

# Properties and mechanism of solar absorber CdTe thin film synthesis by unipolar galvanic pulsed electrodeposition

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**Abstract** Electrochemical deposition of CdTe semiconductor thin films over transparent conducting glass substrates by sequential unipolar current pulses is described. The magnitude of pulsed current and pulse periodicity affects the crystalline structure, morphology, optical absorbance and composition of CdTe films. CdTe films formed under high magnitude pulsed current density  $\sim 5\text{--}15\text{ mA cm}^{-2}$  are crystalline with dominant cubic structure having (111) plane oriented parallel to the substrate. Stoichiometric CdTe film growth occurs with current pulses of short 25–300 ms periodicity and 3–50 ms duration. A mechanism of the CdTe growth involving in situ cathodic tellurization process step involving  $\text{H}_2\text{Te}$  formation and reaction with electrochemically deposited Cd monolayer is described. CdTe film growth in the pulsed electrodeposition occurs under mass transport conditions under strong influence of high magnitude pulsed current. This results in much higher growth rates  $\sim 5\text{--}8\text{ }\mu\text{m h}^{-1}$  for CdTe films which is attractive for CdTe solar cells in a production environment.

**Keywords** Pulsed electrodeposition · CdTe thin films · Optical absorption · CdTe solar cells · Tellurization

## 1 Introduction

Cadmium telluride (CdTe) is a promising p-type semiconductor solar absorber material for the heterojunction photovoltaic devices. Its optical energy gap, 1.5 eV, provides an optimal match with the solar spectrum favoring efficient utilization of the terrestrial solar radiation. High absorption coefficient due to the direct mode optical transitions makes it most useful for the fabrication of thin film solar cells [1, 2]. There is a considerable interest in the low cost, large area deposition of thin films for solar cells. Although CdTe thin films have been deposited by a variety of techniques, namely, closed space sublimation, CSS [3], sputtering [4] and physical vapor deposition, PVD [5], electrodeposition is the most potential technique for fabrication of thin film solar cells [6]. Electrodeposition of several II–VI compound semiconductor thin films have been extensively studied in acidic electrolytes mostly by direct current (DC) cathodic electrodeposition route involving co-reduction of the metal and chalcogen ions. In particular, CdTe thin films have been formed by both cathodic and anodic DC electrodeposition methods [7, 8] as well as by cathodic electrodeposition in organic [9], ammoniacal [10] and acidic electrolytes [11, 12]. Typically, these methods yield extremely slow  $\sim 0.1\text{--}0.3\text{ }\mu\text{m h}^{-1}$  deposition rates due to Te diffusion limitation and also require a complex control of the potential domain, positive with respect to the cadmium deposition potential in order to maintain a stoichiometric Cd/Te composition. For CdTe solar cells in the production environment, these factors are important in order to achieve a higher throughput and yield. In this paper we show that using the sequential high magnitude current pulses instead of the DC, CdTe electrodeposition can be carried out under the mass transport conditions which can yield a higher deposition rates for the

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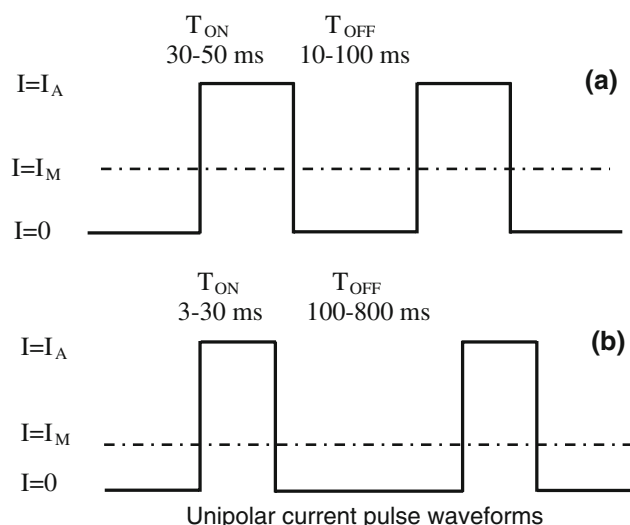
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CdTe films. Pulsed electrodeposition of the semiconductor thin films is relatively less studied although the technique has been extensively used to deposit metallic thin films [13–15]. The pulsed current electrodeposition has the potential advantage of three process parameters, the amplitude, ON time and the OFF time of the current pulses which can be independently varied compared to only the over-potential parameter in DC electrodeposition [13]. Therefore, pulsed current variables can be used to create a mass transport situation and also manipulate the ion adsorption and desorption effects on the substrate to create conditions for electro-crystallization of films. Except for a few reports on the properties of pulsed electrodeposited CdTe films [16, 17], a detailed understanding of the binary compound semiconductor film formation by pulsed current is completely lacking. Our studies show that the growth rates and deposit composition of CdTe films are effectively controlled by the pulsed current magnitude as well as pulse ON/OFF times. More specifically the morphology, monolayer surface coverage and crystallinity of CdTe films are directly affected by the pulse OFF time. This paper describes the properties of CdTe semiconductor thin films with a focus on the mechanistic aspects of the pulsed current electrodeposition and suggests a mechanism for CdTe film formation based on in situ electrochemical tellurization of the Cd monolayer over the substrate.

## 2 Experimental

Pulsed current electrodeposition of CdTe thin films was carried out in an electrochemical cell of 0.6-L capacity Pyrex glass cylindrical vessel fitted with three-electrode assembly. Working electrode (cathode) was the substrate used for CdTe film growth, counter electrode (anode) was a  $20 \times 50$  mm platinum foil placed at a distance 50 mm away facing the substrate and a saturated calomel reference electrode (SCE) was used for the potential measurements. Electrolyte for the CdTe film growth was 2.5 M aqueous solution of  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (Aldrich 99.99%) and 120–180 ppm  $\text{TeO}_2$  at pH  $\sim 1.7$ – $1.8$  adjusted by electronic grade  $\text{H}_2\text{SO}_4$ . Prior to the CdTe film deposition, impurities in the solution were plated out by DC electrolysis at a potential  $-0.58$  V (SCE) for 24 h over a platinum cathode. All depositions were made in the unstirred solution heated to  $75$  °C. The CdTe films were deposited over fluorine doped tin oxide (FTO) coated transparent conducting glass substrates of nominal sheet resistance  $10$ – $15$   $\Omega/\square$ . A thin  $\text{SiO}_2$  layer was coated between the glass and FTO as a barrier for alkali-ions diffusion into CdTe during various process stages.

