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# Thin-film CdTe for imaging detector applications

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## Abstract

Using the method of electrodeposition from aqueous electrolyte, we are able to grow thin films of CdTe as the basis of a direct semiconductor converter for large area X-ray imaging applications. This growth technique has the advantage of operating at low temperature with relatively low current densities and is therefore compatible, in principle, with a large-area hydrogenated amorphous silicon active matrix readout. Such a hybrid detector could prove to be an excellent optical sensor in the near term, and in the long-term advances in growth techniques may allow large area X-ray sensors to be fabricated. Currently, we are able to grow films to a thickness of 1  $\mu\text{m}$  with reasonable mechanical quality. Problems that we have been identified in growing CdTe films include achieving good substrate adhesion and maintaining good stoichiometry over the full substrate area. Results will be presented to describe our approach to CdTe film growth and to show how film quality depends on both deposition time and electrolyte stirring rate. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** CdTe thin-film growth; Electrode position; Application in imaging

## 1. Introduction

The continuing technological advancement towards improvements in digital X-ray imaging using active matrix image sensors requires research into techniques for the growth of suitable X-ray converters. The main semiconductors of interest are CdTe, CZT,  $\text{HgI}_2$ ,  $\text{PbI}_2$  and  $\text{TlBr}$ . Interest in these materials results from their high  $Z$  and density and their wide band gap produces a low leakage current across the detector. Among these, CdTe and its ternary alloy  $\text{CdZnTe}$ , have the best charge transporting properties for a single crystal [1]. Allied to this are the well-known technologies for plating

CdTe over large areas and it is arguably the best understood of the above semiconductors.

Thin films of CdTe have previously been prepared by various techniques such as vapour evaporation [2,3], sputtering [4], close-spaced vapour transport [5,6], screen printing [7], spraying [8], chemical vapour deposition [9] and electrodeposition [10,11]. Among these techniques, electrodeposition shows promise for the growth of CdTe thin films over large areas. It is a relatively simple technique that can be researched and optimised on the small scale and easily expanded to the large scale. It does not require any particularly expensive equipment and plating is carried out only on the substrates so as to minimise the material costs.

It has also been shown that if care is taken to purify the electrolyte prior to deposition, the

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impurities in the resultant electrodeposited films are less than in 99.999%, pure CdTe is available from commercial sources [12,13]. The thickness of the film can also be controlled by monitoring the quantity of charge passed during the deposition [14].

For CdTe there exists the possibility of production of both n- and p-type layers which are obtained through a simple change in the deposition potential [15,16]. Further, doping can be achieved through the addition of desired species to the electrolyte [17].

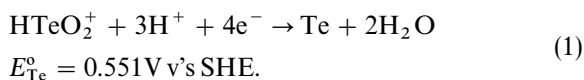
The majority of previous work carried out on CdTe growth by electrodeposition is motivated by the solar cell industry. The optical band gap of 1.5 eV and the direct mode of transition are highly desirable for this application. Indeed, small area solar cells based on the n-CdS/p-CdTe junction have produced efficiencies as high as 15.8% [18].

The cathodic electrodeposition of CdTe was successfully carried out from an aqueous electrolyte by Panicker et al. [10] and Kroger [19] at or near room temperature. The deposition normally takes place using an acidic aqueous solution containing  $\text{CdSO}_4$  and/or  $\text{CdCl}_2$  and  $\text{TeO}_2$ .

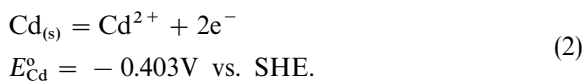
In this paper we discuss our initial study of the deposition process of CdTe as a growth technique for a suitable X-ray interaction medium.

## 2. Theory

Various mechanisms for CdTe electrodeposition have been proposed in the past. Most commonly, the first step is thought to involve the  $4e^-$  reduction of  $\text{HTeO}_2^+$  to Te. Eq. (1) shows this and the standard potential against a standard hydrogen electrode, SHE.



This reaction is followed by Cd deposition and reaction to form CdTe. For Cd the relevant electrochemical reaction and standard potential are



The deposition of Cd and Te in the ratio of 1 : 1 is carried out as follows. The potential is applied at a value more positive than that required to deposit the less noble species, in this case Cd. This leads to a reduction in the concentration of the more noble element Te, at the interface. The energy required to deposit Cd is achieved through the large free energy associated with the formation of CdTe from Cd and Te.

The free energy of formation of CdTe,  $G_{\text{CdTe}}$ , is as large as  $98.4 \text{ kJ mol}^{-1}$ . CdTe can therefore be grown from the standard value of the CdTe/Cd boundary,  $-0.403 \text{ V vs. SHE}$ , to the CdTe/Te boundary of  $-0.403 + G_{\text{CdTe}}/2F = 0.143 \text{ V vs. SHE}$ .  $F$  is the Faraday constant.

