Cadmium stannate conductive layer with high optical transmittance and tunable work function

Ziyao Zhu¹, ², Zhongming Du³, Xiangxin Liu⁴, ⁵, Yufeng Zhang¹, Quchen Wu¹, ² and Xinlu Lin¹, ²

¹ The Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
² University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
³ School of Physics and Electron Science, Zunyi Normal University, Zunyi 563002, People’s Republic of China

E-mail: shinelu@mail.iee.ac.cn

Keywords: cadmium stannate, magnetron sputtering, phonon density of states, x-ray photoelectron spectroscopy

Abstract

200 nm cadmium stannate (Cd₂SnO₄) transparent conductive layer films with a sheet resistance of 6.35 Ω/sq and resistivity of 1.27 × 10⁻⁴ Ω · cm are deposited by magnetron sputtering coupling with adjustable target bias voltage followed by 620 °C 30 min annealing. The lowest resistivity of Cd₂SnO₄ films reported before was 1.28 × 10⁻⁴ Ω · cm, achieved with 510 nm Cd₂SnO₄. The average transmission rate of 200 nm sputtering Cd₂SnO₄ films between 400–800 nm is 94%. The deposition rate increase target bias voltage can the and electrical performance of Cd₂SnO₄ films. The surface work function of Cd₂SnO₄ films is also tunable by target bias voltage. The Cd₂SnO₄ phonon spectrum and phonon density of states combined with Raman microscope shows the Cd₂SnO₄ films with most ideal electric properties has a identical phonon response. XPS shows the chemical component of as-deposited Cd₂SnO₄ films and Cd₂SnO₄ films after annealing with 120 V target bias voltage is Cd₂₀.₀SnO₆.₃₆ and Cd₁₂.₅SnO₄.₃₅ respectively, which is contrary to the general conclusions that interstitial cadmium atoms and oxygen vacancies are the main self-doping defects in Cd₂SnO₄ films.

1. Introduction

Cadmium stannate (Cd₂SnO₄, or CTO) is a high quality transparent conductive metal oxide (TCO) material for high performance optoelectronic devices, such as thin film solar cells [1] and light emitting diode [2]. Highly conductive Cd₂SnO₄ films suffer from low deposition rate [3]. Conductive Cd₂SnO₄ films must be deposited in an atmosphere containing oxygen, while the presence of oxygen will suppress the deposition rate of Cd₂SnO₄ films. To achieve low resistivity, most Cd₂SnO₄ fabrication process also requires a post-deposition annealing step in the atmosphere of Ar, CdS, He and/or H₂ [4, 5].

In our previous work, the lowest resistivity we have achieved was 1.79 × 10⁻⁴ Ω · cm for RF-sputtered Cd₂SnO₄ films with a nitrogen post-deposition annealing process, which helps to reduce the production costs [6]. The lowest resistivity of Cd₂SnO₄ films reported so far is 1.28 × 10⁻⁴ Ω · cm for 510 nm Cd₂SnO₄ deposited by magnetron sputtering followed by an annealing process in the atmosphere of argon and capped with cadmium sulphide [4]. In this work, radio frequency generator coupling with tunable target bias voltage is used for Cd₂SnO₄ deposition and both high deposition rates and improved electrical and optical properties can be acquired at the same time. The lowest resistivity of 200 nm Cd₂SnO₄ films acquired in this work is 1.27 × 10⁻⁴ Ω · cm. The electrical and optical properties, phonon response and self-doping defects of sputtering Cd₂SnO₄ films followed by annealing process are discussed. A unique Raman peak change is discovered in the lowest resistivity sample. The cadmium vacancies may be the main defects of self-doping.
2. Experiments

Homemade round targets with 3 mm thickness and 3-inch diameter were used for sputtering. Cd$_2$SnO$_4$ films were deposited on alkali free borosilicate glass (Corning 7059) at 1.5 Pa, in a flowing gas of 20 sccm Ar mixed with 5 sccm O$_2$. The substrate was not intentionally heated during the sputtering, and target-substrate distance is 7 cm. Then Cd$_2$SnO$_4$ films were annealed in a rapid thermal process chamber (E-star RTP600). Before annealing, the chamber was heated to 500 °C for 30 min, to purge possible contamination residual in the chamber. The Cd$_2$SnO$_4$ films were annealed at 620 °C for 30 min. The detailed annealing atmosphere and setting is discussed in detail in our previous work [6].

