# Preparation of CdTe coatings using the chemical deposition method

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## Abstract

CdTe coatings have been prepared by the reaction between films of cadmium hydroxide deposited on glass and a solution prepared by the dissolution of tellurium in hydroxymethane sulfinic acid. The films of CdTe having thicknesses in the range of 1 μm have been deposited by immersing the cadmium hydroxide coatings in an alkaline solution containing a tellurium compound at 5°C, which is warmed to 70°C. Annealing at ca. 150°C for 24 h gives highly crystalline, cubic CdTe. The preparation of an aqueous solution containing tellurium, which remains stable, is essential for the success of the process. Conditions for the preparation of such a solution are described. Details for the preparation of thin films of $Cd(OH)_2$ on glass, essential for the success of the process, are also described. The CdTe obtained was cubic, has a band gap energy of 1.51 eV, but does not display high photosensitivity. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Cadmium telluride is a II–VI semiconductor compound which is considered of great importance due to its applications in optoelectronic devices. In particular, it is a very promising material for use in photovoltaic devices because of its optimum bandgap (ca. 1.5 eV) for energy solar conversion and its high optical absorption coefficient ($> 10^4$ cm$^{-1}$). Several reports in the last few years have described solar cell efficiencies as high as 15.8% [1–3] based on CdTe/CdS heterojunctions, with CdTe as the absorber layer and CdS as the window layer. This application of CdTe films has increased the importance of research concerning the properties of this material and chemical deposition technique, which lead to the formation of CdTe films.

CdTe thin films have been prepared by several techniques, including MBE, CSVT, r.f. sputtering, thermal evaporation and electrodeposition. A search of the literature reveals that among these techniques the aqueous chemical bath deposition method has not lent itself to the preparation of CdTe thin films. This is one of the simplest and most economical techniques for the preparation of semiconductor thin films. It consists in the deposition of a semiconductor film on a substrate immersed in an aqueous solution which contains a source of the chalcogenide and dissolved metal ions. This technique of thin film preparation has been utilized for the preparation of semiconducting binary chalcogenides. Among these are PbS, PbSe, CdS, CdSe, CuS, ZnS and others. The preparation of semiconducting thin films of CdSe [3], serves to illustrate the method. The success of the chemical deposition method for the synthesis of thin films of sulfides and selenides utilizes a thiocarbonyl such as thiocetamide or a selenocarbonyl, such as *N,N*-dimethylselenourea. The only inorganic source of selenium has been selenosulfate, $SeSO_3^{2-}$.

Recently, Schreder et al. [4], have described the preparation of CdTe/CdS clusters which utilize a chemical deposition method. They prepared a CdTe/CdS suspension in dichloromethane by the addition of

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[(CH)$_3$Si]$_2$Te to a CdCl$_2$/CdS suspension in this solvent. This results in the formation of a liquid colloidal phase containing an optically transparent CdTe/CdS heterosol. These heterosols were used to prepare thin films using the spin-on technique. Pehnt and co-workers [5] prepared solutions containing nanoparticles of CdTe in butanol. The CdTe was prepared by the reaction of Cd(CH$_3$)$_2$ with (C$_8$H$_{17}$)PTe in the presence of ($n$-C$_8$H$_{17}$)$_3$P and ($n$-C$_8$H$_{17}$)$_3$PO. Schulz et al. [6] also described the use of CdTe nanoparticles prepared by the reaction of CdI$_2$ with Na$_2$Te. In both of these investigations a colloidal suspension of CdTe was converted to a CdTe thin film by the spray pyrolysis technique.

The main reasons for the lack of success in the preparation of CdTe films by chemical reaction in an aqueous solution have been the difficulty in the synthesis of tellurocarbonyls and the oxidative instability of aqueous solutions containing the telluride ion. Tellurocarbonyls have only been synthesized recently [7,8]. Our attempts to prepare thin films of metal tellurides utilizing tellurocarbonyls were unsuccessful owing to the extreme instabilities of these compounds. They undergo almost immediate decomposition in aqueous solution with the rapid deposition of elemental tellurium. In this work, we describe the successful preparation of thin films of CdTe by an exchange reaction described by the following equation:

$$Cd(OH)_2 + TeQ^* \rightarrow CdTe + 2OH^-$$
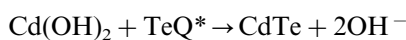
(*TeQ will be the designation used to describe the source of tellurium since its chemical form is not known.) The success of the method depends on the ability to prepare thin, adherent films of cadmium hydroxide on glass by means of the chemical bath deposition technique and the preparation of stable aqueous solutions containing tellurium, which do not oxidize to elemental tellurium upon atmospheric exposure. Both of these procedures are described here.

