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Raman and Photoluminescence Investigation of Films of Solid Solutions $Zn_{1-x}Mn_xTe$

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In this paper, we have investigated some structural properties, Raman spectra and photoluminescence spectra of $Zn_{1-x}Mn_xTe$ films deposited by the closed space vacuum sublimation under different growth conditions. The obtained results of the Raman spectroscopy and XRD analysis show single phase composition of the samples. The presence of phonon replicas in the Raman spectra of the films indicates their high structural quality. The manganese content (about 7 %) in the layers was determined according to shifting the relative peaks positions.

1. INTRODUCTION

The semimagnetic semiconductor solid solutions are promising materials for the micro-, optoelectronics, photovoltaics and spintronics due to their unique photoluminescent, magnetic and magneto-optical properties [1, 2]. However, the properties of solid solutions $Zn_{1-x}Mn_xTe$ thin films are not well studied because of difficulty in thin layers deposition.

The obtaining of the $Zn_{1-x}Mn_xTe$ films with controllable Mn content and optimized characteristics is complicated by the substantial difference in components' pressures. Thus, typical methods for the $Zn_{1-x}Mn_xTe$ films depositions are laser [3] and flash evaporation [4], high frequency magnetron scattering [5], metal-organic deposition [6]. These methods are characterized by the high non-equilibrium of the growth process. As a result the layers have low crystal quality which is not suitable for application in photodetectors, hard radiation detectors and solar cells. In some cases, the manganese is not incorporated into the crystal lattice which is lead to formation of Mn precipitates or MnTe secondary phase. It has strong influence on films performance.

Along with the X-ray diffractometry the Raman spectrometry is widely used for the analysis of the chemical and phase composition of the material.

The goal of present work is to study Raman and photoluminescence spectra of the $Zn_{1-x}Mn_xTe$ solid solutions thin films with the different Mn concentration, obtained by the closed space vacuum sublimation under different growth conditions. This method allows to obtain high-quality thin films under close to equilibrium conditions [7-8]. The results were compared with the data obtained for the undoped ZnTe thin films.

2. EXPERIMENTAL DETAILS

Thin $Zn_{1-x}Mn_xTe$ films were deposited on cleaned glass substrates under residual gas pressure of about $5 \cdot 10^{-3}$ Pa. The detailed description of the growth setup is presented in [11-12]. The $Zn_{1-x}Mn_xTe$ powder with 10% Mn content was evaporated under the evaporator temperature $T_e = 1073$ К. The substrate temperature

was changed in the range $T_s = (423\text{-}823)$ К. The time of condensation was 15 min.

Surface morphology of the films was studied using REMMA-103-01 scanning electron microscopy (SEM).

The structural investigations of the films were performed by using the diffractometer DRON 4-07 in Ni-filtered K_a radiation of the copper anode in the angle range 2θ from 10^0 to 80^0, where 2θ is the Bragg angle. The focusing procedure was according to the Bragg-Brentano mode. The experimental curves were normalized by the intensity of the (111) peak of the cubic phase. The phase analysis was done by comparison of interplane distances and arbitrary intensities of the X-ray peaks from the examined samples and the reference data according to the JCPDS data [11].

The Raman spectra were measured at room temperature (293 K) with two different devices, which allow us to provide more reliable experimental data.

In a first case, we have used Witec Alpha SNOM with exciton laser with a wavelength of 532 nm. The measurements were made over the frequency range of 100-900 cm^{-1}.

Samples were also examined using a spectrometer TRIAX 550 (1800 grooves / mm) with an argon laser ($\lambda = 514.5$ nm). The laser power was 50 mW. The measurements were made over the frequency range of 100-700 cm^{-1}. The dispersed signal was detected with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector. Each spectrum was accumulated 30 times with an acquisition time of 10 sec. each. Long-pass Raman edge filters were used to eliminate Rayleigh scattered light from the laser.

The same equipment was used for the study of photoluminescence spectra of layers of $Zn_{1-x}Mn_xTe$.

The optical properties of the $Zn_{1-x}Mn_xTe$ layers were compared with undoped ZnTe films, obtained under similar growth conditions.

