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Physical characterization of CdMnS nanocrystalline thin films grown by vacuum thermal evaporation

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CdMnS ternary alloys have attracted much attention because they permit to tune the energy gap, the effective mass and the lattice constant by varying the concentration of the magnetic material. Growth and physical characterization of $Cd_{1-x}Mn_xS$ thin films, prepared in different conditions on glass and silicon substrates by thermal evaporation technique is presented. The starting powders, CdS and Mn, were mixed in a crucible in various molar ratios. The samples were characterized by XRD, AFM and XPS. The blue shift of band gap of thin films might be ascribed to the size effect of the small grains and to the fact that Cd was substituted by Mn in the CdS structure.

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1. Introduction

The most studied diluted magnetic semiconductors (DMSs) are $A^{II}_{1-x}Mn_xB^{VI}$ alloys which are direct-gap semiconductors [1]. $Cd_{1-x}Mn_xS$ is distinguishable from other DMSs because it has a *p-d* exchange integral value considerably large that causes various abnormal phenomena experimentally observed [2].

Because of the half-filled 3*d* shell, manganese can contribute to the s-p^3 bonding and can substitutionally replace Cd atoms in CdS by forming a solid solution and allowing the possibility of tailoring its properties.

The variation of the energy gap, E_g, was found to be linear with respect to x for a certain composition range ($x \geq 1$) and to have an anomalous behavior at low x, called band-gap bowing. The minimum of the band-gap energy was attributed to chemical disorder or to exchange interaction of the conduction and valence bands electrons with the Mn^{2+} *d* electrons [4].

CdMnS thin films have attracted considerable interests because of their novel magnetic and magneto-optical properties derived from this hybridization between the Mn 3*d* and *sp*-hexagonal CdS. The introduction of large mole fraction moves the intrinsic edge through the visible region and dominates the optical properties.

Several preparative routes of synthesis of CdMnS thin films were reported in the literature: electro-deposition, vacuum evaporation, screen printing, photochemical deposition, chemical bath deposition, spray pyrolysis, sputtering [5]. This paper presents the influence of Mn doping on the structure and optical properties of CdS thin films, deposited on glass or Si substrates, by using the vacuum thermal evaporation technique.

2. Experimental

A mixture made from 0.15 g CdS powder and x g Mn powder (x = 0.005, 0.01, 0.03) was evaporated, by using the quasi-closed volume technique, from a resistive molybdenum crucible onto pre-cleaned and unheated glass or p-doped Si single crystal substrates. The deposition process was performed in three steps. In the first step the source temperature was kept for 7 min at 873 K; in the second step the temperature was increased to 973 K and kept at this temperature for 3 min. In the third step, the temperature was increased to 1100 K and maintained at this temperature for 7 min. The source to substrate distance was 8 cm. The thin films were coded as CdS/substrate and CdS:Mnx/substrate (substrate = glass, Si). A post deposition thermal treatment was performed at 423 K (T_1), 573K (T_2) and 450 K (T_3) for 2h. The resulted samples were labeled as T_yCdS/substrate and T_yCdS:Mnx/substrate ($T_y = T_1, T_2, T_3$). The film thickness, determined by an interferometric method, was around 280 nm. The film structure was examined by X- ray diffraction technique (DRON2 diffractometer, Co K_α, λ = 1.7889 Å) and the film morphology and roughness were investigated by using a home made AFM equipment.

X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific ESCA-3 Mk-II spectrometer, by using unmonochromatized Al K_α radiation (1486.7 eV). The photoelectrons were collected at a take-off angle of 50°. The pass energy of the electron hemispherical analyzer was 50 eV. The measurements were done at room temperature and a pressure of about 10^{-7} Pa in the analysis chamber.

For the study of the optical properties the optical transmittance was recorded using a UV-VIS Spectrophotometer in the wavelength range 300 – 1400 nm.

3. Results and discussion

3.1. X-Ray diffraction studies

Fig. 1 shows the XRD results of the as deposited and heat treated CdS and CdMnS thin films deposited on glass substrates. The thin films have a hexagonal structure with a (002) preferred orientation. It is visible that by adding 0.005 – 0.01 g Mn to the 0.15 g CdS into the crucible, the thin film crystallinity increases, and it decreases when the content of Mn was of 0.03 g (Fig. 1).

The XRD study of thin films thermal treated at different temperatures evidenced that the thermal treatment made at 423K, for 2h enhances the peak intensity. Thermal treatments for 2h at higher temperatures have an opposite effect. The situation was similar for all the studied thin films (Fig. 2).

