

SOME PROPERTIES OF NANOSTRUCTURED CdTe FILMS FROM CHOLINE CHLORIDE - MALONIC ACID IONIC LIQUID

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This paper reports the electrodeposition of CdTe films on platinum and copper using ionic liquids based on choline chloride: malonic acid mixture at various temperatures. CdCl₂ and TeO₂ were dissolved in ionic liquid at concentrations in the range of 0.1-1M and 0.1-1mM, respectively. The mechanism of CdTe electrodeposition was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The results indicated that the CdTe compound films were obtained by induced codeposition of Cd and Te on Pt substrate. Nyquist and Bode impedance spectra show differences in Pt behavior due to its polarization at various cathodic potentials. The morphology and chemical composition of CdTe films potentiostatically deposited on Cu were determined by SEM and TEM microscopy.

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1. Introduction

The electrodeposition of semiconducting materials still represents, even after decades of study, a challenge, from both academic and economical points of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials [1].

Cadmium telluride, with its direct bandgap of 1.45 eV, is a material of great technological interest for application in photovoltaic cells; Cd Te is one of the few II–VI binary compounds which can act as both n- and p- semiconductor [2]. Its direct optical transition results in a large absorption coefficient that makes it a very attractive material, not only for photovoltaic conversion, but also for gamma-ray and infrared detectors, as well as electronic and optoelectronic devices [3].

The electrodeposition of CdTe semiconductor thin films is usually performed from aqueous alkaline solutions [4-6]; the mechanism of the formation of CdTe compound in ammonia electrolytes was discussed in the papers of Murase et al. [7, 8]. Optimum conditions of CdTe electrodeposition from ammonia–chloride buffer solutions with pH 8.4 have been determined by Dergacheva et al. [9] to be: the deposition potential -1.1 V vs. Ag/AgCl; 80°C and concentration ratio Cd(II):Te(IV) = 1:1 – 0.8:1. Pandey et al. [10, 11] have demonstrated the advantage of ethylene glycol based baths over aqueous baths. In their work they have shown that CdTe films can be electrodeposited on different substrates at relatively high temperatures (up to 140°C) from CdCl₂, KI and TeCl₄ in ethylene glycol; as a non-aqueous electrodeposition bath, it is much less influenced by hydrogen evolution. Also, Lade et al. [12] have prepared very good quality (compact, uniform and crack-free) polycrystalline CdTe thin films with hexagonal crystal structure by galvanostatic electrodeposition method using a similar ethylene glycol bath at 80 °C.

It has been shown recently that ionic liquid media based on mixtures of choline chloride are very promising, being very attractive as non-aqueous environments for the electrodeposition of metals, alloys or semiconductor electrodeposition [13, 14]. The advantages of these novel baths

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include: electroplating of very electronegative metals (which are difficult to be electrodeposited from aqueous solutions); significantly reduced hydrogen evolution at cathode; low water activity, which may lead to very different deposit structures and precise control of materials' composition and thickness. While somewhat lacking in conductivity (depending on their composition and/or working temperature), these ionic liquids are nevertheless electrochemically robust, with a rather large potential window and a very low vapor pressure. The good thermal stability of these ionic liquids is useful, as it allows one to obtain crystalline semiconductor films through direct electrodeposition at higher temperatures without subsequent annealing.

Semiconductor electrodeposition from ionic liquids is still underdeveloped; the electrodeposition of Cd and CdTe was investigated at glassy carbon, polycrystalline tungsten and platinum electrodes in a basic 1-ethyl-3-methylimidazolium chloride:tetrafluoroborate room temperature molten salt [15, 16].

Recently it has been shown that an ionic liquid can be formed as eutectic mixture of choline chloride (2 hydroxy-ethyl-trimethyl-ammonium, ChCl) with a hydrogen bond donor species such as a glycol, amide or carboxylic acid [17]. The present work reports the deposition of CdTe films using the choline chloride (ChCl) + malonic acid (1:1 moles) eutectic as supporting electrolyte; to the best of our knowledge such semiconductor films were not reported in literature as being electrodeposited from ChCl ionic liquids; this ionic liquid mixture is air and moisture stable, biodegradable and economically viable to be used in large-scale processes.

It was shown in earlier work [18-20] that TeO₂ dissolves well in both ChCl-malonic acid and ChCl-urea eutectics; the present study was confined only to ChCl: malonic acid (1:1 moles) ionic liquid. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence electrochemical couples of deposition/dissolution of Cd and CdTe, respectively.

