

## **CYCLIC VOLTAMMETRY STUDIES OF COPPER (II) AND TELLURIUM (IV) IONS IN ACIDIC AQUEOUS SOLUTIONS FOR THIN FILM DEPOSITION**

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**Abstract:** Cyclic voltammetry studies of copper (II) and tellurium (IV) ions in acidic aqueous solutions were carried out to determine the optimum condition for copper telluride thin film deposition. The voltammetry studies include reversible scans at different solution pH. Based on the voltammogram, suitable deposition conditions was determined to be in the range of -0.35 V to -0.45 V versus Ag/AgCl at pH values between 2.0 to 2.2 under non diffusion-limited conditions.

**Keywords:** *copper telluride, cyclic voltammetry, electrodeposition, metal chalcogenide, thin films*

## INTRODUCTION

The field of photoelectrochemical (PEC) cells for energy storage was initiated in 1972 by Fujishima and Honda [1]. PEC cells requirements for an efficient solar conversion system require reproducible deposition technique, consists of readily available material, good conversion efficiency, long-term stability and suitable for large scale production. The synthesis and characterization of metal chalcogenides thin films of different groups have attracted considerable attention due to their wide application prospects. These compounds are reported to be used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials [2]. They also possess certain criteria to make them potential candidates in PEC solar cells. These materials are usually prepared through electrochemical and chemical deposition method and are quite attractive for designing systems for electro-optics and PEC solar cells. An intensive research and development phase is the key to clarify important factors for module efficiency, environmental stability and production yield [3]. Copper chalcogenide thin films have number of applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes and microwave shielding coating [4-9]. Copper-tellurium alloys exhibit interesting behaviors like structural phase transition and variation of band gap as a function of component composition [10]. The Cu-Te system is reported to be the most complex among the copper-chalcogen systems, as shown in the Cu-Te phase diagram [11]. Copper telluride thin films have been prepared by chemical bath deposition [4], flash or vacuum evaporation [10], electrochemical method [12, 13], RF-sputtering [14], Cu/Te co-evaporation [15, 16] and by direct reaction of Cu evaporated on the top of a Te-enriched CdTe layer [17-19].

Electrodeposition has emerged as a simple, economical and viable technique, which produces films of good quality for device applications. Electrodeposition can be carried out using substrates with different sizes and shapes. Reactions involved occur closer to the equilibrium and the deposition process can be controlled more easily than in many high temperature gas phase methods. In addition, toxic gaseous precursors do not have to be used unlike in chemical gas phase methods [20, 21]. The only major limitation of electrodeposition is that the substrate has to be conductive. To our knowledge no detailed cyclic voltammetry studies has been performed for copper telluride systems prior to the electrodeposition process. In light of this, the goal of the present work is to study reaction mechanisms on the substrates which could provide better understanding on the deposition process.

