

EFFECT OF CHLORINE DOPING ON CdTe THIN FILMS

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Abstract

This paper analyzes the effect of chlorine treatment on the structure and resistance of CdTe layers. The morphology, chemical composition, and structure were studied using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD). Both non-activated and activated CdTe layers are polycrystalline with an average grain size being three times higher after chlorine activation and thermal treatment. All CdTe thin layers regardless of the treatment temperature have a cubic crystal structure.

1. Introduction

CdTe is an ideal material for some applications, such as photovoltaic cells and nuclear detectors. It can exhibit both n- and p-types of conductivity, which makes diode and field effect transistors technology possible [1]. Hard X-ray and gamma ray detectors for imaging have been demonstrated from CdTe [2]. CdTe is one of the most thoroughly studied thin film semiconductors for photovoltaic application in the last five decades. CdTe is a group II–VI compound semiconductor with a direct band gap of 1.5 eV at room temperature. Many investigators have shown that CdCl₂ activation promotes recrystallization of CdTe films and leads to a significant increase in grain size associated with an increase in the junction photovoltaic efficiency by approximately an order of magnitude [3, 4]. This compound exhibits a very sensitive and complex dependence of film microstructure on preparation method and deposition conditions [5–7]. In this connection, many studies have recently been conducted to establish deposition conditions in order to obtain CdTe films having a particular crystalline structure and morphology [8–10]. In this paper, we extended these investigations by studying the effect of the post-deposition chloride treatment at different temperatures on the microstructural and electrical properties on CdTe films.

2. Results and Discussions

In order to find the best conditions for CdCl₂ activation, we varied the temperature and the annealing duration. CdCl₂ was applied to the surface of the CdTe structures by dipping in a methanol/CdCl₂ solution. The top cover of the CdTe was porous to allow a regulated flow of CdCl₂ vapor to the substrate. The sheet resistance of as-grown CdTe thin films is higher than 10⁹ Ω/□. The investigation of the sheet resistance with CdCl₂ concentration (Fig. 1) shows that the lowest resistance of CdTe can be achieved at a CdCl₂ concentration of 15–30 wt %. A reduction in resistance is caused by an increase in the grain size along with an increase in the annealing temperature, which is confirmed by the XRD analysis (see table).

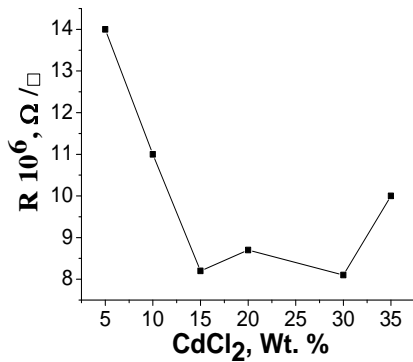


Fig. 1. The sheet resistance of 8-μm CdTe thin film grown on CdS/SnO₂/glass versus CdCl₂ concentration.

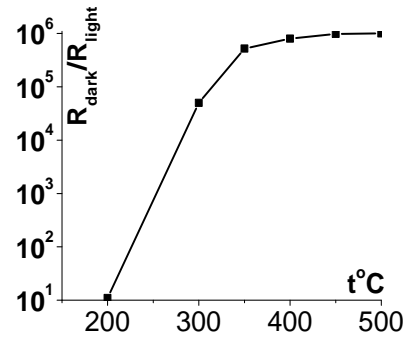


Fig. 2. The relative photosensitivity $\frac{R_{dark}}{R_{light}}$ dependence of the CdTe layer with annealing temperatures.

The investigation of the dependence of dark sheet resistance R_{dark} and light sheet resistance R_{light} on the annealing temperature of the CdTe layer grown on a glass substrate indicated that the dark resistance increases with increasing annealing temperature, while the light resistance decreases. It is evident from Fig. 2 that relative photosensitivity $\frac{R_{dark}}{R_{light}}$ increases with

annealing temperature until 400°C and then becomes nearly constant. It was established that the relative photosensitivity is highest in the case where the CdTe layer is activated for 35 min at 390–450°C (Fig. 3). Figures 4 and 5 compare the morphology and composition of CdTe films grown on glass before and after CdCl₂ activation, respectively. One can see that the CdTe films consist of crystallites with different sizes. For as-grown CdTe on glass substrates (Fig. 4), the grain size varies in a range of 1.5–5 μm before treatment and changes by 2–10 μm after CdCl₂ activation.

The chemical composition analysis before CdCl₂ activation reveals the presence of only Cd and Te. After CdCl₂ activation, CdTe contains an oxygen impurity at the sensitivity level of the EDX system, as illustrated in Fig. 5. In addition, CdTe films before and after annealing of CdCl₂ contain excess Te. We suppose that, since the diffusion coefficient of Cl in CdTe is small ($7.6 \times 10^{-14} \text{ cm}^2/\text{s}$), it is possible to get balance between the substitution of Cl and native defect concentrations in CdTe and to bind almost all chlorine to the shallow acceptor complexes, such as $(V_{Cd}^{2-} - Cl_{Te}^+)^-$.