Instead of the potentiostatic mode, as in the conventional DC electrodeposition of CdTe films, the present



**Fig. 1** Schematic of unipolar pulsed current waveforms corresponding to (a) longer pulse duration (30–50 ms) and shorter pulse intervals (10–100 ms) and (b) shorter pulse periods (3–30 ms) and longer intervals between pulses (100–800 ms) used in the electrodeposition of CdTe films

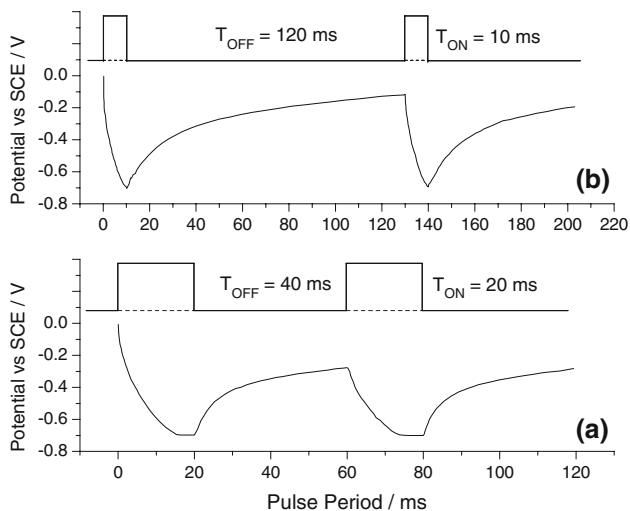
technique uses sequential unipolar square shape current pulses of high current density  $\leq 3$   $\text{A dm}^{-2}$  of different periodicity as schematically shown in Fig. 1. Usually the DC electrodeposition of CdTe films of proportionate composition is done under controlled overpotential condition as Cd and Te reduction processes are potential dependent. In the pulsed current electrodeposition, the interval between the pulses,  $T_{OFF}$ , pulse duration,  $T_{ON}$ , applied pulse current density;  $I_A$  and mean current density  $I_M = \Phi \cdot I_A$ , where  $\Phi$  is pulsed duty cycle given by  $\Phi = [T_{ON}/(T_{ON} + T_{OFF})]$  are controlled to obtain stoichiometric CdTe films. Mean current density for electrodeposition of CdTe can be changed either by varying the applied current  $I_A$  or the duty cycle ( $\Phi$ ) individually or both. Growth of CdTe films was carried out typically under pulse conditions; (i) longer pulse duration,  $T_{ON} \sim 30$ – $50$  ms and shorter interval between pulses,  $T_{OFF} \sim 10$ – $100$  ms and (ii) shorter pulses,  $T_{ON} \sim 3$ – $30$  ms and much longer pulse intervals,  $T_{OFF} \sim 100$ – $800$  ms, schematically depicted at (a) and (b) respectively in Fig. 1. In this case, homogeneous, adherent, crystalline and morphologically coherent CdTe films were deposited with applied pulse current density  $\sim 10$ – $20$   $\text{mA cm}^{-2}$ . At low  $I_A \leq 10$   $\text{mA cm}^{-2}$ , some growth studies were also done with  $T_{ON} \approx 3$  ms and  $T_{OFF} \approx 10$ – $100$  ms. The pulsed current electrodeposited CdTe films were characterized for the crystalline structure by powder X-ray diffraction and its morphology and composition was determined by scanning electron microscope SEM (LeO 440) in conjunction with energy dispersive X-ray analysis (EDAX-Oxford Link-ISIS -300). Optical absorption studies of the CdTe films were carried out using

Shimadzu double beam UV-VIS spectrophotometer using uncoated substrate as the reference.

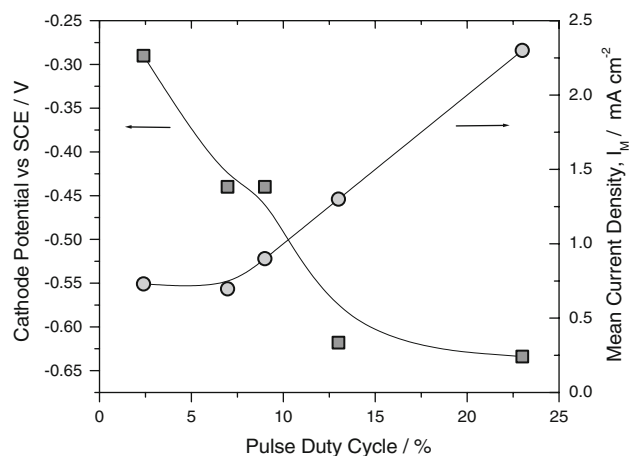
### 3 Results and discussion

#### 3.1 Film growth

The trains of current pulses applied between the cathode (substrate) and anode have a square and unipolar waveform. The corresponding over potential is however modulated due to an electric double layer at the cathode-electrolyte interface forming a capacitor of molecular dimension [18]. Figure 2a and b show experimentally observed potential curves corresponding to specific pulse parameters also shown in the figure. Due to charging and discharging of the double layer capacitor, the potential waveform shown in Fig. 2 has characteristic rise and decay times determined by the pulsed current magnitude and ON-OFF time. CdTe film deposition occurs when the overpotential is large enough, such that a larger free energy is available for the formation of CdTe nuclei [19]. During the short period the pulse is on, deposition occurs at a faster rate due to high instantaneous current. During the interval between the current pulses when applied current is zero, CdTe film growth continues as long as the magnitude of the decaying potential, Fig. 2 favors CdTe deposition. During pulse OFF period, double layer capacitor is discharged with a time constant,  $T_D$ . If  $T_{OFF} \ll T_D$ , a condition is reached when potential has a finite value although applied pulsed



**Fig. 2** Variation of cathode potential (SCE) in pulse current deposition of CdTe films corresponding to the pulsed current waveforms as shown (a) longer  $T_{ON} = 20$  ms and shorter  $T_{OFF} = 40$  ms,  $I_A = 4$  mA cm $^{-2}$  and (b) shorter  $T_{ON} = 10$  ms and longer  $T_{OFF} = 120$  ms,  $I_A = 12$  mA cm $^{-2}$ . CdTe films were deposited in an aqueous solution of 2.5 M CdSO $_4$  with 160 ppm TeO $_2$  at pH  $\sim 1.8$