## 2. Experimental

### 2.1. Preparation of a soluble tellurium solution

This procedure yields a solution containing dissolved tellurium which is very stable. The procedure represents a modification of that described by Tschugaeff and Chlopin [9].

In a 250 ml flask equipped with a reflux condenser, under an atmosphere of nitrogen, is added 1 g of tellurium powder, 8.5 g of sodium hydroxide, 12.5 g of hydroxymethane sulfinic acid (monosodium salt dehydrate) also known as Rongalite and 50 ml of distilled water. The mixture is taken to reflux, stirred vigorously and the nitrogen atmosphere is maintained.

The reaction is terminated after about 45 min. At this time the deep purple solution fades to a faint pink color. The solution is transferred to a capped plastic bottle. The bottle is chilled in an ice bath which results in the separation of colorless crystals. The container is kept at 5°C until its use.

### 2.2. Preparation of cadmium hydroxide films

Cadmium hydroxide films on glass were prepared using a major modification of the method described by Call et al. [10]. The coating solution was made up of 5 ml of 0.5M Cd(NO$_3$)$_2$ in 30% H$_2$O$_2$, 15 ml of aqueous 1 M sodium citrate solution, 15 ml of 0.5M KOH in 30% H$_2$O$_2$, 8 ml of 30% H$_2$O$_2$ and 37 ml of distilled water. The components were stirred at room temperature. Four clean, microscope slides were immersed vertically along the wall of a beaker containing the freshly prepared coating solution and allowed to remain there for 2 h at 40°C. The glass slides became coated with adherent films of Cd(OH)$_2$, and were dried for 24 h in the air. The coated slides were coated for a second time by placing them in a freshly prepared coating solution for an additional 2 h. The thickness of the films thus prepared are of the order of 1 μm. The slides prepared in this manner, i.e. following two successive coats, were dried in air for 24 h prior to their conversion to CdTe.

### 2.3. Preparation of CdTe coatings

A beaker of 25 ml volume is filled with the cold TeQ solution (5°C). A cadmium hydroxide coated slide is placed in the beaker so that one edge rests against the bottom edge of the beaker while the upper edge rests against the upper, opposite wall of the beaker. The angle between the floor of the beaker and the resting slide is 45–60°, depending upon the geometry of the beaker. Immediately upon contact with the TeQ solution, the white Cd(OH)$_2$ film changes to a brown color and gradually intensifies in color to the dark brown color of cadmium telluride. The beaker containing the coating solution and the slide is immediately transferred to a water bath kept at 70°C. Following a total elapsed time of 5 min, the slide, now coated with cadmium telluride, is removed, rinsed with distilled water and dried in air at ca. 150°C for 24 h.

The steps required for the preparation of CdTe deposits on glass are summarized as follows:
1. A film of Cd (OH)$_2$ on glass is first prepared;
2. A solution containing a source of dissolved tellurium, designated as TeQ is prepared;
3. The Cd(OH)$_2$ film on glass is immersed in the TeQ solution where it is converted to CdTe.

