

Development of new CdTe based hybrid semiconducting layers produced in one step by electro-codeposition

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Thin layers of new hybrid organic-inorganic semiconductors, exhibiting photoconductive properties have been produced by a new, one step method. The films result by the combination of a CdTe semiconductor with an appropriate slightly water soluble fullerene salt. The layers were prepared using a cathodic electro-codeposition technique from an electrolytic bath containing both the convenient inorganic and organic chemical species. Using XRD and SEM-EDAX techniques the development of a new hybrid semiconductive system was confirmed. The photoconductive behavior of the new materials obtained was confirmed by photoelectrochemical measurements. The electro-codeposition technique applied could permit the achievement of various new hybrid materials with interesting semiconducting behavior, selecting either the appropriate inorganic and organic reagents or the imposed electrolysis conditions.

1. Introduction

Hybrid inorganic-organic semiconductors, developed through various methods [1], possess interesting semiconductive behavior and functionality, generally different to those exhibited by their ingredient compounds, due to a synergic combination of their properties. The mixing of the starting materials in a single product could modify, combine and ameliorate many of the usable characteristics presenting by each of them. The properties of hybrid semiconductors can be regulated via a variety of functional groups, which can be incorporated in the organic part. Photoconductors, photovoltaic devices, sensors, opto-electronics, etc. might represent some of the most important applications of these novel materials [1,2].

In our previous work [2] the production of hybrid semiconductive materials was accomplished by deposition of a thin organic film from appropriate fullerene derivatives onto thin films of CdSe and CdTe, well-known semiconductive compounds [2–10] presenting direct energy gaps (1.7 and 1.5 eV, respectively). The fullerene moiety incorporated into the hybrid system, being an electron acceptor, had introduced a significant change of the semiconductive behavior by the final hybrid in relation to the pure inorganic material.

In this work, a simple electrochemical method, the electro-codeposition, is applied to produce in one-step hybrid semiconductors. Similar efforts have also been attempted by several researchers, however using other methods than the electrodeposition one [11]. Specifically, the final products were electrodeposited from an electrolytic bath containing, except from the necessary chemical species for the CdTe deposition, a slightly water soluble fullerene salt derivative [12]. Thus, a simultaneous deposition of the inorganic and the organic part of a hybrid system has taken place. So, it is expected that hybrid materials obtained

in this way should appear, if not better, modified semiconducting properties in comparison to the pure inorganic semiconductors.

It is noticeable that the largely flexibility characterizing the described above electro-codeposition technique (i.e. the appropriate choice of the electrolytic bath composition and the electrolysis parameters) allows developing a wide variety of products with the desired useable properties.

2. Experimental

Electrodeposited thin films were developed potentiostatically, using a potentiostatic system (Wenking PGS 81R) with a conventional three electrode set-up. The cathode was a rotating Ti disc electrode ($\varnothing 12$ mm; cathode's rotation rate: 500 rpm). The counter electrode was a large platinum plated grid. The potential of the working electrode was monitored against an Hg/HgSO₄ saturated sulfate reference electrode (SSE). The electrolytic bath for CdTe/fullerene salt derivative plating was an aqueous solution containing typically 0.2 mol/l CdSO₄, $2 \cdot 10^{-3}$ mol/l SeO₂ saturated with TeO₂, a source of tellurium ions (HTeO₂⁺) and a slightly water soluble salt of a fullerene derivative. The electrodeposition had taken place at constant temperature $85 \pm 1^\circ\text{C}$, whereas the electrolyte pH was equal to 2.2. At these conditions the calculated concentrations of HTeO₂⁺ and fullerene salt for saturated solutions are about $5 \cdot 10^{-4}$ mol/l and $4 \cdot 10^{-4}$ mol/l, respectively.

The fullerene salt derivative, having a molecular formula C₆₉H₂₂Cl₂N₂O₂ and molecular weight 981.83, was synthesized according to previous works [13,14]. Its structural formula appears in Scheme 1.

