTe thin films grown on top of (A) sample a and (B) sample b

Fig.7 SEM images of Cl-treated CdTe thin films grown on top of (A) sample a and (B) sample b

Fig.8 XRD patterns of (a) Cl-treated CdTe and (b) as-grown CdTe grown on top of sample b

show cubic structure (well indexed based on CdTe with PDF #65-8879) with (111) preferred orientation growth characterized by the XRD patterns (Fig.8).

4 Conclusions

In conclusion, the effect of O incorporation into CdS was investigated. It was found that the CdS thin film deposited with 0.88% (φ) O_2 in the sputtering $Ar+O_2$ gas showed higher crystalline quality, larger band gap, and smaller grain size than CdS deposited without O_2 . The O incorporation into the CdS also leads to much more closely packed and much larger CdTe grains.

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