## 2.4. Thin film characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Perkin–Elmer PHI 5500 ESCA system with Mg–K$_\alpha$ radiation and argon-ion sputtering. Optical transmission spectra were measured on a Hewlett–Packard UV–vis spectrometer with a glass substrate as the reference. X-ray powder diffraction patterns were measured on the Pad-4-Sintag in the Cu–K$_\alpha$ radiation region (1.541 Å) and electron microprobe analysis was
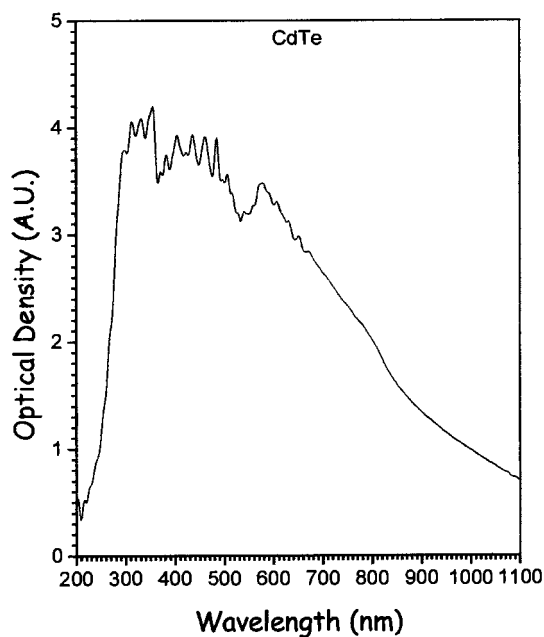
Fig. 1. Optical absorption spectrum of CdTe film.
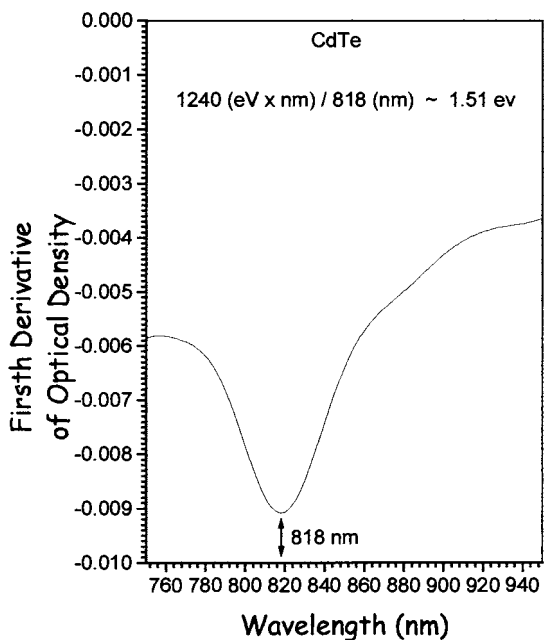
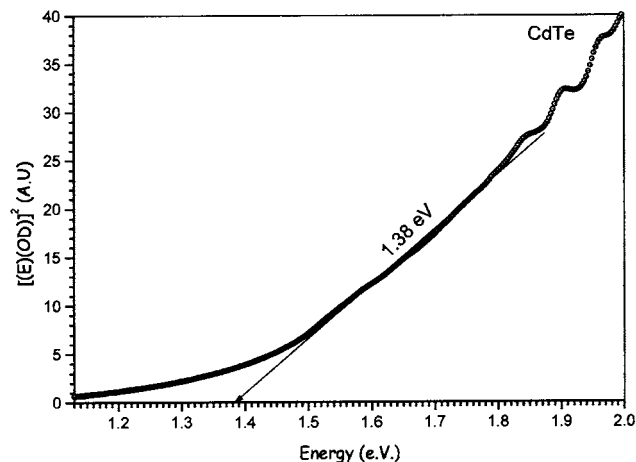Fig. 2. Numerical derivative of the absorption spectrum in Fig. 1.

Fig. 3. Plot of the square of energy times optical density vs. energy.

performed using the four spectrometer Cameca SX50 electron microprobe at an accelerating voltage of 15 kV and a beam current of 10 mA. Photocurrent measurements were performed in a Keithley 236 source measure unit.

## 3. Results and discussion

### 3.1. Characterization of the CdTe coatings

The CdTe coatings were studied using a number of physicochemical techniques. The results are now presented.

The optical absorption spectrum and the first derivative plots of a typical sample are shown in Figs. 1 and 2, respectively. Using the first derivative criterion of the optical absorption spectrum, the absorption edge is placed at a wavelength of 818 nm. This corresponds to a band gap of 1.51 eV, in excellent agreement with accepted values [11,12]. Nevertheless, using linear adjustment of the square of the absorption coefficient yields a value of 1.38 eV for the band gap; this is shown in Fig. 3. It is generally preferable to use the first derivative model in approaching the band gap. The samples we prepared were not sufficiently transparent to be well measured; this can be seen in the weak shoulder of the absorption spectra of the Fig. 1.