The thickness of Cd$_2$SnO$_4$ films was measured by a Veeco Dektak 150 profiler. ZEISS SEM is used for EDX measurement and BRUKER AFM is used for grain morphology measurement and surface work function collection. Cary 7000 ultraviolet-visible infrared spectrometer is used for optical properties analysis and HL 5500 PC is used for Hall measurement. BRUKER XRD and inVia Raman microscope are used for crystal lattice structure study. ESCALAB 250Xi combined with Avantage is used for XPS measurement and element concentration analysis.

The density functional theory (DFT) calculation was performed by the Cambridge serial total energy package (CASTEP) code, in which a plane wave basis set was used. The exchange and correlation interactions were modelled using the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) functional. The Norm-conserving pseudopotential was used with a cut-off energy of 750 eV. Geometric convergence tolerances were set for maximum force of 0.03 eV/Å, maximum energy change of 10$^{-5}$ eV/atom, maximum displacement of 0.001 Å and maximum stress of 0.05 GPa. Density mixing electronic minimization was implemented and the self-consistent field (SCF) tolerance was set to fine with high accuracy of 10$^{-6}$ eV/atom for energy convergence.

3. Results and discussion

3.1. Deposition rate of Cd$_2$SnO$_4$ films

Figure 1 shows the deposition rate of Cd$_2$SnO$_4$ films deposited by magnetron sputtering. The self-bias voltage of a new 3 mm thick Cd$_2$SnO$_4$ target is $-83$ V. Noticing the target bias voltage is discussed with their absolute value and the negative signs are ignored in the rest of this paper. The bias voltage of Cd$_2$SnO$_4$ target is adjusted in a range from self-bias voltage to a maximum of 160 V in this work.

As we discussed in the beginning, one issue for Cd$_2$SnO$_4$ films sputtered for production of transparent conductive layer is that it must be deposited in the presence of oxygen, otherwise crystallization temperature of amorphous Cd$_2$SnO$_4$ films surpasses the softening temperature of most types glass substrate, such as the Corning 7059 of 639 °C [6]. But once oxygen is introduced during deposition, the deposition rate will be suppressed, and deposition time is too long to be suitable for mass production. The detailed deposition rate versus oxygen concentration can be found in our previous work [6].

When there is no extra bias voltage and the deposition atmosphere consists of 20% oxygen and 80% argon, the deposition rate of Cd$_2$SnO$_4$ films is 8.6 nm/min at a RF power density of 1.75 W cm$^{-2}$. When target bias
bias voltage reached 160 V, the deposition rate was increased to 41.7 nm min\(^{-1}\) (figure 1). In this work, all 200 nm Cd\(_2\)SnO\(_4\) films sputtered under various target bias voltage have sheet resistance below 10\(\Omega\)/sq, electrical properties of which can meet the requirement of solar cell industry. Assuming the required sheet resistance for solar cells is 10\(\Omega\)/sq, the shortest deposition time needed is less than 5 min, as shown in table 1. Higher deposition rate could be available if the target bias voltage is further increased, but degradation of electrical performance is expected according to the trend when the target bias voltage exceeds 120 V.

3.2. Optoelectronic properties of Cd\(_2\)SnO\(_4\) films

Before starting the discussion, please note that everything discussed in this article is about the properties of the annealed Cd\(_2\)SnO\(_4\) film. Before annealing the as-deposited film is amorphous and the properties of as-deposited film was discussed in detail in our previous work [6].

Figure 2 gives the electrical properties of 200 nm Cd\(_2\)SnO\(_4\) films deposited with different target bias voltage followed by annealing at 620 °C for 30 min. The detailed values are listed in table 2. The most conductive Cd\(_2\)SnO\(_4\) films obtained by this method has the lowest resistivity of 1.27 \times 10^{-4} \Omega \cdot \text{cm} (conductivity of 8064.52 S cm\(^{-1}\)) and sheet resistance of 6.35 \Omega/sq, which was sputtered with 120 V target bias voltage. Further increase of target bias voltage simultaneously leads to decrease of carrier concentration and carrier mobility. The carrier concentration is approximately 9.7 \times 10^{20} cm\(^{-3}\) and has no obvious change when the target bias is between 83 V and 120 V, and the carrier mobility increased from 44.8 to 50.6 cm\(^2\) \cdot V\(^{-1}\) \cdot s\(^{-1}\). The best electrical performance of 200 nm Cd\(_2\)SnO\(_4\) films in this work is almost the same compared to that of 510 nm Cd\(_2\)SnO\(_4\) films acquired by Wu et al [4], the electrical performance of Cd\(_2\)SnO\(_4\) films deposited with different methods are summarized in attachment 1. When the target bias voltage is further increased, a quick drop of carrier concentration and mobility can be observed, from 9.7 \times 10^{20} to 7.8 \times 10^{20} cm\(^{-3}\) and from 50.6 to 41.1 cm\(^2\) \cdot V\(^{-1}\) \cdot s\(^{-1}\), respectively, both of which dropped approximately 20%. These lead to the deterioration of conductivity, which dropped 52.6%.

