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Deposition and investigation of lanthanum–cerium hexaboride thin films

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Abstract

Thin films of lanthanum–cerium hexaboride, the promising thermoelectric material for low-temperature applications, are deposited on various substrates by the electron-beam evaporation, pulsed laser deposition and magnetron sputtering. The influence of the deposition conditions on the films X-ray characteristics, composition, microstructure and physical properties, such as the resistivity and Seebeck coefficient, is studied. The preferred (100) orientation of all films is obtained from XRD traces. In the range of 780–800 °C deposition temperature the highest intensity of diffractions peaks and the highest degree of the preferred orientation are observed. The temperature dependence of the resistivity and the Seebeck coefficient of films are investigated in the temperature range of 4–300 K. The features appropriate to Kondo effect in the dependences $\rho(T)$ and $S(T)$ are detected at temperatures below 20 K. Interplay between the value of the Seebeck coefficient, metallic parameters and Kondo scattering of investigated films is discussed.

Keywords: Thin films; $(La,Ce)B_6$; Thermoelectric properties; X-ray diffraction; Microstructure

1. Introduction

The thermoelectric effect has numerous applications in science and technology. The problem of obtaining new materials with good thermoelectric properties is urgent and may be a base for either creation of more efficient known thermoelectric devices or development of new types of such devices. Effectiveness of employment in thermoelectric devices depends on the figure of merit of the material, Z, which is defined by the expression $Z = S^2/\rho k$, where S is the Seebeck coefficient, ρ is the electrical resistivity, and k is the coefficient of thermal conductivity of the material. Lanthanum hexaboride with a cerium impurity (~1%) is a Kondo system with a number of anomalies of kinetic properties at low temperatures. So, in the works [1–4] concerning investigation of bulk samples of $(La,Ce)B_6$, anomalous behavior of the electrical conductivity [1,2], a peak in the heat capacity and thermopower [3,4] at low temperatures, were observed. The values of the Seebeck coefficient given in [3,4] (S~80 μV/K at T~1 K) and the corresponding evaluations of the figure of merit, Z~0.47 [5], allow one to consider $(La,Ce)B_6$ as a promising material for creation of thermoelectric refrigerators and thermoelectric detectors in the UV and X-ray ranges [6,7]. There are no data in the literature concerning the deposition of $(La,Ce)B_6$ films, therefore, in our studies, we considered as a base the works on obtaining the LaB_6 films synthesized mainly by the methods of the electron-beam [8,9] and magnetron [10,11] deposition.

In this work, we give the results of investigation of X-ray diffraction and microstructure, as well as results of study of temperature dependence of the resistivity and Seebeck coefficient of $(La,Ce)B_6$ thin films synthesized by the methods of electron-beam evaporation, pulsed laser deposition (PLD) and magnetron sputtering.

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2. Experimental

All films were deposited from a ceramic target with a composition $La_{0.99}Ce_{0.01}B_6$ (CERAC, Inc.), on the substrates of Si, Mo, Al_2O_3, MgO, YSZ, pyrex and glassceramic.

Electron-beam evaporation (arrangement BU-1A) was performed at temperatures 560–950 °C in a vacuum of $1.5–15 \times 10^{-6}$ Torr. The deposition rate was varied within the limits 2–20 Å/s. The target–substrate distance amounted to 19 cm.

Another group of films was deposited by PLD method. A YAG:Nd^{3+} laser with 1.06 μm wave length, 0.1 J energy and 20 ns pulse duration was used as laser radiation source. Pulse repetition rate was 15 Hz. Films were deposited on the substrates of Si, Al_2O_3, MgO, YSZ. Deposition was performed at temperatures 250–400 °C during 40–120 min in a vacuum of $1.5–15 \times 10^{-6}$ Torr. The target–substrate distance amounted to 3 cm. Then films of this group underwent additional annealing in a high-vacuum installation USU-4 under the following conditions: vacuum—10^{-8}–10^{-9} Torr, temperature (T_o)—700–950 °C, duration—3–12 h, temperature increase speed—360 °C/h, temperature decrease speed—600 °C/h. The simultaneous annealing of several samples was performed using resistance furnace with tungsten heater.

$La_{1-x}Ce_xB_6$ films were deposited also in a laboratory magnetron sputtering system in argon atmosphere. The deposition parameters that varied systematically were substrate temperature (600–1200 °C) and argon pressure (1–50 mTorr).

Thickness of all films was measured by the "Tencor Profiler". The phase composition, unit cell parameter, size of crystallites and the texture coefficient of films were determined with use of X-ray diffractometer DRON-4 (CuK_α). The X-ray microanalysis of films was performed by the electron microscope VEGA TS5130MM with the analyzer INCA-Energy-300. The cerium concentration was determined with an accuracy of ±50%, while that of La and B within the limits ±1–2%.

