
Effect of in-situ CdCl₂ treatment on spray deposited CdTe films: Photoluminescence study

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In-situ CdCl₂ treatment for spray deposited CdTe films has been done by spraying a 0.01 M CdCl₂ solution on CdS substrates. Scanning electron micrographs show the improvement in grain growth with the CdCl₂ spray. Photoluminescence spectra for films with the in-situ treatment show a shift in the bandgap by 0.06 eV and a reduction in the defect band intensity as compared to those for the films without the treatment. The shift is due to conversion of CdTe into CdTeS by S diffusion from the CdS substrate. Our studies show that an in-situ CdCl₂ treatment is effective in improving the CdTe thin film properties.

1 Introduction

A post growth CdCl₂ treatment is a critical activation step for the CdTe/CdS solar cells [1, 2]. The improvements in grain growth and inter-diffusion at the CdTe/CdS interface help to improve the minority carrier lifetime and thus the device performance [3]. The treatment is normally done ex-situ using a CdCl₂ solution or vapor. In addition a cleaning step is needed to remove excess CdCl₂, which leads to the formation of oxy-chloride complexes on the surface during annealing and affects the contact formation [4]. For spray deposited CdTe films one can incorporate this treatment easily by doing a CdCl₂ spray before, during or after the CdTe deposition. The effect of this in-situ CdCl₂ treatment can then be observed using photoluminescence (PL). In this article, we report the photoluminescence (PL) studies for spray deposited CdTe films with and without in-situ CdCl₂ treatment.

2 Experimental details

The spray solution is prepared from a mixture of water, ammonium hydroxide, hydrazine hydride and hydrochloric acid. Cadmium and Tellurium are added to this mixture in the form of cadmium chloride (CdCl₂) and tellurium oxide (TeO₂) with concentrations of ~0.02 M. Hydrazine hydride is used as a reducing agent to obtain Te²⁻ ions [5]. A solution pH value of 11.2 and a flow rate of ~1–1.5 ml/min are used for the deposition on CdS coated glass. The substrate temperature is 400 °C. For the in-situ CdCl₂ treatment, prior to the CdTe deposition, 0.01 M CdCl₂ dissolved in methanol is sprayed for 3 min with a flow rate of 5 ml/min on CdS coated substrates at 400 °C, more details of CdTe film preparation are presented elsewhere [6]. SEM studies are carried out with a Hitachi S - 2300 microscope. A Midac FT-Photoluminescence Spectrometer system is used for the PL measurements from 0.6 to 1.6 eV at 4.2 K with an argon ion laser ($\lambda = 514.5$ nm) as the excitation source. Films without CdCl₂ spray are denoted as sample A and those with in-situ CdCl₂ spray as sample B.

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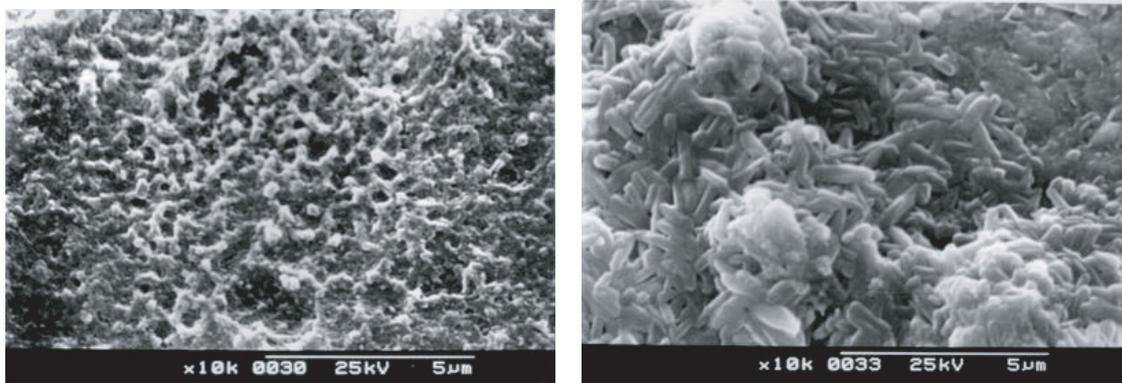


Fig. 1 SEM micrographs of CdTe films a) deposited without CdCl₂ and b) with CdCl₂ spray.