2. Experimental

The supporting electrolyte was prepared by mixing choline chloride (ChCl, Aldrich 99%, used as received) with malonic acid (Aldrich 99%); by heating the two components in 1:1 molar proportions at above 80°C for 30 min, a homogeneous colorless liquid is formed. CdCl₂ (Merck) and TeO₂ (99%, Alfa Aesar) reagents as precursors of Cd²⁺ and Te⁴⁺ ions were also used as received, and were dissolved in the supporting electrolyte ChCl-malonic acid (ChCl-MA). In order to calculate the solution molarities the densities of ChCl-malonic acid ionic liquids reported in literature [21] were used.

An AUTOLAB PGSTAT 12 Ecochemie electrochemical workstation was used for all electrochemical measurements. A platinum sheet (0.5 cm²) was used as working electrode, whereas the auxiliary electrode was a platinum mesh. A platinum wire immersed in the working electrolyte (*i.e.* ionic liquid containing cadmium and/or tellurium ions) served as quasireference electrode. The Pt working electrode was polished with alumina paste, rinsed and dried before every measurement. The cyclic voltammograms were recorded at various scan rates from 2 to 100 mVs⁻¹. Electrodeposition processes were performed on the platinum working electrode at different polarization potentials (versus Pt quasireference electrode), different temperatures or time durations. EIS characterization was carried out in 100 kHz ≥ f ≥ 0.1 Hz frequency range with an *ac* voltage amplitude of ±10 mV; the impedances were represented as Bode spectra.

For a full characterization CdTe films were potentiostatically electrodeposited onto commercial copper sheets from ChCl-MA ionic liquids, without stirring. The Cu cathode had an exposed area of 1-2 cm²; a parallel Pt sheet was the anode and a Pt wire was used as quasireference electrode. The CdTe film's morphology was studied using SEM microscope (Bruker AXS Microanalysis provided with EDX) and TEM microscope (EM-410 Philips, 60 kV).

3. Results and discussion

It has been reported previously that tellurium compounds, such as BiTe, SbTe and BiSbTe, can be successfully electrodeposited from eutectic ionic liquids with choline chloride and

either urea [19] or malonic acid [20]. In chloride-rich and low water content media (as all eutectics containing choline chloride are), we assume that tellurium species may exist in solution as TeCl_x^{4-x} complex ionic species, most likely as TeCl_6^{2-} anion [16]. The mechanism for the electrodeposition of CdTe from aqueous solutions is still not very well understood, but most authors agree that the first step involves the reduction of Te(VI) species to elemental Te, followed by the reduction of Cd^{2+} and formation of CdTe with various stoichiometries [2, 22, 23]. For low water contents a direct discharge to elementary Te presumably takes place according to eq. (1):



When both Cd^{2+} and Te^{4+} ions are present in ChCl-malonic acid ionic liquids the recorded cyclic voltammograms have a complex appearance. A typical example is given in Fig. 1 where a comparison at 60°C of the system Pt/ 0.5M CdCl_2 + 0.5mM TeO_2 dissolved in ChCl-malonic acid (1:1 moles) at different scan rates is presented. For some systems the cathodic peaks are rather broad and ill-defined, but for all others the cathodic peak currents depend linearly on the square root of the scan rate, indicative of diffusion control.