For measurement of thermopower of $(La,Ce)B_6$ thin films we used the method based on direct measurement of the voltage along the film on which temperature gradient is created. In this case we realized the measurement scheme similar to that described in [12]. The temperature difference was measured by a differential copper–constantan thermocouple. As potential outlets were copper wires, the Seebeck coefficient of the films (S_{film}) was determined from the expression $S_{film} = \Delta U/\Delta T + S_{Cu}$, where ΔU and ΔT are the potential and temperature differences measured on the sample, and S_{Cu} is the Seebeck coefficient of the copper wire. We note that S_{Cu} was determined preliminarily from the experiment with the same scheme where the film sample was a superconducting film $YBa_2Cu_3O_{7-\delta}$ with the critical temperature $T_c \sim 90$ K. At $T < T_c$ the thermopower of the superconducting film is known to vanish and S_{Cu} may be determined. At temperatures above 90 K the values of S_{Cu} depend weakly on impurities and are taken from [13].

The resistivity of the films has been measured by a standard AC four-probe technique. Measurements of either resistivity or Seebeck coefficient were conducted in vacuum in the temperature range 4–300 K which was provided by a closed-cycle ST 405 "Cryomech" refrigerator. The studied films had average size 10×10 mm. We also measured for comparison the characteristics of a $La_{0.99}Ce_{0.01}B_6$ ceramic rod with sizes $14 \times 1.5 \times 1.5$ mm.

3. Results and discussion

3.1. $(La,Ce)B_6$ thin films obtained by e-beam evaporation method

3.1.1. Study of X-ray diffraction and microstructure

The X-ray diffractograms of $(La,Ce)B_6$ films on the glassceramic substrates at the deposition temperature (T_d) 560 °C are demonstrated in Fig. 1. It is just the temperature at which we observed transition from the amorphous to the crystalline structure. The study of diffractograms allows one to make several conclusions. A crystalline structure inherent to LaB_6 was revealed in films with the thickness above 170 nm ($T_d = 560$ °C) and the intensity of the diffraction peak (100) increased practically linearly with the increase in the thickness. It should be noted that at $T_d = 600$ °C the LaB_6 structure was revealed also in the 70 nm films. The predominant (100) orientation is observed in all obtained films and the orientation degree essentially varies with the increase in T_d. Films obtained at $T_d = 560$ °C contain also the phase LaB_4. However, with the increase in the film thickness the strength of the diffraction peaks of LaB_4 remained practically unchanged. One may assume the presence of the phase LaB_4 in only a thin layer close to the substrate. The films obtained at $T_d > 600$ °C were single-phase; the diffraction peaks of LaB_4 were not observed. Exceptions were the films on Si at $T_d > 770$ °C which gave a pattern with an additional peak at $2\theta \approx 25.6°$.

Fig. 2 shows the results of T_d-dependence measurements of the strength of the diffraction peak $I_{(100)}$ for the $(La,Ce)B_6$ films with equal thickness on the Si and Mo substrates. The maximal value of $I_{(100)}$ was obtained on the Si films at $T_d = 780$ °C; in this case the crystal lattice parameter was $a = 0.416$ nm (Fig. 3). At $T_d > 780$ °C for Si and at $T_d > 800$ °C for Mo reduction of $I_{(100)}$ and broadening of diffraction peaks near bases took place. Such a behavior of $I_{(100)}$ is typical also for the films on MgO and Al_2O_3; other substrates have not been used at $T_d \geqslant 700$ °C. The crystal lattice parameter in the films on Si substrates decreased with the increase in T_d and at $T_d \geqslant 900$ °C it approached the a value for a bulk sample (Fig. 3). For other substrates an increase in the a value is recorded at $T_d \geqslant 800$ °C, which may be caused by the change in the ratio B/(La,Ce).

The 70-nm-thick films ($T_d = 600$ °C) and those of 170 nm thickness ($T_d = 560$ °C) had equal values of $I_{(100)}$ and slightly differing texture coefficients $KT_{(100)} \approx 1.3$, which

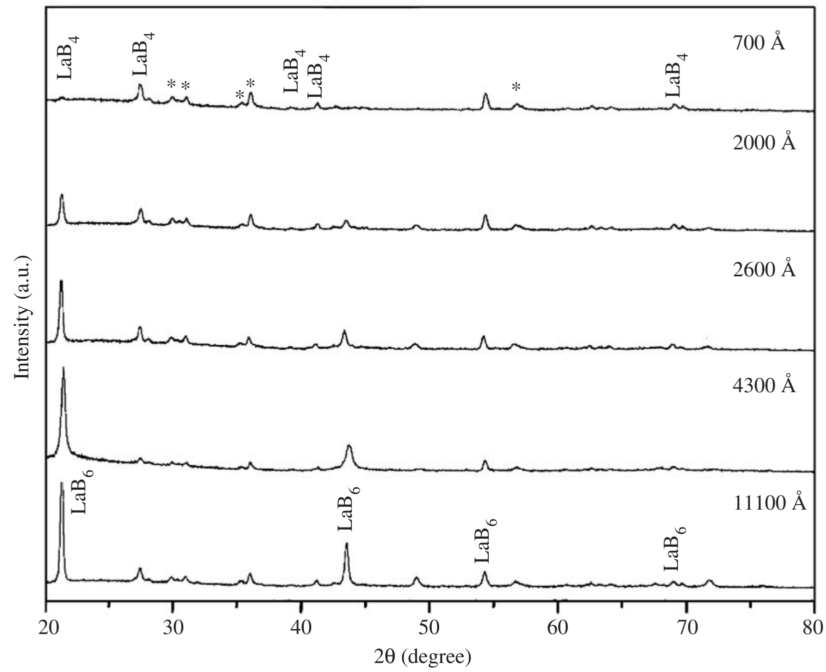

Fig. 1. X-ray diffraction patterns of (La,Ce)B_6 films of different thicknesses; (*) denote the peaks of the substrate (glassceramic); the deposition temperature 560 °C.

