

Studying the Elemental Composition and Manganese Distribution in $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ Films Using the μ -PIXE and EDAX Methods

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Abstract—The methods of proton-induced X-ray emission (μ -PIXE) and energy-dispersive X-ray analysis (EDAX) are used to study the elemental composition and areal distribution of manganese in $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ films. The μ -PIXE technique is implemented using a nuclear scanning microprobe with a proton-beam energy of 1.5 MeV and cross-sectional dimensions of $4 \times 4 \mu\text{m}$. The semimagnetic solid solution films are obtained under different operating modes of thermal vapor deposition in the quasiclosed volume of a manganese-containing blend.

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INTRODUCTION

The solid solutions $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ are presently attracting the special interest of material scientists, as these solutions have unique magnetic and magneto-optic properties (giant Zeeman and Faraday effects) and are capable of anomalous photoluminescence [1, 2]. The lattice constant, band-gap width (E_g), and other parameters of these materials may be altered by varying the transition-metal (Mn) concentration. This makes them promising for the construction of heterojunctions with small mismatches between lattice constants and an optimized band structure [2, 3].

However, films of manganese-containing semimagnetic solid solutions are studied insufficiently due to the fact that it is rather difficult to produce them [4–6]. The difficulties are attributable to the dissociation of A^2B^6 compounds upon sublimation and the large differences in the saturation vapor pressures of components of the solid solutions (Zn, Mn, S, and Te). This hinders the production of stoichiometric condensates with a controlled admixture content [7]. It is these factors that determine the significance of identifying the interrelation between the chemical composition and physical and technological conditions of the manufacturing of films of semimagnetic solid solutions.

EXPERIMENTAL

Films of the solid solutions $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ were produced in accordance with the method of sublimation in a quasiclosed volume on

cleaned glass substrates [8, 9]. The deposition temperature (T_s) varied from 373 to 723 K when layers of $Zn_{1-x}Mn_xS$ were deposited, and the evaporator temperature (T_e) equaled 1273 K. A semiconductor-grade blend with a manganese content of about 7% was evaporated. The temperatures T_s and T_e were equal to 623–823 and 1073 K, respectively, when the films of $Zn_{1-x}Mn_xTe$ were deposited. A blend with a manganese content of 30% was used.

The samples were studied using a microanalytical accelerator complex based on the compact electrostatic accelerator Sokol with a proton-beam energy of up to 2 MeV (Institute of Applied Physics, National Academy of Sciences of Ukraine, Sumy). This complex provides analytical channels for ion luminescence, nuclear reactions, Rutherford backscattering (with a magnetic spectrometer), and a nuclear scanning microprobe (with secondary-electron-emission detectors, a semiconductor detector of characteristic X-ray radiation, and a charged particle detector) [10].

The characteristic X-ray radiation induced by a proton beam was used to study the films [11, 12]. Such methods were earlier applied to semiconductors and materials of other types [13, 14]. Aggregate spectra from several areas of the sample surface (μ -PIXE) were first obtained, and then they were scanned pointwise with a microbeam (μ -PIXE). Film regions with a size of $200 \times 200 \mu\text{m}$ were normally scanned. The probe cross-sectional dimensions were $4 \times 4 \mu\text{m}$, and the charge Q equaled $4 \times 10^{-10} \text{C/pixel}$. Scanning was carried out with a 50×50 pixel raster, a step of $4 \mu\text{m}$, and a proton-beam energy of $E_p = 1.5 \text{ MeV}$. These studies resulted in a map of the doping-element (Mn) distri-