3 Results and discussion

SEM studies indicate that the grain size in sample B is larger than in sample A, which can be seen in Fig. 1. This means that the presence of the CdCl₂ during CdTe deposition decreases the inter-grain pore size and increases the grain size. This recrystallization will in turn affect the defect density (Cd and Te vacancies/interstitials) as well as promote inter-diffusion between CdS and CdTe layers to form CdTe_{1-x}S_x. The change in defect density and their activation energies are quite visible in the PL spectrum shown in Fig. 2a and b. In sample A, a weak band with peak at 1.585 eV and three defect related bands with peaks at 1.404, 1.106 and 0.843 eV are observed. In sample B these peaks are shifted to lower energies (1.527, 1.347, 1.056 and 0.828 eV respectively) and the peak intensities are considerable lower. In both the samples the 1.4 eV band emission is always the prominent one and by de-convoluting the emission lines, each defect band can be identified as a combination of two sub bands.

In sample A, the peak at 1.585 eV is due to the radiative recombination of excitons bound to shallow neutral acceptors (A⁰X), since the CdTe band gap at 4 K is 1.610 eV [7]. All the defect bands observed in sample A have been observed in PL spectra of CdTe crystals after different treatments and in CdTe films deposited by other techniques [8, 9]. The 1.4, 1.1 and 0.8 eV defect bands are due to the formation of native defects or interstitials or defect complexes (DX and AX) which introduce either acceptors or donors in the band gap depending on the formation energies [10]. V_{Cd} is the most prominent intrinsic acceptor because the formation of energy (2.67 eV) is less than that for other intrinsic defects [10]. The

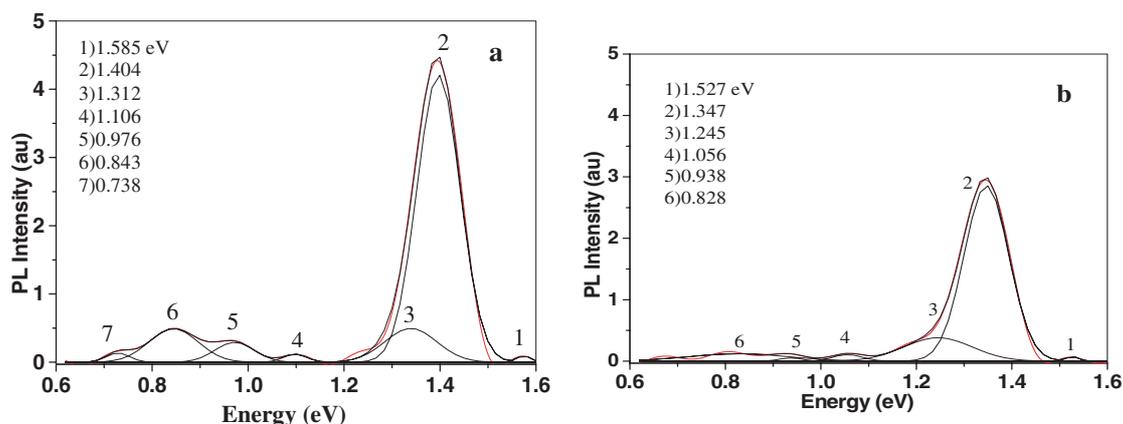


Fig. 2 (online colour at: www.interscience.wiley.com) Photoluminescence spectra of CdTe films a) without CdCl₂ and b) with in-situ CdCl₂ spray.

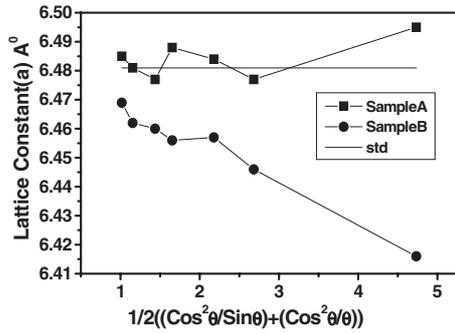


Fig. 3 Lattice parameters of different planes for samples A and B.

