NANOSCALE ZnS AND CdS THIN FILMS FROM SINGLE-SOURCE MOLECULAR PRECURSORS

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II-VI semiconducting materials like ZnS and CdS have been used as phosphors and photoconductors for many years. In particular, CdS thin films have been employed in photovoltaic solar cells as wide band-gap window layers (E_G=2.42 eV) (1), while ZnS (E_G=3.80 eV) coatings are potential candidates for applications in thin film luminescent devices emitting in the UV and deep-blue spectral regions (2). The optoelectronic properties of these materials can be tailored by varying the composition of the ternary phase $Cd_{1-x}Zn_xS$, obtaining thus promising systems for photoconductive devices, as well as for photo- and electroluminescence in the visible spectral region (3).

The growth of II-VI sulphides thin films by Chemical Vapor Deposition (CVD) has attracted much attention as a possible method for the production of optoelectronic devices at moderate temperatures and in controlled conditions. Moreover, CVD results particularly suitable in order to obtain nanoscale semiconductor thin films, that might exhibit peculiar properties as a function of their nanostructure and morphology.

The present work describes the most relevant results on the CVD synthesis and characterization of nanocrystalline ZnS and CdS coatings. To this aim, *O*-isopropyl xanthates [$M(O\text{-}^iPrXan)_2$; M = Zn, Cd; *O*-^{i}PrXan = $S_2COCH(CH_3)_2$] were synthesised, characterized and used as *single-source* precursors. Besides being appreciably volatile and stable to air and moisture, these compounds contain pre-formed M-S bonds that enable their clean conversion into the corresponding sulphides in an inert atmosphere, as proved by thermal and mass spectrometry analyses (4). Moreover, they allow to avoid toxic multiple-source systems and to achieve a better control over composition and microstructure of the final product.

ZnS and CdS films were deposited on SiO_2 by a cold-wall low-pressure CVD reaction system at temperatures between 200 and 450°C. Electronic grade N_2 was used as carrier gas. For the deposition of MS coatings (M=Zn, Cd), the precursor $M(O\text{-}^iPrXan)_2$ (whose detailed syntheses and characterizations will be reported elsewhere (4)) was vaporized at 120°C. For ZnS films, total pressure and N_2 flow rate were set at 5 mbar and 110 sccm respectively, while for CdS coatings the total pressure was 1.5 mbar and the gas flow rate was 150 sccm. Film crystallinity was studied by Glancing Incidence X-Ray Diffraction (GIXRD), while their chemical composition was analyzed by X-ray Photoelectron (XPS) and X-ray Excited Auger Electron (XE-AES) Spectroscopies. Their surface morphology was analyzed by Atomic Force Microscopy (AFM). Finally, UV-Vis optical properties were also investigated.

GIXRD investigations showed that all the obtained films contained both the hexagonal (*wurtzite*) and cubic (*sphalerite*) polimorphs (fig. 1). For both ZnS and CdS coatings, estimation of the average crystallites size yielded values ranging from ≈10 and ≈25 nm, indicating that the adopted CVD route gave rise to the formation of nanoscale sulphide thin films.

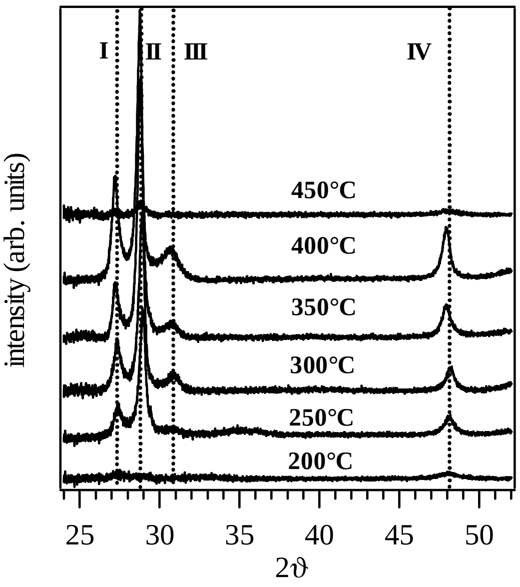

Figure 1. GIXRD patterns of ZnS thin films deposited on silica (incidence angle = 1.5°). Peaks (**I**) and (**III**) corresponded with *wurtzite* reflections, while signals (**II**) and (**IV**) arose from overlapped *wurtzite* and *sphalerite* peaks.

XPS and XE-AES analyses allowed to ascertain the formation of pure ZnS and CdS in the obtained coatings. In fact, evaluation of the Auger parameters yielded very similar values for all zinc sulphide (≈2011.4 eV) and all cadmium sulphide coatings (≈786.4 eV). These features agreed to a good extent with GIXRD results.

AFM measurements (fig. 2) showed that film surface texture was characterized by the presence of well interconnected globular grains. For both ZnS and CdS coatings, typical r.m.s.-roughness values fell in the range 2÷5 nm. This result might be interesting in view of potential film applications in optoelectronic devices like solar cells, where a smooth and regular morphology is required (5).

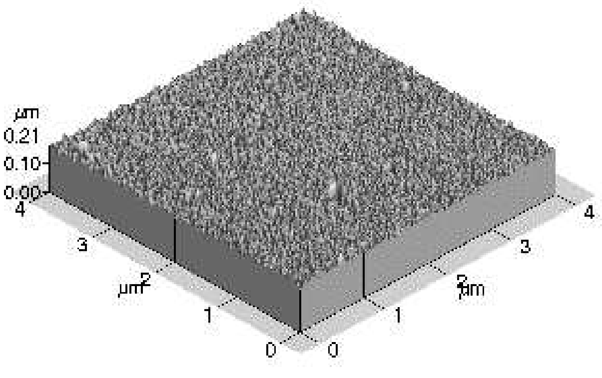

Figure 2. Representative AFM surface micrograph (4x4 $\mu m^2$of a ZnS film deposited on silica at 300°C.

Finally, optical spectra evidenced a *red shift* of the absorption thresholds, which might be related to film policrystallinity and defect presence in the metal sulphide band gap.

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