## 3. Experimental

### 3.1. Choice of substrate

The majority of work carried out on CdTe electrodeposition has used metallic or CdS-coated glass as the substrate. Our eventual aim is the growth onto the metal readout pixels of an active matrix array. However, metal foils compromise measurement of transmission through the growing film, which can be a useful diagnostic. Therefore, we grow films on metal-coated glass. The metal is thin enough ( $< 40 \text{ nm}$ ) to be transparent at visible wavelengths.

### 3.2. Substrate preparation

Substrates were borosilicate glass with a thickness of  $0.7 \text{ mm}$  and an area of  $12 \text{ cm}^2$ . The glass was cleaned with an isopropanol vapour cleaner for 2 hr before immersion in a sonic bath with distilled water. The substrates were then heated in a vacuum oven for several hours to outgas any absorbed water. A titanium layer (99.9 % pure, Sigma) was then evaporated on to the surface of the glass using an Edwards E306 thermal evaporation coater and allowed to cool in vacuum for several hours.

### 3.3. Electrolyte solution

Bath solutions were contained in a Teflon tank of capacity  $1.2 \text{ dm}^3$ . The solution is made from A.C.S

water, analytical grade cadmium sulphate, sulphuric acid and  $\text{TeO}_2$  (99.999%). Such solutions can be used for a long period of up to 8–9 months [20].

The solubility of  $\text{TeO}_2$  in an aqueous electrolyte is known to be very poor, but can be enhanced by the addition of sulphuric acid. According to Pourbaix [21] the solubility of tellurium dioxide is then given by

$$\log_{10}[\text{Te}] = -1.0\text{pH} - 2.0. \quad (3)$$

To maintain a constant amount of Te ion concentration in the solution,  $\text{TeO}_2$  in lump form was added to the electrolyte to maintain the concentration. The  $\text{TeO}_2$  was supplied in powdered form and converted to lumps in a quartz tube under heating.

### 3.4. Electrodeposition tank

The electrodeposition tank included the standard three-electrode system controlled with our own potentiostat. A platinum foil was used as the counter electrode.

The reference electrode was a cadmium reference electrode of our own design to avoid contamination of the solution. A standard calomel electrode would normally be used, but has been identified as a possible source of contamination leaking upto  $5 \text{ mM h}^{-1}$  of KCl into the electrolyte [22]. Our Cd

electrode comprises a glass tube with a Cd wire immersed into a 1 M solution of pH2  $\text{CdSO}_4$ . The electrode is separated from the electrolyte by a permeable membrane.

The working electrode was our metal-coated glass held in a Teflon holder with contact being made through a platinum pressure pad.

The electrolyte was continuously stirred using a 7.5 cm long Teflon coated magnetic rod with a minimum rotational speed of  $1 \text{ rev s}^{-1}$ . This introduces fresh electrolyte to the surface of the substrate. Further agitation was achieved with a  $\text{N}_2$  supply of  $0.21 \text{ min}^{-1}$  to the electrolyte to purge any dissolved oxygen.

The entire tank sat on a heater mat with a Teflon-covered platinum resistor used to maintain the temperature of the electrolyte to within  $\pm 1^\circ\text{C}$  in the range ambient to  $95^\circ\text{C}$ .

## 4. Results

Standard growth conditions were used for all data presented here. In each case, the growth substrates were immersed in the electrolyte at the appropriate potential for 1 hr. At the end of this period, the substrates were removed from the electrolyte and thoroughly rinsed with de-ionised

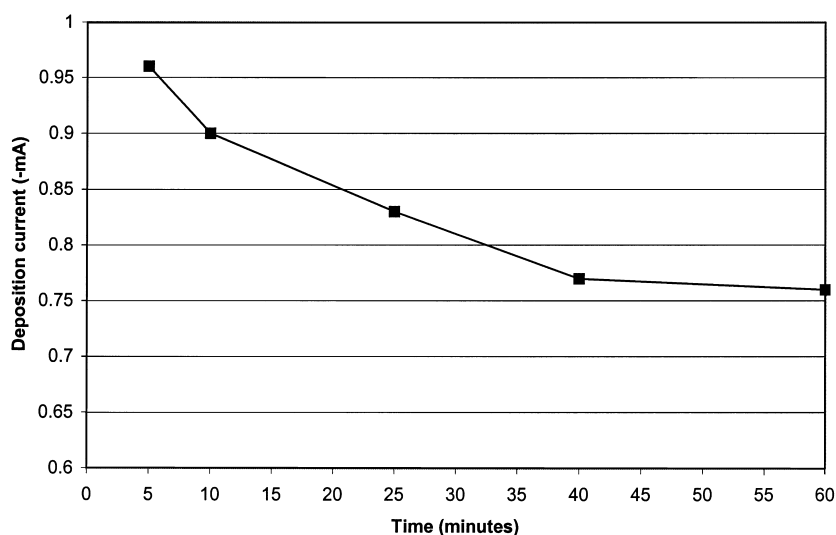


Fig. 1. Deposition current as a function of growth time. The grown area was  $12 \text{ cm}^2$  with the growth electrode held at a potential of  $-0.1 \text{ V}$  with respect to an  $0.1 \text{ M}$  Cd reference electrode.

water, dried with a nitrogen gun and sealed in dust tight containers.

