Наносистеми, наноматеріали, нанотехнології
Nanosystems, Nanomaterials, Nanotechnologies
2014, т. 12, № 3, сс. 623–632

PACS numbers: 72.20.Pa, 73.22.-f, 73.50.Lw, 73.61.-r, 81.15.Fg, 81.16.Mk, 85.80.Fi

Pulsed Laser Deposition of Thin Iron and Chromium Silicide Films with Large Thermoelectromotive Force Coefficient

S. A. Mulenko

G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
Academician Vernadsky Blvd., 36,
03680 Kyyiv-142, Ukraine

Nanostructures in the form of thin films exhibiting the semiconductor properties with a narrow energy-band gap are deposited from the $CrSi_2$ and β-$FeSi_2$ targets by means of the pulsed laser deposition (PLD) assisted with an excimer KrF laser. The films deposited from $CrSi_2$ target on the ⟨100⟩Si substrate at 293 K and 740 K manifest the band gaps $E_g \cong 0.09$ eV and 0.18 eV, respectively. The films deposited from β-$FeSi_2$ target on the ⟨100⟩Si substrate at the same conditions manifest the band gaps $E_g \cong 0.16$ eV and 0.31 eV, respectively. The upper-range value of thermoelectromotive force coefficient (Seebeck coefficient), S, for the $CrSi_2$-based films deposited on heated substrate at 740 K is about 1.4 mV/K at $300\ \mathrm{K} \leq T \leq 340$ K. The largest S coefficient for the β-$FeSi_2$-based films deposited on heated substrate too is about 1.5 mV/K within the same temperature range. With the higher E_g, the higher S coefficient is obtained. The XRD analysis reveals that films deposited on the Si substrates have a polycrystalline structure, and films deposited on the SiO_2 substrates are amorphous. As regards the S coefficient for films deposited on the Si and SiO_2 substrates, this coefficient is higher for polycrystalline films than for amorphous deposits. The larger the semiconductor-phase concentration in the deposited films, the higher the S coefficient. So, the PLD based on an excimer KrF laser is an effective method for the deposition of nanostructures in the form of thin films, which are quite suitable for thermal sensors operating at moderate temperatures.

Наноструктури у формі тонких плівок, що проявили напівпровідникові властивості, з вузькою енергетичною забороненою зоною було осаджено методом імпульсного лазерного осадження (PLD) з мішеней $CrSi_2$ і β-$FeSi_2$ із застосуванням ексимерного KrF-лазера. Плівки, яких було осаджено з мішені $CrSi_2$ на підложжя ⟨100⟩Si при температурах у 293 К і 740 К, мали ширину забороненої зони $E_g \cong 0{,}09$ еВ і 0,18 еВ відповідно. Плівки, яких було осаджено з мішені β-$FeSi_2$ на підложжя ⟨100⟩Si за таких же умов, мали ширину забороненої зони $E_g \cong 0{,}16$ еВ і 0,31 еВ відповідно. Найбільше значення коефіцієнта термоерс (Зеєбекового коефіцієнта) S плівок на основі $CrSi_2$ при осадженні на нагріте підложжя при 740 К складає біля 1,4 мВ/К при 300 К $\leq T \leq$ 340 К. Найбільше значення коефіцієнта S плівок на основі β-$FeSi_2$ при осадженні на нагріте також підложжя складає біля 1,5 мВ/К у тому ж інтервалі температур. Чим більше E_g, тим більше значення було встановлено для коефіцієнта S. Рентґенодифракційний аналіз показав, що плівки, яких було осаджено на Si-підложжя, мали полікристалічну структуру, а плівки, яких було осаджено SiO_2-підложжя, були аморфними. Що стосується коефіцієнта S для плівок, яких було осаджено на SiO_2-підложжя, то він виявився більшим для полікристалічних плівок, аніж для аморфних. Таким чином, PLD-метод із використанням ексимерного KrF-лазера є ефективним методом осадження наноструктур у формі тонких плівок, які є вельми придатними для термосенсорів, що працюють за помірних температур.