3. RESULTS AND DISCUSSION

SEM images of the surface and cross-section of $Zn_{1-x}Mn_xTe$ films, obtained at different substrate temperatures are shown in Figure 1.
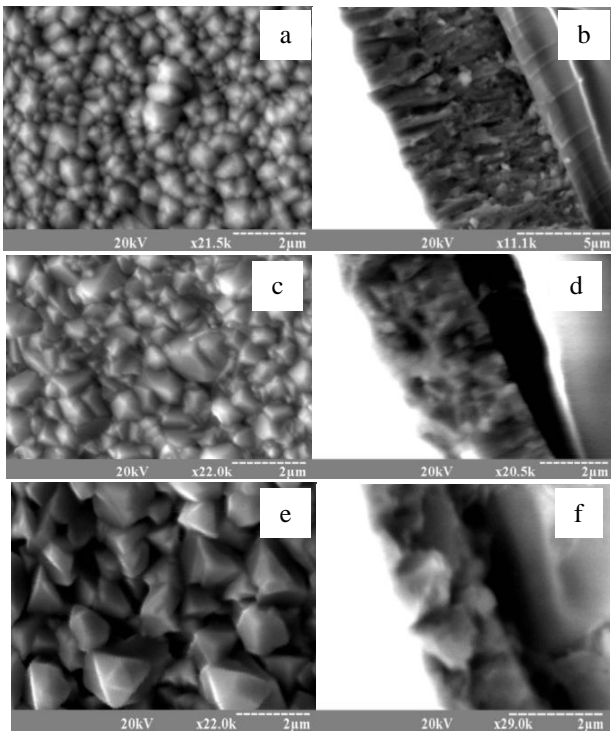
Fig. 1. – SEM images of the surface (a, c, e) and cross section of the $Zn_{1-x}Mn_xTe$ films (b, d, f) obtained at substrate temperature T_s : 423 K (a, b), 623 K (c, d) and 823 K (e, f) respectively

As was shown earlier [15], the obtained films have polycrystalline structure with the stable cubic modification and contained 1.61-3.04 at. % of manganese. The grain size of the films was $D = (0.50\text{-}1.12)$ mm and thickness $l \sim (2\text{-}4)$ um, the D is increase with substrate temperature. The calculated value D in the layers of solid solutions were somewhat smaller than for the films ZnTe, deposited under similar growth conditions [22-23].

The diffraction patterns of Mn doped zinc telluride films deposited at different substrate temperatures are shown in Figure 2.
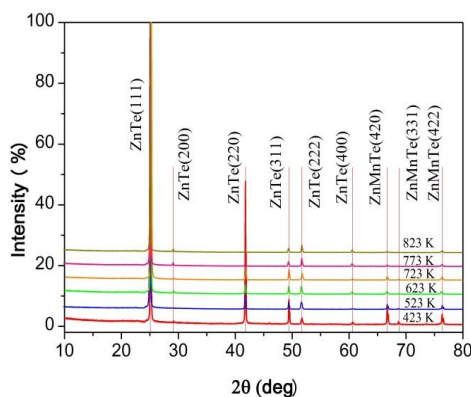

Fig. 2 - X-ray diffraction of the films $Zn_{1-x}Mn_xTe$ obtained under different growth conditions

The films have single-phase cubic structure. The low intensity line (0.7% of the (111) line intensity) at 73.49^0 was observed for the film obtained at $T_s = 423$ this line can be identified as the reflection from the crystal plane (444) of manganese. It should be noted

that the additional lines were not observed for the other samples.

The Raman spectra of the films $Zn_{1-x}Mn_xTe$, obtained using the Witec Alpha SNOM are shown in Figure 3. The spectra show a number of intense lines at 177, 211, 417 and 621 cm^{-1} frequencies. According to the reference data, these lines have been interpreted as 1TO, 1LO, 2LO, 3LO phonon modes [16, 17]. The half-width of the 1LO peak is varied from 12.5 to 16.9 cm^{-1} for the different samples.
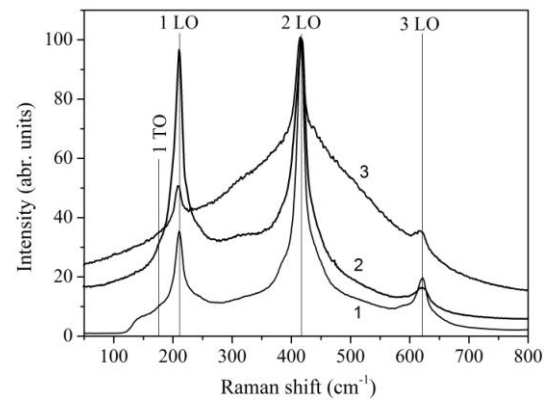

Fig.3 – Raman spectra of films $Zn_{1-x}Mn_xTe$, deposited at different substrate temperatures: $T_{s,}$ K: 623 (1); 723 (2); 823 (3)

Raman spectra were obtained using a spectrometer TRIAX 550 are shown in Figure 4. are similar to the results of the previous Raman experiment. The spectra are show intense peaks at frequencies of 176, 204, 410, and 616 cm^{-1}. These peaks were also interpreted as 1TO, 1LO, 2LO, 3LO phonon modes. In addition, a weak intensity peak at frequencies of 381 cm^{-1} was observed, this peak was not interpreted. The presence of several orders of phonon replicas in the spectra indicates their high structural quality.
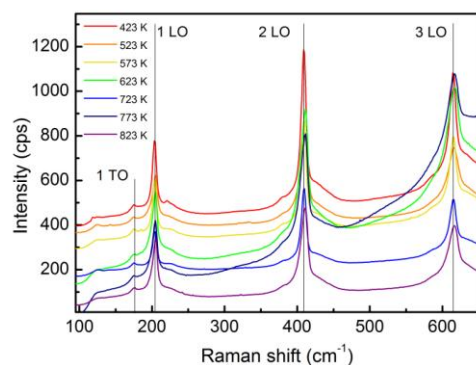