All semiconductive deposits of typically 1 to 4 μm thickness, were examined by XRD (Siemens D5000) using a Cu K α X-ray source and SEM (FEI-Quanta 200) techniques. Compositional data were obtained by SEM-EDAX analysis. Photoresponse studies were performed in a Photoelectrochemical Cell (PEC) with a three electrode

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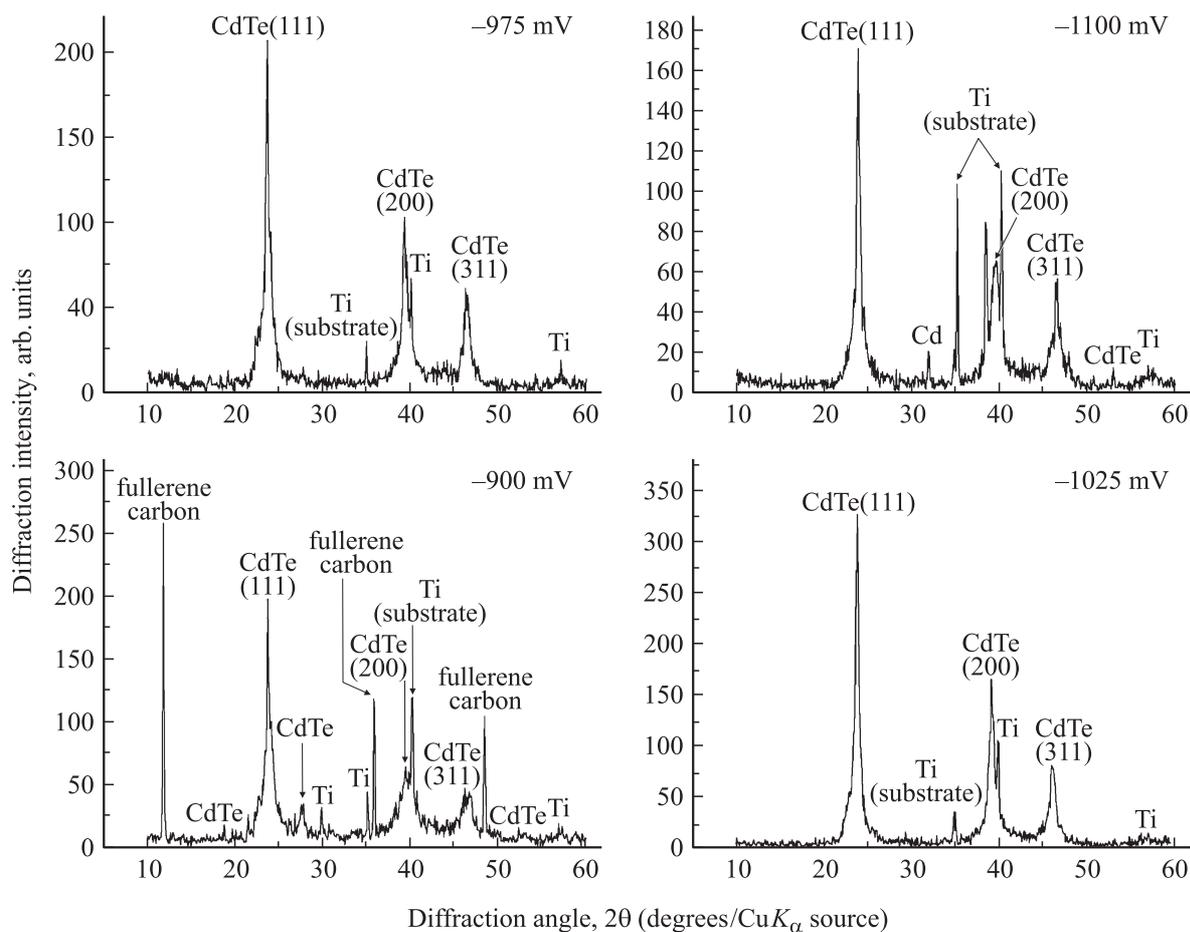
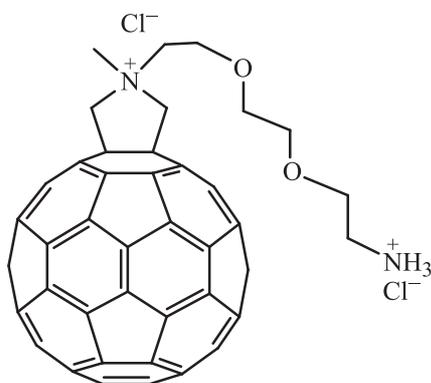


Figure 1. XRD diagrams given by CdTe/(fullerene salt electro-codeposits) prepared at -900 , -975 , -1025 and -1100 mV/SSE.

configuration comprising platinum wire rods as counter and reference electrodes. An alkaline sulfidepolysulfide solution (S_x^{2-} 1M NaOH, 1M Na_2S , 1M S) was the red-ox electrolyte. The PEC measurements were conducted under a white illumination generated by a halogen lamp and focused in front of the quartz window of the cell. Illumination intensity was 1.000 W/m^2 .



Structural formula the fullerene salt derivative introduced in the electrolytic bath.

