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Effect of the substrate temperature on the physical properties of sprayed-CdS films by using an automatized perfume atomizer

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ABSTRACT

Cadmium sulfide (CdS) thin films were deposited onto glass substrates at different temperatures by the spray pyrolysis technique. A home-made experimental setup with an automatized perfume atomizer was implemented for the spray pyrolysis deposition. The temperature of the substrates was varied from 300 °C to 500 °C prior to the CdS deposition. The automatization and precise control of the spraying process produce CdS thin films with stable and controlled physical properties. The CdS stoichiometric ratio [S]/[Cd] and the bandgap energy were independent of the temperature of the substrate while the surface roughness decreased with increased temperature. The optical transmittance of the CdS films increased with increased substrate temperature, reaching values above 70% for wavelengths > 500 nm. A hexagonal crystalline structure was observed for the CdS films for all the substrate temperatures, however, the crystalline orientation of the CdS was dependent on the substrate temperature. Hall Effect measurements in Van der Pauw configuration confirmed low electrical resistivity values ($\sim 10^{-1}$ Ω-cm) and negative Hall coefficients (i.e. n-type) for the semiconducting CdS films. From the presented results, the samples deposited at 500 °C showed most adequate morphological, optical, electrical and structural conditions for potential implementation in photovoltaic applications. A good control and understanding of the physical properties of semiconducting thin films grown by low-cost and scalable techniques, such as the spray pyrolysis, represents an important step towards the development of nanostructures with high functionality.

1. Introduction

Cadmium binary semiconductor compounds, such as the CdS, CdSe and CdTe, have received great attention due to their advantageous optical and electronical properties and their potential implementation in photovoltaic applications and optoelectronics [1]. Cadmium sulfide (CdS) grows normally as a n-type semiconductor with a wide bandgap energy (2.42 eV), and exhibits a high absorption coefficient, high stability and can be produced at relatively low cost [1–4]. Such characteristics make the CdS an appropriate material to be used as an optical window layer for solar cells along with other semiconductors such as CdTe, Cu_2S, $CuInSe_2$ and Cu(In, Ga)Se_2 [5]. CdS can also be used as photodetectors [6], transparent semiconductors [7], light emitting diodes [8] and diluted magnetic semiconductors in spintronic devices [9].

CdS in thin film geometry can be obtained by different techniques such as the chemical bath deposition (CBD), successive ionic layer absorption and reaction (SILAR), RF sputtering, metal organic chemical vapor deposition (MOCVD), pulsed laser ablation (PLA), closed space sublimation, vacuum evaporation and spray pyrolysis, among the most relevant ones [10]. However, in the majority of the mentioned techniques, the requirements of high vacuum conditions along with complexity and cost of the experimental setups are the main drawbacks for their implementation. Thus, the use of low-cost and scalable techniques such as the CBD and spray pyrolysis techniques [10–14] has gained important attention and several efforts have been carried out for the implementation, reproducibility and validation of the resulting materials. Among the mentioned techniques, the spray pyrolysis emerges as a very convenient one to deposit semiconducting materials in thin and thick film geometry, powders and coatings, with high quality and stability [13–17]. Such a methodology allows the deposition of specific materials on large areas in a relatively small amount of time, being this, the main reason for its usage for several decades in the photovoltaic and solar cell industry [10].

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The original application of sprayed films was in the area of photoconductivity, where CdS, Cd(*S*,Se) and CdSe films achieved important sensitivities with remarkable performance, comparable to other materials made by other processes [16,18]. The spray pyrolysis technique has also been implemented in the areas of photoluminescence and cathodoluminescence, where the resulting deposited films are used as constituents of thin film solar cells [16,19]. In general, a typical spray pyrolysis system consists on an atomizer, a precursor solution, a substrate heater and a temperature controller [10,16]. Different types of commercial atomizers have been reported such as the *air blast* type, where the liquid is exposed to a stream of air [20], the *ultrasonic atomizer*, where ultrasonic frequencies produce the short wavelengths necessary for fine atomization [21], and the *electrostatic atomizer*, where the liquid is exposed to a high electric field in order to accelerate the charged powdered particles or atomized liquid towards the pre-heated substrate [22].

Albeit the use of commercial systems for the spray pyrolysis technique is common, some groups have reported the use of low-cost home-made spray pyrolysis systems [17–19]. For example, Bouaoud et al. [23], deposited Ni-doped zinc oxide (ZnO) thin films by spray pyrolysis using a perfume atomizer. Authors prepared the precursor solution with anhydrous zinc acetate and hexahydrate nickel chloride as sources of zinc and nickel. The films were deposited onto pre-heated glass substrates (450 °C) and the effect of the Ni and Zn ratio on the structural, morphological, optical and electrical properties was evaluated. In other work Ortel et al. [24], deposited ZnO layers with a similar perfume atomizer system and investigated their optical absorbance and surface morphology. Authors reported a high mobility of $5\,cm^2V^{-1}s^{-1}$ and an excellent switching behavior for the ZnO layers, finding a strong correlation of the electrical performance with the growth rate.