Fig. 4 – Raman spectra of the films of $Zn_{1-x}Mn_xTe$, caused by various physical and technological regimes of condensation

The Raman data of the $Zn_{1-x}Mn_xTe$ films was compared with the undoped ZnTe (Fig. 5). There are 4 peaks were observed at the frequencies 175, 204, 409 and 615 cm^{-1}. According to reference data [18-20] observed peaks are correspond to 1TO, 1LO, 2LO and 3LO phonon modes zinc telluride (177, 210, 420, 630 cm^{-1} [20]).
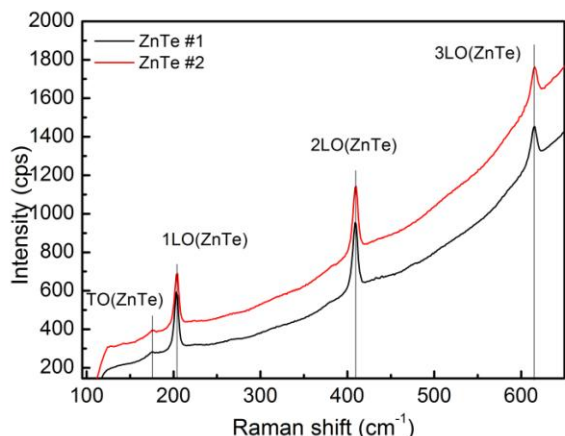
Fig. 5 – Raman spectra of the films of ZnTe, deposited at a substrate temperature $T_s = 623$ К (1), 823 К (2). $T_e = 973$ К

The presence of manganese impurity in ZnTe leads to a shift of Raman peaks comparatively with pure material. The Mn (about 7%) concentration was determined by the lines shift.

The photoluminescence spectra of the solid solution films are shown in Fig. 6. These results are similar to data obtained in [21-22]. Most of them show several peaks with the energy which are listed in Table 1. These peaks are due to the Raman effect, since the laser light that was used was 514.5 nm.

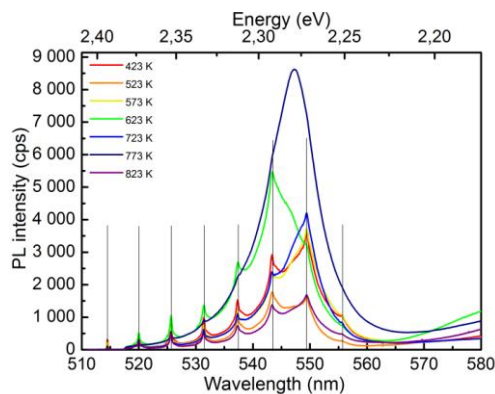The photoluminescence spectra of undoped ZnTe show only one peak at 549.61 wavelength.

Fig. 6 – Photoluminescence spectra of the films $Zn_{1-x}Mn_xTe$, obtained at different growth conditions
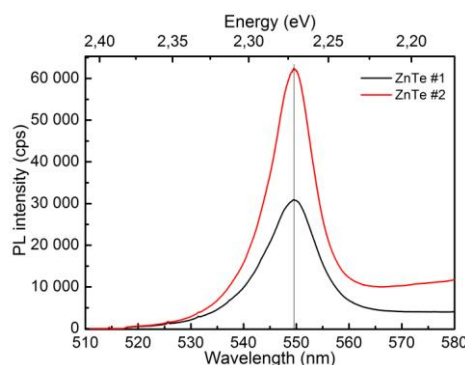

Fig. 7 – Photoluminescence spectra of the films of ZnTe, deposited at T_s=623 К (1), 823 К (2). T_e=973 К substrate temperatures

Table 1 - Energies of the photoluminescence peaks observed on the $Zn_{1-x}Mn_xTe$ films spectra.

λ, nm	514.5	520	525.65	531.4	537.3	543.35	549.44	555.65
E, eV	2.41	2.39	2.36	2.33	2.31	2.28	2.26	2.23

4 CONCLUSIONS

The present study of the $Zn_{1-x}Mn_xTe$, obtained by the closed space sublimation under different growth conditions shown that films with a thickness of $l \sim (2\text{-}8)$ have a grain size m $D = 0.50\text{-}1.12$ microns and it increases with the substrate temperature. The obtained films were single phase with a stable cubic structure. The results of Raman spectroscopy confirm single-phase composition of the samples. The presence of several orders of phonon replicas in the spectra of solid solution films indicates their high structural quality.

According to the shift of the relative position of the peaks in Raman spectra of the $Zn_{1-x}Mn_xTe$ comparatively to the undoped ZnTe allow us to estimate Mn concentration in a samples (about 1-3 %).

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