Investigation of the deposition current as a function of growth time in the electrolyte consistently shows a reduction in deposition current over the 1 hr growth period. Representative data for a film grown with an electrolyte temperature of 25°C on a Ti-glass substrate held at a potential of  $-30$  mV with respect to the 1 M Cd reference electrode are shown in Fig. 1. These data are consistent with the previous observation [13] and the reduction in current is believed to be due to adsorbed hydrogen and oxygen initially present at the growth surface.

To analyse film stoichiometry, Energy Dispersive X-ray Analysis (EDX) was used. A result for a CdTe film grown at 25°C with the substrate held at  $+30$  mV with respect to a 0.1 M Cd reference electrode is shown in Fig. 2. The data indicate a Te: Cd ratio of 2:1 in the grown film with some Si signal due to the underlying borosilicate glass substrate and Ti from the contact metal. To date, a Te: Cd ratio of 2:1 has been achieved on all grown films and improved growth conditions that will achieve a 1:1 ratio are currently under investigation.

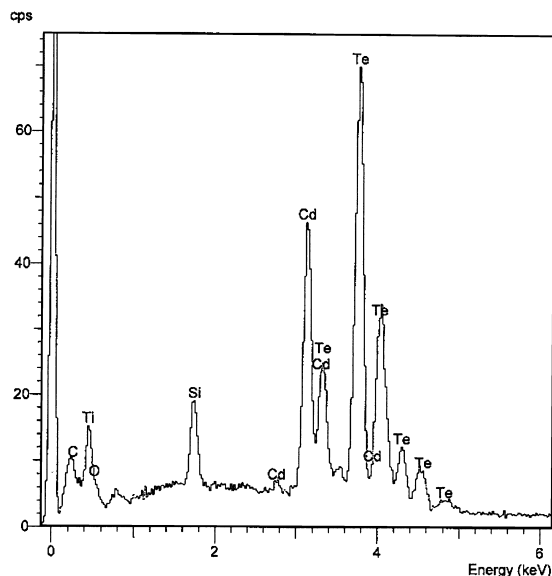


Fig. 2. Energy Dispersive X-ray Analysis (EDX) data for a CdTe film approximately 1  $\mu$ m thick. This result shows a Te: Cd ratio of approximately 2:1.

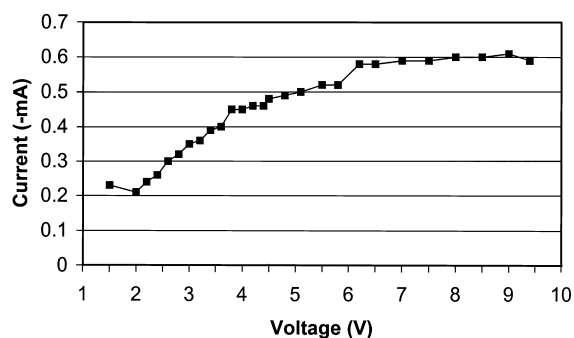


Fig. 3. Deposition current as a function of stirring rate. Stirring rate is parameterised in terms of the voltage used to drive the motor that spun a magnetic stirring rod.

As a further check on the growth process, an investigation of deposition current as a function of electrolyte stirring rate was conducted. Deposition current is directly proportional to the rate of film growth and consequently is an important parameter to optimise. Fig. 3 shows the result of such a study. Stirring rate is parameterised in terms of the voltage applied to the motor that spun the Teflon coated stirring bar. As expected [13] the deposition current increases approximately with the square root of stirring rate towards an asymptote. At slow stirring rate, deposition current is limited by the availability of  $\text{HTeO}_2^+$  at the growth surface. As rotation of the stirring rod increases, agitation of the electrolyte near the growth electrode tends to stabilise due to the presence of a boundary layer between the film surface and moving electrolyte.

## 5. Conclusions

This programme to deposit thin films of CdTe by electrodeposition is still at an early stage but has already demonstrated that films containing both Cd and Te can be grown using electrodeposition. The EDX measurements shown in Fig. 2 indicate that the required stoichiometry has not yet been achieved although the trends in deposition current with time and stirring rate match with other published data.

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