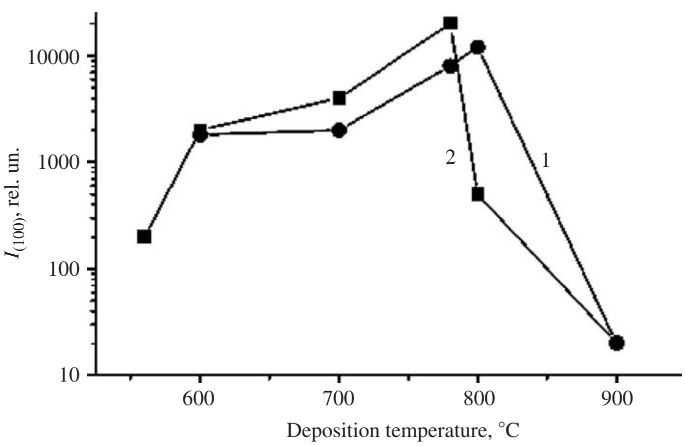

Fig. 2. Deposition temperature dependence of the intensity of the peaks (100); films on substrates: 1—Mo; 2—Si.

have been calculated using the strengths of peaks (100) and (210) in the relation,

$$KT_{(hkl)i} = \frac{I_{(hkl)i}/I_{(hkl)i,0}}{1/n\sum_{j=1}^{n} I_{(hkl)j,0}}, \qquad (1)$$

where I and I_0 are the intensities of peaks (hkl) of the film and powder X-ray pattern, respectively, n is the number of peaks taken into account [10]. In the two-peak calculation the quantity $KT_{(hkl)}$ varies from 1, in the case of absence of a predominant orientation direction, to 2, in the case of complete orientation. The quantity $KT_{(100)}$ for the films with the highest value of $I_{(100)}$ (Si, $T_d = 780$ °C) reaches the value 1.999. However, the results of measurements did not give a possibility to make an unambiguous conclusion on the deposition temperature dependence of $KT_{(100)}$, since the value $KT_{(100)} \approx 1.998$ was obtained at already $T_d = 600$ °C. There is also no obvious correlation between the quantities $KT_{(100)}$ and $I_{(100)}$. The T_d-dependence of the width at half-maximum ($\Delta\Omega$) of the curves of crystallite distribution around the direction of the predominant orientation (100) seems to be more demonstrative. In this case the angle between the sample surface and emission direction varies by the quantity Ω. For the films obtained at $T_d = 560$ °C the value of $\Delta\Omega$ exceeds 9.2°, for those at $T_d = 600$ °C it reduces down to 2.7°, while for the films with $T_d = 780$–800 °C it reaches 1.6°. At further increase in T_d the value of $\Delta\Omega$ increases up to 6–10° ($T_d = 950$ °C).

The average size of crystallites was calculated using Sherrer's formula and full width at a half maximum intensity of diffraction peak (100). Upon change of T_d in the range 600–900 °C size of crystallites of films on Si

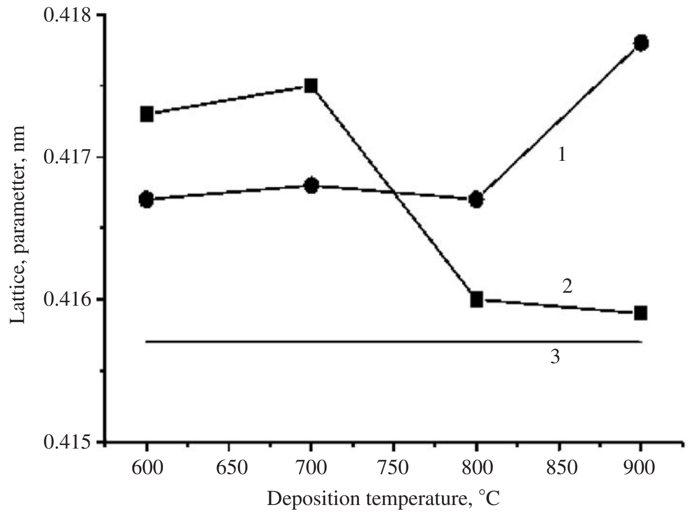

Fig. 3. Deposition temperature dependence of the lattice parameter; films on substrates: 1—Mo; 2—Si. Lattice parameter of the bulk sample—3.

substrates changed from 50 to 100 nm. Obtained results are typical also for films on other substrates.