3. Results and discussion

As it is known by previous works [3–5], CdTe prepared by cathodic electrodeposition, present a cubic sphalerite (zinc blende) structure with a predominating crystalline orientation towards the [111] axis, as derived by XRD data. Well crystallized electrodeposits are obtained at negative potentials vs.SSE. At these conditions, the corresponding photocurrents are anodic, that is characteristic of an n -type behavior due to the variations of stoichiometry.

The as-prepared hybrid materials also present a zinc blende cubic structure as derived by their XRD diffraction patterns. Moreover, in some XRD diagrams, new diffraction peaks clearly appear, that might correspond to the fullerene salt, due to the fact that many fullerene derivatives exhibit peaks in these areas of diffraction angles. In Fig. 1 the XRD diagrams of the CdTe based hybrid semiconductor, prepared at -900 , -975 , -1025 and -1100 mV vs. SSE are presented. The surface morphology of the above specimens is shown in Fig. 2.

Additionally, the SEM-EDAX investigations confirmed the presence of carbon in all the electro-codeposited layers and consequently the preparation of a hybrid system (Fig. 3). It is worth noting that exchanges of the chloride

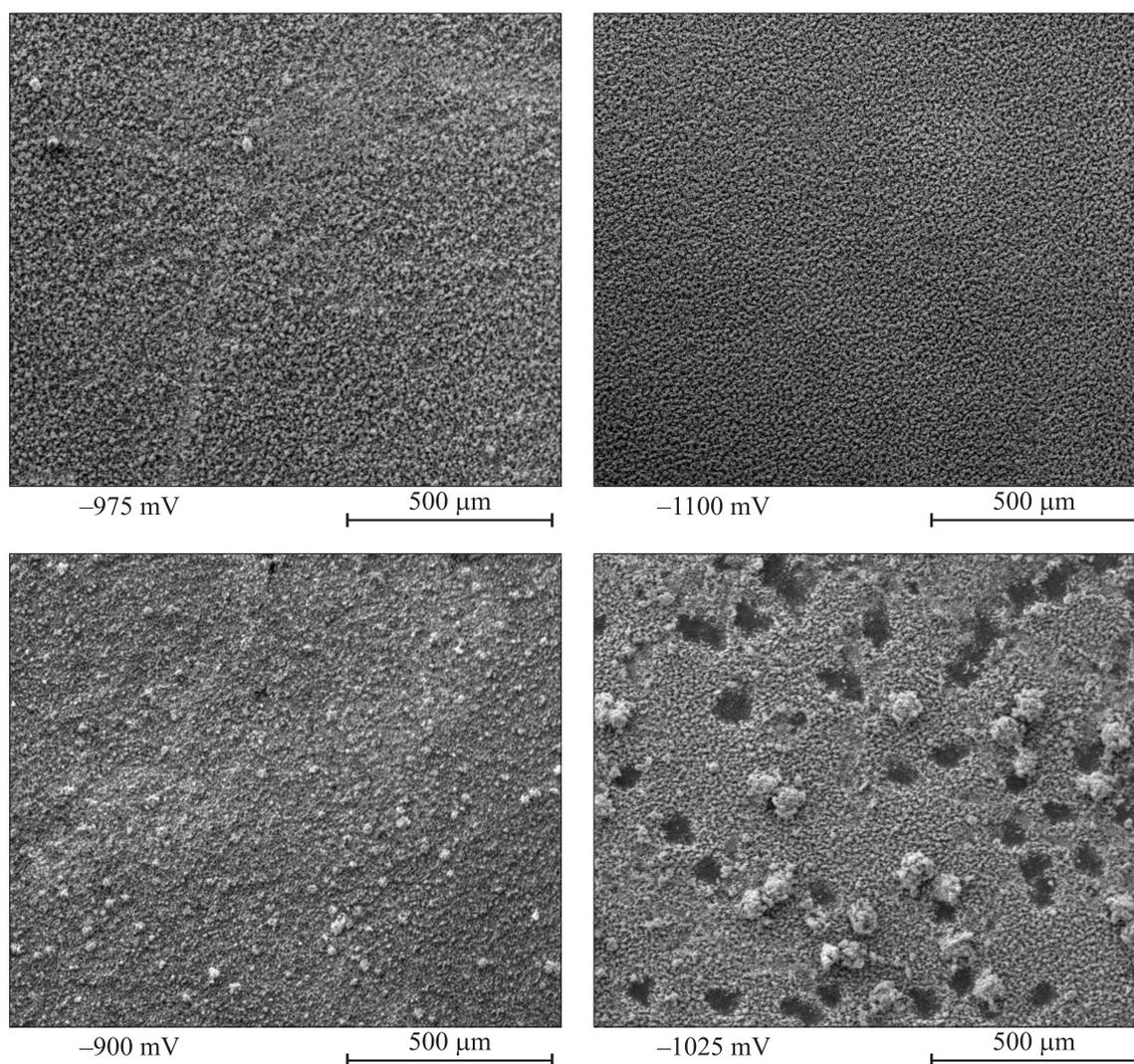


Figure 2. SEM micrographs of CdTe/(fullerene salt electro-codeposits) prepared at -900 , -975 , -1025 and -1100 mV/SSE.