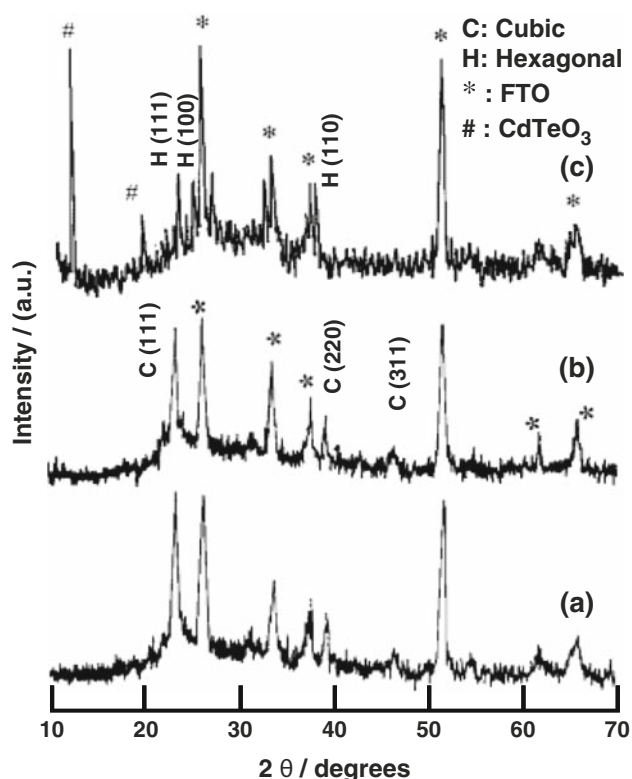


**Fig. 3** Development of peak cathodic potential with pulsed current of different duty cycles extracted from generalized polarization data for electrodeposited CdTe films. Applied pulse current density,  $I_A = 10$  mA cm $^{-2}$  (all solid data points) and 30 mA cm $^{-2}$  (encircled data point) was used in with constant pulse duration  $T_{ON} = 3$  ms. Duty cycle variation is obtained by varying  $T_{OFF}$  in the range 10–120 ms. CdTe films were deposited in an aqueous solution of 2.5 M CdSO $_4$  with 160 ppm TeO $_2$  at pH  $\sim 1.8$

current drops to zero (see Fig. 2a). Consequently, the potential and hence Faradic current,  $i_F$  has a finite value and decays slowly during OFF period. If  $T_{OFF} \gg T_D$ , potential as well as  $i_F$  drops to zero or an insignificant value as shown in Fig. 2b. Interrelationship between the unipolar pulsed current parameters (duty cycles and mean current density) and the peak cathodic over potential (COV) extracted from generalized polarization curves for CdTe film deposition at different duty cycle,  $\Phi$  and mean current  $I_M$  values is shown in Fig. 3. A more negative cell potential develops as  $I_M$  increases linearly with  $\Phi$ . The effect of  $I_M$ ,  $T_{OFF}$  and  $T_{ON}$  on the properties and mechanistic aspects of film growth are discussed in the following sections.

#### 3.2 Crystalline structure

X-ray diffraction studies show that the pulsed current electrodeposited CdTe thin films formed under varied  $T_{ON}/T_{OFF}$  and  $I_M$  parameters are generally polycrystalline with mixed cubic and hexagonal phases. Figure 4 shows typical X-ray diffraction patterns from films deposited with a low (5 mA cm $^{-2}$ ) and a high (15 mA cm $^{-2}$ ) magnitude applied cathodic current pulses. The pulse  $T_{ON}$  was 3 ms and the  $T_{OFF}$  was varied as  $\sim 40$  and 120 ms to keep the mean current density  $I_M$  for the film growth in the two cases nearly constant at  $\sim 0.36$  mA cm $^{-2}$ . Diffraction patterns in curves (a) and (b) show that both CdTe films are polycrystalline having dominantly cubic structure with preferred orientation of (111) planes parallel to the substrate. It may be mentioned that DC electrodeposited CdTe films generally form in the hexagonal phase. The peaks



**Fig. 4** X-ray diffraction patterns of CdTe films deposited at different applied current density and pulse OFF times. Curve (a)  $I_A \sim 5 \text{ mA cm}^{-2}$ ,  $T_{ON} \sim 3 \text{ ms}$ ,  $T_{OFF} \sim 40 \text{ ms}$ ; curve (b)  $I_A \sim 15 \text{ mA cm}^{-2}$ ,  $T_{ON} \sim 3 \text{ ms}$ ,  $T_{OFF} \sim 120 \text{ ms}$ ; and curve (c)  $I_A \sim 15 \text{ mA cm}^{-2}$ ,  $T_{ON} \sim 1 \text{ s}$  and  $T_{OFF} \sim 39 \text{ s}$ .  $I_M$  is nearly constant in all depositions  $\sim 0.36 \text{ mA cm}^{-2}$ . CdTe films were deposited in an aqueous solution of 2.5 M  $\text{CdSO}_4$  with 160 ppm  $\text{TeO}_2$  at pH  $\sim 1.8$

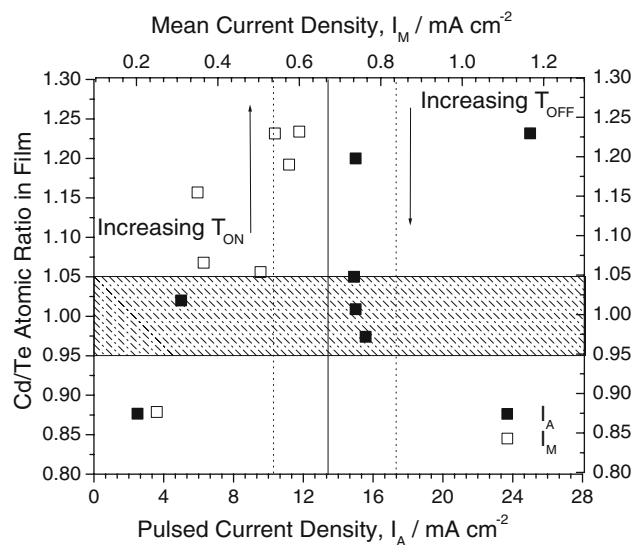
marked (\*) are due to conducting FTO coating over the substrate. No diffraction lines from secondary phases belonging to either Cd or Te or their oxides were observed. The effect of more drastic changes in  $T_{ON}$  and  $T_{OFF}$  periods of the current pulses on the crystalline structure of films are shown by curve (c). Here, the CdTe film deposition was carried out with  $T_{ON} \sim 1 \text{ s}$  and  $T_{OFF} \sim 39 \text{ s}$ . With this choice of pulse periods, the mean deposition current is also similar to that for curves (a) and (b). It is evident that increase in  $T_{ON}$  and  $T_{OFF}$  has resulted in CdTe films with hexagonal crystalline structure. Prominent hexagonal CdTe diffraction lines from (101), (110), (103) and (210) diffraction planes are observed. No diffraction peaks belonging to the cubic CdTe, as in curves (a) and (b) are seen. Apparently, such longer deposition periods are more akin to DC conditions, which are known to result in hexagonal CdTe growth phase. Two lines at lower two values belonging to  $\text{CdTeO}_3/\text{TeO}_2$  system are also seen indicating high pulsed current with longer  $T_{ON}$  periods leads to the inclusion of minor secondary oxide phases. It seems that

$I_M \sim 0.36 \text{ mA cm}^{-2}$  represents an upper limit to form crystalline-CdTe film without secondary phases.