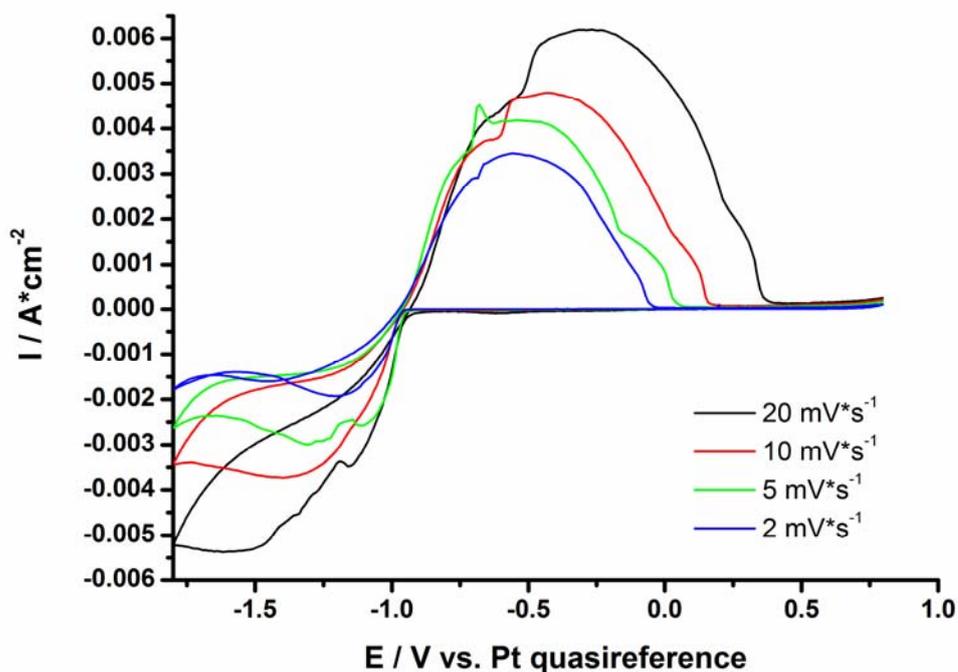


Fig. 1. Cyclic voltammograms for 0.5M CdCl_2 and 0.5 mM TeO_2 dissolved in ChCl-malonic acid (1:1 moles) eutectic at different scan rates; Pt electrode (0.5 cm^2), temperature 60°C .

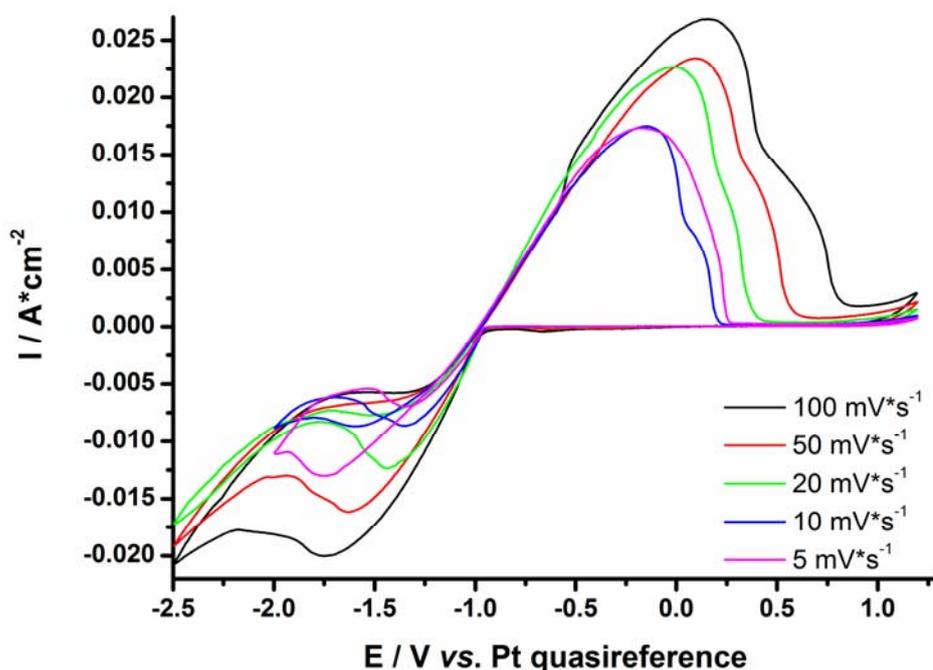


Fig. 2. Cyclic voltammograms for 0.5M CdCl₂ and 0.25 mM TeO₂ dissolved in ChCl-malonic acid (1:1 moles) eutectic at different scan rates; Pt electrode (0.5 cm²), temperature 40°C.

On the cathodic scan the bulk deposition of CdTe takes place as the current starts to rise significantly at around -0.9 V. An ill-defined, rather broad electrodeposition peak is noticed, with another broad, dissolution-like peak on the anodic branch.

Cyclic voltammograms for systems having a lower Te concentration are presented in Fig. 2. For this ionic liquid solution less rich in Te ions (0.25mM TeO₂) the voltammograms show somewhat lower peak currents (peak currents proportional to the concentration of TeO₂ have been reported previously [22]); the same is noted for the anodic dissolution peaks as well. Note that in Fig. 2 the rather large cathodic peak at -1.75 V at 5 $\text{mV} \cdot \text{s}^{-1}$ is seen on the reverse scan; this behavior is likely due to nucleation (the regular reduction peak is quite small at this scan rate, but it is still visible around -1.3 V). At 10 $\text{mV} \cdot \text{s}^{-1}$ the cathodic peak on the reverse scan is much smaller, but still visible, while at larger scan rates this peak virtually disappears.