The kinetic energy of particles condensing on the substrate is the most important parameter describing the deposition process and essentially affecting the microstructure of thin films. As a result of a strong covalent bond of boron in hexaborides of rare earths, a need appears to have the substrate temperature sufficiently high in order to provide efficient diffusion processes for the particles on the surface and inside the film. The size of crystallites is, in turn, affected by T_d. Growth of middle size cubic crystallites in LaB_6 films with raising the substrate temperature was observed in [8] and at raising the temperature from 730 to 790 °C a tendency appeared towards predominant growth of crystallites in the direction perpendicular to the substrate, and a little separation of those from each other. Appearance of a column microstructure was also reported in [10] where LaB_6 films were obtained by magnetron deposition. Microphotographs of surfaces of $(La,Ce)B_6$ films on Si indicate the transition from the glassy structure of the surface ($T_d = 780$ °C) to the lumpy one ($T_d = 860$ °C). Such a behavior is typical for only the films on Si. The films on the MgO, Al_2O_3, and Mo substrates remained smooth at even $T_d > 800$ °C. Exceptions were the films on SiO_2 the surface of which had splits at already $T_d = 680$ °C because of essential difference in the thermal expansion coefficients of quartz and $(La,Ce)B_6$. Change in surface morphology of films on Si is caused by diffusion of silicon into the films and, probably, by formation of a new phase which is displayed in X-ray patterns via a peak with $2\theta \approx 25.6°$.

Results of X-ray microanalysis of three samples are shown in Table 1. The table contains data concerning the substrate, on which the films are deposited, the deposition temperature, the electron accelerating voltage (U), the element composition of the film, and the B/(La + Ce) ratio. All the films had ~700 nm thickness. Measurements were performed at three different values of the accelerating voltage, which corresponds to different depths of electron penetration into the sample. Results of analysis show that at the voltage 10 kV the electron beam does not practically get into the substrate (there is no Mg in the MgO substrate and the content of Al in the Al_2O_3 substrate is very low) and these data correspond mostly to the realistic content of elements in the film. However, analysis of the sample on Si shows that the content of silicon measured at different U is practically unchanged. This is, apparently, the result of silicon diffusion into the film.

Table 1
Data of the X-ray microanalysis of $(La,Ce)B_6$ films

Substrate	T_d[a] (°C)	U[b] (kV)	Contents of elements (at%)					B/(La + Ce)
			La	Ce	B	O	Mg, Si, Al	
MgO	780	10	11.93	0.2	87.6	0.27	—	7.2
		15	11.2	0.25	86.94	1.13	Mg–0,66	7.7
		20	7.4	0.19	88.05	2.34	Mg–1,98	11.5
Si	950	10	13.2	0.4	70.81	7.05	Si–8,22	5.1
		15	10.8	0.16	77.75	4.45	Si–6,85	7.1
		20	5.5	0.06	84.22	2.66	Si–7,52	15
Al_2O_3	950	10	14.9	0.33	77.74	7.61	Al–0,03	5.3
		15	13.9	0.26	80.91	5.47	Al–0,27	6.06
		20	9.1	0.22	84.64	4.91	Al–1,13	9.08

[a] T_d: deposition temperature.
[b] U: accelerating voltage.

Analysis also demonstrates that at $T_d = 780$ °C the film does not contain oxygen, whereas at $T_d = 950$ °C a partial oxidation of the film takes place. Oxygen is present also in the film on Si and may not be ascribed to the influence of substrate. The ratio B/(La + Ce) varies at $U = 10$ kV from 7 at $T_d = 780$ °C to 5.1 at $T_d = 950$ °C. In this temperature range, an exact B/(La + Ce) = 6 stoichiometry may obviously be achieved.

3.1.2. Study of resistivity

Results of measurement of the temperature dependence of the resistivity $\rho(T)$ for (La,Ce)B_6 films on different substrates are given in Fig. 4. Resistance of all films decreases with temperature decrease. The least values of ρ, most close to those of bulk samples, have the films on Si substrates (Fig. 4b). The resistivity of films decreases monotonically down to the temperature 20 K and then begins to increase. Such a behavior of $\rho(T)$ is typical for the (La,Ce)B_6 system and is a feature of the Kondo effect. This effect in this compound is caused by scattering of charge carriers on the magnetic ($s = 1/2$) impurities of Ce^{3+}. In order to compare the films with single crystals we consider dimensionless parameters of metallicity and Kondo scattering which, respectively, are the ratios $\rho(77\,\mathrm{K})/\rho(300\,\mathrm{K})$ and $\Delta\rho/\rho_{\min}$, where $\Delta\rho = \rho(4\,\mathrm{K})–\rho_{\min}$, $\rho_{\min} \approx \rho(20\,\mathrm{K})$. Single crystals of $La_{0.99}Ce_{0.01}B_6$ have resistivities $\rho(300\,\mathrm{K}) = 8–9\,\mu\Omega\,\mathrm{cm}$ and $\rho(77\,\mathrm{K}) = 1.8\,\mu\Omega\,\mathrm{cm}$ and parameters of metallicity and Kondo scattering, respectively, 0.21 and 1.5. In this case the parameter $\rho(77\,\mathrm{K})/\rho(300\,\mathrm{K})$ is minimal, while $\Delta\rho/\rho_{\min}$ is maximal at the Ce^{3+} concentration 1 at%. For a ceramic $La_{0.99}Ce_{0.01}B_6$ sample the parameters $\rho(77\,\mathrm{K})/\rho(300\,\mathrm{K})$ and $\Delta\rho/\rho_{\min}$, amounted to, respectively, 0.22 and 0.88. The parameter $\Delta\rho/\rho_{\min}$ in ceramics is smaller than in a single crystal due to the presence of additional scattering on the boundaries of grains. The (La,Ce)B_6 films on the Si substrate have the highest values of Kondo scattering and the best metallicity among the films on other substrates, but even these films yield to ceramics in mentioned parameters. This is, probably, caused by either non-optimum value of the cerium ion concentration in the films or the presence in them of non-controlled impurities, stresses, and weakly bound grains.

