THERMOELECTRIC POWER IN EPITAXIAL $Ga_{1-x}Mn_xAs$ FILMS

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The thermoelectric power (TEP) in epitaxial $Ga_{1-x}Mn_xAs$ (x =0.03÷0.055) films 0.3 to 3 μm in thickness grown by the low-temperature molecular-beam-epitaxy (LT-MBE) technology on semi-insulating GaAs (100) substrates has been measured in the temperature range 10—300 K. The current carriers (holes) in the films under investigation had the concentration of $(1 \div 4) \times 10^{20}$ cm^{-3} and possessed the mobility of $1 - 10$ cm^2/(V × s). The analysis of the temperature dependences of TEP brought us to the conclusion about the presence of three contributions to the total TEP value, namely, the standard diffusion, ferromagnetic contribution, and exchange one. The model of a non-uniform distribution of magnetic phases has been considered for the film consisting of a paramagnetic phase and ferromagnetic clusters.

1. Introduction

A significant number of works devoted to studying the electronic, magnetic, optical, and transport properties of diluted magnetic (semimagnetic) semiconductors has been published for last decades [1]. The interest in those materials has grown in connection with the discovery of ferromagnetism in $A^{III}B^{V}$ compounds at the beginning of the 1990s. Ferromagnetic semiconductors enable one to use two degrees of freedom of current carriers — a charge and a spin — simultaneously, which presents new functional potentialities. The diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$ attracts a special attention owing to the perspective to attain a high temperature of the ferromagnetic ordering and the opportunity of its simple integration into the existing technologies.

Ferromagnetism in $Ga_{1-x}Mn_xAs$ requires very high concentrations of holes ($10^{20} - 10^{21}$ cm^{-3}), the latter serving for the indirect exchange interaction between manganese ions [2]. Contrary to the diluted magnetic $A^{IV}B^{VI}$ semiconductors with Mn ions, manganese forms electrically active acceptor centers in $Ga_{1-x}Mn_xAs$ which provide both the existence of local magnetic moments and the high concentrations of current carriers (holes) [3]. The highest Curie temperature (T_C) achieved by the group of authors [4] amounts to 175 K for $x = 0.08$ at.% and the hole concentration of 1.5×10^{21} cm^{-3}.

As a rule, $Ga_{1-x}Mn_xAs$ films are grown by the MBE method under ultrahigh vacuum. In so doing, manganese atoms with low concentration are distributed statistically over the lattice and independently of gallium ones [3]. At large Mn concentrations, the formation of a ferromagnetic phase MnAs with $T_C = 321$ K is more convenient energetically. To produce alloys with high contents of Mn (up to 10%), the LT-MBE method is used, with the temperature of a substrate being about 250°C [5].

In the prepared films, manganese atoms occupy mostly electrically non-active interstitial positions in the GaAs crystal lattice. In order to replace gallium by manganese, the films are annealed. In the course of this procedure, the hole concentration grows sharply, and the film becomes ferromagnetic.

This work aims at studying the thermoelectric properties of epitaxial $Ga_{1-x}Mn_xAs$ films in order to

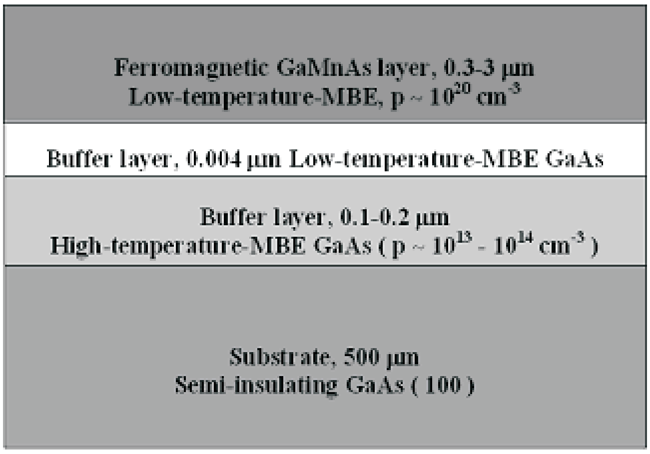


Fig. 1. Structure of specimens with a ferromagnetic $Ga_{1-x}Mn_xAs$ layer (LT-MBE)

elucidate the effect of Mn on the TEP in them and the character of exchange interaction between current carriers and Mn ions.