Наноструктуры в форме тонких плёнок, которые проявили полупроводниковые свойства, с узкой энергетической запрещённой зоной были осаждены методом импульсного лазерного осаждения (PLD) из мишеней $CrSi_2$ и β-$FeSi_2$ с применением эксимерного KrF-лазера. Плёнки, осаждённые из мишени $CrSi_2$ на подложку ⟨100⟩Si при температурах 293 К и 740 К, имели ширину запрещённой зоны $E_g \cong$ 0,09 эВ и 0,18 эВ соответственно. Плёнки, осаждённые из мишени β-$FeSi_2$ на подложку ⟨100⟩Si при тех же условиях, имели ширину запрещённой зоны $E_g \cong$ 0,16 эВ и 0,31 эВ соответственно. Наибольшее значение коэффициента термоэдс (коэффициента Зеебека) S для плёнок на основе $CrSi_2$ при осаждении на нагретую подложку при 740 К составляет около 1,4 мВ/К при 300 К $\leq T \leq$ 340 К. Наибольшее значение коэффициента S для плёнок на основе β-$FeSi_2$ при осаждении на нагретую так же подложку составляет около 1,5 мВ/К в том же интервале температур. Чем больше E_g, тем большее значение было установлено для коэффициента S. Рентгенодифракционный анализ показал, что плёнки, осаждённые на Si-подложки, имели поликристаллическую структуру, а плёнки, осаждённые на SiO_2-подложки, были аморфными. Что касается коэффициента S для плёнок, осаждённых на подложки Si и SiO_2, то он для поликристаллических плёнок оказался больше, чем для аморфных. Чем больше концентрация полупроводниковой фазы в осаждённых плёнках, тем больше коэффициент S. Таким образом, PLD-метод с применением эксимерного KrF-лазера является эффективным методом осаждения наноструктур в форме тонких плёнок, которые весьма удобны для термосенсоров, работающих при умеренных температурах.

Key words: thin films, laser-assisted deposition, silicides, thermoelectric effects, thermoelectric devices, thermal sensors.

(Received 25 March, 2014)

1. INTRODUCTION

One of the most important parameters for thermosensors is the thermoelectromotive force coefficient (Seebeck coefficient, S). Thermoelectric converters based on silicides of transitional metals are up-to-date materials owing to their narrow band gap result in a large thermo-electromotive force (e.m.f.) coefficient, S. Chromium silicide ($CrSi_2$) and iron silicide (β-$FeSi_2$) in bulk single crystalline form are semiconductors with the band gaps $E_g \cong 0.35$ eV and 0.85 eV, respectively [1–3]. In general, chromium and iron silicides are attractive materials because of their semiconducting, electrochromic and photochromic properties [4]. However, the electrical properties of $CrSi_2$ depend strongly on the film deposition method and on its stoichiometry (Cr:Si) [5]. The thermoelectric conversion properties of these silicides deposited in the form of thin films and layers depend on E_g. In turn, the value of E_g depends on the structure of the deposited materials: amorphous or polycrystalline. The aim of this work is to study chromium and iron silicide thin films' characteristics, which depend on their nature and temperature. These thin films are suitable structure for the fabrication of thermosensors operating at moderate temperature. The pulsed laser deposition (PLD) method was used, since it allows a very efficient fabrication of films from compound materials.