Study of dependences of parameters of Kondo scattering and metallicity on the film deposition temperature (T_d) showed that the parameter of Kondo scattering, independently of the substrate, has a tendency to increase with the

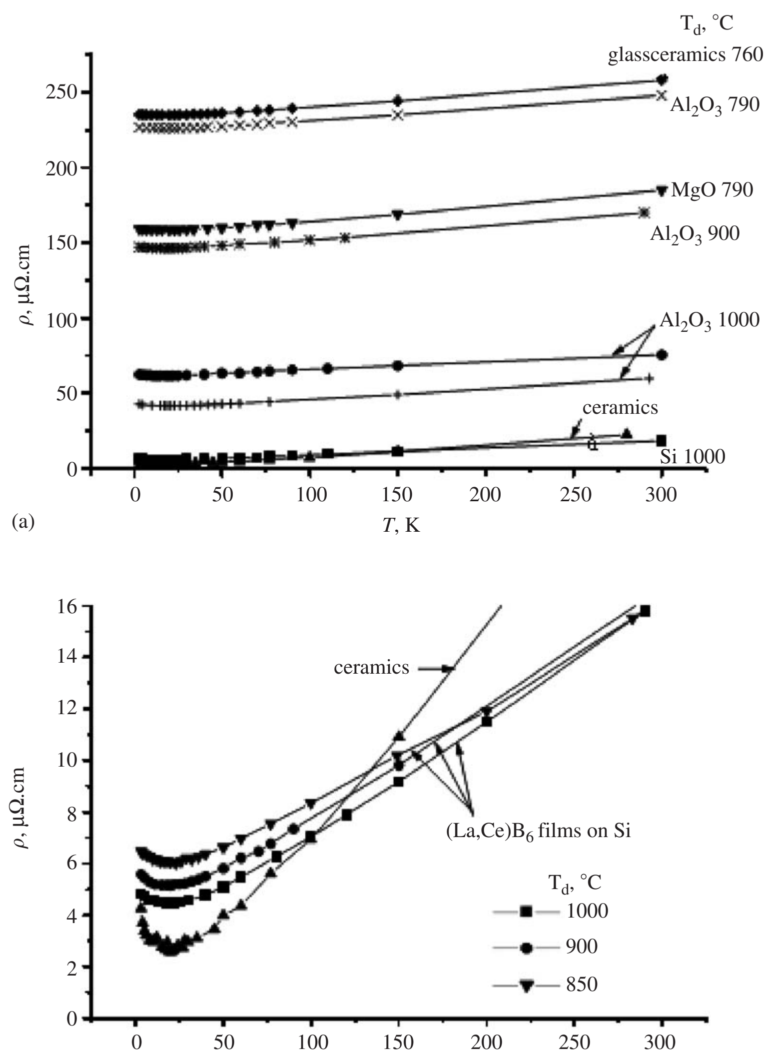

Fig. 4. Temperature dependence of the resistivity of (La,Ce)B_6 films on various substrates (a), the ceramic $La_{0.99}Ce_{0.01}B_6$ sample and the films on Si substrates (b).

raising of T_d and is maximal at $T_d \sim 1000\,^{\circ}C$. So, the obtained maximal values of the Kondo-scattering parameter for films on substrates of Si, Al_2O_3, MgO, glassceramics amount to, respectively, 0.16, 0.013, 0.006, 0.002. In this case the parameter of Kondo scattering for the films on Si at all values of T_d remains sufficiently higher than for the films on other substrates. The metallicity parameter of the films improves, independently of the substrate, as the T_d rises reaching the values of 0.36, 0.74, 0.87, 0.92 for the films on the substrates of Si, Al_2O_3, MgO, glassceramics, respectively. The metallicity parameter of the films on Si is smaller in the overall deposition temperature range than that of the films on other substrates. Improvement of parameters of either Kondo scattering or metallicity with the rise of deposition temperature is probably caused by the change of the ratio La/Ce/B in the films and improvement of intergrain links. For the films on the Si substrates, at high T_d diffusion of Si from the film into substrate occurs which causes the essential distinction of ρ in these films from that in the films on other substrates.

3.1.3. Study of the Seebeck coefficient

In Fig. 5 we demonstrate the temperature dependences of the Seebeck coefficient $S(T)$ of the (La,Ce)B_6 films. The character of these curves is determined by either the substrate material or the deposition temperature. Note that each figure contains information on the samples, i.e., the substrate, ρ, T_d, as well as $S(T)$ of the ceramic $La_{0.99}Ce_{0.01}B_6$ sample.