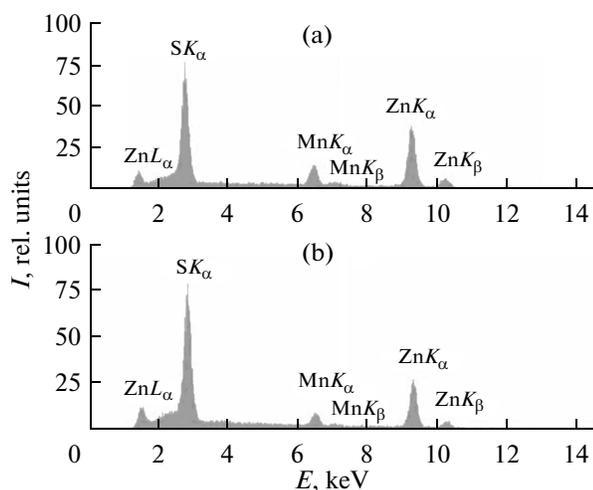


Fig. 1. (a) Fragments of characteristic X-ray spectra (EDAX) from the blend and (b) the film of the $Zn_{1-x}Mn_xS$ solid solution obtained at $T_s = 673$ K and $T_e = 1273$ K.

bution over the sample area and made it possible to determine the elemental composition of condensates in several regions of the films. The PIXE spectra were processed using GUPIX software. The specifics of the scanning and focusing system of the microanalytical accelerator complex are described in [10].

The elemental composition of the solid-solution films was also studied with the use of a scanning electron microscope (REMMA-103-01) via the energy-dispersive X-ray analysis (EDAX) method. The con-

centration of elements was determined for no less than 5 points on the sample surface with subsequent averaging of the results. A standard expression cited in [15] was used to convert the mass concentration into the atomic (C_i) one. The atomic concentration ratios C_A/C_B and C_{A+Mn}/C_B were used to estimate the deviation of the film composition from stoichiometry.

RESULTS AND DISCUSSION

The typical characteristic spectra of X-ray spectroscopic microanalysis of the blend and the $Zn_{1-x}Mn_xS$ film sample are shown in Fig. 1. It can be seen that only the lines of major solid-solution components are manifested in the spectra. Uncontrolled and residual impurities were not observable within the limits of the method accuracy.

By processing the spectra, we determined the mass concentrations of the constituent elements of the $Zn_{1-x}Mn_xS$ films. The corresponding results for a series of samples obtained under different physical and technological condensation conditions are presented in the table.

Figure 2 shows the dependences of (a) the atomic concentration of manganese (C_{Mn}) in the $Zn_{1-x}Mn_xS$ films and (b) the ratios C_{Zn}/C_S and C_{Zn+Mn}/C_S on the material condensation temperature. The dashed lines correspond to the values in the initial blend.

The studies showed that the atomic concentration of manganese in the $Zn_{1-x}Mn_xS$ films was monotonically reduced from 5.82 to 1.75 at % as the T_s conden-

Elemental composition of $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ films

Zn _{1-x} Mn _x S (EDAX)									
T_s , K	T_e , K	Zn, wt %	Mn, wt %	S, wt %	Zn, at %	Mn, at %	S, at %	C_{Zn}/C_S	C_{Zn+Mn}/C_S
Blend		72.50	6.86	20.64	59.06	6.65	34.29	1.72	1.92
373	1273	20.94	8.55	70.51	11.97	5.82	82.21	0.15	0.22
523	1273	73.09	3.00	23.91	58.27	2.85	38.88	1.50	1.57
623	1273	69.70	3.17	27.14	54.11	2.93	42.96	1.26	1.33
673	1273	69.06	2.61	28.33	53.15	2.39	44.46	1.20	1.25
723	1273	66.69	1.96	31.35	50.16	1.75	48.08	1.04	1.08
Zn _{1-x} Mn _x Te (PIXE)									
T_s , K	T_e , K	Zn, wt %	Mn, wt %	Te, wt %	Zn, wt %	Mn, wt %	Te, wt %	C_{Zn}/C_{Te}	C_{Zn+Mn}/C_{Te}
623	1073	28.9	1.70	69.40	43.47	3.04	53.49	0.81	0.87
723	1073	30.55	1.09	68.36	45.68	1.94	52.38	0.87	0.91
823 (Sample 1)	1073	26.22	1.02	72.76	40.51	1.88	57.61	0.70	0.74
823 (Sample 2)	1073	26.34	0.88	72.78	40.72	1.62	57.66	0.71	0.73