2. Experimental Results and Their Discussion

Epitaxial $Ga_{1-x}Mn_xAs$ films with $0.01 < x < 0.06$ and 0.3—3 μm in thickness were grown by the LT-MBE method on GaAs (100) substrates with a buffer semi-insulating GaAs film 0.1—0.2 μm in thickness deposited using the high-temperature MBE (HT-MBE) method. A thin 4-nm GaAs layer was deposited using the LT-MBE method between the GaMnAs film and the buffer layer [6] (see Fig. 1). The holes in the film had the concentration $p \approx (1 \div 4) \times 10^{20}$ cm^{-3} and the mobility $\mu \approx 1 \div 10$ cm^2/(V $\times$ s). The TEP of the $Ga_{1-x}Mn_xAs$ films was studied in the temperature interval 10—300 K. The characteristics of the specimens obtained are quoted in the table.

While analyzing the TEP of $Ga_{1-x}Mn_xAs$, we considered the role of the buffer GaAs layer which, together with $Ga_{1-x}Mn_xAs$ one, can govern the conductivity of the heterostructure.

The thermoelectric parameters of the considered structure with two conducting layers were calculated in work [7]. The experimentally investigated "effective" TEP of two conducting layers, $\alpha_{\rm exp}$, can be presented in the form

$$\alpha_{\rm exp} = \frac{\alpha_L \sigma_L d_L + \alpha_B \sigma_B d_B}{\sigma_L d_L + \sigma_B d_B}, \qquad (1)$$

where α_i, σ_i, and d_i are the TEP, conductivity, and thickness of the $Ga_{1-x}Mn_xAs$ ($i = L$) and buffer ($i = B$) layers, respectively.

In our case, $\sigma_L d_L / \sigma_B d_B \approx 10^3$; therefore, practically, $\alpha_{\rm exp} \approx \alpha_L$. The low-temperature MBE-layer of GaAs which is located on the buffer layer is 100 times thinner than other layers. Hence, the contribution of this layer to the total TEP can be neglected.

Parameters of the p-$Ga_{1-x}Mn_xAs$ films

N of sample	Thickness, μm	x	T_C, K	$\alpha_{\rm FM}$ in maximum, μV/K	α_e μV/K
A378	2.0	0.03	15	11.5	−12
A377	2.0	0.04	6	10.5	−9
A375	1.6	0.055	20	13	−11