The influence of target bias voltage to electrical properties could manifest in different ways. First, it might change the chemical potential of different element component on the target surface, which may lead to a deviation of chemical ration between the target and the film. Second, the target bias voltage increases the deposition rate, which could establish a new balance between the nucleation rate and growth rate of Cd\(_2\)SnO\(_4\) films, thus influence the film properties from the aspect of grain structure and morphology. Target bias voltage could also increase the kinetic energy of atoms sputtered off the target which are more easily to overcome energy barriers to form effective dopants, such as Cd and Sn interstitial sites (Cd\(_i\), Sn\(_i\)) or O vacancies (V\(_{\text{O}}\)) [7]. These effects that may influence the electrical properties will be discussed later in the XPS analysis part.

Figure 3 are the optical properties of 200 nm Cd\(_2\)SnO\(_4\) films with different target bias voltage after annealing. All the Cd\(_2\)SnO\(_4\) films have an average optical transmission rate of over 94% between 400–800 nm after subtract glass reflectance and absorbance. The noise between 800–900 nm is caused by the low intensity of light source in the ultraviolet-visible infrared spectrometer. The light intensity of both light sources in the Cary 7000 spectrometer are insufficient in this wavelength range, which causes low signal/noise ratio.

The optical band gap of Cd\(_2\)SnO\(_4\) films is slightly higher than 3.8 eV when the target bias voltage is between self-bias voltage and 120 V. When the target bias voltage exceeds this range, the optical band gap decreases from 3.81 eV to 3.75 eV when the target voltage is increased. Due to Burstein-Moss effect, \(\Delta E_g = \left(\frac{e^2}{2\pi}\right)\left(\frac{S_{ni}}{8e}\right)^{2/3}\), higher carrier concentration corresponds to larger optical band gap, as shown in figure 2(b).

One interesting phenomenon is that the optical band gap of Cd\(_2\)SnO\(_4\) films reported by many independent researches varies a lot, from 2.75–3.65 eV, and the relationship between carrier concentration and optical band gap satisfies the Burstein-Moss shift trend [8–13]. We guess this may be cause by the degree of crystallization process of Cd\(_2\)SnO\(_4\) films. In this work, the as-deposited Cd\(_2\)SnO\(_4\) films is in amorphous state, presenting a deep yellow color with an optical band gap of 2.83 eV [6]. The crystal and grain structure of Cd\(_2\)SnO\(_4\) films will be discussed later. Based on the carrier concentration and optical band gap data, if the effective mass is assumed to

| Resistivity \((10^{-4} \Omega \cdot \text{cm})\) | Sheet resistance \((\Omega/sq)\) | Thickness (nm) | Deposition rate (nm/min) | Deposition time (min) |
|---|---|---|---|---|
| 1.44 | 10 | 143.5 | 8.65 | 16.59 |
| 1.32 | 10 | 132.3 | 13.89 | 4.57 |
| 1.27 | 10 | 127 | 22.63 | 5.61 |
| 1.52 | 10 | 151.6 | 33.2 | 4.57 |
| 1.94 | 10 | 193.8 | 41.66 | 4.65 |
be a constant, and ignore the upper limit of the applicable range of carrier concentration for Burstein-Moss effect, the band gap of polycrystal Cd$_2$SnO$_4$ film without self-doping at room temperature can be derived from Burstein-Moss equation, is around 3.35 eV, as shown in figure 4. Noticing the optical band gap of Cd$_2$SnO$_4$ film deposited with total bias voltage no greater than 120 V is all 3.81 eV, which is overlapped at the rightmost point position in figure 4. The calculated reduced effective mass is 0.795 m$_e$.

The Cd$_2$SnO$_4$ films fabricated by this method provide a new option of TCO films for thin film solar cell industry. The lowest sheet resistance of 200 nm Cd$_2$SnO$_4$ films is 6.35 Ω/sq sputtered at target bias of 120V, which means the sheet resistance of 100 nm Cd$_2$SnO$_4$ films is about 12-13 Ω/sq. Since the sheet resistance of TCO layers for thin film solar cells is usually below 15 Ω/sq. 100nm Cd$_2$SnO$_4$ film of 12-13 Ω/sq is proper for thin film PV devices. The deposition time for 100 nm Cd$_2$SnO$_4$ is less than 5 min, and the deposition time could be reduced to less than 1 min by co-sputtering with 5 targets. The annealing temperature is close to the substrate temperature of CSS or VTD CdTe layer deposition. Cd$_2$SnO$_4$ films have been found to be robust in previous work, resistivity of which only increases 2.24% after chlorine treatment at 400 for 60 min [6].