Fig. 3 and Fig. 4 show comparatively the voltammograms for the same Cd²⁺ and Te⁴⁺ ions concentrations at different temperatures. The shapes of cathodic and anodic branches are quite similar, with increasing currents as the temperature rises, as expected. A current crossover is observed on the cathodic branches at potential values ranging from -0.75 to -1.5 V (depending on both temperature and composition), indicative of a typical nucleation process (see *e.g.* [24, 25]). Note also from **Error! Reference source not found.** that the cathodic peak seen on the reverse scan becomes much more pronounced as the temperature increases, which is likely due to a faster nucleation at higher temperatures. At larger concentrations and also a higher Te/Cd ratio in solution (Fig. 4) the cathodic curves become featureless, while the anodic dissolution peaks show that some CdTe is still deposited [26].

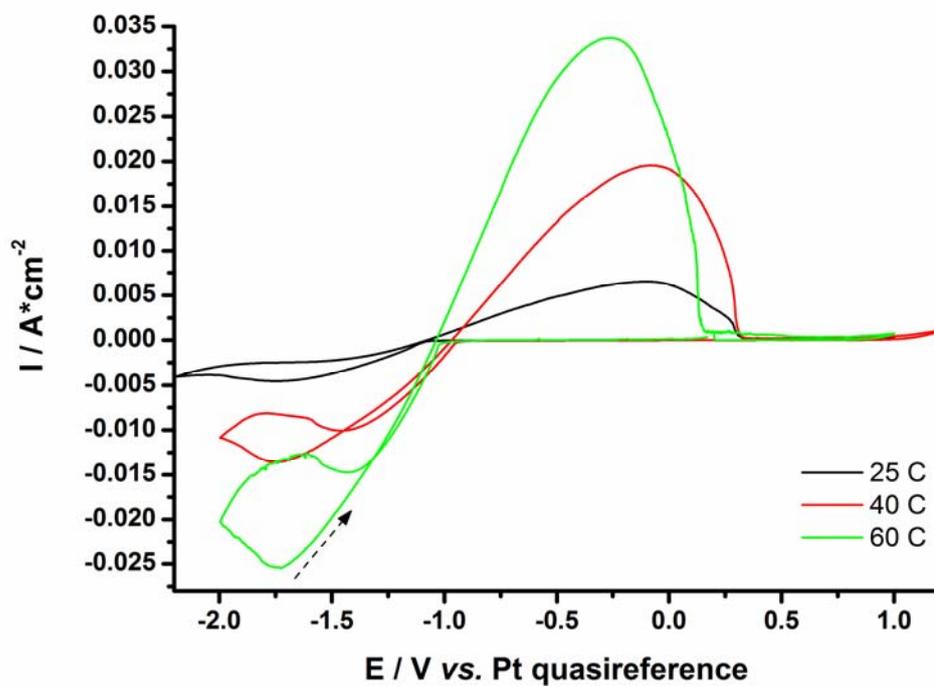


Fig. 3. Cyclic voltammograms showing the influence of temperature for 0.5M CdCl₂+0.1 mM TeO₂ dissolved in ChCl-malonic acid (1:1 moles) eutectic at constant scan rate of 10 mVs⁻¹.

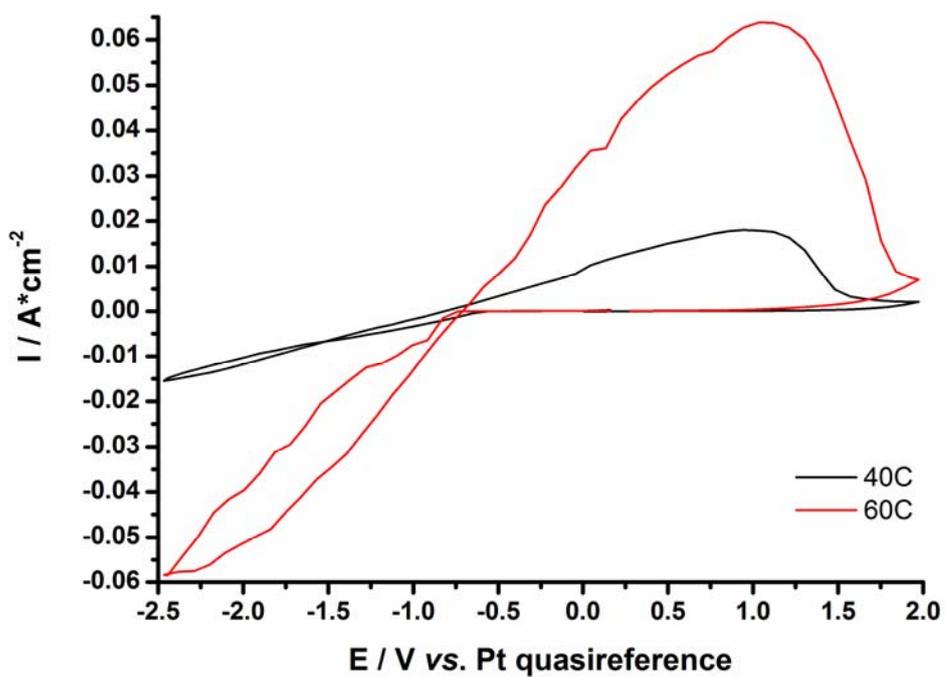


Fig. 4. Cyclic voltammograms showing the influence of temperature for 1M CdCl₂+1 mM TeO₂ dissolved in ChCl-malonic acid (1:1 moles) eutectic at constant scan rate of 5 mVs⁻¹.