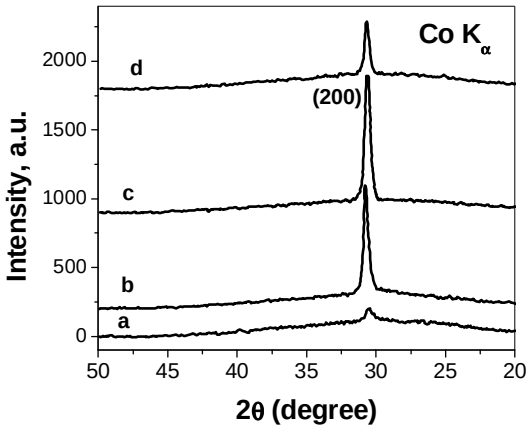

Fig. 1. XRD patterns of CdS/glass and CdS:Mnx/glass a) x=0.00 g; b) x=0.005 g; c) x=0.01 g; d) x=0.03 g.

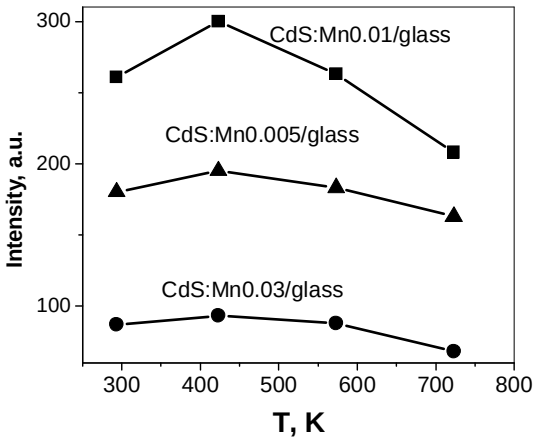

Fig. 2. Dependence of XRD peak intensity on temperature of heat treatment.

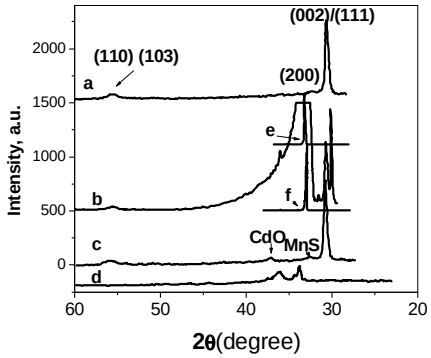

Fig. 3. Comparison of XRD patterns: a) CdS:Mn0.03/glass, b) CdS:Mn0.03/Si, c) T3CdS:Mn0.03/glass, d) p-doped Si wafer, e) attenuated XRD pattern of T3CdS:Mn0.03/Si, f) attenuated XRD pattern of CdS:Mn0.03/Si.

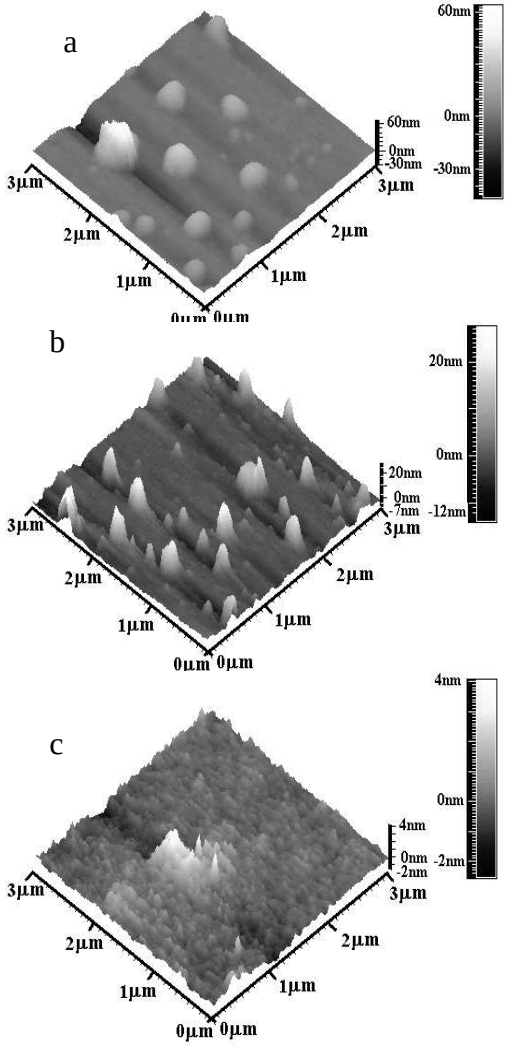

Fig. 4. Atomic force micrographs of heat treated CdS:Mn0.01/glass thin films at: a) 423K, RMS=7.53 nm; b) 573K, RMS=3.52 nm; c)723K., RMS=0.48 nm.