![Resistivity and sheet resistivity of 200 nm Cd$_2$SnO$_4$ films with different deposition target bias voltage after annealing.](image1)

![Carrier mobility and carrier concentration of 200 nm Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing.](image2)

| Target bias (V) | Resistivity ($\times 10^{-4}$ Ω·cm) | Sheet resistance (Ω/sq) | Carrier mobility (cm$^2$·V$^{-1}$·s$^{-1}$) | Carrier concentration ($\times 10^{20}$ cm$^{-3}$) |
|----------------|--------------------------------------|--------------------------|------------------------------------------|------------------------------------------|
| 83             | 1.44                                 | 7.17                     | 44.8                                     | 9.714                                    |
| 100            | 1.32                                 | 6.61                     | 48.3                                     | 9.767                                    |
| 120            | 1.27                                 | 6.35                     | 50.6                                     | 9.707                                    |
| 140            | 1.52                                 | 7.58                     | 48.5                                     | 8.495                                    |
| 160            | 1.94                                 | 9.69                     | 41.1                                     | 7.838                                    |
Figure 3. (a) Optical transmission of 200 nm Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing; (b) Tauc analysis of $(h\nu \alpha)^2$ versus $h\nu$ plots of 200 nm Cd$_2$SnO$_4$ films with different total deposition target bias voltage after annealing.

Figure 4. Calculated optical band gap of Cd$_2$SnO$_4$ spinel polycrystal film with no self-doping.
Figure 5 is the surface morphology and corresponding electron potential of 200 nm Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing. Figure 6 shows the work function derived from electron potential. A standard Au film sample was used to calibrate the baseline of electron potential. The work function of standard Au is 5.08 eV [14] and the electron potential measured by SKPM is $-96$ mV, thus the work function of Cd$_2$SnO$_4$ films can be calculated through the relative values of electron potential.

On the macroscale level, the average electron potential or work function of Cd$_2$SnO$_4$ films can be adjusted by the total deposition target bias voltage. In the structure of CdTe and CIGS thin film solar cells, TCO layer is usually contacted with a n-type window layer like CdS, or a thin highly resistive transparent (HRT) layer, which is adjacent to n-type window layer (such as CdS in CIGS) or the absorber (such as CdSeTe). The HRT layer is usually made of metal oxide solid solution, such as MgZnO in recent high efficiency CdSeTe/CdTe solar cells. The work function of CdS is 4.9 eV [15] and the work function of MgZnO is 3.9–4.4 eV, depending on the ratio of Zn and Mg [16]. The electron affinity of MgZnO adopted in solar cells, CdS and CdTe is 4.1, 4.5 and 4.4 eV, respectively [17]. When the spike in conduction band mismatch at interface is below 0.3 eV, there is little influence on cell performance [18]. There is no available data of electron affinity of Cd$_2$SnO$_4$ film, but due to the high carrier concentration it is reasonable to assume the electron affinity of Cd$_2$SnO$_4$ film in this work is close to 4.9 eV because of the heavy self-doping. A cliff conduction band alignment may be expected between Cd$_2$SnO$_4$ and MgZnO or CdS window layer. Even if a spike forms at this interface, the conduction band mismatch greater than 0.3 eV may not be possible.

On the microscale level, the electron potential of Cd$_2$SnO$_4$ films is not uniform when the target bias voltage is less than 120 V, as shown in figure 5. Electron potential of larger grains is about 40 mV higher than small grains, the detailed cross-grain scanning data is shown in attachment 2. When the target bias voltage is higher than 120 V during deposition, there is no obvious non-uniformity of both grain morphology and electron potential.
These may suggest the work function of Cd$_2$SnO$_4$ films could be further reduced by more sophisticated controlling of nucleation and grain growth process to form more large grains. The non-uniform large grains may be caused by the discontinuous grain growth during annealing. Noticing a common misconception is that there are no grains if no fluctuations are observed in the morphology picture. Morphology picture only tells the difference in height, if the roughness is low enough, it is impossible to observe the grain boundaries by AFM or SEM of the smooth polycrystalline film without using chemical corrosion or thermal corrosion to pre-treat the sample, as we demonstrate here and before [19].