Fig. 5 shows clearly that solutions with higher concentrations of Cd^{2+} show a significant increase in current; when the concentration becomes very large the cathodic peak becomes very ill-defined and the shape of the voltammogram is „stretched”, with cathodic peaks shifted negatively and anodic ones shifted positively. The electrodeposition peak which is clearly visible in Fig. 5 can be associated with CdTe electrodeposition. At higher Cd ion concentrations the peak becomes ill-defined and Cd is deposited onto CdTe; this behavior has been reported previously [22]. The electrodeposition at very negative potentials (below -1.5 V) also yields Cd deposits onto CdTe (see Fig 8 and also the discussion below).

The mechanism for the electrodeposition of CdTe likely involves first the deposition of a tellurium layer on Pt and the subsequently cadmium telluride deposition according to the process:



If either the concentration of Te ions is low or the electrodeposition potential too negative (or both), excess Cd metal is electrodeposited directly onto a CdTe layer. Unfortunately, the co-deposition potentials in choline chloride + malonic acid eutectic obtained experimentally for CdTe, are very difficult to compare with literature values, as the differences in standard potential scales are specific to each ionic liquid.

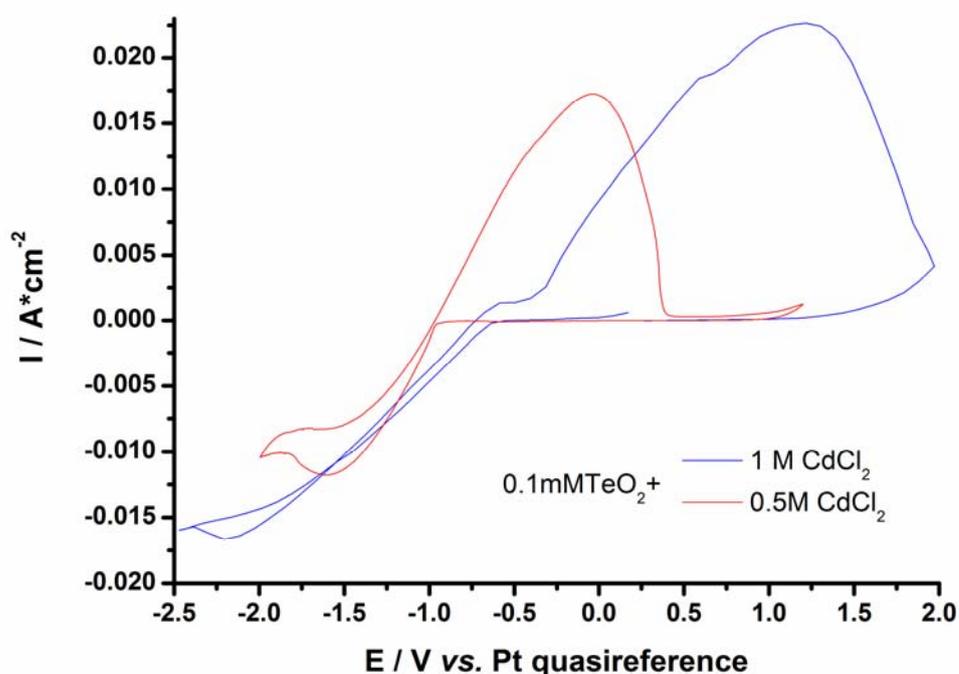


Fig. 5. Cyclic voltammograms showing the influence of Cd concentration for 0.1 mM TeO_2 + x mM CdCl_2 dissolved in ionic liquid at constant scan rate of 20 mVs^{-1} , temperature 40°C .