In Fig. 4 is shown an X-ray diffraction (XRD) pattern of a cadmium telluride film, which was annealed in air at 150°C for 24 h, and also a XRD pattern of its glass substrate. The results show that a crystalline material is obtained. The three peaks at $2\theta = 23.88$, 39.48 and 46.60° correspond very closely to those reported for cubic CdTe [13], viz. 23.76, 39.31 and 46.43°. Nevertheless, one Cd(OH)$_2$ peak and one CdTe$_3$O$_8$ peak, appear.

An electron micrograph of the chemically deposited CdTe film is shown in Fig. 5. In this figure, it can be seen that the crystalline aggregates are fairly uniform in size and the their mean size is about 500 nm. The individual crystal size, as calculated from the Debye–Scherer equation [14], is approximately 21 nm.

In Fig. 6, a cross-sectional photograph by BSEM of the CdTe films, including graphs of ion distributions, are shown. From this, it is possible to conclude that the conversion to CdTe is not 100%.

The results of XPS measurements, Fig. 7, demonstrate the presence of Te and Cd with binding energies of 579.2 and 412 eV, respectively. In the same figure,
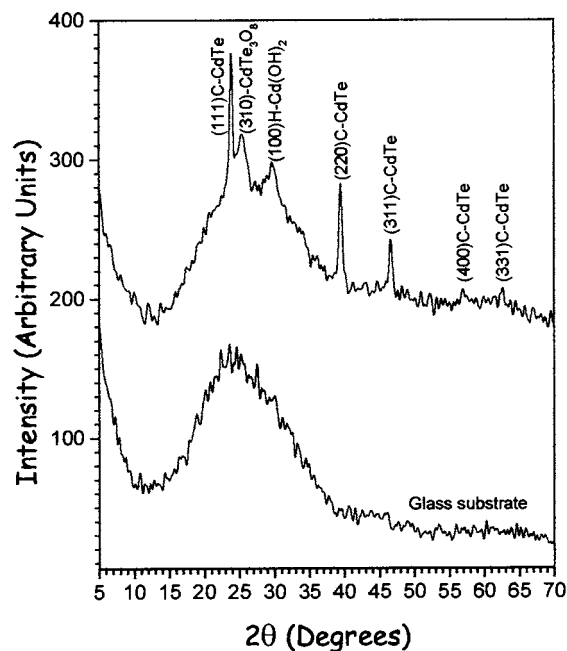


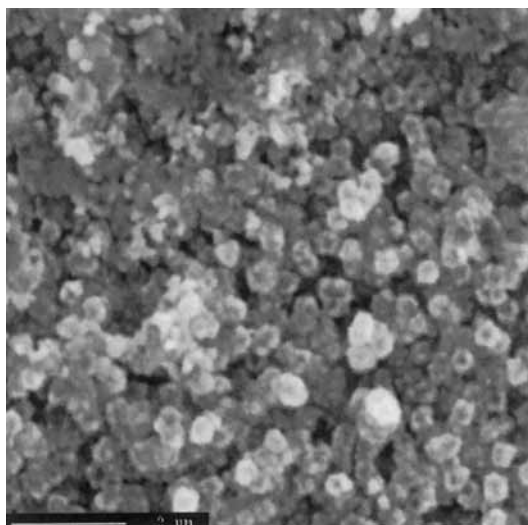Fig. 4. XRD spectrum of CdTe film and glass substrate.



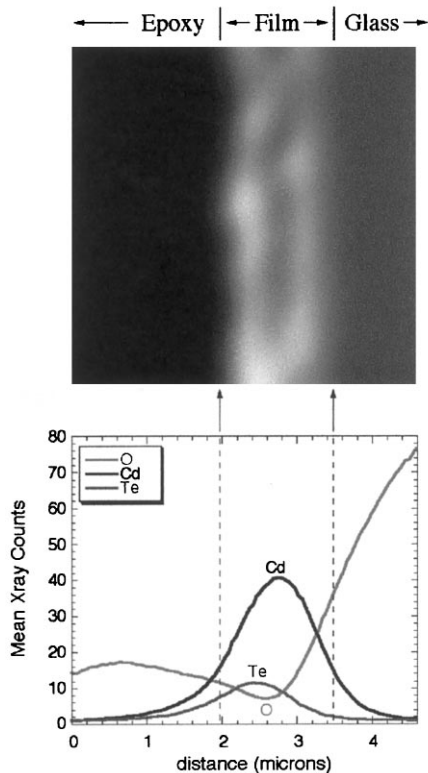Fig. 5. SEM photograph of CdTe film.