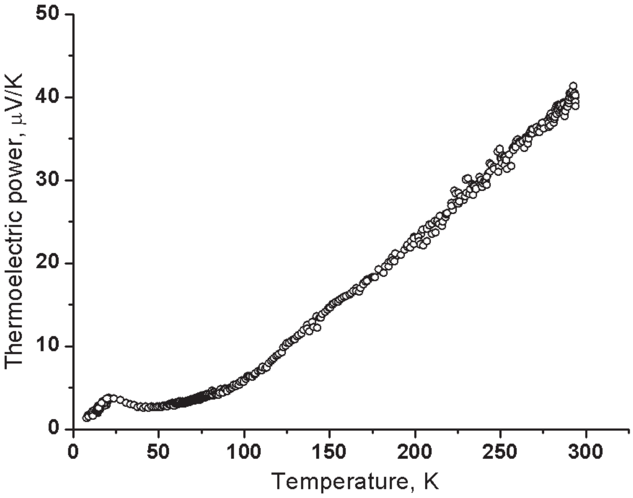


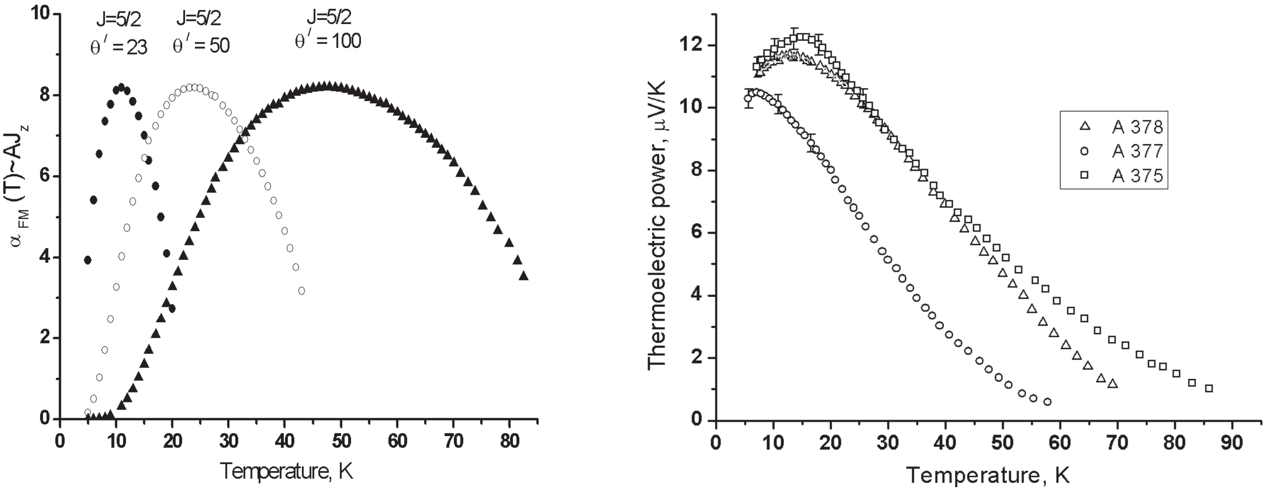
Fig. 2. Temperature dependence of TEP in $Ga_{0.945}Mn_{0.055}As$

Fig. 2 shows a typical temperature dependence of the TEP of $Ga_{1-x}Mn_xAs$ films. The TEP sign evidences for the conductivity of the p-type within the whole researched temperature interval. At $T > 100$ K, the temperature dependences of α for specimens with the Mn content $x = 0.03$ and 0.04 were superlinear, and linear for $x = 0.055$. At $T < 100$ K, the dependences $\alpha(T)$ of all specimens have a tendency to saturation.

The experimentally measured TEP in a diluted magnetic semiconductor is composed of three terms: the ordinary diffusion contribution α_D, the contribution of the exchange TEP α_e, and the ferromagnetic contribution $\alpha_{\rm FM}$.

The ordinary (diffusion) contribution to the TEP in a degenerate hole gas with a parabolic energy band looks like

$$\alpha_D = \frac{\pi^2 k_{\rm B}^2 T}{3 e E_{\rm F}} \left(r + 3/2\right), \qquad (2)$$



a **b**

Fig. 3. Temperature dependences of the ferromagnetic contribution α_{FM} to TEP in various specimens of the Ga$_{1-x}$Mn$_x$As films: (a) the calculation in the framework of the Kasuya theory and (b) the experimental results

where E_{F} is the Fermi energy, r the parameter of scattering, e the electron charge, and k_{B} the Boltzmann constant.

Expression (2) describes TEP in the case where the current carrier scattering does not depend on the spin and where the relaxation time τ is reciprocal to the density of states ρ_{F} at the Fermi level: $\tau(E) \sim 1/(\rho_{\mathrm{F}}(E))^{-1/2}$.