The shapes of the curves $S(T)$ of a film are divided into three groups. The first group (Fig. 5a) are the films for which the temperature dependences have no anomalies typical for Kondo systems and the $S(T)$-shape at $T > 50$ K is similar to that of a ceramic sample. The second group (Fig. 5b) are the films for which $S(T)$ has no low-temperature anomalies typical for Kondo systems, but there is a prominent peak in the Seebeck coefficient at $T = 80$ K. The third group (Fig. 5c) constitute the films for which in $S(T)$ a peak of the thermopower at $T = 80$ K, a little smaller in value than for the second group, is revealed along with an abrupt rise in the values of the Seebeck coefficients when lowering the temperature down to 4 K. Note that the films of the second and third groups are synthesized on the Si substrates.

The value of S of films at $T < 25$ K is smaller than that of ceramics (Fig. 5c) which may be caused by a non-optimum concentration of Ce ions, the presence in the films of non-controlled impurities, stresses, weakly bound grains, and the phase responsible for the 80 K-peak in S. The presence of this phase may considerably reduce the value of S of third-group films at $T < 25$ K, since $S(T)$ of second-group samples have a tendency for transition of S-values into the negative range (Fig. 5b).

The values of the Seebeck coefficient at $T = 4.5$ K depend essentially on the deposition temperature T_d and for all measured samples the increase in S-values with the

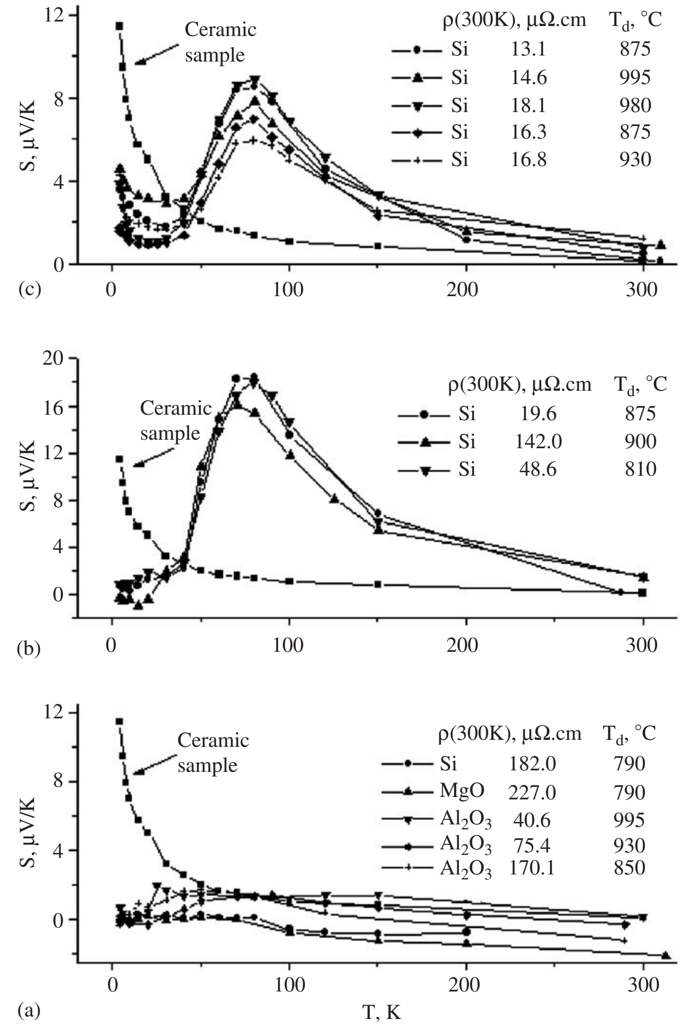

Fig. 5. Temperature dependence of the thermopower of (La, Ce)B_6 films. (a,b)—films without Kondo anomaly, (c)—films showing Kondo anomaly.

increase in T_d is observed. Study of dependences of the Seebeck coefficient at $T = 4.5$ K on $\rho(300\,K)$ and the parameter of Kondo scattering $\Delta\rho/\rho_{min}$ shows that the coefficient of thermopower increases with the decrease in $\rho(300\,K)$ and with the increase in $\Delta\rho/\rho_{min}$. Investigations revealed also that the greatest values of the Seebeck coefficient at $T = 4.5$ K are obtained for the films synthesized on Si substrates.

3.2. (La,Ce)B_6 thin films obtained by PLD

3.2.1. Study of X-ray diffraction and microstructure of thin films deposited by the pulsed laser deposition method

The X-ray diffractograms of (La,Ce)B_6 films show that the films are amorphous. The transition from the amorphous to the crystalline structure occurs after additional annealing in USU-4. A crystalline structure inherent to LaB_6 was revealed in films starting with annealing temperatures above 700 °C. Films have predominant orientation (100).

Electron microscope analysis showed that the surface of (La,Ce)B_6 films on MgO, YSZ and Al_2O_3 substrates remains smooth at all annealing temperatures. The only exception were films on Si substrate the surface of which changed from mirror surface to lumpy one at annealing temperatures above 850 °C. Change of surface morphology of films on Si is due to diffusion of silicon from the substrate into the film like in case of e-beam deposition. We have observed pores and fractures on the surface of some films, besides the micron-size particles which are typical for PLD method.