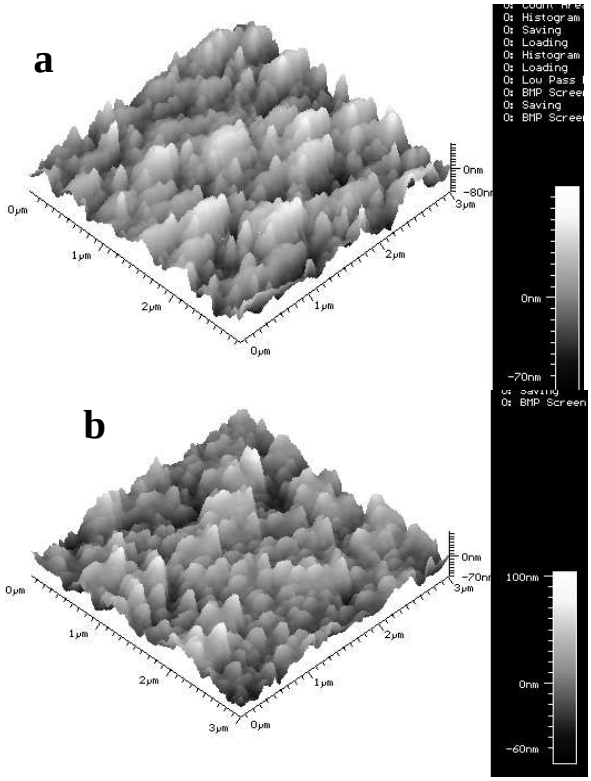

Fig. 5. Atomic force micrographs of CdS:Mn0.03/Si: a) as deposited RMS = 26.43 nm , b) heat treated at 723K RMS=22.14 nm.

3.2. Atomic force microscopy

In order to investigate the morphology of thin films deposited on glass or on Si wafers, atomic force micrographs were recorded for 3 x 3 μm^2 regions. The RMS surface roughness measured for the studied thin films indicate a smooth surface in the nanometer scale (Figs. 4 and 5). The surface morphology correlates well with the XRD results. The as deposited thin films deposited on glass substrates are composed by isolated nanocrystals in an amorphous matrix. It is visible that during the heat treatment performed at 723 K a recrystallisation process takes place and thin films become more compact and smooth. Fig. 5 evidence the effect of Si substrate in the growth of thin films. As compared with the thin films deposited on glass, the thin films deposited on Si are more crystalline.

3.3. X-Ray photoelectron spectroscopy (XPS)

The XPS analysis focused on the Cd 3*d* and S 2*p* core-level spectra, for the characterisation of the CdS host, and on the Mn 2*p* spectra, in order to evidence the chemical interaction of the dopant atoms with the host. XPS analysis was performed on high-*j* component of each well spin-orbit separated doublet (Cd $3d_{5/2}$, Mn $2p_{3/2}$), and on both ($2p_{3/2}$ and $2p_{1/2}$) lines for the S 2*p* core level.

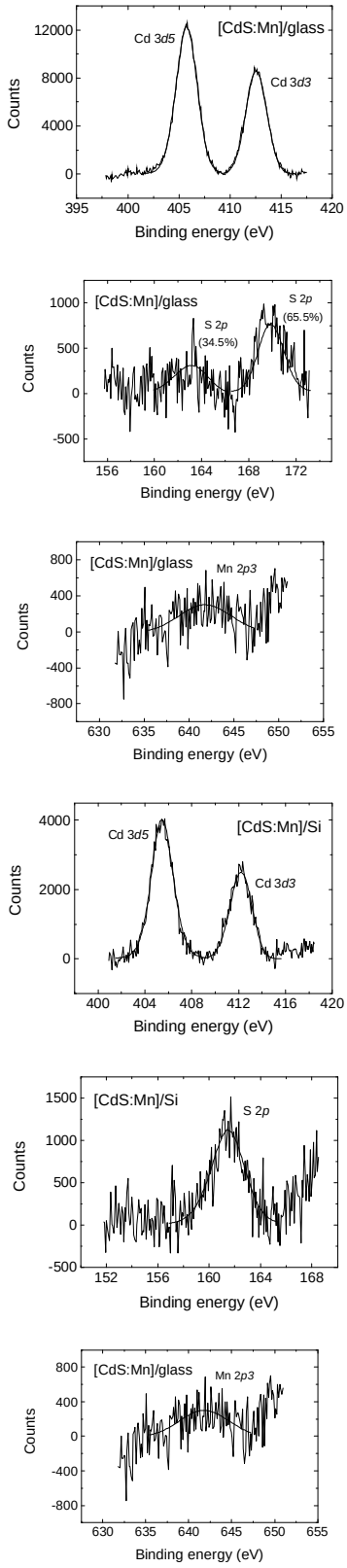

Fig. 6. Cd 3d, S 2p and Mn 2p core-level spectra of the T_3CdS:Mn0.03 thin films on glass and Si substrates.