2. EXPERIMENTAL

Film depositions were performed in a stainless-steel chamber, evacuated down to 10^{-5} Pa. Pure $CrSi_2$ and β-$FeSi_2$ monocrystalline targets were ablated with an excimer KrF laser pulses ($\lambda = 248$ nm; $\tau_p \cong 20$ ns) at a fluence $F \cong 5.5$ J/cm^2 and repetition rate of 10 Hz. The target was rotated at 3 Hz to obtain a smooth ablation procedure. Before each deposition, the target surface was cleaned using 600 laser pulses, with a shutter shielding the substrate. The ablated material was collected on $\langle 100 \rangle$Si or SiO_2 substrates, either at room temperature (RT) or heated to 740 K. Film deposition on heated substrate was carried out at 5000 pulses and while film deposition on the substrate at RT the number of laser pulses (N) was 6500. Such conditions were used to obtain 40 nm film thicknesses. Optical measurements were carried out to find out the real part of the dielectric constant ($\varepsilon_1 > 0$) of the deposited films with ellipsometry and prove the existence of a semiconductor phase in these deposits [6]. The direct current (DC) electrical resistance of Si samples with the deposited films was measured by using a two-probe technique in the range 340–78 K. An indium or silver coating formed ohmic contacts. Electrical resistance was measured in plane of the deposited film. The substrate temperature was measured by thermocouple. Temperature dependences of specific conductivity (σ) were evaluated from measurements of the electrical resistance of the samples as a function of temperature and film geometry. Film thickness was measured with Dectak-3080 profilemeter or by RUMP simulation of experimental Rutherford backscattering (RBS) spectra [7]. The crystalline structure of deposited films was studied with X-ray diffractometer (XRD) 'Stoe' at 45 kV and 33 mA (CuK_α radiation). The DC electrical resistance of deposited films was measured by two-probe technique. Ohmic contacts were made from indium or silver coatings. Temperature dependence of the electrical resistance, specific conductivity (σ) of the deposited films, the S coefficient were measured in the range 78–340 K with a high resistance multimeter. The heating temperature and its difference between the two ends of the substrate were measured by two thermocouples. Calculations of the specific conductivity were performed taking into account the geometrical shape of Si and SiO_2 substrates. The temperature dependence of the S coefficient was measured after producing a thermal gradient along the sample. The value of the S coefficient was measured from thermoelectromotive force existing between heated or cooled end of the sample and its end at RT.

3. RESULTS AND DISCUSSION

Film deposition from $CrSi_2$ target was carried out on both SiO_2 and Si substrates. It is seen for films deposited on the heated Si substrate ($T_S \cong 740$ K) that a semiconductor trend of these films reveals from 340 down to 227 K, and then a metallic one down to 78 K (Fig. 1, curve 1 and 2). Semiconductor trend of temperature dependences of σ is evident also for the film deposited from β-$FeSi_2$ target on the heated Si substrate ($T_S \cong 740$ K) and on the Si substrate at RT from 340 to 78 K (Fig. 1, curve 3 and 4) can be described by the well-known expression [8]

$$\sigma = \sigma_g \exp\{-E_g/(2kT)\} + \sigma_i \exp\{-E_i/(kT)\}, \quad (1)$$

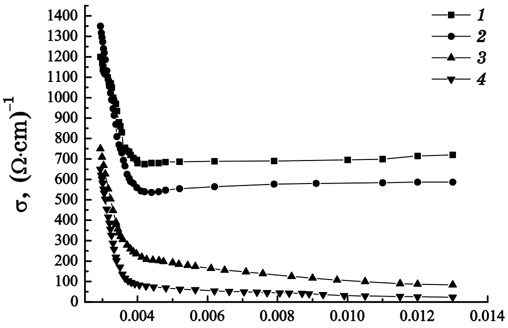

Fig. 1. Temperature dependences of the specific conductivity of films deposited by PLD on Si substrates from: (*1*) $CrSi_2$ target, $E_g \cong 0.09$ eV, $T_S \cong 293$ K, $N = 6500$; (*2*) $CrSi_2$ target, $E_g \cong 0.18$ eV, $T_S \cong 740$ K, $N = 5000$; (3) β-$FeSi_2$ target, $E_g \cong 0.16$ eV, $T_S \cong 293$ K, $N = 6500$; (*4*) β-$FeSi_2$ target, $E_g \cong 0.31$ eV, $T_S \cong 740$ K, $N = 5000$.

where σ_g is intrinsic specific conductivity; σ_i is the specific conductivity determined by impurities; E_g is the band gap for intrinsic conductivity; E_i is the band gap assigned for impurities. The band gap E_g in the range 340–293 K was calculated by using the following expression

$$E_g = \frac{2k \ln\left[\sigma(T_1) / \sigma(T_2)\right]}{1/T_2 - 1/T_1}, \tag{2}$$

where $\sigma(T_1)$ is the specific conductivity at the temperature T_1 and $\sigma(T_2)$ is the specific conductivity at the temperature T_2 ($T_1 > T_2$). The temperature dependence of σ essentially depends on the substrate nature (Si or SiO_2) [6]. It was shown by XRD that deposited films on SiO_2 substrate display an amorphous structure (Figs. 2, 4). However, deposited films on Si substrate display a polycrystalline structure (Figs. 3, 5).