We neglect the contribution of the phonon capture to TEP, because it is important for semiconductors or metals, in which a phonon has a large mean free path due to the weak electron–phonon interaction.

We consider the saturation of α at low temperatures as a result of the exchange interaction between current carriers and magnetic centers. The exchange component of TEP, α_e, has been discovered experimentally for the first time by us in a Mn-doped solid solution Pb$_{1-x}$Sn$_x$Te ($0.18 < x < 0.23$) [8]. The sign of this component was negative and coincided with that of the diffusion TEP. The value of α_e does not depend on temperature and looks like [9]

$$\alpha_e = 4\pi^2 \frac{k_{\mathrm{B}}}{e} \rho_{\mathrm{F}}^2 IV \frac{\rho_e}{\rho}, \tag{3}$$

where I is the integral of the exchange interaction between holes and magnetic centers, V the amplitude of potential scattering, and ρ_e/ρ the ratio between the exchange portion of the specific resistance to its total value.

The negative value of α_e in Ga$_{1-x}$Mn$_x$As, provided that it does not depend on temperature, was determined by extrapolating the linear section of the dependence $\alpha(T)$ down to $T = 0$. We note that the negative sign of α_e differs from that of α_{D}. The data of α_e for various Mn contents are quoted in the table.

In the range of ferromagnetic ordering, an anomalous component of TEP appears and looks graphically like an arch with the maximum at $T = T_{\mathrm{C}}$. Such a phenomenon has been observed by us in PbSnMnTe [10].

The quantitative analysis of the ferromagnetic contribution to the TEP of Ga$_{1-x}$Mn$_x$As specimens was carried out in the framework of the Kasuya theory for ferromagnetic metals and alloys with a magnetic component. This theory is based on the molecular field approximation and considers the exchange interaction between the localized d-electrons of manganese atoms and free carriers to be responsible for the ferromagnetic ordering. Current carriers are responsible for the indirect exchange between magnetic ions. We calculated the magnetic contribution to TEP making use of the expression [11]

$$\alpha_{FM} = -FA\overline{J_z^2}, \tag{4}$$

where F is a certain function independent of the temperature,

$$A(x) = \frac{2x^2}{e^x + e^{-x} - 2},$$

$$\overline{J_z^2}(x) = \left(J + \frac{2J+1}{e^{(2j+1)x} - 1} - \frac{1}{e^x - 1} \right),$$

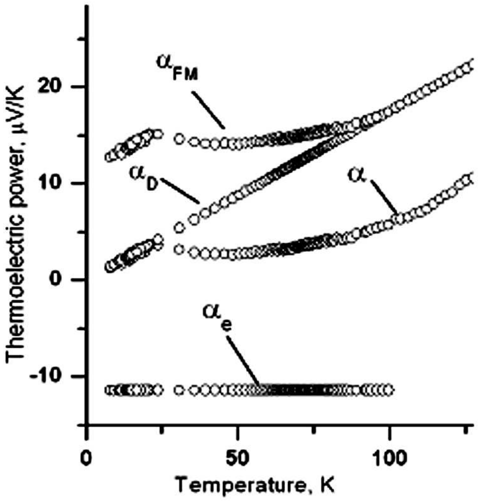


Fig. 4. Temperature dependences of various contributions to TEP in the $Ga_{0.945}Mn_{0.055}As$ film

$$x = H_0/k_{\mathrm{B}}T, \quad H_0 = 3k\theta/J(J+1),$$

and J the total quantum number of the magnetic impurity.

The theoretical calculations for the temperature dependence of α_{FM} by expression (4) for $J = 5/2$ and various Curie temperatures θ are depicted in Fig. 3,*a*. At the same time, subtracting the exchange and diffusion contributions from the experimental values of $\alpha_{\mathrm{exp}}(T)$, we singled out the "experimental" ferromagnetic contribution $\alpha_{\mathrm{FM}}(T)$. The "experimental" contributions to the TEP of $Ga_{1-x}Mn_xAs$, connected to the ferromagnetic transition and determined in such a way, are shown in Fig. 3,*b*.