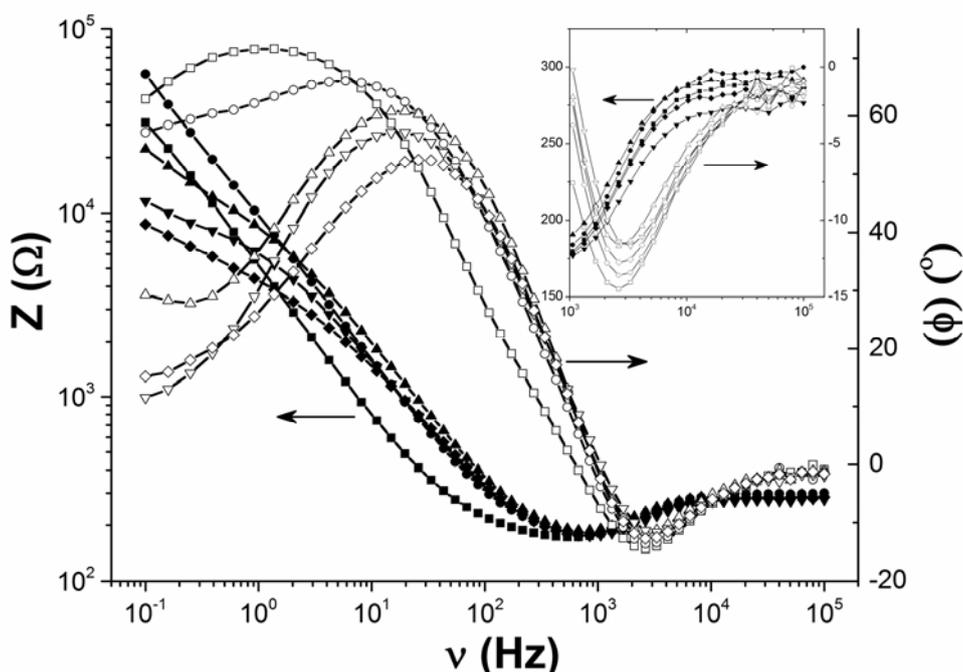


Fig. 6. Impedance spectra for 0.1M CdCl_2 +1 mM TeO_2 dissolved in ChCl-malonic acid (1:1 moles) eutectic at 40 °C and different polarization potentials: -0.2 (□), -0.4 (○), -0.6 (△), -0.7 (▽) and -0.8 V (◇). The inset shows the high-frequency region.

EIS measurements (only the ones at 40 °C are presented – see Fig. 6) show a rather featureless region characteristic of UPD (above ~ -0.6 V) [27, 28] and one (below -0.6 V) where the curves' shape seems to be closer to a classical Randles circuit (phase angle close to 45°), with the charge transfer resistance lowering as the temperature increases. All spectra at all temperatures do show however a high-frequency inductive loop (Fig. 6), which cannot be ascribed to a faulty reference electrode [29] since the quasi-reference electrode used has a very low impedance. One may try to ascribe this small inductive loop to some nucleation process, as theoretical descriptions have shown this to be possible under certain circumstances [24]. However, since the significance of some parameters in ref. [30] is not very clear, no fitting of the experimental data are reported, even though in some cases a good fit is obtained. The impedance spectra for the electrodeposition of CdTe are quite complicated though, especially at lower frequencies: the shapes of the Nyquist curves (not shown) are similar to the ones in ref. [23] (except for the high-frequency inductive loop) for potentials below ~ -0.4 V, with a marked deviation from a Warburg-element at low frequencies, which has been ascribed to a slow surface reaction [23].'

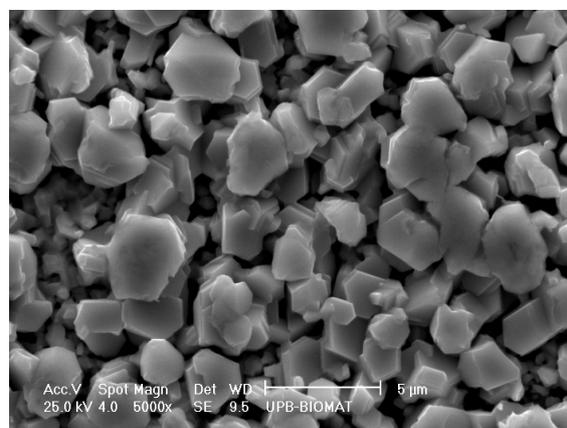
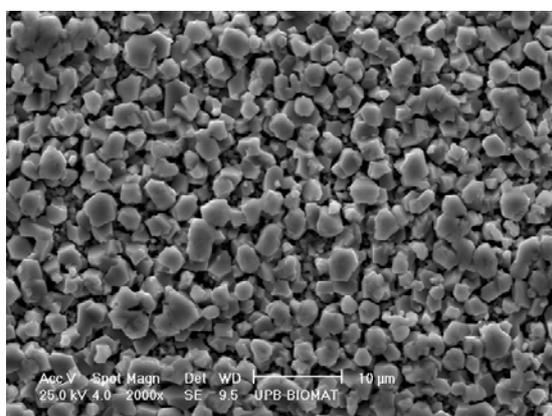


Fig. 7. SEM micrograph of a film deposited at -1.25V vs. Pt quasireference from ionic liquid containing 0.5M CdCl_2 and 0.1 mM TeO_2 , time 30 minutes, temperature 60°C.