Fig. 6. Cross-section photograph by BSEM of the CdTe film, including graphs of ion distributions.
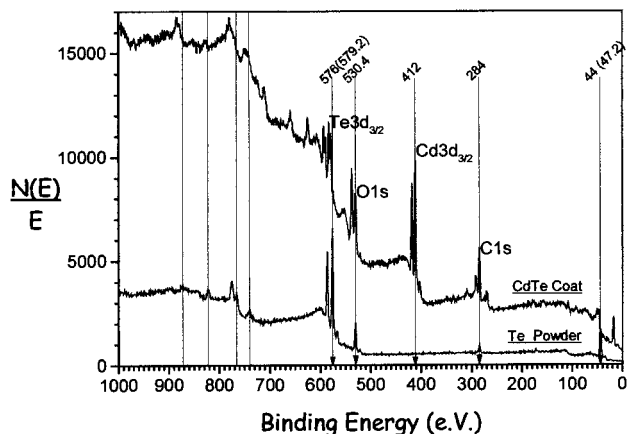


Fig. 7. XPS-measured spectra of CdTe film and Te° powder.

we can see a 3.2 eV shift from Te° (44 and 576 eV) powder peaks, measured with the same equipment. In Fig. 8 is shown an expanded portion of XPS spectra for the Te region of our material, from this it is possible to conclude that tellurium is bonded to cadmium.

For the photocurrent measurements we use a large enough surface of the CdTe film to print two parallel silver electrodes of 5 mm length each, and of 5 mm separation distance. The dark–light–dark intervals, the

photocurrent measurements and a 10 V bias voltage used were done in the direct way, by using a Keithley 236 source measure unit. In Fig. 9 these measurements of the material are shown. They show a characteristic current step under 300 lux of illumination. This material was not as photosensitive as materials shown in Refs. [3,15]. Also, the sheet resistance ($R_\square$) in the dark and under illumination (photo) were measured, $R_{\square\text{dark}} = 4.34 \times 10^{10}$ $\Omega$, and $R_{\square\text{photo}} = 6.57 \times 10^9$ $\Omega$. Therefore, the electrical conductivity ($1/R_\square d$) of the film may be estimated using a film thickness ($d$) of 1 $\mu$m, $\sigma_{\text{dark}} \simeq 2.3 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$, $\sigma_{\text{photo}} \simeq 1.52 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$.

### 3.2. Nature of the tellurium species

It has been assumed, based on the work of Tschugaeff and Chlopin [9], that when elemental tel-



Fig. 8. Expanded portion of XPS spectra for the Te region of our material.



Fig. 9. Photocurrent response of CdTe film.

lurium is dissolved in hydroxymethane sulfinic acid it is converted to telluride. However, based on our observations, this may not be true.

When the solution prepared in the manner described in Section 2 is chilled in ice, long, colorless needles separate. In solution, these crystals are quite stable, but they are extremely unstable in air. Immediately upon exposure to the air, they become dark. The dark color intensifies upon exposure, the crystals appearing black.

It was possible, in a dry, inert atmosphere, to separate and mount crystals suitable for the collection of X-ray data. At this time, the only definitive characterization that can be made is that tellurium is present at a level of 34.5% and hydrogen at a level of 5.49%. The large concentration of hydrogen suggests the presence of considerable amounts of water. The complete structure has not been solved. Sulfur and carbon are absent. Until the structure is solved, the source of tellurium is being designated as TeQ.

### 3.3. Exchange reactions

The use of exchange reactions for the synthesis of semiconducting thin films has been reported previously [16]. In this report, it was demonstrated that zinc selenide, when immersed in a solution of Cu(II) ions, converted to CuSe. Similar attempts were made in this investigation. Thus, films of CdS, CdSe and CdS/CdSe, all prepared by chemical bath deposition, showed a maximum percentage of exchange of 2–5% when immersed in a solution of TeQ prepared in the manner described in this report. The degree of exchange was measured by electron microprobe analysis.