It is worth noting that the pulsed current electrodeposited CdTe films are highly crystalline in the as-deposited state which is of significant advantage for solar cells compared the DC electrodeposited CdTe films which are either amorphous or display poor crystalline structure [20]. Thus to use in solar cells, the DC electrodeposited CdTe films are first subjected to a  $\text{CdCl}_2$  flux annealing at  $400^\circ \text{C}$  which enhances crystallinity and grain structure [21]. It seems that such crystallization step is not required for the pulsed current electrodeposited CdTe films.

### 3.3 CdTe film composition

Figure 5 conveys the effects of  $I_M$  and  $I_A$  on the Cd/Te ratio in the films. CdTe films deposited with  $5 \leq I_A \leq 18 \text{ mA cm}^{-2}$  have the Cd/Te ratio  $\approx 1 \pm 0.05$  as shown by the horizontal band. This is acceptable stoichiometric range for application of CdTe films as absorber in hetero-junction solar cells. Deposition with  $I_M \approx 0.35\text{--}0.45 \text{ mA cm}^{-2}$  results in more stoichiometric CdTe films although near stoichiometric films are still formed over a broader range,  $0.3\text{--}0.5 \text{ mA cm}^{-2}$ .  $I_M$  values can be changed by changing either  $I_A$ ,  $T_{ON}$  or  $T_{OFF}$  independently. Figure 5 also illustrates the trend of current pulse  $T_{ON}$  and  $T_{OFF}$  parameters on the Cd/Te ratio in the film. A trend towards deviation from the stoichiometry with  $T_{OFF}$  for CdTe films deposited at a fixed applied current density  $\sim 15\text{--}16 \text{ mA cm}^{-2}$  is depicted by the dotted vertical column in Fig. 5. Pulse OFF time,  $300 \geq T_{OFF} \geq 120 \text{ ms}$ ,



**Fig. 5** Effect of mean current  $I_M$  and applied pulse current density  $I_A$  on CdTe film composition. Horizontal band shows region of stoichiometric CdTe growth. Vertical band traces the trend of pulse OFF and ON time on the Cd/Te composition in the deposited films

results in CdTe films in near stoichiometric composition. Similarly, the trend of variation in  $T_{ON}$  is depicted for  $I_M$  values within a range  $\sim 0.3\text{--}0.5 \text{ mA cm}^{-2}$  which shows that with increase in the ON time of current pulses, the CdTe film growth tend to have excess Cd.

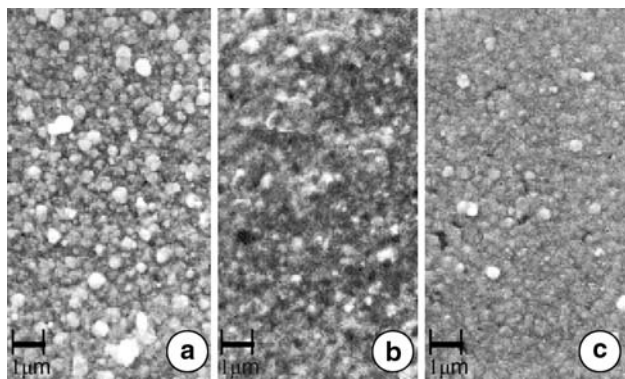
### 3.4 CdTe film morphology

Figure 6 shows the effect of pulsed current density and pulse off time on the morphology of the CdTe films. The film formed at  $T_{OFF} \sim 20$ ,  $T_{ON} \sim 3$  ms and the pulsed current density  $\sim 15 \text{ mA cm}^{-2}$  within the upper bound of stoichiometric composition have nodular shape three-dimensional crystallites of average lateral size,  $0.4\text{--}0.5 \mu\text{m}$ , closely packed and uniformly distributed over the entire surface as seen in Fig. 6a. As the  $T_{OFF}$  period is increased to  $\sim 120$  ms, the nodular crystallites appearance changes to that of the flat lateral crystallites and growth morphology becomes relatively smoother as in Fig. 6b. The morphology of the film deposited with reduced pulsed current density near the lower bound of the stoichiometry range is shown in Fig. 6c. Although nodular shaped crystallites are still visible, these do not have a three-dimensional appearance indicating a slower vertical growth.

Morphological changes can be related to the effect of pulsed current parameters on CdTe nucleation. Nucleation rate  $R_n$  of depositing species (Cd) is given by [22],

$$R_n = 2\pi r_c N^2 \sqrt{\left(\frac{kT}{2\pi m}\right)} \exp\left[-\frac{\Delta F_c + E_a}{2kT}\right]$$

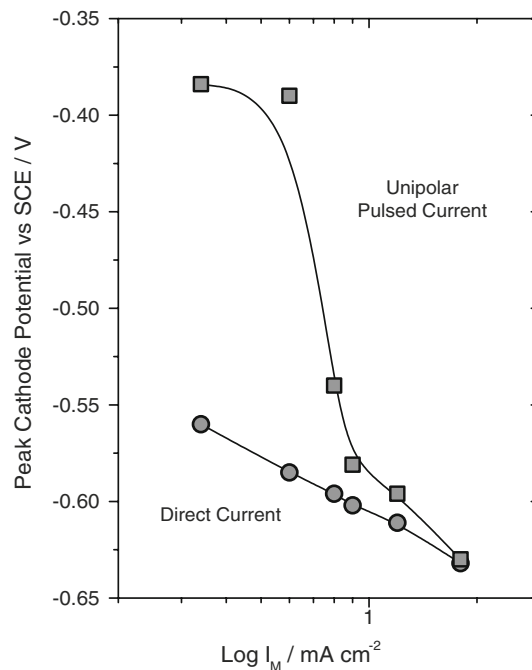
where  $r_c$  is the critical radius of the nuclei,  $N$  is the number of adions  $\text{cm}^{-2}$ ,  $\Delta F_c$  is free energy change for the nucleus and  $E_a$  is the activation energy of surface diffusion. A lower current density translates into a lower charge (number of Coulombs) per pulse, which implies reduction



**Fig. 6** Scanning electron micrographs showing surface morphology of CdTe thin films formed under varied pulsed current parameters, (a)  $I_A \sim 15 \text{ mA cm}^{-2}$ ,  $T_{ON}/T_{OFF} \sim 3/20$  ms, (b)  $I_A \sim 15 \text{ mA cm}^{-2}$ ,  $T_{ON}/T_{OFF} \sim 3/120$  ms (c)  $I_A \sim 2.5 \text{ mA cm}^{-2}$ ,  $T_{ON}/T_{OFF} \sim 3/20$  ms

in the density of impinging ionic species  $N$  on the substrate. A reduction in  $N$  reduces the nucleation rate in proportion to  $\sqrt{R_n}$ . It is known that the adsorption and hence nucleation of cations (Cd) over a substrates is extremely sensitive to the overpotential. Referring to the Fig. 2 for short  $T_{OFF}$  periods, due to capacitive nature, the decay in overpotential is still above the threshold ( $-0.403 \text{ V SHE}$ ) for Cd deposition. Thus, provided  $T_{OFF}$  is short, impingement of ionic species is still maintained resulting in a continuous film growth with granular morphology as seen in Fig. 6a. For longer  $T_{OFF}$ s, the period between the current pulses allows the overpotential to decay below the growth activation level. Thus, with the cessation of adsorption of ionic species, unstable CdTe nuclei tend to desorb during the OFF period between the current pulses. Selective etch back and a well balance sequence of deposition during  $T_{ON}$  and partial etch back during  $T_{OFF}$  in the repetitive current pulses results in the loss of granular character and growth of CdTe films appears smoother as evidenced in Fig. 6b. As applied current density is lowered, the ion impingement density is correspondingly reduced and if a lower  $T_{OFF}$  period is maintained, a slower three-dimensional growth in the vertical direction results in smoother morphology shown in Fig. 6c.