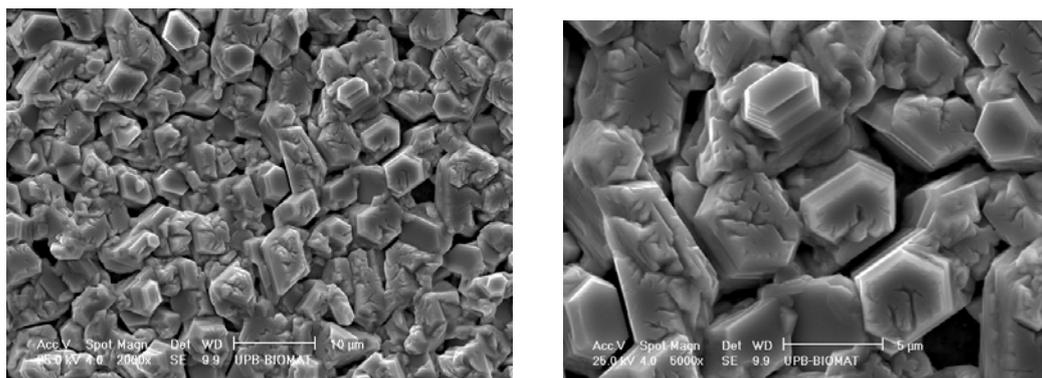


Fig 8. SEM micrograph of a film deposited at -1.35V vs. Pt quasireference from ionic liquid containing 0.5M CdCl₂ and 0.25 mM TeO₂, time 60 minutes, temperature 60°C.

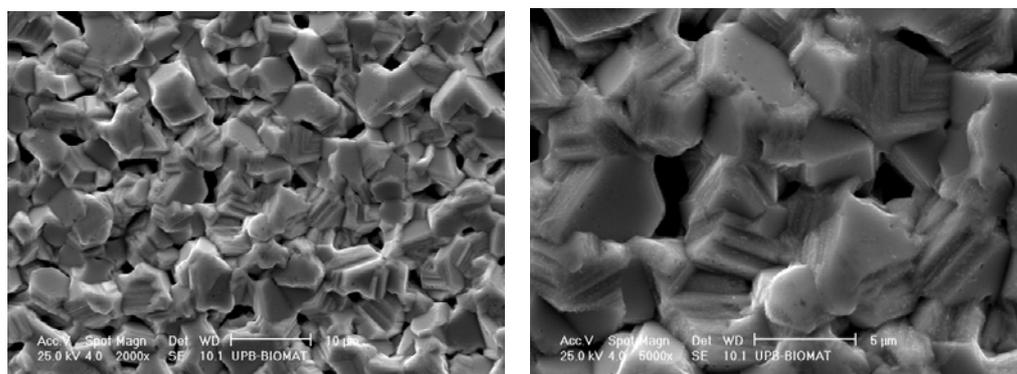


Fig. 9. SEM micrograph of a film deposited at -1.45V vs. Pt quasireference from ionic liquid containing 0.5M CdCl₂ and 0.1 mM TeO₂, time 60 minutes, temperature 60°C.

The surface morphology of the deposits obtained from choline chloride based ionic liquid containing 0.5M CdCl₂ with different additions of Te⁴⁺ at 60°C and different applied potentials was analyzed by scanning electron microscopy (Figures 7–9). For the first sample (shown in Fig. 7) obtained from a mixture of 0.5 M CdCl₂ + 0.5mM TeO₂ at -1.25 V one can observe a granular surface structure, also observed for other CdTe electrodeposition processes [11, 22, 31]; the EDX analysis performed on these samples revealed an atomic ratio Cd/Te approximately equal to 1.

For the second sample (Fig 8), obtained at a more negative potential, potential corresponding to the value at which was observed from CV the codeposition of Cd with CdTe; one can notice the appearance of typical hexagonal surface structures, characteristic of Cd metal deposits [32]. At even more negative potentials and a much lower concentration of Te ions (Fig. 9) the polycrystalline CdTe film seems to be entirely covered by elemental Cd, with hexagonal Cd deposits which coalesce into a 3D network of grains and forming a sponge-like structure.