### 3.3. Crystal structure and phonon response

In this part, we will discuss the structure of magnetron sputtered Cd$_2$SnO$_4$ films followed with annealing. Figure 7 is the XRD patterns of these Cd$_2$SnO$_4$ films after annealing. The high baseline from 15 to 40 degree is from the amorphous phase of borosilicate glass substrate. The general patterns of Cd$_2$SnO$_4$ films are in good alignment with the standard card (PDF#80-1469) of spinel Cd$_2$SnO$_4$ phase. The peak fitting results of peak (511) are listed in attachment 3. The peak position shifts towards higher degree, which indicates compression of lattice plane along the normal direction of the film. There is basically no difference in peak shift between films sputtered at target bias of between self-bias and 120 V, except for the one at 160 V. There are three plausible
explanations for the peak shift: residual compressive stress after the annealing, mismatch between glass substrate and Cd$_2$SnO$_4$ lattice, and/or doping (more likely self-doping). The XRD pattern of Cd$_2$SnO$_4$ films sputtered with 120 V target bias has the smallest FWHM, which means the Cd$_2$SnO$_4$ lattice has the largest sub-grain volume. While, the one sputtered with 160 V shows a relatively large FWHM and an obvious drop of peak intensity, which may suggest more defects and low degree of crystallinity. The higher the target bias voltage, the larger the kinetic energy of particles and the higher the deposition rate of films. The larger kinetic energy of particles could generate more lattice defects. The higher deposition rate could also lead to more lattice defects due to the high kinetic energy of particles could break the chemical bond of ideal Cd$_2$SnO$_4$ lattice and induce self-doping. Therefore, the high defects density in films sputtered at high target bias voltage may not be removed completely during the annealing process and cause the decrease of peak intensity and broaden of FWHM. We speculate remnant lattice defects could also explain the deterioration of the electrical properties in Cd$_2$SnO$_4$ films deposited with high target bias voltage.

The morphology of Cd$_2$SnO$_4$ films deposited with different target bias voltage is shown in figure 8. The 3D images give the morphology and amplitude images partly enhance the contrast of edge and slope of grains. The roughness of Cd$_2$SnO$_4$ films decreases with the increase of target bias voltage, from 19.4 nm deposited with self-bias voltage (83 V) to 3.72 nm deposited with 160 V. Also, large particles are not observed when the target bias voltage...
voltage is relatively high. These results indicate the roughness of Cd₂SnO₄ film is tunable by controlling the target bias voltage. When coupled with extra target bias voltage, the total deposition power density is increased, and the growth rate of CTO grains is increased due to larger flux of sputtered species reaching the substrate, but the nucleation rate remains the same, thus leads to reduce the roughness of Cd₂SnO₄ films.

Although XRD patterns and AFM height images could give a preliminary evidence for the quality of crystal lattice, it’s still limited to establish a connection to the electrical properties of Cd₂SnO₄ films. Another way to
Figure 12. Raman shift of Cd$_2$SnO$_4$ films deposited on Corning 7059 glass substrate with different target bias voltage after annealing.

Figure 13. DFT calculated and measured phonon response spectrum of Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing.

Figure 14. Full XPS spectrum of Cd$_2$SnO$_4$ films deposited with 120 V target bias voltage before and after annealing.
study the degree of crystallinity is phonon response spectrum. We first calculated the density of phonon states of ideal spinel Cd$_2$SnO$_4$ lattice, the crystal structure is reported in database of [20]. The results are listed in figures 9–11. Then the phonon response of Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing is acquired by Raman microscope. The original results are shown in figure 12.

Before further discussing, please note that many studies often ignore the influence of the thermal history of the substrate material during Raman spectrum analysis. When the film is thin enough and/or transparent in the laser wavelength range, laser cannot be accurately focused on the film surface and substrate can also contribute to Raman response. Another common misconception is that glass is not Raman active under any circumstances. As we discussed in previous work [6], the soften point or secondary phase transition temperature of Corning 7059 glass is about 639 °C, that is also why our annealing temperature cannot change much. We found after annealing at 620 °C for 30 min, the Corning 7059 glass showed multiple broad Raman peaks in the 100–4000 wave number range. The contributions of substrate must be removed before further discussing.

The peaks of substrate are determined through peak fitting from the Raman spectrum of Corning 7059 glass, then the Raman shift patterns of Cd$_2$SnO$_4$ samples are deconvoluted by keeping the peak positions of substrate unchanged. All the deconvolutions are given in attachment 4. And the separated Cd$_2$SnO$_4$ Raman spectrum is then plotted with the density of phonon states, as shown in figure 13.