1.4 eV emission band is broad due to polycrystalline nature and can be resolved into two sub-bands with peaks at 1.404 and 1.312 eV. The 1.4 eV peak is assigned to the formation of complex $[V_{Cd}-Cl_{Te}]$, the D–A transition from shallow donor state (Cl_{Te}) to acceptor level (V_{Cd}) [11]. The second peak at 1.312 eV can arise due to the transition involving from the shallow donor level due to Cadmium interstitials (Cd_i), these two defect bands exist separately only if the E_F is located far from the valence band [12]. The 1.10 eV band, also consisting of two peaks at 1.106 and 0.976 eV, arises due to the $V_{Te}-Te_i$ complex, where V_{Te} is acting as a donor and Te_i as an acceptor [8]. The 0.8 eV band, consisting of peaks at 0.843 and 0.738 eV, is also associated with V_{Cd} states [13].

In sample B the near band edge PL peak is shifted to a lower energy (1.527 eV). This shift can happen because of S diffusion into CdTe, which leads to the formation of $CdTe_{1-x}S_x$ phase. Since the band gap of $CdTe_{1-x}S_x$ is smaller than the band gap of CdTe [14], the formation of this phase shifts the PL peak positions to lower energies. A similar shift with ex-situ $CdCl_2$ treatment done at 410 °C has been reported by Aslan et. al. [15]. However, the shift (~ 0.03 eV) is less than ~ 0.06 eV shift for in-situ $CdCl_2$ treatment. Also, since the shift is observed for unetched surface in our samples, it suggests that S is present uniformly in the entire CdTe film. It should be pointed out that a uniform shift of 0.03 eV requires an annealing temperature of 460 °C for ex situ $CdCl_2$ treatment. The presence of a uniform $CdTe_{1-x}S_x$ phase throughout the CdTe film is also confirmed by the depth profile study using Glancing angle Incidence X-ray Diffraction. This suggests that the presence of $CdCl_2$ during CdTe film growth is more effective for S diffusion into CdTe. In fact, a shift of ~ 0.058 eV corresponds to S concentration of $\sim 5.32\%$, which is close to the thermodynamical solubility limit of S in CdTe at 410 °C. A reduction of lattice mismatch and passivation of defects in the CdTe by the presence of S may also occur [16]. The shift of the peak positions of the defect bands can also be related to the reduction in band gap. The reduction in defect band intensities could be due to reduction of defect concentration and change in grain growth process. The larger grains may enhance the scattering on the surface and grain boundaries are known to act as a non-radiative recombination centres [17].

No such reduction in the major 1.4 eV peak intensity has been reported for CdTe films deposited by other techniques [9]. This means that the presence of $CdCl_2$ during CdTe growth is instrumental in eliminating Cd vacancies, it will also result in stress reduction in the film. This effect can be seen from Taylor & Nelson plots [18], the lattice constant ‘a’ derived from each of the X-ray diffraction peaks is plotted against $1/2[(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta)]$ which is shown in Fig. 3. For sample A the ‘a’ values are oscillating around a standard bulk value of 6.481 Å, which suggests that the presence of stacking faults and compressive stress in the film due to the lattice mismatch [19]. On the other hand for sample B the ‘a’ values are less than the standard value and the values follow a straight line. The reduction in ‘a’ has also been observed in situ $CdCl_2$ treated CSS CdTe films [20] and is due to the tensile stress in the film. The lattice constant ‘a’ of CdTe is also calculated from the Vegard’s law ($a = 6.477 - 0.657 X$) [21]. Where X is the S concentration. The $X = 5.32\%$ value is estimated from the difference in near band edge emission value of CdTe before and after the $CdCl_2$ treatment [$\Delta E_g = 0.058$ eV = $1.74 X^2 - 1.01 X$] [14]. The ‘a’ value is 6.442 Å, which is very much consistent with the ‘a’ value of $CdTe_{1-x}S_x$ pellets prepared with $X = 0.056$ [22].

4 Conclusions

In conclusion an in situ CdCl₂ treatment can become an integral part of CdTe deposition by spray pyrolysis. This treatment is more effective for the grain growth, recrystallization and interdiffusion in CdTe and CdS films than ex-situ treatments. The defect density is also affected. It allows uniform line-of sight delivery of CdCl₂ for uniform reactions in the CdTe/CdS structure, which also leads to chemically clean surface for back contacts. Introducing an appropriate amount of CdCl₂ can effect the interdiffusion at the CdS/CdTe interface. In fact, one can introduce the CdCl₂ spray during the CdTe deposition, to achieve controlled interdiffusion along with the increasing grain size.

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