The XPS spectra of thin films are shown in Fig.6, after subtraction of a background of Shirley type. The photoelectron lines were fitted by Gaussian-Lorentzian convolutions (Voigt profiles) (G/L) curves, with the G weight ranging between 80% and 100%. The positions of the fitted peaks (Table 1) probes the chemical state of the emitting atoms, while the element composition (atomic concentration) is calculated from the areas of the photoelectron peaks.

For the CdS film, deposited on glass, the binding energy (BE) of the Cd $3d_{5/2}$ peak (Table 1), at 405.7 eV, is close to the range of the previously reported values for CdS [6]. The S 2*p* photoelectron peak lies at 162.4 eV, also in the vicinity of the BE values characteristic of CdS. The sample composition (Table 2) indicates an enrichment of the film surface by sulfur (S:Cd = 1.24), with respect to the CdS stoichiometry. This is changed for the doped CdS films, with a systematic sulfur depletion of the surface, in favour of cadmium. The depletion effect observed for the T_3CdS:Mn0.03 film on glass substrate (Cd:S ~ 5.5) is probably influenced by thermal treatments of the films, and also by the dopant concentration. Samples deposited on Si substrates have a larger dopant concentration (T_3CdS:Mn0.03/Si) and manifest a less marked sulfur depletion.

Table 1. Binding energies (BE) of the Cd $3d_{5/2}$, S 2p and Mn $2p_{3/2}$ photoelectron peaks in the XPS The most plausible assignment of each line was indicated between parentheses.

Sample	Cd-$3d_{5/2}$ BE (eV)	S-2*p* BE (eV)		Mn-$2p_{3/2}$ BE (eV)
Reference data	CdS: 405.5 [6]	CdS:162.2 [7] MnS: 162.0 [8]	$CdSO_4$: 168.8 [9] $MnSO_4$: 169.6 [10]	MnS: 641.9 [11] $MnSO_4$: 642.7 [10] Mn_2O_3: 642.0 [12] MnO_2: 642.2 [12]
CdS/glass	405.7	162.4		
T3CdS:Mn03/glass	405.8	163.2	169.5	641.9
T3CdS:Mn/Si	405.4	161.6		642.3

For the sample T_3CdS:Mn0.03/glass, a fraction of the S atoms (34.5%) contributes by a lower BE peak to the XPS spectrum (Fig. 6), corresponding to CdS and MnS. The other S fraction, dominant, is manifested at higher energies, pointing out the formation of significant amounts of $CdSO_4$ and $MnSO_4$ on the film surface. The Cd $3d_{5/2}$ photoelectron peak, at 405.8 eV, includes the superposed contributions of CdS and $CdSO_4$. Similarly, the weak Mn $2p_{3/2}$ peak, at 641.9 eV, corresponds to the compounds MnS and $MnSO_4$. One must remark that the Mn $2p_{3/2}$ peak could also include contributions of oxidized forms (e.g. Mn_2O_3, MnO_2) in the outermost layers of the film [7,8].

The deposition of the CdS:Mn film on Si substrate has some significant effects on the surface composition: (i) sulfur is entirely included in CdS and MnS, with no evidence of the compounds $CdSO_4$ and $MnSO_4$; (ii) the Cd:S ratio (~1.3) is close to the CdS stoichiometry; (iii) the Mn concentration is about twice that of Mn in the film deposited on glass.

The chemical formula for the as deposited thin films CdS:Mn0.03 on glass or silicon are well described by $Cd_{0.88}Mn_{0.12}S$ and $Cd_{0.7}Mn_{0.3}S$ respectively.

Table 2. Element composition (atomic concentration) of the analyzed samples, calculated from the areas of the XPS peaks.