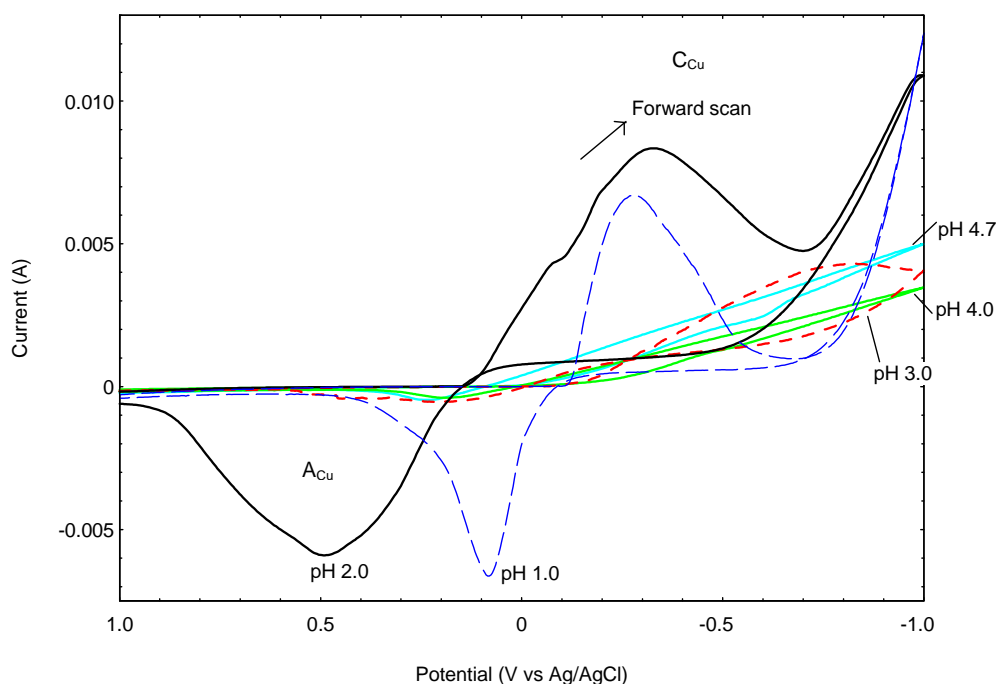
## MATERIALS AND METHODS

The solutions used contained dissolved 0.01M  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (R&M), 0.01 M  $\text{TeO}_2$  (Stream Chemicals). The pH value of the solution was adjusted with HCl (R&M). The electrolytes were prepared using analytical grade reagents and deionized distilled water. A potentiostat/galvanostat model EG&G PAR 263A with a three-electrode cell was used for cyclic voltammetry measurements. The electrodes were titanium substrates (0.8 cm diameter) as a working electrode, platinum wire (1 mm diameter) as a counter electrode and Ag/AgCl (KCl saturated) as a reference electrode. The reference electrode

was placed as close as possible to the working electrode. Cyclic voltammetry (CV) was used for studying deposition reactions and finding the appropriate deposition potential range. Cyclic voltammetry studies were performed on individual solutions containing copper and telluride ions to determine reduction and oxidation potentials ranges at different  $pH$ . CV studies on solution mixture at different  $pH$  were done to determine optimum condition to produce quality copper telluride thin films. The studies were done at room temperature ( $27\text{ }^{\circ}\text{C}$ ) and in unstirred solution condition. Purified  $\text{N}_2$  gas was purged into the electrolyte solution for at least 5 min to remove the dissolved oxygen before the experiment.

## RESULTS AND DISCUSSION

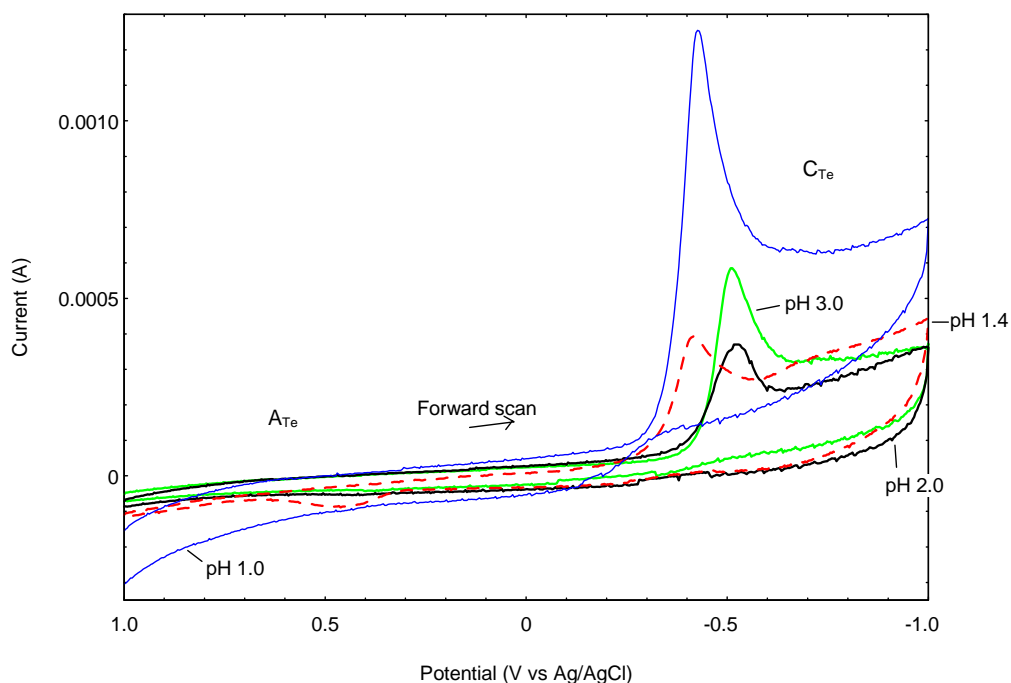
Figure 1 shows the CV plot for  $0.01\text{ M CuCl}_2$  solution at various  $pH$ . The forward scan was initiated from  $+1.00\text{ V}$  to  $-1.00\text{ V}$  and reversed to the initial potential. The voltammogram obtained for solution  $pH\ 1.0$  indicate reduction peak starting from  $-0.15\text{ V}$ . As the potential was swept to more negative regions, the cathodic peak increases to a maximum value at about  $-0.30\text{ V}$  before reducing to a lower value. These values are almost similar to values reported elsewhere at extremely low  $pH$  [22].



