

## Single-Phase Cadmium Telluride Thin Films Deposited by Electroless Electrodeposition

Gennadiy Khrypunov\*, Natalja Klochko, Neonila Volkova<sup>1</sup>, Viktor Lyubov, and Tatyana Li

National Technical University "Kharkiv Polytechnic Institute", 61002, Frunze Street 21, Kharkiv, Ukraine

<sup>1</sup>National Aerospace University "Kharkiv Aviation Institute", 17 Chkalov Street, 61070 Kharkiv, Ukraine

Received September 17, 2010; accepted January 21, 2011; published online May 20, 2011

By means of analysis of electrochemical processes taking place during electroless electrodeposition have elaborate method for obtaining of well adherent smooth and stoichiometric single-phase CdTe films with cubic structure. Illumination of the growing layers has increased their thickness and improved film crystallinity. Following improvement of CdTe structure was riched by "chloride treatment" of the films. So, the novel electroless electrodeposition technique gives possibilities for the manufacture of CdTe absorbers suitable for  $\eta$ -solar cells.

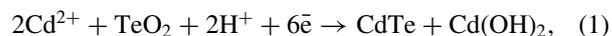
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Now cadmium telluride (CdTe) is a leading base material for fabrication of thin film solar cells.<sup>1)</sup> Equally with the creation of traditional thin film photovoltaic devices on the base of CdTe in recent years several approaches have been investigated to develop solar cells with extremely thin (80–500 nm) CdTe absorber (so-called  $\eta$ -solar cells) that offer a potential to reduce recombination losses in the base layers and thus use low cost materials.<sup>2,3)</sup> Until today CdTe depositions for  $\eta$ -solar cells manufacture were performed by vapour phase epitaxy under dynamical vacuum<sup>2)</sup> at working temperature 750 °C or by electrodeposition in a special electrochemical cell equipped with a potentiostat.<sup>3)</sup> Development research of simple and inexpensive method for obtaining of the single-phase stoichiometric cadmium telluride films has required an improvement of the electroless electrodeposition technique.<sup>4)</sup> So, for the showing up synthesis of doped or stoichiometric cadmium telluride films conditions and in order to decide a problem of the deposition of single-phase CdTe layers we have researched electrochemical processes going during electroless electrolysis in sulfate solutions with different acidities and CdSO<sub>4</sub> concentrations. In addition we investigated influence of illumination on the film growth as such as the impact of the illumination and "chloride treatment" on the film crystallinity.

In this research approximately 100 nm thick CdTe films were deposited on tin oxide film (SnO<sub>2</sub>) coated glass substrates (Pilkington), inserted in aluminum frames. Electroless electrolysis was fulfilled in accordance with<sup>5)</sup> in aqueous solutions contained 0.05–0.5 M CdSO<sub>4</sub>,  $2 \times 10^{-4}$  M TeO<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub> (to adjust pH 2 or 4) at 95 °C. Some film samples during deposition were illuminated by 500 W halogen lamp. A following treatment of the CdTe structure was fulfilled by air annealing during 1 h at 200 °C or by the use of "chloride treatment" through vacuum deposition of CdCl<sub>2</sub> film onto CdTe surface and subsequent air annealing at 430 °C for 20 min. The phase composition and structure of the deposited films were determined by X-ray diffraction (XRD) method using an X-ray diffractometer DRON-4M with Co K $\alpha$  radiation according to  $\theta$ –2 $\theta$ -scheme. Preferable orientations of the films were researched by analytical treatment of the X-ray diffractions.<sup>6)</sup> Precise measuring of cadmium telluride base layer lattice spacing a was fulfilled by using of extrapolating function a versus  $\cos^2 \theta (\sin \theta^{-1} + \theta^{-1})$ .<sup>7)</sup> Average crystalline size  $t$  and lattice strain  $\Delta d/d$  of the electroless electrodeposited CdTe films

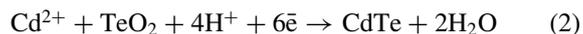
were determined by the Williamson–Hall formula for adherent deposits.<sup>8)</sup> The transmittance spectra of the samples were measured by double beam spectrophotometer SF-46 in the spectral range 0.6–1.1  $\mu$ m. Surface morphology of the films was researched by scanning electron microscope REM-100U.

With the object to prevent the excess of free tellurium in CdTe films we deposited the first cadmium telluride sample in slightly acidic solution (pH 4) characterized by great surplus of cadmium ions (0.5 M CdSO<sub>4</sub>). XRD spectra showed side by side with cadmium telluride a commensurable quantity of cadmium hydroxide  $\gamma$ -Cd(OH)<sub>2</sub> impurity. To our opinion, in this case the deposition of cadmium telluride was happened owing to aluminum oxidation in accordance with tellurium reduction electrochemical reaction:

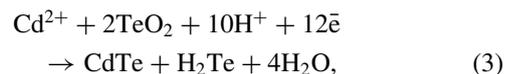


and caused a joint deposition of CdTe and cadmium hydroxide.