In addition, it is known that the chemical bond between Cl and Te is strong, but the chemical bond between Cl and S is weak. Hence, another similar shallow acceptor complex $(Te_i^{2-} - Cl_{Te}^+)^-$ can be formed in CdTe. Therefore, the $(V_{Cd}^{2-} - Cl_{Te}^+)^-$ or/and $(Te_i^{2-} - Cl_{Te}^+)^-$ shallow acceptor complex is believed to be responsible for the high *p*-type conductivity in CdTe layers formed with CdCl₂ activation [8]. From the above analysis, it follows that a decrease in resistivity in an air atmosphere is caused by a decrease in the Cd content rather than by oxygen doping [3, 4].

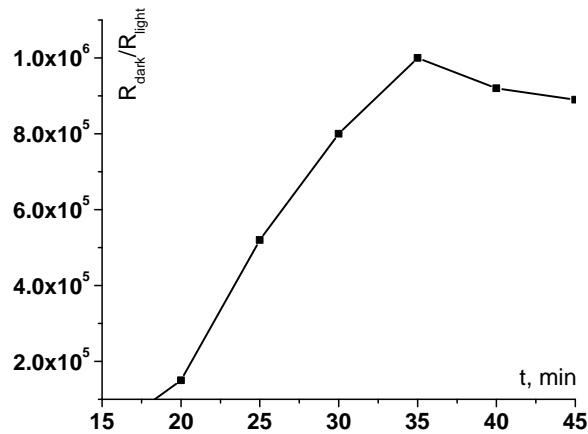


Fig. 3. Relative photosensitivity $\frac{R_{dark}}{R_{light}}$ dependence of the CdTe layer of the duration of annealing.

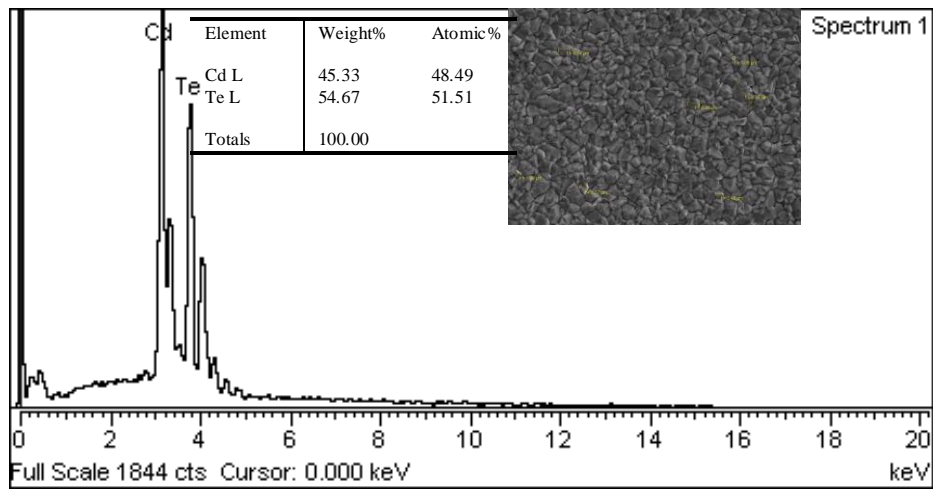


Fig. 4. SEM image of as-grown CdTe on a glass substrate deposited at 320°C before CdCl₂ activation and results of the EDX analysis.

Figures 6 and 7 show XRD patterns of chloride annealed CdTe thin films at different temperatures and as-grown and powder CdTe.

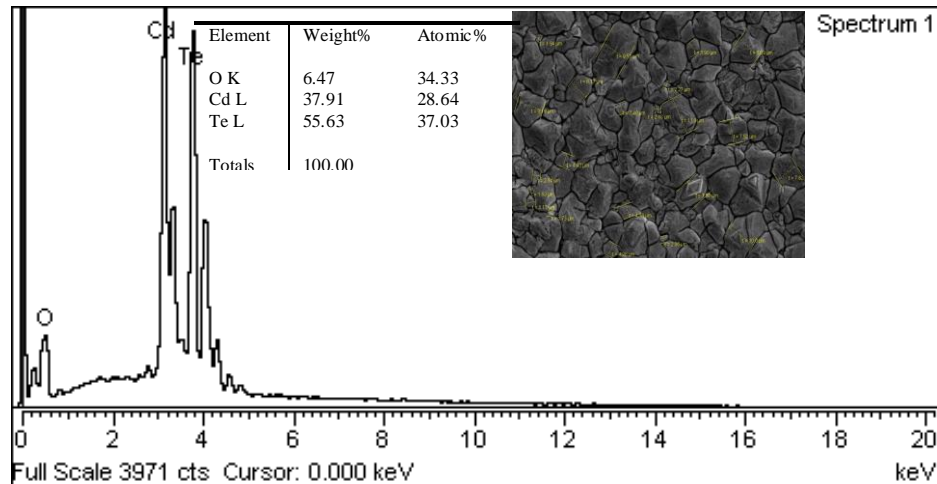


Fig. 5. SEM image of CdTe on glass substrates deposited at 320°C after CdCl₂ activation and results of the EDX analysis.