**Figure 1.** Cyclic voltammogram of  $\text{CuCl}_2$  solution at different  $pH$  (scan rate:  $30\text{ mVs}^{-1}$ );  $C_{\text{Cu}}$  – cathodic peak,  $A_{\text{Cu}}$  – anodic peak

$\text{Cu}$  film is deposited in this potential range. A sharp increase in the cathodic current was observed when the potential proceeds to more than  $-0.75\text{ V}$  which indicate hydrogen evolution reaction that normally occurs at higher potentials. Any deposition carried out at these high negative potentials would produce low quality films that would not adhere strongly onto the substrate [21, 23]. During the reverse scan, anodic current could be

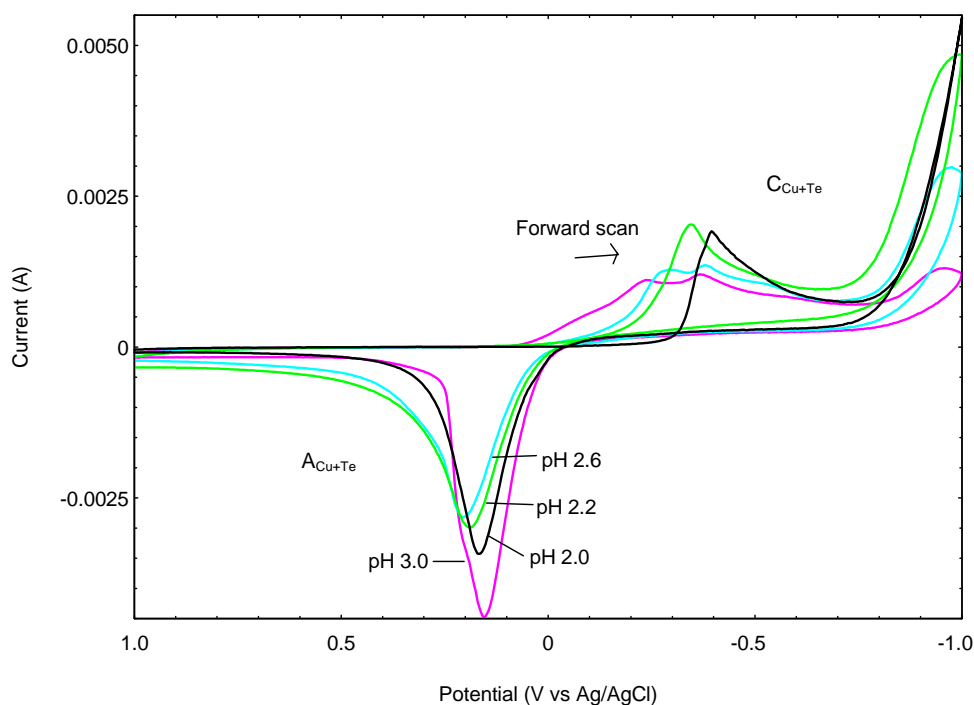
observed after  $-0.15$  V. The rise in the anodic current indicates oxidation process whereby deposited Cu element dissolves into the bath. When the experiment was performed at  $pH$  2.0, the forward scan produces broader cathodic curve with higher cathodic peak current indicating more Cu material being deposited onto the substrate. The cathodic peak potential was shifted to higher negative value of  $-0.40$  V. Further increase in the cathodic current beyond  $-0.75$  V supports hydrogen evolution process and thus could not be used as one of the deposition potentials for Cu films. During the reverse scan, the anodic curve starts at the same potential as the cathodic curve. However lower anodic peak current shows less dissolution of Cu film that was deposited during the forward scan. The anodic peak potential was shifted to more positive value compared to the scan performed at  $pH$  1.0. The anodic peak potential of  $+0.45$  V at this  $pH$  is very close to the cathodic peak potential of  $-0.40$  V which supports reversible redox process. Further increase in the solution  $pH$  (3.0, 4.0, 4.7) produced peaks corresponding to irreversible process. There was an absence of stripping anodic peak during the reverse scan indicating that Cu film deposited onto the working electrode surface failed to dissolve into the electrolyte. Specific working range for Cu deposition could not be determined at these  $pH$  conditions. The cathodic current increases continuously and proceeds into hydrogen evolution region. Thus, these  $pH$  values are not suitable for Cu deposition under the current condition. Figure 2 shows the CV plot for tellurium (IV) oxide solution at different  $pH$  conditions. The cathodic current profile looks similar at all  $pH$  values. The  $pH$  value could not be raised further due to difficulty in dissolving  $TeO_2$ . At  $pH$  1.0, the cathodic current increases beyond  $-0.35$  V and recorded the highest cathodic peak current at about  $-0.45$  V. Lower  $pH$  is also needed to maintain an appreciable amount of  $HTeO^{2+}$  in solution [24].



