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Hexagonal electrodeposited CdSe in new multi-layer hybrid organic–inorganic semiconductive systems with remarkable high photoconductivity

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ABSTRACT

Thin films of new hybrid organic–inorganic semiconductors have been developed, presenting noticeable photoconductive properties. They result by the combination of a CdSe semiconductor with an appropriate organic compound, commercially available, such as ferrocene or ferrocene aldehyde. The organic layer of the hybrid system is either deposited over the inorganic one or enveloped between two inorganic layers in a sandwich-like structure. The inorganic layers were produced using a cathodic electro deposition technique. The full characterization of the final products confirmed the development of the hybrid semiconductive system. The external electrodeposited CdSe layer of the sandwich-like materials exhibits a definite hexagonal structure. A clear amelioration of the photoresponding behavior of the three-layered products comparing to that of the two-layered ones as well as the pure electrodeposited cubic CdSe is observed. Finally, as derived from the XRD data of the materials prepared, the development of chemical bonds between the inorganic and the organic parts seems to be confirmed.

1. Introduction

A combination of inorganic semiconductors with appropriate organic compounds might lead to a new class of chemical compounds, known as hybrid semiconductors, which might present interesting physicochemical properties and functionality. Indeed, as a synergic combination of the properties of their components always exists, hybrid systems usually present a particular semiconductive behavior. The mixing of the starting materials in a single hybrid material could modify, combine and ameliorate many of the usable characteristics presenting by each of them. Moreover, the incorporation of various functional groups in the organic part of the hybrid semiconductor could permit a regulation of the final product's properties. These novel materials could find several interesting applications into various scientific fields, some of them presenting considerable industrial interest, as in photoconductors, photovoltaic devices, opto-electronics, such as organic light-emitting diodes and field-effect transistors, sensors, photodetectors, *etc.* [1,2].

As presented in our previous works, the development of hybrid semiconductive products was managed either by deposition of an appropriate thin organic film (specifically a fullerene derivative) onto thin films of cadmium chalcogenides [2] or, in one step, by an electro-codeposition technique from an electrolytic bath containing both the convenient inorganic and organic chemical species [3,4].

CdSe and CdTe, constituting the inorganic part of the hybrid system, developed by both techniques mentioned above, are well-known semiconductive compounds, as referred in our previous works [2,3,5,6,8], presenting direct energy gaps (1.7 and 1.5 eV, respectively). Concerning their crystal structures, they display a duality: the telluride is more stable in the zinc blende form, whereas the selenide analogous is more stable in the wurtzite form, consisting of two interpenetrating hexagonal close packed lattices. However, preparation of CdSe by electrochemical means generally leads to deposits with a well-developed cubic structure with a strong (1 1 1) preferred orientation [5,7], behaving as a metastable kinetically controlled phase, which can easily be transformed to the thermodynamically stable hexagonal one by annealing [5]. A substantial decrease in the photoresponse stability – in a PEC – and a high sensitivity in photocorrosion occurs yet, when the cubic phase is the dominant one, at a given stoichiometry. This is surprising in view of the very close structural relation between the two phases, though it may be attributed partly to the stronger bonding of the hexagonal one [5,8,9]. The preferable wurtzite structure of CdSe has been observed in films prepared by other techniques including sublimation of the compound, vacuum deposition, sputtering, *etc.* Moreover, using a much more acidic electrolyte and a higher selenium concentration, a mixture of the two phases has been obtained [10], though accompanied by serious hydrogen evolution problems.