Relationship of cathodic potential  $\eta$  with current  $I_M$  in Fig. 7 shows that activated pulsed electrodeposition is described by the Tafel region in which the current shows



**Fig. 7** Typical polarization curves plotted as peak cathodic potential versus log mean current for unipolar pulsed current and DC electrodeposition of CdTe films over FTO coated substrates

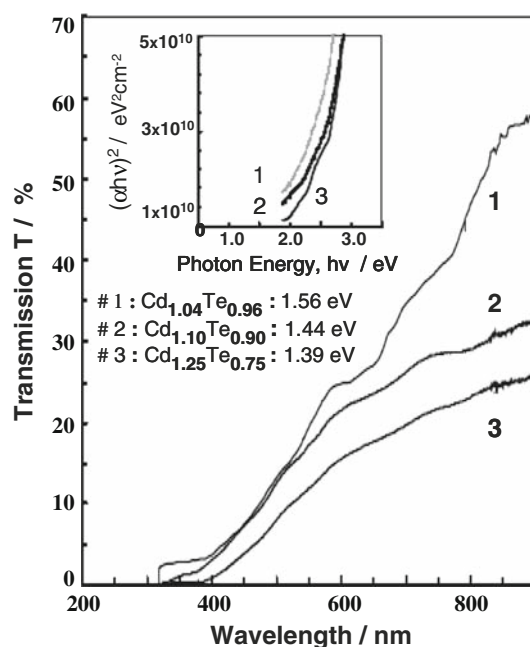
linear logarithmic dependence according to the relation,  $\eta = a \pm b \ln I_M$  where,  $b$  is the Tafel coefficient. Compared to DC, the limiting current densities in pulsed current electrodeposition are higher. Tafel coefficient,  $b$  for pulsed current and DC electrodeposition of CdTe films is 18.8 and 0.013 V/decade, respectively. A higher  $b$  value implies higher rates of CdTe film deposition in the pulsed current deposition process. The pulsed current electrodeposited CdTe films are also more uniform compared to the DC deposited films. Film uniformity depends on the distribution of current across the substrate surface, conductivity of the electrolyte and the electrodeposition kinetics and could be described in terms of the uniformity quotient  $U_Q$  which takes into account all these factors [23],

$$U_Q = \frac{\sigma}{\lambda} \cdot \left( \frac{\partial \eta}{\partial I} \right) = \frac{\sigma}{\lambda} \cdot \left( \frac{b}{I_M} \right)$$

where,  $\sigma$  is electrolyte conductivity ( $S\text{ cm}^{-1}$ ) and  $\lambda$  is characteristic length. A higher Tafel coefficient is associated with higher uniformity quotient for the films which translates into increased throwing power for the ionic species in the pulsed current electrodeposition. Similarly, lower mean deposition current density optimizes the uniformity quotient of the films which is consistent with the morphological studies presented in Fig. 6.

### 3.5 Optical absorption

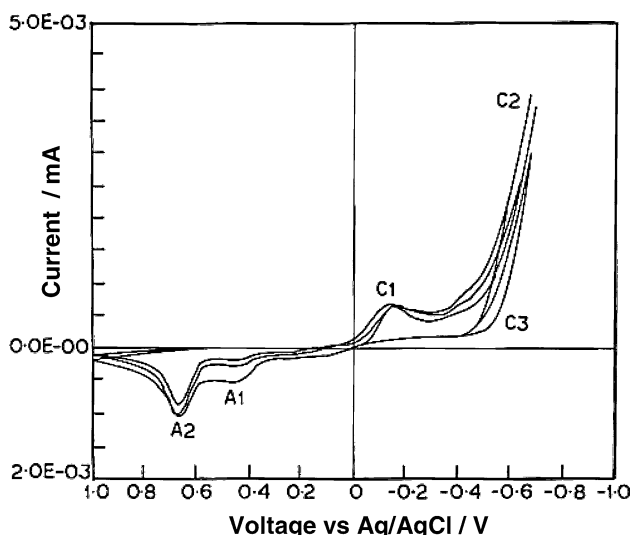
CdTe films of a higher absorption coefficient are needed for solar cells to act as an efficient harvester of solar radiation and to minimize the thickness for absorber layer for efficient transport and collection of photo-generated minority carriers across the heterojunction. Characteristic optical transmission spectra of the pulse electrodeposited CdTe thin films formed at pulsed current densities 15, 20 and  $25\text{ mA cm}^{-2}$  in the wavelength region 320–900 nm are shown by the curves 1, 2 and 3, respectively in Fig. 8. The period of current pulse  $T_{ON}$  and  $T_{OFF}$  were  $\sim 3$  and  $\sim 120$  ms, respectively. Films deposited at lower range of pulsed current show a higher absorption coefficient ( $\alpha$ ), typically  $\sim 9.2 \times 10^4\text{ cm}^{-1}$  which decreases to  $6.9 \times 10^4\text{ cm}^{-1}$  for films formed at a higher pulsed current density  $\sim 25\text{ mA cm}^{-2}$ . Deposition conditions of these films fall within a broad  $I_M \sim 0.36\text{--}0.6\text{ mA cm}^{-2}$  range, which favor a near stoichiometric growth of CdTe films. CdTe films show direct band gap absorption with optical band gap ( $E_g$ ) determined by Tauc's relation as shown in the inset of the Fig. 8. Optimum optical gap energy  $E_g \sim 1.56\text{ eV}$  determined for film deposited at  $15\text{ mA cm}^{-2}$  is in agreement with the bulk data [24]. The marginal decrease in  $E_g$  is consistent with the deviation in the film composition as pulse current density used for CdTe electrodeposition increases.