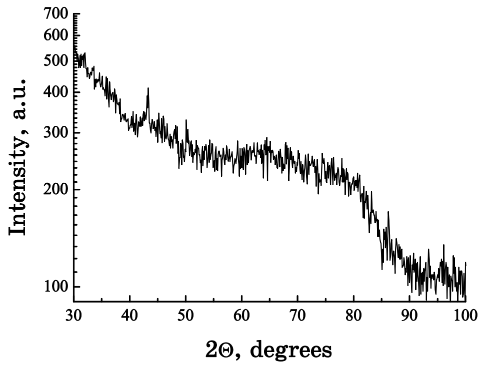

Fig. 2. XRD diagram of film deposited by PLD from $CrSi_2$ target on SiO_2 substrate at $T_S \cong 293$ K.

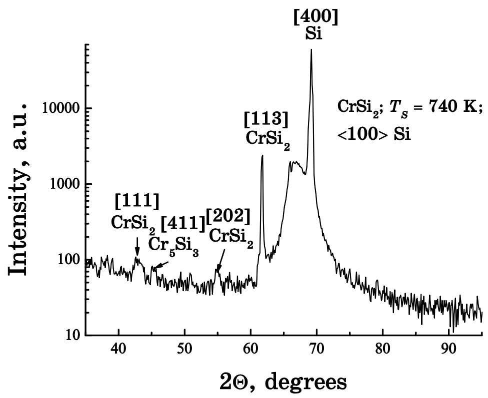

Fig. 3. XRD diagram of film deposited by PLD from $CrSi_2$ target on Si substrate at $T_S \cong 740$ K.

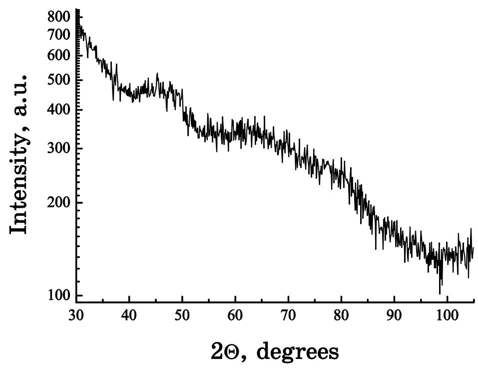

Fig. 4. XRD diagram of film deposited by PLD from β-$FeSi_2$ target on SiO_2 substrate at $T_S \cong 293$ K.

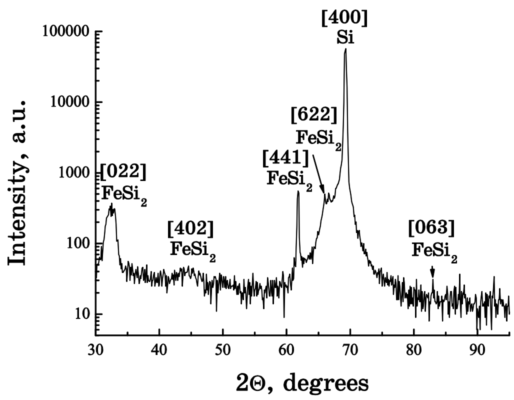

Fig. 5. XRD diagram of film deposited by PLD from β-$FeSi_2$ target on Si substrate at $T_S \cong 740$ K.

The SiO_2 native layer on Si substrate is about 3 nm thickness and has no a significant influence on the growth of deposited film from $CrSi_2$ and β-$FeSi_2$ targets [9]. The optical properties of films deposited from $CrSi_2$ and β-$FeSi_2$ targets on SiO_2 and Si substrates prove the existence of a semiconductor phase in these deposits as the real part of the dielectric constant ($\varepsilon_1 > 0$) [6].