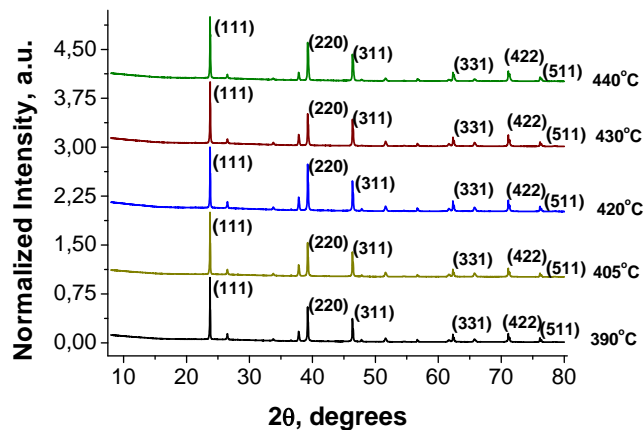


Fig. 6. X-ray diffraction patterns of CdTe deposited on CdS/SnO₂/glass after annealing for 30 min in air at different temperatures.

It is observed that all thin films are polycrystalline in nature having a cubic crystal structure, a preferred orientation along (111) together with other planes (220), (311), (331), (422), and (511). Other peaks shown in Fig. 6 correspond to diffraction from the SnO₂ and CdS layers. Structural parameters such as lattice parameter, grain size, and strain (ϵ) of CdTe thin films deposited on CdS/SnO₂/glass before and after annealing for 30 min in air at different temperatures are shown in Table 1.

All the activated samples exhibit a slight decrease in the lattice parameters compared to the as-grown ones. For all treatment conditions, the lattice parameters were found to be greater than for a powder CdTe sample (6.4810 Å).

For the as-grown CdTe, the value of lattice parameter a (6.4905 Å) is larger than that of the powder sample (6.4810 Å) (Fig.7), which suggests that the film is subjected to a compressive stress in the plane parallel to the substrate surface. This stress has been observed before [5] and is caused by the lattice mismatch and/or differences in the thermal expansion coefficients

between the CdTe and the underlying film. Also, a reduction in the lattice constant in activated layers is due to lattice strain. It can be seen from the table that the strain increases as the annealing temperature achieves a maximum at 440°C. The average crystallite sizes (*D*) increase compared to the as-deposited ones. Therefore, the chlorine activation improves the CdTe grain size. This beneficial effect of chlorine activation on CdTe thin films presented in this study is in good agreement with earlier reports [6].

Table 1. Structural parameters of chlorine doped CdTe thin films.

T(°C)	<i>a</i> (Å)	<i>D</i> (Å)	Strain%
as-grown	6.4905	319.9	
390	6.4890	1230.1	0.073(10)
405	6.4892	1086.6	0.070(7)
420	6.4876	1156.7	0.073(7)
430	6.4871	1042.7	0.078(9)
440	6.4869	1149.2	0.118(9)

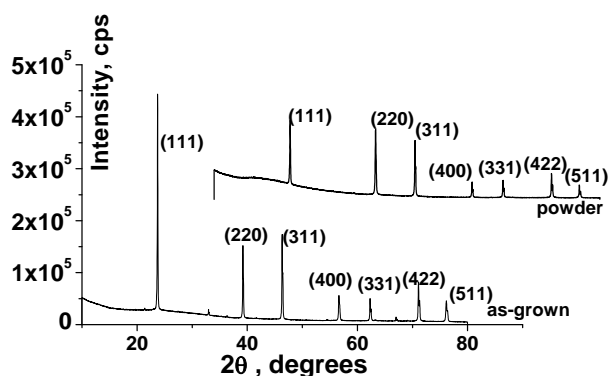


Fig. 7. X-ray diffraction patterns of the CdTe powder and as-grown CdTe thin films.

3. Conclusions

The XRD reveals that the as-grown CdTe layers were polycrystalline with a cubic structure. The chloride treatment of the CdTe increases the average grains size and decreases the resistance of the CdTe thin films. Variations in lattice constants for the CdTe films over the bulk values suggest that film grains are strained. The results show a decrease of the electrical resistance with immersion in chlorine and treatment at about 390–400°C.

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