We concluded that in order to diminish cadmium hydroxide impurity contention in the cadmium telluride films the tellurium electrochemical reduction process (1) must be exchanged by following electrochemical process:



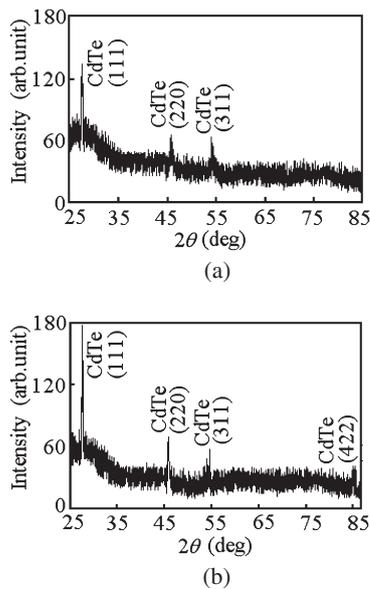
With this object we decreased cadmium sulfate concentration in the solution to 0.05 M and diminished pH to 2. However, it turned out that in the case of the 0.05 M CdSO<sub>4</sub> concentration and even if the cadmium sulfate concentration was 0.1 M the creation of cadmium telluride film was very significantly delayed, so in this interval of the concentrations we have not obtain whatever CdTe film for 45 min. The possible cause of this was the reaction with the development of water soluble hydrogen telluride:



which, on the same time, etched ITO substrate.

On purpose to fulfill process (2) we have increased cadmium sulfate concentration to 0.2 M. XRD spectra confirm that the last change of the electroless electrodeposition conditions allowed almost full avoiding the joint deposition of the additive phases with CdTe. So, in the last case it was a success to deposit near-stoichiometric cadmium telluride films. X-ray investigations of the CdTe film samples crystal structures have revealed that irrespective of the mode of the deposition all films consisted of cubic

\*E-mail address: khrip@ukr.net

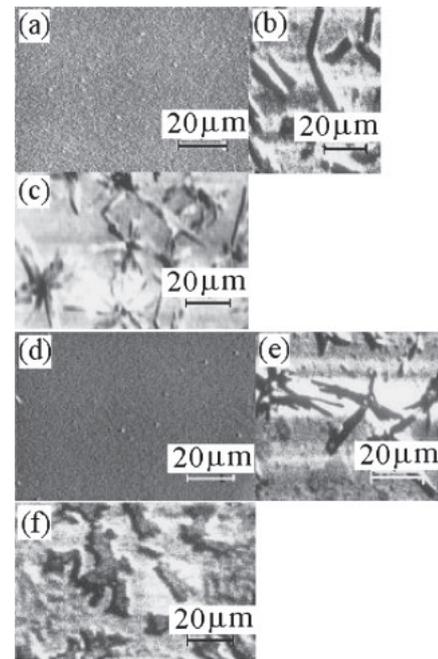


**Fig. 1.** XRD spectra of electroless electrodeposited CdTe film (sample 101) before (a) and after (b) “chloride treatment”.

phase CdTe. The illumination of the growing cadmium telluride layers increased their deposition rate and slightly improved film crystallinity. The sample, which was electroless electrodeposited under illumination by 500 W halogen lamp, has the most intensive peaks (111), (220), and (311) of cubic CdTe [Fig. 1(a)]. All films were preferably oriented in [111] direction, degree of preferable orientation reached  $G = 0.54$ . The surface morphology of as-deposited CdTe films was illumination-independent.

As it has been shown by optical estimations, the CdTe absorption coefficients  $\alpha$  for visible light were in order  $10^5 \text{ cm}^{-1}$ . The optical band gap  $E_g$  values near 1.52–1.56 eV for the CdTe films obtained from transmission measurements and by plotting  $[(-\ln T)h\nu]^2$  versus  $h\nu$  indicated that the electroless electrodeposited films represented direct band gap material, but the intercept on the energy axis gave  $E_g$  values rather more than 1.49 eV, which is characteristic for CdTe. To our opinion, such “blue shift” may be a result of nano-scale grain structure of the films. Air annealing at moderate temperatures has no effect on the film properties.

At the same time, the influence of the “chloride treatment” is extraordinary as such as it induced film recrystallization. In the case of excessive  $\text{CdCl}_2$  layer thickness a structural self-organization was especially evident in the thinnest CdTe films (Fig. 2), because such films became disrupt. XRD spectrum of the electroless electrodeposited cadmium telluride film has shown [Fig. 1(b)] that after “chloride treatment” diffraction peaks of stable cubic CdTe phase became more intensive, the only other line (422) has appeared. Calculations by the Williamson-Hall formula displayed that average crystalline size  $t$  was near 2 nm as before such as after “chloride treatment”, but the film lattice strain  $\Delta d/d$  of the electroless electrodeposited CdTe films diminished from 0.23 to 0.16. Simultaneously degree of preferable orientation in [111]



**Fig. 2.** Surface morphology of CdTe films electroless electrodeposited without illumination (a–c) and under illumination by 500 W halogen lamp (d–f): (a,d) as-deposited CdTe films; (b,c,e,f) after “chloride treatment”.

direction decreased to  $G = 0.37$ . As a result of the “chloride treatment” lattice spacing increased from  $a = 6.448 \text{ \AA}$  up to  $6.465 \text{ \AA}$ , thereby it approached to the theoretic data  $6.481 \text{ \AA}$  for cubic CdTe single crystal (JCPDS card 15-0770) that is an evidence of the compressive stress lowering owing to the “chloride treatment”.

As a result of our researches, the stoichiometric single-phase CdTe films were obtained by electroless electrodeposition and subsequent “chloride treatment”. Intensive illumination during deposition was favorable condition as it accelerated CdTe deposition rate. In whole, the novel electroless electrodeposition technique gives possibilities for the manufacture of the CdTe absorbers suitable for  $\eta$ -solar cells.

**Acknowledgement** The work was supported by STCU under Project 4301.

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