The best fitting of the experimental curve of the specific conductivity for deposited films from $CrSi_2$ target shows a semiconductor trend. Using the expression (2), one can obtain $E_g \cong 0.09$ and $E_g \cong 0.18$ eV for $T_S \cong 293$ K and 740 K, respectively. The best fitting of the experimental curve of the specific conductivity for deposited films from β-$FeSi_2$ target shows a semiconductor trend too. Using the expression (2), one can get $E_g \cong 0.16$ and $E_g \cong 0.31$ eV for $T_S = 293$ K and 740 K, respectively (Fig. 1). These energy band gaps were calculated with an er-

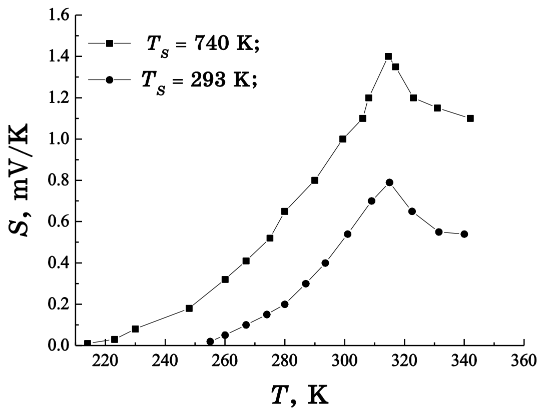

Fig. 6. Temperature dependence of the thermo-e.m.f. coefficient for the film deposited by PLD on Si substrate from $CrSi_2$ target; substrate temperature $T_S \cong 293$ K and 740 K.

ror of 10%.

The highest value of the S coefficient for films deposited from $CrSi_2$ target on Si substrate is 1.4 mV/K at $T \leq 340$ K (Fig. 6). The highest value of this coefficient for films deposited from $CrSi_2$ target on SiO_2 substrate was about 0.010–0.015 mV/K at 293 K $\leq T \leq$ 340 K [6].

The highest value of the S coefficient for films deposited from β-$FeSi_2$ target on Si substrate is 1.5 mV/K at $T \leq 340$ K (Fig. 7). The highest value of the S coefficient for films deposited from β-$FeSi_2$ target on SiO_2 substrate was about 0.008–0.010 mV/K at 295 K $\leq T \leq$ 340 K [6]. Measurement method for the S coefficient provides the uncer-

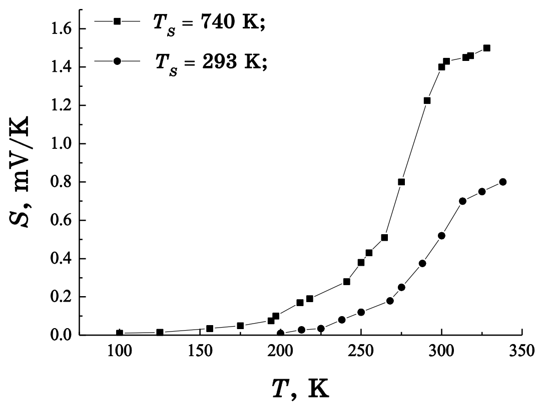

Fig. 7. Temperature dependences of the thermo-e.m.f. coefficient for the film deposited by PLD on Si substrate from β-$FeSi_2$ target; substrate temperature $T_S \cong 293$ K and 740 K.

tainty in determining of its value of no more than 10% in the temperature range $100 \text{ K} \leq T \leq 340 \text{ K}$.

One can see that, for films deposited from $CrSi_2$ and β-$FeSi_2$ targets, the crystalline structure of the Si substrate promotes the growth of polycrystalline films, while the amorphous structure of the SiO_2 substrate promotes the growth of amorphous films. Deposition of films on heated substrates results in the formation of films with a higher content of semiconductor phase: value of E_g is higher for films deposited on heated substrate. In general, polycrystalline films deposited from iron silicide target have higher values of E_g than films deposited from chromium silicide target. This is congruent with the fact that E_g for bulk single crystalline form β-$FeSi_2$ has a higher value (0.85 eV) than the one for bulk single crystalline form $CrSi_2$ phase (0.35 eV). As regards the S coefficient for films deposited from $CrSi_2$ and β-$FeSi_2$ targets, this coefficient is higher for the polycrystalline film with higher values of E_g.

