Structural Modifications of Nanostructured Cubic CdS Thin-Films due Cu²⁺ Doping

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The development of II-VI semiconductor nanocomposites doped with metallic ions has gained a lot of attention in different investigation groups given the possibilities of modification of the structural, optical and electrical properties, thanks to the quantum confinement effect [1]. Particularly, using the copper ion Cu^{2+} , remarkable changes in the optical properties of the nanocomposite were noticed [2].

The undoped CdS thin-film was obtained using the chemical bath deposition (CBD) technique, with a constant temperature of 60°C without special atmosphere, aqueous solutions of CdCl₂ (0.01 M, 20 mL) as Cd²⁺ ions precursor, NaOH (0.05M, 10mL), NH₄NO₃ (0.5M, 15mL) as complexing agent and SC(NH₂)₂ as S²⁻ ions precursor. Deposition of the thin-films was performed in a recirculating bath. The Cu-doped (CdS:Cu) nanocomposite was obtained by the addition of the metallic ion Cu²⁺ Precursor Cu(NO₃)₂ before the complexing reaction.

The SEM micrographs of both samples illustrated in Fig.1a and 1b allows qualitative comparison of the particle cluster sizes and densities, showing smaller sizes and higher densities in the doped sample (CdS:Cu) as shown in Fig. 1b.

The high resolution XPS superficial analysis of the CdS matrix shows a strong, symmetrical and clean signal of cadmium 3d doublet $3d_{3/2}$ (411.7 eV) and $3d_{5/2}$ (404.95eV), who has a slight widening illustrated in Fig. 1c, typical of the CdS II-VI binary [3]. The XPS spectra of the 2p doublet of sulfur shown in Fig. 1d shows a chemical shift of 2.4 eV to lesser binding energies from elemental sulfur [4] with the photoelectron peaks of $2p_{1/2}$ (162.8 eV) and $2p_{3/2}$ (161.6 eV), also characteristic of cadmium sulfide. The copper ions were found in the surface of the CdS:Cu film, as possible CuS compounds with a 2p doublet with binding energies $2p_{1/2}$ (913.2 eV) and $2p_{3/2}$ (933.2 eV)[5] (Fig. 1e).

The monocrystalline nature of the undoped CdS thin film can be observed in the TEM micrograph shown in Fig. 2a with an interplanar distance of 3.35 Angstrom associated by Bragg's law with the angular position 2θ of the (111) CdS cubic phase. A typical particle diameter of around 5.87 nm was measured. The effects of doping are clear in the micrograph of the CdS:Cu sample shown in Fig. 2b, where the quantum confinement is evident, due the reduction of the particle diameter to an average size of 4.76 nm. The change to a polycrystalline structure of the CdS:Cu sample is confirmed in the micrograph in Fig 2b, with different crystalline domains that are clearly visible.

The results presented in the present work highlight the viability of the CBD technique for structural modification of CdS thin films via doping [6].

References:

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Figure 1. SEM micrographs of a) CdS and b) CdS:Cu thin-films. High resolution photoelectron spectra of the binding energy ranges of c) cadmium in CdS d) sulfur in CdS and d) copper in CdS:Cu



Figure 2. TEM micrographs of a) CdS and b) CdS:Cu samples.