The results in figure 13 brings several preliminary speculations. First, although it is often understood as the characteristic vibration of certain chemical bond, the Raman shift is the atom oscillation mode of lattice wave. The calculated phonon density gives the phonon density distribution of ideal spinel Cd$_2$SnO$_4$ lattice. The Raman scattering curves of Cd$_2$SnO$_4$ films can be treated as two parts, a sharp peak at 625–630 cm$^{-1}$ and a wide peak from 450–750 cm$^{-1}$. The sharp peak corresponds to the phonon density distribution in the range of 610–650 cm$^{-1}$ (figure 11). The wide peak corresponds to the phonon density distribution from 500–600 cm$^{-1}$.
Combined with XRD results, since the Cd$_2$SnO$_4$ films deposited with 120 V target bias voltage has the highest phonon response and an obvious high intensity between 500–550 cm$^{-1}$, the films deposited under this condition may have the relatively most intact lattice structure. Hall measurement showed that the best electrical performance and largest carrier mobility of Cd$_2$SnO$_4$ films appear in those deposited with target bias voltage of 120 V. XRD results also indicates that the Cd$_2$SnO$_4$ films deposited with 120 V have the smallest deviation from powder form. One possible explanation of why 120 V Cd$_2$SnO$_4$ films have the best performance may be that Cd$_2$SnO$_4$ films deposited with these parameters has the most relatively intact crystal lattice, thus leads to less defect scattering. Lower or Higher deposition target bias voltage may cause the film growth process deviate from ideal conditions, introducing more defects and damaging electrical performance. Since the post-deposition annealing process in this work is fixed, it might be possible that such annealing time or temperature is not enough for high bias voltage sputtering, such as 140 and 160 V. Optimization of post-deposition annealing for high bias voltage sputtering is necessary for future work.

3.4. Chemical composition and doping defects

The final part of this work is to study the chemical composition of Cd$_2$SnO$_4$ films deposited with 120 V target bias voltage and then after annealing in at 620 °C for 30 min, which is the optimum electrical performance sample in this work. Previous studies reported during annealing amorphous Cd$_2$SnO$_4$ will partly form CdO and CdSnO$_3$ besides spinel Cd$_2$SnO$_4$ phase, and the main intrinsic defects are interstitial cadmium atoms and oxygen vacancies [21, 22]. There are also thin film solar cell manufacturers who deliberately introduce excess cadmium in targets to make cadmium rich Cd$_2$SnO$_4$ films [23]. The full spectrum of Cd$_2$SnO$_4$ deposited with 120 V target bias and after annealing are given in figure 14. The full XPS spectra could give a half-quantitative description of the chemical composition at surface. It is reasonable to assume the chemical stoichiometric number of Sn is constant, since there is no tin source during annealing. The chemical ratio of as-deposited amorphous Cd$_2$SnO$_4$ film derived from XPS full spectrum is Cd$_{2.03}$SnO$_{6.36}$, the ratio of Cd/Sn is close to 2 and...
Oxygen is about 59% over the ideal chemical stoichiometric ratio. The chemical stoichiometric ratio of Cd$_2$SnO$_4$ film after annealing is Cd$_{1.25}$SnO$_{4.15}$, where Sn/O reaches ideal value, but the concentration of cadmium is 37.5% less. Noticing these values are not accurate values, it only indicates a trend of how a specific element deviates from ideal chemical composition. These preliminary results may suggest the main intrinsic defects of Cd$_2$SnO$_4$ films deposited with sputtering after annealing is cadmium vacancies-V$_{Cd}$, instead of interstitial cadmium-C$_{di}$ and oxygen vacancies-V$_O$. During annealing the excess cadmium may sublime in the form of CdO. The saturated vapor pressure of CdO is around 1.3 × 10$^{-2}$ Pa at 620 °C [24].

Another interesting phenomenon is that the intensity of as-deposited Cd$_2$SnO$_4$ inelasticity scattering step of cadmium at around 425 eV is higher than that of annealed Cd$_2$SnO$_4$. This suggests the emitted electrons from cadmium are more prone to leave the atom in Cd$_2$SnO$_4$ films after annealing, while the electrons emitted from tin and oxygen atoms are either reluctant to leave. The electron configuration of cadmium is [Kr]4d$^{10}$5s$^2$, so there is no final-state effect for cadmium ions. The decrease of inelasticity scattering of Cd may suggest the valence of cadmium decreases after annealing.