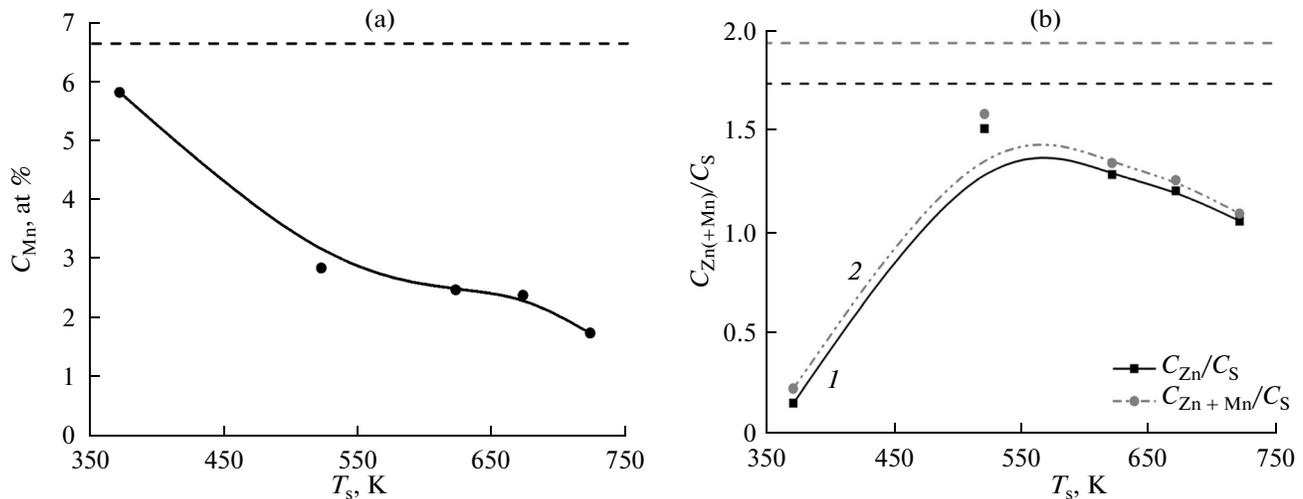


Fig. 2. Dependence of (a) the atomic concentration C_{Mn} and (b) stoichiometry C_{Zn}/C_S (1) and C_{Zn+Mn}/C_S (2) on the T_s deposition temperature.

sation temperature was increased from 373 to 723 K, while the ratio of the aggregate atomic concentration of zinc and manganese (C_{Zn+Mn}) to the atomic concentration of sulfur (C_S) first rose from 0.22 to 1.57 ($T_s = 623$ K) and then started decreasing as the substrate temperature was increased further and went down to 1.08 ($T_s = 723$ K). It can be seen from the table that the concentration of manganese in the initial blend equaled 6.65 at %.

A typical aggregate PIXE spectrum (on the logarithmic scale) from the $Zn_{1-x}Mn_xTe$ films irradiated with a proton beam is shown in Fig. 3. The irradiated-region size was $200 \times 200 \mu m$.

It can be seen that only the lines of the solid-solution components (Zn, Mn, and Te) are present in the spectra. The results of analyzing the elemental composition of the samples are presented in the table. The table shows that the $Zn_{1-x}Mn_xTe$ films, as well as the $Zn_{1-x}Mn_xS$ films, exhibit a trend towards a decrease in the manganese concentration from 3.04 to 1.62 at % when the layer condensation temperature T_s is increased from 623 to 823 K. The obtained films were at the same time enriched with tellurium ($C_{Zn+Mn}/C_S = 0.73-0.91$).

The averaged calculation data are also presented in the table. As already pointed out, the measurements were conducted at several points on the sample surfaces. It should be noted that the used method revealed no changes in the solid-solution composition over the film area.

The maps of manganese distribution in $Zn_{1-x}Mn_xTe$ films obtained at different deposition temperatures T_s are shown in Fig. 4. The scales next to the maps (0–15 and 0–50) denote the number of quanta of characteristic X-ray radiation induced by the focused proton

beam in the range of energies corresponding to the MnK_α peak in the spectrum in Fig. 3.