anions of the fullerene salt with sulfate ones always take place to a large extent in the hybrid material, as concluded from the presence of sulfur and oxygen peaks in the SEM-EDAX diagrams.

Table summarizes the four parameters of the photo-conversion curves (short circuit current, j_{sc} , open circuit potential, V_{oc} , fill factor, FF , and photoelectrochemical efficiency, η) for the CdTe based hybrid semiconductors prepared at -900 , -975 , -1025 and -1100 mV *vs.* SSE, used directly as absorbed electrodes in a conventional PEC. For comparison, the corresponding data of the pure inorganic semiconductors, taken at the same conditions, are provided, too. Fig. 4 illustrates the current-potential photoresponses for the hybrid layers prepared at -975 , -1025 and -1100 mV *vs.* SSE.

The as-prepared CdTe based hybrid semiconductors do not exhibit, as derived from the data of Table, an obviously improved photoconductive character, although they are characterized by neighboring magnitude efficiencies. However,

the more negative are their deposition potentials the better is their semiconductive behavior (Fig. 4).

Thus, we may conclude that, in the presence of the fullerene salt derivative in the electrolytic bath, a displacement of the Cd deposition potential versus more negative values takes place. So, CdTe based hybrid semiconductive layers can be obtained even at negative enough potentials (e.g. 1100 mV/SSE), where pure CdTe deposits are not produced, exhibiting a rather improved photoconductive behavior in comparison to them taken at less negative potentials.

4. Conclusions

New hybrid organic-inorganic semiconducting systems, constituting the combination of a CdTe semiconductor with a selective fullerene derivative, have been developed in one step using a simple cathodic electro-codeposition technique. In particular, they result as thin layers over Ti substrates