### 3.4. Success of the cadmium telluride deposition

The success of the chemical bath deposition technique depends upon the slow, controlled precipitation of the desired metal chalcogenide. It was attempted to produce cadmium telluride coatings by anion-exchange between a metal salt film and a solution of telluride (TeQ), in water. But soluble Te$^{-2}$ salts undergo a very rapid oxidation accompanied by the deposition of elemental tellurium. Because of the extreme instability of telluride with respect to atmospheric oxidation, such attempts were unsuccessful. In the present report the success of the procedure can be attributed to two factors. The first is the stability of the TeQ solution and the second is the use of cadmium hydroxide thin films.

The TeQ solution, prepared in the manner described, contains an excess of sulfinic acid (Rongalite) which functions as a reducing agent. It appears that the oxidation of the sulfinic acid occurs more easily than the oxidation of the tellurium. A similar observation has been made with respect to the action of sulfite, which inhibits the oxidation of selenourea [17].
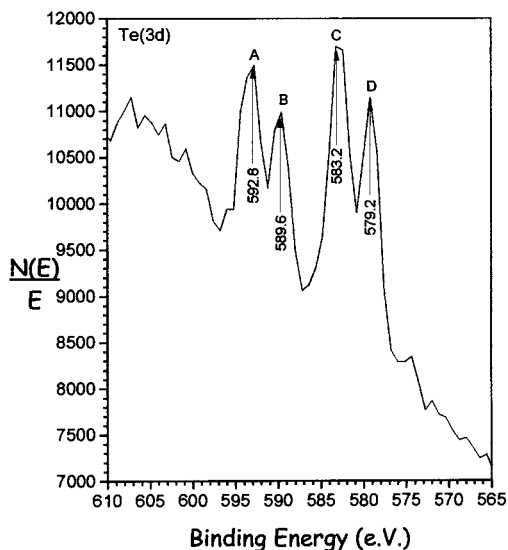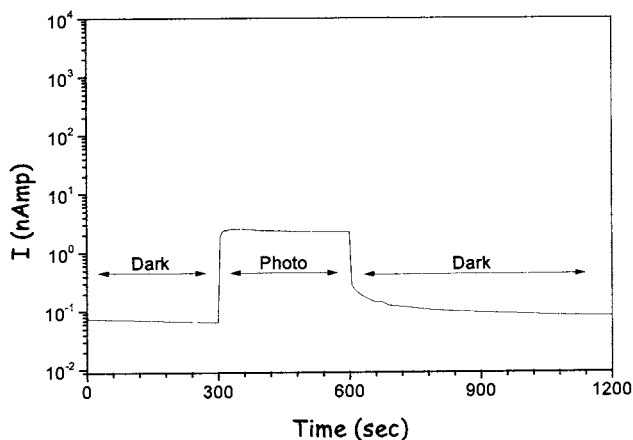
The cadmium hydroxide films on glass very likely convert to the oxide on drying at 150°C or 200°C. The $Cd(OH)_2$ films are uniform and adhere strongly to the glass substrate. Because the telluride solution is strongly basic, the oxide film remains fixed and stable in the alkaline medium. Although a solubility product constant is not reported for CdTe, it is likely that it is much less soluble than the oxide. Thus, the reaction may be given by:

$$Cd(OH)_2 + TeQ \rightarrow CdTe + 2OH^-$$
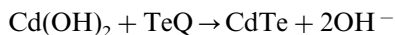
Many variables including time of immersion, temperature, tellurium concentration and others were investigated. Optimum results were obtained when films were prepared in the manner described.

## 4. Conclusion

A procedure is described which allows for the preparation of films of cadmium telluride on a glass surface. The success of the method depends upon the manner of preparation of a glass surface coated with cadmium hydroxide and the synthesis of a tellurium solution, which remains stable (i.e. no deposition of elemental tellurium due to atmospheric oxidation) during the coating procedure. Details are given for the preparation of the reactants.

If the procedure can be adapted so as to make possible the deposition of cadmium telluride on a film such as CdS, the potential for practical photovoltaic applications exists.

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