These studies showed that the distributions of Mn denoted with different shades of grey in Figs. 4a and 4b were somewhat different from each other, as its concentration decreases with increasing film-deposition temperature. However, the differences in the characteristic X-ray radiation yield in each pixel are at the level of statistical variability. Therefore, we may conclude that manganese is rather evenly distributed over the sample area.

Thus, the analysis carried out in the present work allows one to predict the manganese content and stoichiometry of films of $Zn_xMn_{1-x}S$ and $Zn_{1-x}Mn_xTe$

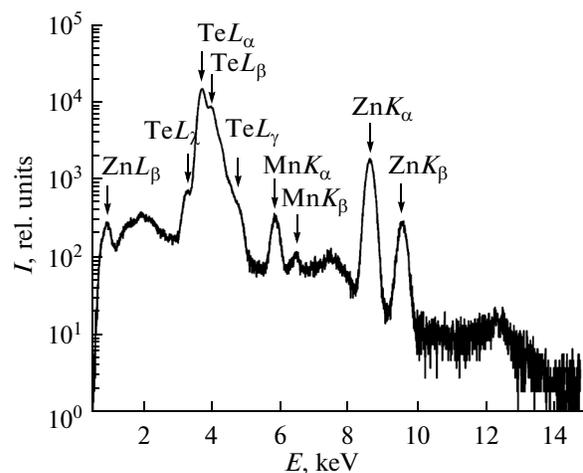


Fig. 3. Typical aggregate PIXE spectrum induced by a proton beam from a $Zn_{1-x}Mn_xTe$ film ($T_s = 823$ K and $T_e = 1073$ K).

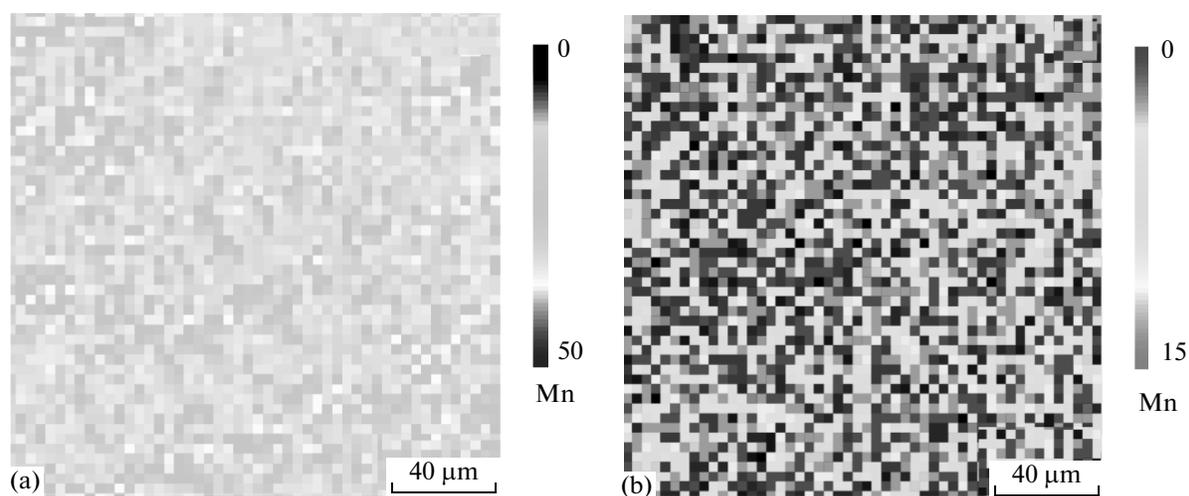


Fig. 4. Maps of Mn distribution in $Zn_{1-x}Mn_xTe$ films at a scanning step of $4\ \mu m$ for (a) $T_s = 723\ K$ and (b) $T_s = 823\ K$.

solid solutions deposited via thermal evaporation in a quasiclosed volume.

CONCLUSIONS

The elemental composition and area distribution of manganese in $Zn_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xS$ films obtained via thermal evaporation in a quasiclosed volume under various technological deposition modes were studied using the μ -PIXE and EDAX methods. It was shown that the manganese concentration in the films varied from 1.62 to 5.82 at % depending on the layer condensation temperature. It was found that manganese was evenly distributed over the film area.

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