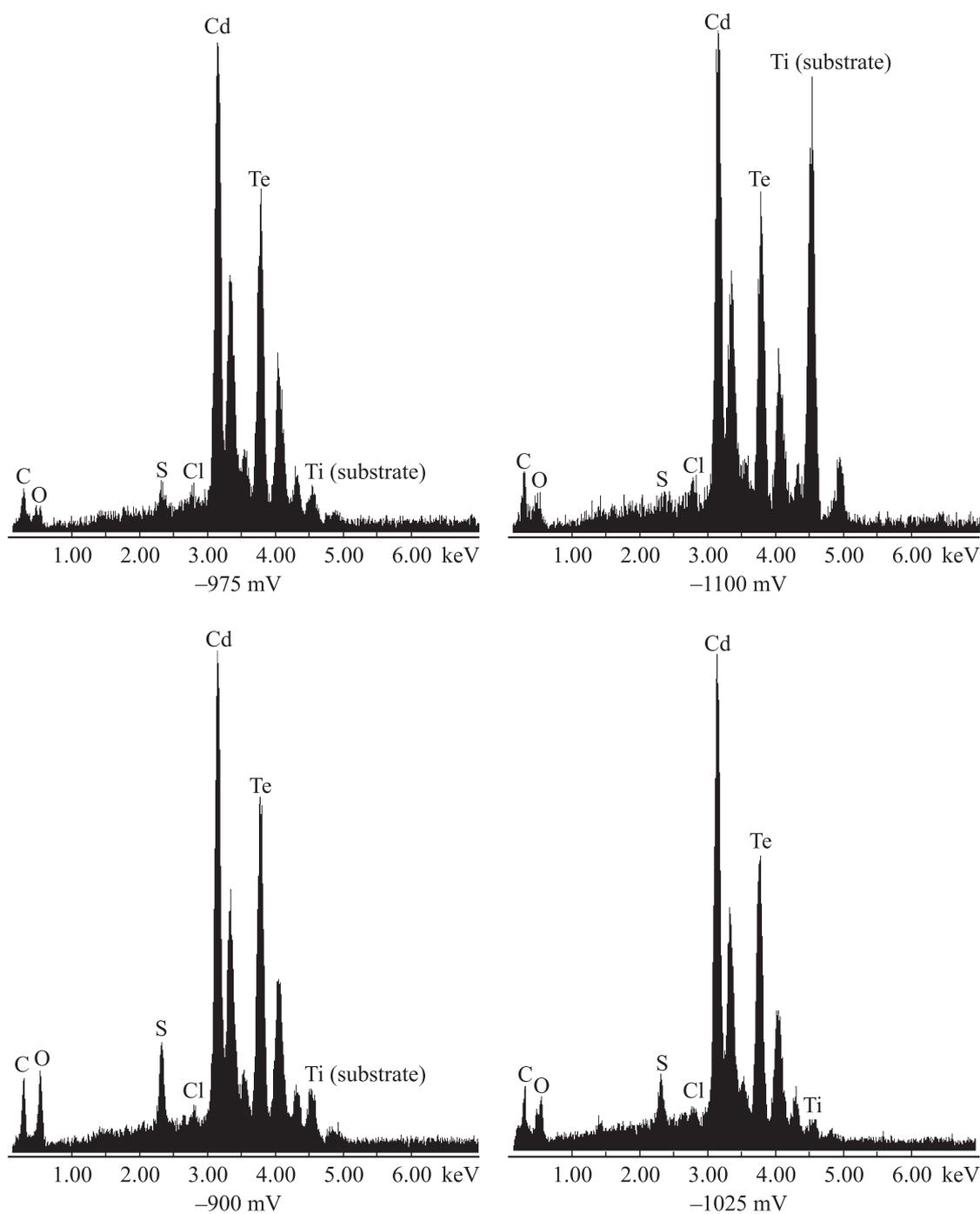


Figure 3. EDAX diagrams of CdTe/(fullerene salt electro-codeposits) prepared at -900 , -975 , -1025 and -1100 mV (SSE).

Photoelectrochemical parameters of CdTe based inorganic and hybrid semiconductors

Deposition Potential (mV)	Pure CdTe electrodeposits				Hybrid CdTe/fullerene salt electro-codeposits			
	-900	-975	-1025	-1100	-900	-975	-1025	-1100
J_{SC} (μA)	*	759	504	**	*	164	329	1033
V_{OC} (mV)	*	-329	-351	**	*	-306	-365	-316
FF	—	0.136	0.164	—	—	0.345	0.204	0.195
η (%)	—	0.030	0.026	—	—	0.015	0.022	0.052

Notes. * No photoresponse. ** Pure metal (Cd) deposition.

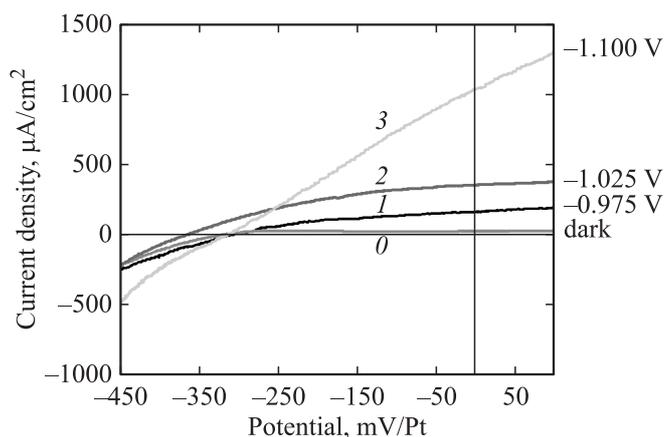


Figure 4. Current density *vs.* electrochemical potential given by CdTe/(fullerene salt electrocodeposits) prepared at -975 , -1025 and -1100 mV (SSE) used directly as absorbed electrodes in a conventional PEC in the dark (curve 0, approximately the same for all specimens) and under illumination of 1.000 W/m^2 (curves 1, 2 and 3, respectively).

from an electrolytic bath containing both the convenient inorganic and organic chemical species. SEM-EDAX and XRD investigations verified the presence of carbon in all the electro-codeposited layers and consequently the preparation of a hybrid system. Hybrid semiconductive layers obtained do not appear a clearly improved photoconductive character, in comparison to the pure inorganic ones. However, the more negative are their deposition potentials the better is their semiconductive behavior. Moreover, in the presence of the fullerene salt derivative in the electrolytic bath, a displacement of the Cd deposition potential versus more negative values takes place.

The electro-codeposition technique could permit the development of a variety of new hybrid semiconductive products, many of which are expected to exhibit interesting properties and provide important applications either selecting the appropriate ingredients or controlling the imposed electrolysis parameters.

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