It should be noted that the $Pb_{0.16}Sn_{0.72}Mn_{0.12}Te$ specimens, which manifest a ferromagnetic transition [10], do not demonstrate the exchange contribution to TEP. In our opinion, this can be a result of the following reasons. Contrary to the PbSnMnTe system , $Ga_{1-x}Mn_xAs$ compounds are highly doped compensated semiconductors, where, owing to their growing under nonequilibrium conditions of MBE, a lot of defects is created [12]. Therefore, the energy spectrum of $Ga_{1-x}Mn_xAs$ is very complicated and has not been established ultimately until now. Here, one may expect for the Kondo mechanism to be realized, which would result in the exchange interaction between current carriers and isolated centers, i.e. in the appearance of the α_e component. Simultaneously, provided that the ferromagnetic ordering takes place, the component α_{FM}, which describes the interaction between current carriers and the molecular field of magnetic clusters (the Kasuya mechanism), appears.

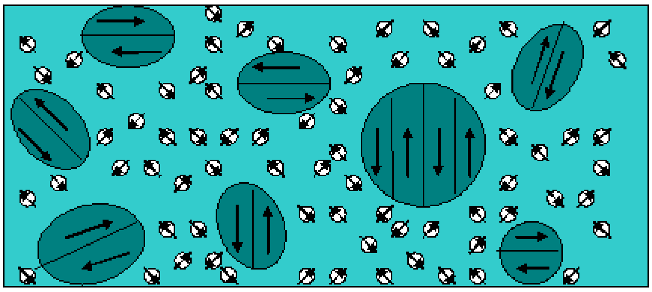


Fig. 5. Schematic image of the non-uniform distribution of magnetic phases in $Ga_{1-x}Mn_xAs$ films: magnetic clusters and localized spins

Thus, we revealed the existence of three contributions to the total TEP in a $Ga_{1-x}Mn_xAs$ compound (Fig. 4): 1) the diffusion one which is proportional to the temperature for the degenerate gas of current carriers with a parabolic band in their energy spectrum; 2) the exchange contribution and 3) the ferromagnetic one.

The complete expression for TEP has the form

$$\alpha = \alpha_D + \alpha_{\mathrm{FM}} + \alpha_e = \frac{\pi^2 k_{\mathrm{B}}^2 T}{3eE_{\mathrm{F}}}(r + 3/2) -$$

$$-FA\overline{J_z^2} - 4\pi^2 \frac{k^2}{e} \rho_{\mathrm{F}}^2 IV \frac{\rho_e}{\rho}. \tag{5}$$

From formula (3), one can see that the sign of α_e is defined by the sign of the current carrier charge and the sign of the exchange integral. It means that the negative sign of the exchange TEP in $Ga_{1-x}Mn_xAs$ of the p-type is caused by a negative sign of the exchange integral ($I < 0$). On the contrary, the negative value of α_e in PbSnMnTe specimens of the n-type testifies to that $I > 0$.

Thus, the thermoelectric studies of $Ga_{1-x}Mn_xAs$ films grown by the MBE method under known nonequilibrium conditions and PbSnMnTe single crystals evidence for different characters of the manganese ion distributions in those two materials.

In the case of PbSnMnTe, the manifestation of the α_e and α_{FM} components is precisely determined. Provided the manganese concentration $p = 2 \times 10^{18} \div 5 \times 10^{19}$ cm^{-3} and low temperatures $T < 20$ K, only the exchange component of TEP is observed. If the content of manganese in the cation sublattice amounts to 10—12% ($p = 1 \times 10^{20} \div 3 \times 10^{21}$ cm^{-3}), the experiment reveals only the ferromagnetic component [10].