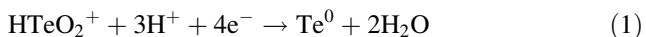
**Fig. 8** Optical transmission spectra of CdTe films deposited at pulse current density, curve (1) 15, curve (2) 20 and curve (3)  $25\text{ mA cm}^{-2}$  resulting in films of different compositions marked in the figure. Inset shows direct optical energy gaps determination using the Tauc's relation for direct transitions

### 3.6 Electrochemical studies

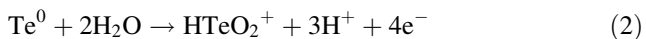
For understanding the pulsed current electrodeposition process of CdTe films, the tellurium electrochemistry is quite important. Voltammetric studies of tellurium reduction were carried out in  $0.10\text{ mM TeO}_2$  aqueous solution at  $\text{pH} \sim 2$ , without  $\text{CdSO}_4$ . Figure 9 shows a representative voltammogram scanned at the  $100\text{ mV s}^{-1}$  rate in the  $+1.0$  to  $-0.7\text{ V}$  range. First cathodic wave  $C_1$  at  $-0.12\text{ V Ag/AgCl}$  followed by a second cathodic process corresponding to a higher current wave  $C_2$  with current peak at  $-0.65\text{ V}$  and onset at  $-0.56\text{ V}$  was observed. In the anodic wave, no nucleation loop was seen except for a weak anodic wave at  $-0.45$  to  $-0.5\text{ V}$  range. Incursion towards the positive potentials shows two anodic waves. Anodic peak  $A_1$  at  $+0.46\text{ V (Ag/AgCl)}$  is a characteristic anodic stripping peak complimentary to cathodic process  $C_1$ . The second anodic process occurs at  $+0.65\text{ V (Ag/AgCl)}$ . In multiple scans, each time an excursion to  $C_2$  process is made, intensity of the anodic stripping peak increases. Electrochemical processes give strong peaks and wave plateau in the voltammetric plots in acidic aqueous solution. Tellurium exists in electrochemically active  $\text{Te}^{2-}$ ,  $\text{Te}^0$ ,  $\text{Te}^{4+}$ ,  $\text{Te}^{6+}$  valence states [25]. The peak  $C_1$  is identified with the reduction of Te (IV) specie into  $\text{Te}^0$  involving a four electron process [26],



**Fig. 9** Cyclic voltammogram scanned at 100 mV s<sup>-1</sup> in the potential range +1.0 to -0.70 V with Ag/AgCl reference electrode in electrolyte comprising of 0.1 mM TeO<sub>2</sub> aqueous solution in H<sub>2</sub>SO<sub>4</sub>



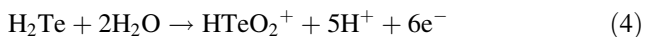
The correlated anodic peak A<sub>1</sub> is assigned to anodic stripping wave of Te<sup>0</sup> as follows,



The cathodic peak C<sub>2</sub> at higher negative potentials is associated with H<sub>2</sub>Te formation as follows

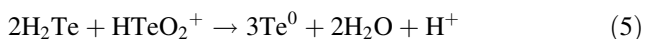


This cathodic reaction is not due to H<sub>2</sub> evolution, since such a process should give peak at >0.9 V (Ag/AgCl) which is well separated from the C<sub>2</sub> peak position. Formation of H<sub>2</sub>Te is not unusual and has been seen in Pt electrodes around the same potential [24, 26, 27]. The reverse wave manifests as anodic wave A<sub>2</sub> as follows,



The six electron anodic process is seen if an excursion to cathodic wave C<sub>2</sub> is made, which is due to the combined reaction given by Eqs. 1 and 3.

Anodic peak A<sub>1</sub> increases and peak C<sub>2</sub> decreases with each incremental scan. This suggests additional pathways for the deposition of more Te. During the anodic cycle after C<sub>2</sub>, plateau C<sub>3</sub> indicates that the recovery process is rather weak. As suggested by Mori et al. [24], this may be due to partially irreversible chemical reaction between electro generated H<sub>2</sub>Te after cathodic wave C<sub>2</sub> and adsorbed HTeO<sub>2</sub><sup>+</sup> species on the FTO coated cathode, which is given by [28],

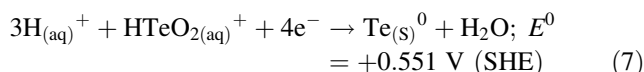
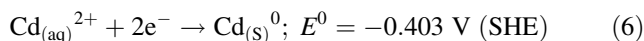


This gives additional deposition of Te<sup>0</sup> in each voltammetric scans. Incremental increase in the anodic stripping

peak A<sub>1</sub> (Eq. 2) is reflective of this process. H<sub>2</sub>Te forms at potentials <-0.68 V (Ag/AgCl) or ~-0.7 V (SCE), which reacts with adsorbed HTeO<sub>2</sub><sup>+</sup> ions to form Te<sup>0</sup> over cathode surface. In summary, the voltammetric results show sequential reduction of Te from Te (IV) to Te (0) and onto Te (-II) species.

### 3.7 CdTe film growth mechanism

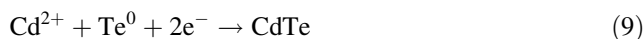
Present understanding of the electrodeposition of various compound semiconductor CdTe [24, 29], ZnTe [30] and MnIn<sub>2</sub>Te<sub>4</sub> [31, 32] thin films is based on the DC method. With Te in acidic (H<sub>2</sub>SO<sub>4</sub>) electrolytic medium present as stable HTeO<sub>2</sub><sup>+</sup> ionic species, DC electrodeposition of, say, CdTe films takes place primarily by cathodic reactions involving Cd<sup>2+</sup> and HTeO<sub>2</sub><sup>+</sup> which occur at widely differing potentials E<sup>0</sup> given by [19, 33],



Once the precursors are reduced to elemental Cd<sup>0</sup> and Te<sup>0</sup>, CdTe formation takes place by solid-state reaction over the substrate as shown below [33, 34],



The Gibbs free energy of formation ΔG<sup>0</sup>, causes a shift in the Cd deposition potential from -0.403 V (SHE) at the CdTe/Cd phase boundary to -0.403 V + 0.546 V (ΔG/2F) = 0.143 V at the CdTe/Te phase boundary. Thus, to deposit CdTe films in stoichiometric proportion by the DC method, more positive potentials are used as Cd under potential deposition (UPD) is driven by free energy gain due to Te deposition. Following the adsorption of HTeO<sub>2</sub><sup>+</sup> and subsequently its reduction over the electrode surface as described by Eq. 7 [27, 29, 35], Cd<sup>2+</sup> ions immediately assimilate into growing Te nuclei to form CdTe. A mere nucleation rather than the monolayer Te deposition is sufficient to initiate CdTe formation as follows [24],



Thus, as CdTe formation in DC electrodeposition is preceded by Te<sup>0</sup> nucleation over the substrate, CdTe film growth is HTeO<sub>2</sub><sup>+</sup> diffusion controlled and Te<sup>0</sup> formation process determines the rate of CdTe film deposition. As the solution concentration of HTeO<sub>2</sub><sup>+</sup> is extremely low in most DC CdTe electrodeposition baths and practically reduces to zero at the cathode/electrolyte interface, the rate of film deposition is very slow, typically 0.1 – 0.3 μm h<sup>-1</sup>. Furthermore, as the CdTe deposition is usually carried out at a potential more positive than the redox potential of the less noble species Cd<sup>2+</sup> [24, 29], this also contributes to

the reduction in the rates of film formation. Composition of the CdTe films also critically depends on the deposition potential. More negative potentials may result in an increase in Cd concentration and more positive potentials into Te rich CdTe film formation.