X-ray microanalysis results of the samples showed the presence of C, O, Si impurities in the films and considerable distortion from precise stoichiometric ratio B/La = 6 of main elements. A significant amount of oxygen contained in the surface of LaB_6 thin films obtained by PLD was observed also in [14].

3.2.2. *Investigation of the resistivity and Seebeck coefficient*

Results of measurement of the temperature dependence of the resistivity $\rho(T)$ for films annealed in high vacuum are given in Fig. 6. $\rho(T)$ of films show typical metallic behavior. Resistivity of some films decreases monotonically down to the temperature ~20 K and then practically does not change down to 4 K. Such a behavior of $\rho(T)$ is typical for the LaB_6 system [4] and is a feature of absence of the Kondo effect. Parameter of metallicity $\rho(77\,K)/\rho(300\,K)$ of these films is >0.77 and the resistivity values of films $\rho(300\,K) \geqslant 100\,\mu\Omega\,cm$. Resistivity of some films on Si substrate decreases monotonically down to the temperature ~90 K, then begins to increase reaching the highest value (comparable to $\rho(300\,K)$ values) at the temperatures ~22 K and then decreases monotonically down to the temperature ~90 K with a small incline (Fig. 6b). Resistivity values of this group of films are $\rho(300\,K) \geqslant 250\,\mu\Omega\,cm$.

In Fig. 7 we demonstrate temperature-dependence measurements of the Seebeck coefficient $S(T)$ of the same (La,Ce)B_6 film samples. We were not able to observe a rise of values of S at low-temperature range typical for (La,Ce)B_6 Kondo system in any sample. There is a peak in $S(T)$ temperature dependence of films on Si substrates (Nos. 37, 38, 47) at the temperatures ~80 K due to the change of properties of substrate during high-temperature annealing in high vacuum. This conclusion was confirmed by additional measurements of $S(T)$ dependence of Si substrate without deposited film annealed in high vacuum.

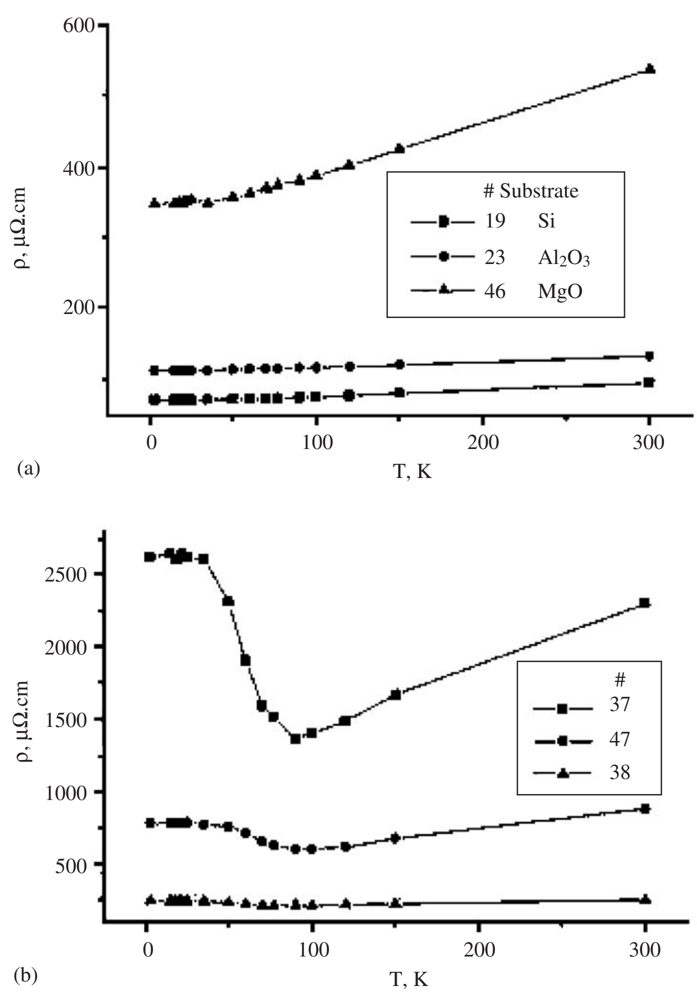

Fig. 6. Temperature dependence of the resistivity ρ for films obtained by PLD on various substrates (a) and on Si substrates (b).