The detailed XPS scanning of Cd is shown in figure 15. For the as-deposited Cd$_2$SnO$_4$ films, the binding energy peak at 405.3 and 411.9 eV of cadmium matches well with NIST database [25, 26]. After annealing, the binding energy peak position of cadmium shifts to 404.9 and 411.6 eV, respectively. The 3d$^5$/2 peak may be composed of two parts, the original 405.3 eV peak and a Cd$^{+}$ peak at 404.6 eV, which has been observed in electrochemically reduced Cd$_2$SnO$_4$ films before [25]. There are no references on the 3d$^3$/2 peak position of Cd$^{+}$, so we fixed one peak position at 411.9 eV, and the Cd$^{+}$ peak derived from peak fitting is 411.3 eV. The atomic ratio of Cd$^{2+}$ and Cd$^{+}$ derived from 3d$^5$/2 peak area is 64.1% and 35.9%, respectively, assuming the sensitivity factor of Cd is unchanged. The decrease in the valence of cadmium may suggest that oxygen could produce free electrons, which is the source of n-type self-doping. The reducing agent could be tin, which will be discussed later.

Figure 16 shows the detailed Sn scanning before and after annealing. The peak positions can be found in [25–27]. The binding energy of tin shows no obvious difference before and after annealing. The chemical valence of tin cannot be sure because Sn$^{2+}$ and Sn$^{4+}$ have the same binding energy peak positions [28]. Based on the XRD patterns and full scanning XPS results, the valence value of most tin is likely +2 in the as-deposited Cd$_2$SnO$_4$ film, and partly become +4 after annealing. Around 0.85% of interstitial tin may exist in the form of interstitial tin (Sn$_i$) with a valence value of 0. According to the deconvolution, the Sn$_i$ increased to around 1.7% after the annealing. The increase of Sn$_i$ may be caused by cadmium vacancies. In general, the main surface intrinsic defects of Cd$_2$SnO$_4$ films in this work is cadmium vacancies instead of interstitial cadmium atoms.

EDX result suggests the Cd vacancies also exist in the bulk of Cd$_2$SnO$_4$ films, increasing with the target bias voltage during deposition. The bulk chemical composition of Cd$_2$SnO$_4$ films contains slightly less cadmium vacancies than surface after annealing, as shown in figure 17. The stoichiometric number of Sn is assumed to be 1. Since oxygen is light element and accuracy of the concentration measured by EDX is low, we only listed the ratio of Cd/Sn. Combined with XPS and EDX results, it is cadmium vacancy that leads to n-type self-doping in the sputtered Cd$_2$SnO$_4$ films followed with post deposition annealing.

![Figure 17](image_url)

Figure 17: (a) EDX results of bulk chemical composition of Cd$_2$SnO$_4$ films deposited with different target bias voltage after annealing.*
4. Conclusions

200 nm Cd$_2$SnO$_4$ with the resistivity of 1.27 × 10$^{-4}$ Ω cm$^{-1}$ and sheet resistance of 6.35 Ω/sq and over 94% transmission rate between 400–800 nm are deposited by sputtering followed by annealing. Target bias voltage can increase the deposition rate and electrical performance of Cd$_2$SnO$_4$ films. Target bias voltage can also adjust the surface work function of Cd$_2$SnO$_4$ films. But when the target bias voltage is too high, a decreasing in electrical and optical performance can be observed.

XRD and Raman shift combined with DFT calculations shows the Cd$_2$SnO$_4$ samples with most ideal performances has the most intact spinel Cd$_2$SnO$_4$ lattice structure. Contrary to previous studies, XPS analysis shows the main self-doping defects are cadmium vacancies instead of cadmium interstitial vacancies. There are also some interstitial tin atoms. These results may suggest cadmium-poor Cd$_2$SnO$_4$ films is also an option for thin film solar cell application.

Acknowledgments

This work is sponsored by National High Technology Research and Development Program of China (No. 2015AA050609), Research Foundation of IEE, CAS (No. Y710411CSB), Lujiazixi International Team Project of CAS (No. GJTD-2018-05), and Chinese Academy of Sciences President’s International Fellowship Initiative (No. 2020VEC0008).