The electrochemical processes for the CdTe film growth in pulsed current deposition differs from that in the conventional DC electrodeposition. In the unipolar pulsed current electrodeposition of CdTe films, pulses of current of high amplitude  $5\text{--}15\text{ mA cm}^{-2}$  are applied for extremely short duration, which drives the system towards large negative potential conditions. The voltammetric studies described above show  $\text{H}_2\text{Te}$  formation at high cathodic potentials (Eq. 3). Free Cd deposition also occurs under cathodic potentials  $\leq -0.68\text{ V (SCE)}$ . It is thus suggested that in the pulsed current deposition CdTe formation could involve reaction with  $\text{H}_2\text{Te}$  as follows,



The pulsed current electrodeposition conditions favour a direct 6-electron process (Eq. 10) which is a combination of 2-step reaction process given by Eqs. 1 and 3. Deposition potentials in DC electrodeposition never exceed the electrochemical potential for  $\text{Te}^0$  reduction to  $\text{H}_2\text{Te}$  and the CdTe film growth is by reduction of Te with Cd as shown by Eqs. 7 and 9 [36]. The  $\text{H}_2\text{Te}$  formed at the cathode is unstable unless involved in a reaction such as with  $\text{Cd}^{2+}$  reduced at the cathode to form CdTe, a situation which is easily created in pulsed electrodeposition. The pulsed current density determines the reduction rate and the surface coverage of  $\text{Cd}^{2+}$  as well as  $\text{H}_2\text{Te}$  generation and reaction rates. At high-pulsed currents, overpotential conditions needed for  $\text{Cd}^{2+}$  and  $\text{HTeO}_2^+$  reduction to Cd and  $\text{H}_2\text{Te}$  are easily reached. Since surface coverage of  $\text{Cd}^{2+}$  is nearly 100% and there are no sites for Te deposition, CdTe film growth is highly stoichiometric. The total current supplied by the pulse is utilized in charging the double layer capacitor ( $i_c$ ) as well as in the deposition of CdTe, ( $i_F$ ). During the pulse OFF period, the double layer capacitor is discharged with a time constant,  $T_D$ . If  $T_{\text{OFF}} \ll T_D$ , a condition is reached when the potential has a finite value, although the applied pulsed current drops to zero (see Fig. 2a). Consequently, the Faradaic current,  $i_F$ , has a finite value and decays slowly during the OFF period. If  $T_{\text{OFF}} \gg T_D$ , the potential and hence  $i_F$  drops to zero (see Fig. 2b). Alternatively, when  $T_{\text{OFF}} \leq T_D$ ,  $i_F$  oscillates around an average value and is never zero. Thus, the cathodic potential is driven from extreme negative values during the pulse ON period to moderately negative values during the pulse OFF period. The magnitude of oscillations depends on the level of damping effect of  $T_{\text{OFF}}$  over  $i_F$  and

relative difference between  $T_{\text{OFF}}$  and  $T_D$ . Electrochemical steps in the formation of CdTe during the pulse OFF periods are thus different from the pulse ON period. When the OFF period of pulses is extremely short and the damping effect on  $i_F$  is stronger, the corresponding cathodic potential traverses the wave  $C_3$  (Fig. 9). In this case, there is deposition of Te due to reaction given by Eq. 5. Tellurium in the free-state reacts with  $\text{Cd}^{2+}$  until the next current pulse switches the mode of CdTe deposition according to the six electron process given by Eqs. 10 and 11. If the pulse OFF time is such that the damped value of  $i_F$  corresponds to the electrochemical wave  $C_1$  (Fig. 9), then during the early stages (short OFF periods) the CdTe deposition process step would be as in Eqs. 7 and 9 as long as the potential stays within the deposition range. For large cathodic potentials beyond the  $C_1$  wave, during the pulsed current OFF cycle and as a large number of Te nuclei are present, the CdTe growth process is controlled by faster  $\text{Cd}^{2+} \rightarrow \text{Cd}^0$  kinetics [24]. CdTe film growth rate is decided by the  $\text{Cd}^{2+} + \text{Te}^0 + 2\text{e}^-$  process, rather than by the reduction of  $\text{HTeO}_2^+$  into Te. In this case, excess Cd inclusion is a strong possibility. At longer pulse OFF times, as the  $\text{HTeO}_2^+$  concentration is reduced, reduction to  $\text{Te}^0$  (Eq. 7) slows down considerably. At this stage, reaction of the substrate deposited Cd deposited with  $\text{HTeO}_2^+$  in solution results in its oxidative dissolution. The open circuit Cd corrosion reaction at higher pulse off time can be given as follows:

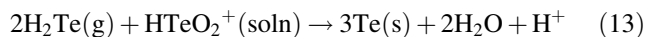


Besides forming CdTe, this reaction involves removal of Cd from the substrate deposited film. Consequently, at longer pulse OFF times (increasing  $T_{\text{OFF}}$ ) the Cd/Te ratio in the films will decrease, as indeed experimentally observed by us (Fig. 5). The Cd/Te composition ratio in the film is therefore determined by the  $T_{\text{OFF}}$  period between current pulses consistent with the results of compositional analysis in Fig. 5. Furthermore, at high applied pulsed current density and at sufficiently longer  $T_{\text{ON}}$  period that current pulse is ON, (increasing mean current density), CdTe film formation with excess Cd is possible as verified experimentally by the EDX data presented in Fig. 5.