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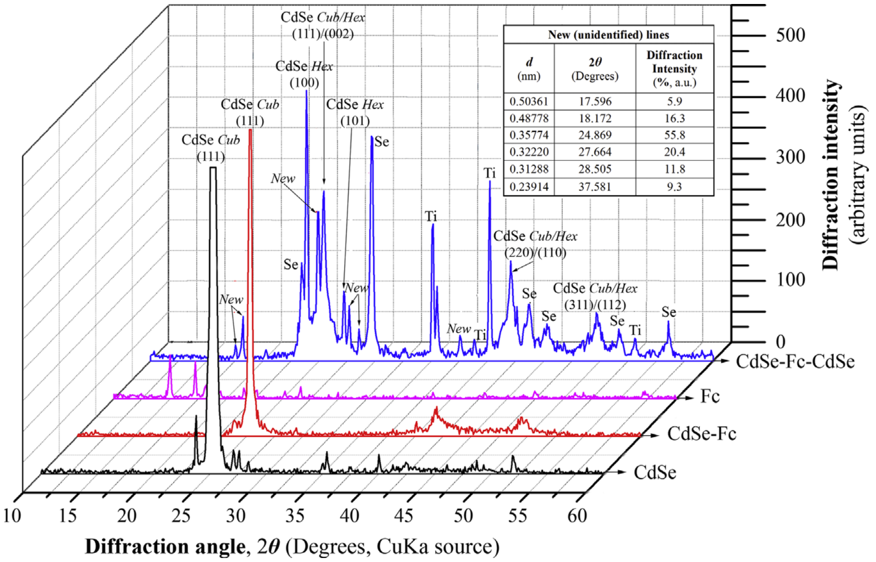
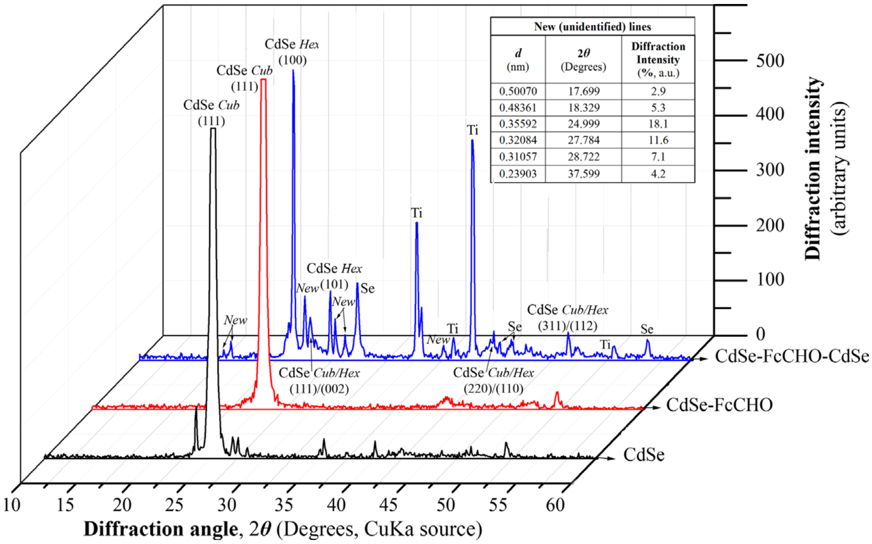


New (unidentified) lines

d (nm)	2*θ* (Degrees)	Diffraction Intensity (%, a.u.)
0.50361	17.596	5.9
0.48778	18.172	16.3
0.35774	24.869	55.8
0.32220	27.664	20.4
0.31288	28.505	11.8
0.23914	37.581	9.3

Fig. 1. XRD diagram of a CdSe/ferrocene (Fc)/CdSe three-layered hybrid semiconductor prepared by electrodeposition/spin coating/electrodeposition in comparison with the diagrams of pure CdSe, Fc and CdSe/Fc two-layered system.



New (unidentified) lines

d (nm)	2*θ* (Degrees)	Diffraction Intensity (%, a.u.)
0.50070	17.699	2.9
0.48361	18.329	5.3
0.35592	24.999	18.1
0.32084	27.784	11.6
0.31057	28.722	7.1
0.23903	37.599	4.2

Fig. 2. XRD diagram of a CdSe/ferrocene aldehyde (FcCHO)/CdSe three-layered hybrid semiconductor prepared by electrodeposition/spin coating/electrodeposition in comparison with the diagrams of pure CdSe and CdSe/FcCHO two-layered system.

The organic part, on the other hand, being an electron acceptor, had induced a significant change in the semiconductive behavior by the final hybrid in relation to the pure inorganic material [2].

In the frame of this work, the development and study of new two- or three-layered hybrid semiconducting systems, involving CdSe thin films in combination with pure ferrocene (an electron donor) or ferrocene aldehyde (formyl group, attached onto the ferrocene molecule, is an electron acceptor), was attained. It is expected that the presence of the organic part, in particular when placed between two CdSe thin films, in a sandwich-like construction, should lead to hybrid materials presenting modified crystal structure and improved or at least modified semiconducting behavior, such as its photoresponse, in comparison to the pure inorganic semiconductors. This fact may be attributed to a type of physicochemical interaction between the layers. It is also assumed that a kind of chemical bond between the organic and the inorganic part of the hybrid system should be deployed.

2. Experimental

CdSe thin films were developed potentiostatically, using a potentio-scan system with a conventional three electrode set-up. The cathode was a rotating Ti disc electrode (⌀ 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 $Hg/HgSO_4$ saturated sulfate reference electrode (S.S.E.). The electrolytic bath for CdSe plating was an additive-free aqueous solution containing typically 0.2 mol/L $CdSO_4$ and 2×10^{-3} mol/L SeO_2 being kept constant at 85 ± 1 °C. The bath pH was adjusted to 2.2.

The organic layers were deposited dropwise, from solutions in toluene of commercially available ferrocene or ferrocene aldehyde, onto the rotating inorganic electrode (spin coating technique). In this way, a thin film of the organic substance can be formed. Three-layered products were also prepared by electrodeposition,