In the case of Ga$_{1-x}$Mn$_x$As, the simultaneous manifestation of two TEP components, α_e and $\alpha_{\rm FM}$, testifies to that the distribution of manganese in the film is exceptionally non-uniform. Together with the regions of the film where the ferromagnetic interaction dominates and, correspondingly, which are ferromagnetically ordered, there exist the regions where manganese ions are spatially separated and play the role of localized magnetic moments not coupled by the exchange interaction forces. The proposed model is schematically imaged in Fig. 5.

As a rule, the fluctuations of a local exchange field are well averaged owing to the long-range exchange interaction. But, in the case of ferromagnetic Ga$_{1-x}$Mn$_x$As, the radius of the exchange interaction is much shorter. Therefore, the averaging of a disorder is less effective, and the fluctuations concerned are strongly pronounced in the alloy [13]. These conclusions of the authors of work [13] confirm our results about the inhomogeneity of the ferromagnetic ordering in Ga$_{1-x}$Mn$_x$As.

Thus, the researches of the TEP of dilute magnetic semiconductors make it possible to obtain the information concerning the inhomogeneity of the distribution of a magnetic component in a material and the character of the exchange interaction between current carriers and magnetic ions.

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1. *Ohno H.* // J. Magn. and Magn. Mater. — 1999. — **200**, N10. — P. 110—129.
2. *Dietl T., Ohno H.* // Physica E. — 2001. — **9**, N 1. — P. 185—193.
3. *Twardowski A.* // Acta phys. pol. A. — 2000. — **98**. — P. 203.
4. *Sawicki M.* // Abstr. XXXIII Intern. School Phys. Semicond. Comp. — Jaszowiec: Inst. Phys., PAS, 2004. — P. 67.
5. *Ohno H.* // Appl. Phys. Lett. — 1996. — **69**, N 3. — P. 363—365.
6. *Sadowski J., Domagala J.Z., Bak-Misiuk J. et al.* // Thin Solid Films. — 2000. — **367**. — P. 165.
7. *Lin-Chung P.J., Reinecke T.L.* // Phys. Rev. B. — 1995. — **51**. — P. 13244.
8. *Lashkarev G.V., Kikodze R.O., Radchenko M.V. et al.* // Fiz. Tekhn. Polupr. — 1979. — **13**, N8. — P. 1548—1555.
9. *Kondo J.* // Solid State Phys. — 1969. — **23**. — P. 183.
10. *Radchenko M.V., Lashkarev G.V., Osinniy V. et al.* // J. Magn. and Magn. Mater. — 2002. — **247**. — P. 77—82.
11. *Kasuya T.* // Prog. Theor. Phys. — 1959. — **22**, N2. — P. 227—246.
12. *Look D.C.* // Thin Solid Films. — 1993. — **231**. — P. 61—73.
13. *Fedorych J. V., Wilanowski Z., Sadowski J.* // Abstr. XXXIII Intern. School Phys. Semicond. Comp. — Jaszowiec: Inst. Phys., PAS, 2004. — P. 70.

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ТЕРМО-ЕРС В ЕПІТАКСІЙНИХ ПЛІВКАХ Ga$_{1-x}$Mn$_x$As

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Резюме

У температурному інтервалі 10—300 К досліджено термоелектрорушійну силу епітаксійних плівок Ga$_{1-x}$Mn$_x$As (x=0,03÷0,055) товщиною 0,3—3 мкм, вирощених за низькотемпературною технологією LT-MBE на напівізолюючих підкладках GaAs (100). Досліджені плівки мали концентрацію дірок $(1\div4)\cdot10^{20}$ см$^{-3}$ з рухливістю 1—10 см^2/(В·с). На основі аналізу температурних залежностей термо-ерс встановлено наявність трьох складових в її сумарній величині: дифузійної, феромагнітної та обмінної. Розглянуто модель, що передбачає неоднорідний розподіл магнітних фаз у плівці, яка складається з парамагнітної фази та феромагнітних кластерів.