Different authors have explored the CdS deposition by spray pyrolysis onto different type of substrates, several works can be found on the literature [16,25–32]. For example, Ma and Bube [26,27] prepared CdS thin films and CdS/CdTe heterojunctions. The CdS thin films were deposited onto amorphous glass at different temperatures, ranging from 320 °C to 570 °C. Authors found that the orientation, cubic/hexagonal phase ratio, and morphology of the films were dependent on the substrate temperature. Furthermore, solar cells CdS/CdTe heterojunctions were prepared by depositing CdS films onto single-crystal CdTe films by spray pyrolysis, achieving solar efficiencies higher than 6%. The performance of the solar cells prepared by this method was comparable with the performance of solar cells conformed by CdS prepared by vacuum evaporation [27]. In Ref. [27], the spraying process of CdS consists on spraying a solution of $CdCl_2$, and thiourea onto a heated substrate at 450 °C, using a spray pyrolysis system similar to that one described by Chamberlin and Skarman [16], which is basically a device to atomize the spray solution with a substrate heater and air pressure control. Other authors have studied the effects of different dopants materials, such as In, Ni, Al, Na, and fluorine atoms, on the optical, electrical, structural and morphological properties of sprayed CdS thin films [5,33–35]. Hiie et al. [36] show a comparative study of CdS thin films prepared by two different techniques (CBD and spray pyrolysis) and the effects of post-deposition thermal treatment at 450 °C on their optical, electrical and morphological properties. For the spraying process, a flow rate of compressed air was used as a carrier gas. Authors observed that the annealing treatment decreased the electrical resistivity of the sprayed CdS films onto glass substrates up to two orders of magnitude, while the films grown by CBD do not exhibit changes on this property. Additionally, the bandgap energy of the annealed CdS films grown by CBD decreased from 2.51 eV to 2.42 eV, whereas the bandgap energy of sprayed CdS films (2.46 eV) did not suffer significant changes with the thermal treatment.

In the spray pyrolysis method, the properties of the deposited films strongly depend on the anion-to-cation ratio, spraying rate, substrate temperature, carrier gas, droplet size, and cooling rate after deposition [6]. In addition, such a technique involves many processes occurring either simultaneously or sequentially during the formation of the films, e.g. aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading and precursor decomposition [10]. The deposition temperature (or substrate temperature) is of great relevance for all the mentioned processes, representing a key parameter on the physico-chemical and morphological characteristics of the sprayed thin films, due to its influence on the thermodynamic parameters during the pyrolysis and nucleation processes [37–39].

The spraying process and its characteristics (spraying area, volume of sprayed reactive, spraying ratio) become very relevant for the control and stability of the deposited samples. However, in most of the cases, the precursor solution is sprayed manually, with intermittent sprayed cycles. Although good results have been reported with manual spraying, a precise control of the spraying rate, sprayed volume and duration would render improved homogeneity on the physical properties of the deposited materials.

In this work, the deposition of CdS thin films by spray pyrolysis using an electronic system to automatize the spraying process is presented. The use of a perfume atomizer has many advantages over other commercial spray pyrolysis systems [40]. For example, the perfume atomizer implementation implies a reduced cost [40,41], no carrier gas is required (which would imply early drying of microparticles, before arriving the substrate [42]), gives fine atomization and improves wettability between the sprayed micro particles and previously deposited layers [40–42]. Moreover, the effect of the substrate temperature on the optical, morphological, electrical and structural properties of CdS thin films deposited onto glass substrates is investigated. The morphology, bandgap energy, optical transmittance, stoichiometry, crystalline structure, electrical resistivity, type of charge carriers and preferential orientation of the deposited samples were investigated, and the dependence of each parameter on the substrate temperature was evaluated.

2. Materials and methods

2.1. CdS deposition by spray pyrolysis

Corning glass substrates of 1.5 cm × 1.5 cm were used for the CdS deposition. The substrates were cleaned following a well-stablished methodology consisting on an initial washing step with soap and water followed by a washing procedure using acetone and isopropyl alcohol in an ultrasonically bath and a final rinsing step with distilled water [43]. For the implementation of the spray pyrolysis process, an automatized home-made system was designed and implemented. The system consists on a perfume atomizer, a power supply and a heating plate. A programmable microcontroller was used to control the time of spraying and the intervals between spraying steps.

Fig. 1 shows a schematic of the implemented system. For the spraying process, the precursor solution is sprayed towards the substrates in a parabolic trajectory (see Fig. 1) similarly to the methodology reported by Ortel et al. [24]. The precursor solution for the spray process consisted on a mixture of 0.05 M of cadmium chloride ($CdCl_2$) and 0.05 M of thiourea ($CS(NH_2)_2$) dissolved in distilled water. The solution was prepared at room temperature and kept on a container

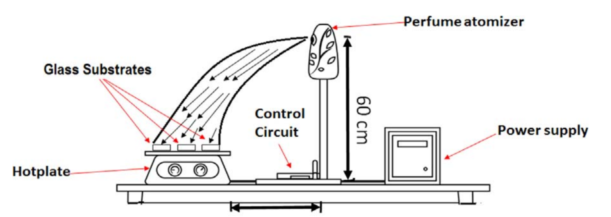

Fig. 1. Schematic of the experimental setup implemented for the CdS films deposition by the spray pyrolysis technique.