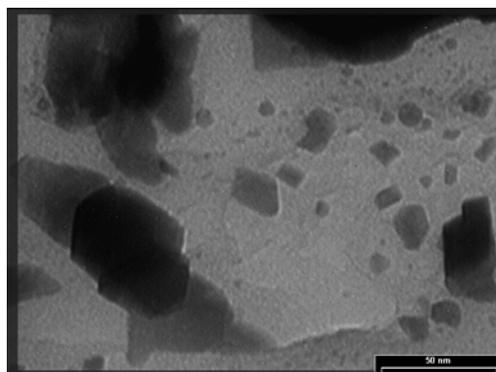


Fig. 10. TEM micrograph of a film deposited at -1.35V vs. Pt quasireference from ionic liquid containing 0.5M CdCl₂ and 0.5 mM TeO₂, at 300 seconds, temperature 60°C.

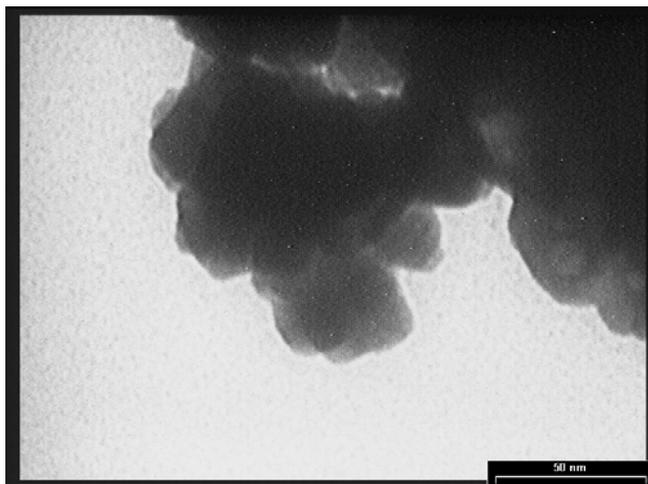


Fig. 11. TEM micrograph of a film deposited at -1.35V vs. Pt quasireference from ionic liquid containing 0.5M CdCl₂ and 0.5 mM TeO₂, at 900 seconds, temperature 60^oC.

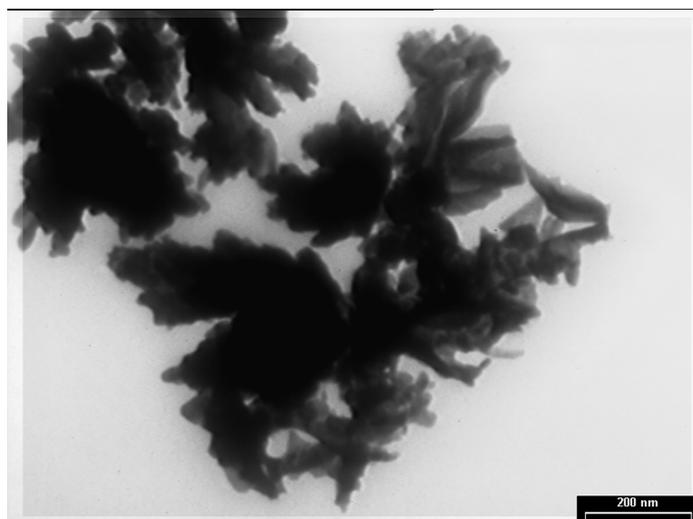


Fig. 12. TEM micrograph of a film deposited at -1.35V vs. Pt quasireference from ionic liquid containing 0.5M CdCl₂ and 0.5 mM TeO₂, at 1800 seconds, temperature 60^oC.

Cadmium telluride films obtained on copper substrate from the same ionic liquid but with different contents of Te⁴⁺ ions and Cd²⁺ ions at different temperatures and applied potentials were submitted to TEM analysis (Figures 10–12). The TEM micrographs clearly reveal nanometric crystallites composed of CdTe; the size of CdTe nanoparticles range between 9–18nm. The nanometric crystallites form especially at shorter deposition times (Fig. 10 and Fig. 11), while at longer times the crystallites tend to coalesce into dendritic, fractal-like structures (Fig. 12).

4. Conclusions

CdTe film has been successfully deposited onto copper substrate from choline chloride - malonic acid ionic liquid. The deposits obtained at negative potentials (below -1.5V vs Pt quasireference) show Cd metal deposits onto CdTe while the ones obtained at more positive potentials are almost entirely composed of CdTe.

The morphology of the deposits shows a nanocrystalline structure which may be due to the random bulk nucleation process observed during impedance measurements.

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