**Figure 2.** Cyclic voltammogram of  $TeO_2$  solution at different  $pH$  (scan rate:  $30\text{ mVs}^{-1}$ );  $C_{Te}$  – cathodic peak,  $A_{Te}$  – anodic peak

The cathodic current reduces beyond that potential and shows a tendency to increase as the potential was swept to more negative regions due to hydrogen gas evolution. During the reverse scan, appearance of anodic current was observed. However, the anodic current increased as the potential was swept to more positive regions without any presence of anodic peak current. The presence of small anodic current does indicate dissolution of tellurium film into the solution at smaller quantity.

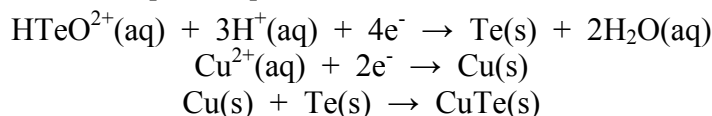
When the  $pH$  was raised to 1.4, presence of small anodic current at about +0.45 V could be observed indicating minor dissolution of telluride films into the solution. Further increase in the solution  $pH$  did not produce any anodic peak indicating strong adherence of the film onto the substrate. The cathodic peak potential at  $pH$  2.0 and 3.0 varied between -0.45 to -0.55 V. These potentials would be suitable for the deposition of telluride films under current conditions. Figure 3 shows the CV plot of solution mixtures containing copper and telluride ions. At  $pH$  values of 2.0 and 2.2, only single cathodic peak current appears between -0.35 to -0.45 V. During reverse scan, deposited film dissolves into the solution around +0.30 V. At higher  $pH$  of 2.6 and 3.0, two cathodic peak currents were observed indicating multiple reduction process. During this multiple reduction process, any deposition of a single element prior to the other element could produce single component film (copper or tellurium) rather than copper telluride film.



**Figure 3.** Cyclic voltammogram of  $CuCl_2$  and  $TeO_2$  mixture at different  $pH$  (scan rate:  $30\text{ mVs}^{-1}$ );  $C_{Cu+Te}$  – cathodic peak,  $A_{Cu+Te}$  – anodic peak

This would produce copper telluride films with the presence of excess copper or tellurium elements. The sharp increase after -0.75 V supports  $H_2$  formation reaction. The  $TeO_2$  added into the bath appears as  $HTeO_2^{2+}$  in the  $pH$  range used. The following

reduction mechanisms lead to the deposition of copper telluride thin films which is also suggested by other researchers [25 - 27]:



## CONCLUSION

Copper telluride thin films could be deposited in acidic condition in the pH range between 2.0 and 2.2. Any pH values below 2.0 would produce films with lower adhering properties that could peel off the substrate. An increase in the pH beyond 2.2 might produce films containing excess copper or tellurium which could change the bandgap value of pure copper telluride thin films.

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