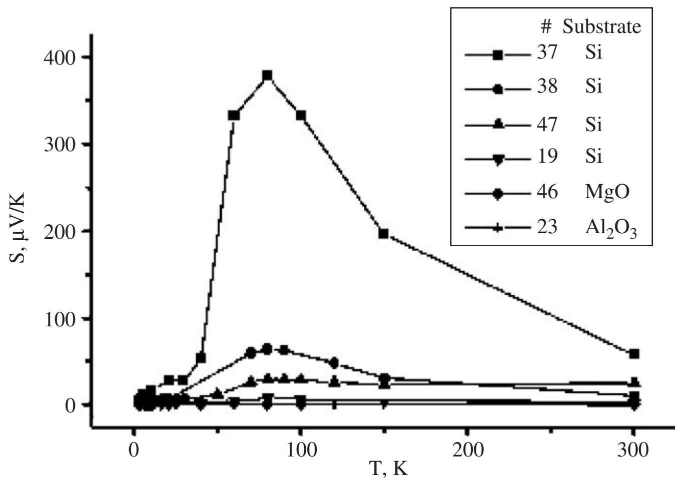

Fig. 7. Temperature dependence of S of films obtained by PLD on various substrates.

In some samples Seebeck coefficient achieved values of ~1500 μV/K at the temperatures ~80 K.

3.3. $(La,Ce)B_6$ thin films obtained by magnetron sputtering

Properties of films obtained by magnetron sputtering are in many respects similar to those of films obtained by e-beam and PLD methods. These films also have predominant (100) orientation and composition that changes depending on deposition conditions. Again the resistivity of films decreases with the increase of deposition temperature and a Kondo feature is clearly observed on the $\rho(T)$ dependence at the temperatures below 20 K. The distinction of these films is the presence of Ar impurity in the composition and the nature of $S(T)$ dependences. But as it is shown on Fig. 8 films obtained by magnetron sputtering method do not exhibit high Seebeck coefficient values either.

In Table 2 main characteristics of films obtained by various methods are shown in order to summarize the obtained results. As one can notice, obtained films possess significantly lower Seebeck coefficient values at 4.5 K than the ceramic sample, while the values of resistivity are comparable. Consequently, in order to use films in thermoelectrical devices at low temperatures, it is necessary to achieve higher Seebeck coefficient values.

4. Conclusions

We revealed an optimum deposition temperature range, 780–800 °C, for producing $(La,Ce)B_6$ films by electron-beam evaporation method with the highest intensity of diffraction peaks and highest degree of predominant orientation which corresponds to best crystallinity of obtained films. On the other hand, the lattice parameter for the films on Si is mostly close to the parameter of bulk samples at higher temperatures. For the films on other substrates the distortion of a from the bulk sample

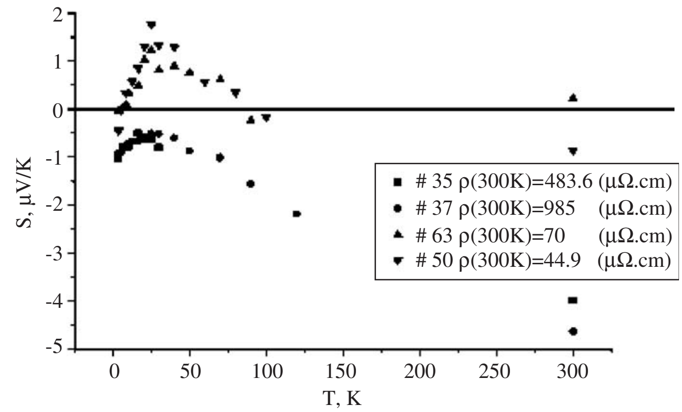

Fig. 8. Temperature dependence of S of films on various substrates obtained by magnetron sputtering.

Table 2
Comparison of properties of best films obtained by different methods and the ceramic sample of $(La,Ce)B_6$

Sample	ρ (77 K)/ ρ (300 K)	$\Delta\rho/\rho_{min}$	ρ (4.5 K), μΩ cm	S (4.5 K), μV/K
E-beam film	0.36	0.16	3.9	4.59
PLD film	0.85	0.007	70.5	1.15
Magnetron sputtering film	0.73	0.03	19.5	−0.05
Ceramic sample	0.22	0.88	4.26	11.42

parameter significantly increases at $T_d > 800$ °C. Substrates of MgO, Si, Al_2O_3, and Mo were employed below $T_d = 950$ °C. Diffusion of silicon from the substrate into the film is established with sufficient reliability. Interaction of the films with other substrates has not been revealed. The obtained results will be used in further search of conditions for synthesizing $(La,Ce)B_6$ films with the properties optimum for applications in low-temperature thermoelectric devices.

The basic result of the work is revealing of the Kondo effect in thin films of nominal composition $(La,Ce)B_6$. The dependences $\rho(T)$ and $S(T)$ of the films deposited on different substrates are investigated. The films on Si substrates at $T_d > 800$ °C have the values of ρ(300 K), S(4.5 K), and parameters ρ(77 K)/ρ(300 K), $\Delta\rho/\rho_{min}$ most close to bulk samples. However, they are still inferior to bulk samples in their electrophysical characteristics. Diffusion of silicon from the substrate into the film occurring at $T_d > 800$ °C results in appearing of a peak in $S(T)$ at 80 K which is, in its turn, one of the reasons of low values of S(4.5 K). Other factors leading to low S(4.5 K) and high ρ values of films are the deviation from stoichiometry (La/B ratio), presence of uncontrolled impurities and peculiarities of microstructure.

Approach of thermoelectric properties of thin films to those of $(La,Ce)B_6$ bulk samples may be expected by choosing proper substrate and by optimizing synthesis conditions.

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