Data availability statement

The data will be provided by the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ORCID iDs

Ziyao Zhu https://orcid.org/0000-0003-4375-2133

References

[1] Wu X et al 2001 16.5% efficient CdS/CdTe polycrystalline thin-film solar cell (C) Proc. of the 17th European Photovoltaic Solar Energy Conf. (London: James & James Ltd) 995
[2] Abrutis A et al 2007 Spray-pyrolysis Cd$_2$SnO$_4$ films for electrochemical applications Thin Solid Films 515 6817–23
[3] Mamazza R J, Morel D L and Ferekides C S 2005 Transparent conducting oxide thin films of Cd$_2$SnO$_4$ prepared by RF magnetron co-sputtering of the constituent binary oxides Thin Solid Films 484 26–33
[4] Wu X, Mulligan W P and Courts T J 1996 Recent developments in RF sputtered cadmium stannate Thin Solid Films 286 274–6
[5] El-Nahhas M M, Atta A A, Abd El-Raheem M M and Hassanien A M 2014 Structural and optical properties of DC sputtered Cd$_2$SnO$_4$ nanocrystalline films J. Alloys Compd. 585 1–6
[6] Du Z et al 2017 High-quality cadmium stannate annealed in N$_2$ atmosphere for low-cost thin film solar cell RSC Adv. 7 18545–52
[7] Liu D et al 2017 Cd$_2$SnO$_4$ transparent conductive oxide: a promising alternative for highly efficient hybrid halide perovskite solar cells RSC Adv. 7 8295–302
[8] Metz A W et al 2004 MOCVD growth of transparent conducting Cd$_2$SnO$_4$ thin films Chem. Vap. Deposition 10 297–300
[9] Li X, Gessert T A and Coutts T 2004 The properties of cadmium tin oxide thin-film compounds prepared by linear combinatorial synthesis Appl. Surf. Sci. 223 138–43
[10] Ismail R A et al 2007 Pulsed laser deposition of crystalline Cd$_2$SnO$_4$ thin film e-Journal of Surface Science and Nanotechnology 5 152–4
[11] Godines C D et al 2014 Transparent conductive thin films of Cd$_2$SnO$_4$ obtained by the sol–gel technique and their use in a solar cell made with CdTe Sol. Energy Mater. Sol. Cells 128 150–5
[12] Ali H M et al 2009 Optical and electrical properties of tin-doped cadmium oxide films prepared by electron beam technique Japan. J. Appl. Phys. 48 041101
[13] El-Nahhas M M et al 2014 Structural and optical properties of DC sputtered Cd$_2$SnO$_4$ nanocrystalline films J. Alloys Compd. 585 1–6
[14] Rose A 1983 The absence of surface dipole contributions to metal work functions Solid State Commun. 45 839–64
[15] Sasakhi K 1974 Study on work function of the [0001] faces of CdS crystal J. Japan. J. Appl. Phys. 13 933
[16] Yin Z et al 2014 Bandgap tunable Zn$_x$Mg$_{1-x}$O thin films as highly transparent cathode buffer layers for high-performance inverted polymer solar cells Adv. Energy Mater. 4 1301404
[17] Kephart J M et al 2016 Band alignment of front contact layers for high-efficiency CdTe solar cells Sol. Energy Mater. Sol. Cells 157 266–75
[18] Sharbati S and Sites J R 2014 Impact of the band offset for n-Zn(O,S)/p–Cu(In,Ga)Se solar cells IEEE J. Photovolt. 4 697–702
[19] Zhu Z et al 2020 Mechanism of chlorine treatment in the resistivity stabilization of high-performance AZO/i-ZnO composite transparent conductive layer Ceram. Int. 46 20819–29
[20] Jain A et al 2013 Commentary: the materials project: a materials genome approach to accelerating materials innovation APL Mater. 1 011002
[21] Miyata N, Miyake K and Nao S 1979 Physical properties of cadmium–tin oxide films deposited by dc reactive sputtering Thin Solid Films 58 385–9
[22] Stapinski T, Leja E and Pisarkiewicz T 1984 Point defects and their influence on electrical properties of reactive sputtered Cd$_2$SnO$_4$ thin films J. Phys. D 17 407
[23] Roberts D et al 2012 Transparent conductive materials including cadmium stannate US Patent 8,198,529[P]
[24] Hincke W B 1933 The vapor pressure of cadmium oxide JACS 55 1751–3
[25] Hashemi T, Hogarth C A and Golestani-Fard F 1988 Characterization of electrochemically reduced dicadmium stannate J. Mater. Sci. 23 2645–8
[26] Danaher W J et al 1986 Chemical etching of crystal and thin film cadmium telluride Appl. Surf. Sci. 27 338–54
[27] Bhuvaneswari P V et al 2013 Effect of fluorine doping on the structural, optical and electrical properties of spray deposited cadmium stannate thin films Mater. Sci. Semicond. Process. 16 1964–70
[28] Crist B V and Crist D B V 2000 Handbook of Monochromatic XPS Spectra[M] (New York: Wiley)