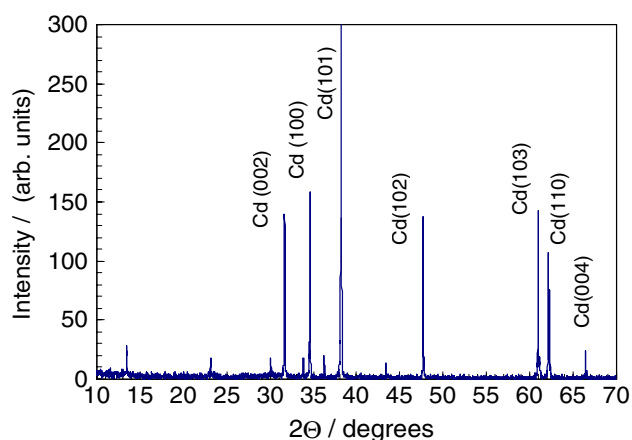
**Cd Tellurization:** The above discussion suggests that the CdTe film growth mechanism under pulsed current during the ON time is through the reaction of  $\text{H}_2\text{Te}$  with  $\text{Cd}^{2+}$  reduced over the cathode surface having 100% Cd coverage. To verify this mechanism, ex situ tellurization of Cd by cathodic electrochemical generation of  $\text{H}_2\text{Te}$  [37] under unipolar pulsed current conditions was investigated. We have carried out two separate tellurizing experiments, one using a Cd film coated Pt cathode and the other with a bare Pt cathode in a 0.1 mM aqueous solution of  $\text{TeO}_2 + \text{H}_2\text{SO}_4$



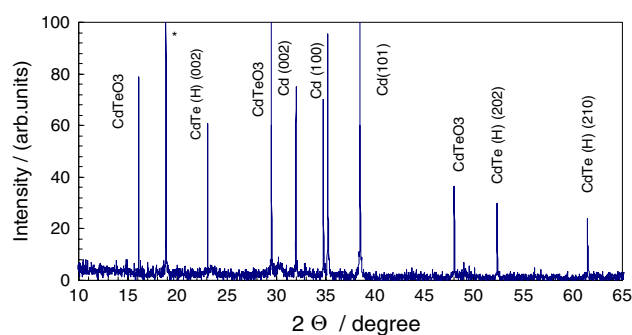
(without  $\text{CdSO}_4$ ) at  $\text{pH} \sim 2$ . For this Cd films of thickness 0.2–0.4  $\mu\text{m}$  were deposited by conventional DC electrodeposition from 1.0 M cadmium cyanate solution at  $\text{pH} 2\text{--}3$  over Si single crystal substrates. Electrodeposition was carried out in a bath that did not contain  $\text{CdSO}_4$  as a source of Cd ions under pulsed current conditions corresponding to transient  $\text{C}_2$  favoring  $\text{H}_2\text{Te}$  formation at the cathode.  $\text{H}_2\text{Te}$  at the cathode is unstable and is consumed by any of the following processes;



If  $\text{H}_2\text{Te}$  could not be adsorbed at the substrate, then according to reaction 13, in reaction with  $\text{HTeO}_2^+$  in the solution, it would result in the precipitation of elemental Te in the solution. We have observed this when pulsed deposition was carried out using a bare Pt cathode without a Cd coating. With a Cd coated Pt cathode, consumption of  $\text{H}_2\text{Te}$  resulted in the formation of CdTe, which was identified by X-ray diffraction studies shown in Figs. 10 and 11. Figure 10 shows diffraction pattern of the Cd-film displaying diffraction peaks (002), (100), (101), (102), (103), (110) and (004) belonging to the hexagonal Cd (ASTM card no. 5–674). Figure 11 shows an X-ray diffraction pattern of the same film after the pulsed current electrochemical tellurization step. Cd peaks at high  $2\theta$  values e.g. (102), (103), (110) and (004) have all disappeared and new lines corresponding to hexagonal CdTe (002), (202) and (210) have emerged. This strongly suggests that in the presence of Cd,  $\text{H}_2\text{Te}$  formed at the cathode by unipolar current pulses-results in the formation of CdTe following reaction 14. Some lower  $2\theta$  Cd diffraction lines (002), (100) and (101) are still seen because, the tellurization process has partially converted the Cd film over the surface into CdTe, since the reaction with  $\text{H}_2\text{Te}$



**Fig. 10** X-ray diffraction pattern of Cd film electrodeposited over Si substrate



**Fig. 11** X-Ray diffraction pattern of the Cd film after tellurization carried out using stream of unipolar pulsed current of peak density  $\sim 15 \text{ mA cm}^{-2}$  and  $T_{\text{ON}}$  and  $T_{\text{OFF}}$  periods of 3 and 100 ms, respectively showing formation of CdTe

progressively slows down in the Cd film bulk. Visualizing a similar situation during electrodeposition from a bath having  $\text{Cd}^{2+}$  and  $\text{HTeO}_2^+$  ions, instantaneous reaction of  $\text{Cd}^{2+}$  ions reducing and nucleating as  $\text{Cd}^0$  over the substrate surface with  $\text{H}_2\text{Te}$  results in CdTe film growth on a continual basis. It may be mentioned that  $\text{H}_2\text{Te}$  is a known reducing agent and widely used to prepare tellurides of several metals such as Bi, Cd, Co, Cu, Fe, etc. by bubbling  $\text{H}_2\text{Te}$  through metal salt solutions [38].

## 4 Conclusions

Pulsed current electrodeposition offers a method to form highly stoichiometric polycrystalline CdTe thin films. Extremely short 25–300 ms periodicity and 3–50 ms duration pulses of high 5–15  $\text{mA cm}^{-2}$  amplitude drive the system towards large negative potential conditions. The growth of CdTe films is a result of cathodic formation of  $\text{H}_2\text{Te}$  and reaction with Cd layer deposited at cathodic potentials  $\leq -0.68 \text{ V}$  (SCE). Pulse periodicity affects the crystalline structure and morphology because etch back process during the pulse OFF period provides a fresh surface (sites) for the arriving adions to deposit and form a well oriented grain structure. Lower current density translates to lower charge (number of Coulombs) per pulse, which implies reduction in the impingement rate of depositing ionic species on the substrate. Periodicity of current pulses also affects the nucleation rate through the damping affect over the Faradaic current due to double layer capacitance. These attributes of the pulsed current electrodeposition process are significant for forming nanocrystalline and nanostructured semiconductor and oxide films as has been shown by some recent studies [39, 40]. Substantial advantages of pulsed current CdTe electrodeposition over the conventional DC electrodeposition method in terms of higher rates of CdTe film growth and improved control of stoichiometric composition makes it

attractive in the production environment for CdTe solar cells. In the DC process deposition potential critical for CdTe stoichiometry is controlled by complex techniques including maintaining constant Te concentration over the entire growth process. In pulsed current electrodeposition potential control is not directly exercised, instead a simple control of the  $T_{ON}/T_{OFF}$  ratio of current pulses is adequate. CdTe film growth in pulsed electrodeposition occurs under mass transport conditions under the strong influence of high magnitude current typically  $\sim 5\text{--}20\text{ mA cm}^{-2}$  pulses which leads to much higher growth rates  $\sim 5\text{--}8\text{ }\mu\text{m h}^{-1}$  for CdTe films. The DC electrodeposition is done under diffusion-limited conditions of Te being the more noble species resulting in lower rates of film deposition.

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