Sample	Cd(at%)	S (at%)	Mn(at%)
T3CdS/glass	44.6	55.4	
T3CdS:Mn0.03/glass	75.6	13.6	10.8
T3 CdSMn0.03/Si	45.9	33.9	20.2

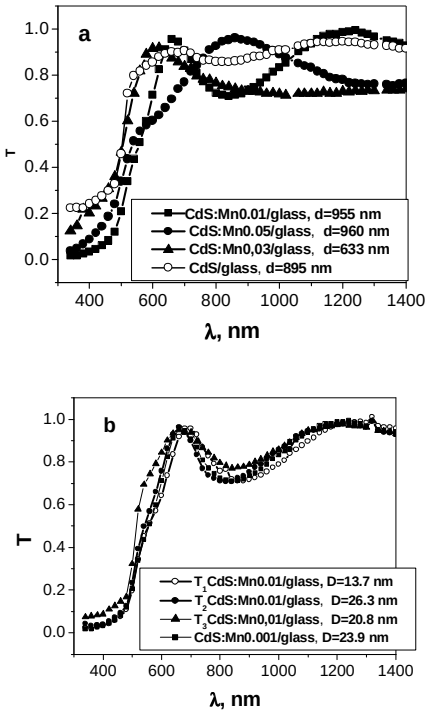

Fig. 7. *Optical spectra as a function of: a) manganese content, d = thin film thickness, b) temperature of thermal treatment, D = grain size.*

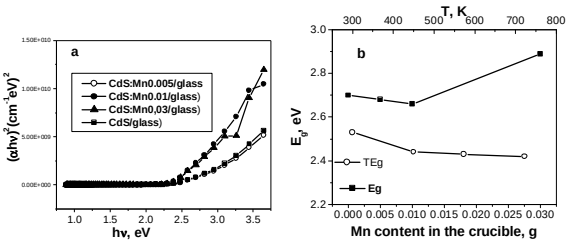

Fig. 8. a) Optical absorption spectra b) Dependence of band gap energy on Mn content, Eg, and on temperature, Teg.

3.4. Optical properties

The optical transmission (Fig. 7 a, b) were carried out for both as-deposited and heat-treated thin films grown on glass substrates. The heat treatment increases the thin film transmission for all the studied samples. The transmittance was in all cases higher than 60%. The data were used to calculate the absorbance and finally to determine the optical band gap energy (E_g, Fig. 8.a,b) using the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$. The relation $(\alpha h\nu)^2$ vs. $h\nu$ yields to a straight line, which means that the fundamental absorption edge can be described by the direct-allowed transition.

The aspect of optical spectra suggests that manganese entered into CdS lattice and also that manganese content induced changes in thin film thickness (Fig. 7). Thickness measurements evidenced an increase in the thin films thickness, in comparison to the undoped thin films (d = 895 nm), when Mn content into the crucible was lower than 0.010g (d = 960 nm) and a decrease in the thickness when the Mn content was 0.030g (d = 633 nm).

The transition at the fundamental absorption region is dependent not only on the Mn content but also on chemical homogeneity and Cd/S ratio [4]. The study of thin film optical properties as a function of temperature evidenced visible changes, in the optical spectra, only when the temperature of heat treatment was 723K (Fig. 7 b). These results correlate well with the structural data, which evidenced the formation of some oxide and sulfoxide species.

The differences in band gap energy values are clearly indicated by the thin film colors. The yellow color of thin films turned to orange or yellowish-red one as much as the value of band gap energy diminishes. The dependence of the band gap energy value on doping atom suggests that doping atoms enter into the CdS structure merely by substitution [9]. The minimum in the band gap energy (Fig. 8 a) could be attributed to exchange interactions of the conduction and valence bands electrons with the Mn^{2+} d electrons {5]. The optical band gap energy is dependent not only on doping content but also on grain size (quantum size effect). The decrease in the band gap with the temperature of the heat treatment (Fig. 8 b) can not be explained only in terms of smaller grains in nanometer scale present in as-deposited thin films forming into larger grains upon heat treatment [11]. Another reason for experimentally observed band gap narrowing after the heat treatment could be due to atomic composition changes.

4. Conclusion

Smooth CdMnS thin films were grown, using a slow rate procedure, by thermal evaporation in vacuum. The influence of support nature, manganese content and thermal treatment was studied by means of XRD, AFM, XPS and optical absorption methods. Si support acts in the growing process as a template, the thin films having a stable crystalline structure. A recrystallisation process takes place when samples are heat treated at 723 K. At low contents, manganese acts as a crystallization center and as a scattering center when content is higher then 0.010g into the crucible. XPS revealed a sulfur depletion in the top layers and confirmed the formation of some oxide and sulfoxide. An approximate stoichiometry of $Cd_{0.7}Mn_{0,3}S$ was found when films were deposited on silicon, and when a mixture of 0.150 g CdS and 0.030g Mn was used. Thin films deposited on glass are highly transparent and have lower Mn content, as compared with thin films deposited on Si. The changes in band gap energy value correlate well with the evidenced structural changes.

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