The S coefficient is important for studying kinetic phenomena of charge transfer in materials [10, 11]. To this purpose, it is necessary to know besides the correlation between the temperature and specific conductivity, the correlation between the temperature and the S coefficient. If one takes into account the expressions for electron and hole concentrations in a non-degenerate semiconductor, it is possible to write the S coefficient in the form [12] as follows:

$$S = -\frac{k}{e}\frac{[2+\ln(N_c/n)]n\mu_n - [2+\ln(N_v/p)]p\mu_p}{n\mu_n + p\mu_p}, \quad (3)$$

where k is the Boltzmann constant; e is electron charge; n, p are electron and hole concentrations; N_c, N_v are effective densities of states in the conduction and valence bands, respectively; and μ_n, μ_p are electron and hole mobilities, respectively. It is seen that the thermo-e.m.f. coefficient of semiconductor materials depends on impurities of two types (n and p), which determine their conductive characteristics (3). The S coefficient is being increased with temperature increasing up to 315 K and then decreased with temperature increasing up to 340 K for films deposited from $CrSi_2$ target (Fig. 6). This behaviour can be explained by the existence of metallic phase in deposited films while this target ablation. During ablation process of $CrSi_2$ target, the stoichiometry of this bulk single-crystalline form is being destroyed, resulting in Cr atomic content in deposited films. Therefore, the value of E_g is decreased. The S coefficient is increased with temperature increasing in the range from 100 K to 340 K for films deposited while β-$FeSi_2$ targets ablation (Fig. 7). During ablation process of β-$FeSi_2$ target, the stoichiometry of this bulk single-crystalline form is being destroyed too, resulting in Fe atomic content in deposited films. Nevertheless, in this case, Fe atomic content in deposited films is not enough to change the specific conductivity of deposited films from semiconductor trend to metallic one while sample cooling. The value of E_g is decreased in this case too. However, in general, released Cr and Fe create impurity levels in the forbidden zone of semiconductor films results in decreasing of energy band gap E_g, which is less than that is for bulk single-crystalline form. Nanometre film deposition on heated Si substrate results in increasing of energy band gap E_g in comparison with one deposited on Si substrate at RT as heat energy promotes crystallization process of semiconductor phase. As the S coefficient is positive in whole temperature range, p-type of charge carriers prevails above n-type ones. Moreover, the increasing the S coefficient for nanometre films is assigned with increasing of effective density of states in the conduction and valence bands results in increasing charge-carriers' gradient at creation of temperature gradient in nanometre films.

4. CONCLUSIONS

Large S coefficient of thin films deposited from $CrSi_2$ and β-$FeSi_2$ targets by PLD using an excimer KrF laser is obtained. The value of this coefficient depends on substrate nature and substrate temperature. The more substrate temperature, the higher value of energy band gap E_g of nanometre films results in increasing of the S coefficient. Therefore, the PLD based on an excimer KrF laser is effective method for the deposition of nanostructures in the form of thin films with large thermoelectromotive force coefficient, which are quite suitable for thermal sensors operating in a wide temperature range. Nanostructures of iron and chromium silicide films in the form of thin films deposited by PLD the form of thin films with a narrow energy-band gap (less than 1.0 eV) can be proposed not only for thermal sensors but for infrared detectors too.

ACKNOWLEDGMENTS

Author thanks to Prof. A. Luches and Dr. A. P. Caricato from the Department of Physics at Salento University, Italy for the help of sample preparation by PLD.

REFERENCES

1. L. F. Mattheiss, *Phys. Rev. B*, **43**: 1863 (1991).
2. H. Lange, *phys. status solidi (b)*, **201**: 3 (1997).
3. J. Chevrier, J. Y. Natoli, I. Berbezier, A. Ronda, and J. Derrien, *Solid State Phenomena*, **39**: 32 (1993).

4. S. P. Murarka, *Silicides for VLSI Applications* (New York: Academic Press, Inc.: 1983).
5. C. D. Lien, M. A. Nicolet, and S. S. Lau, *Thin Solid Films*, **143**: 63 (1986).
6. A. P. Caricato, A. Luches, F. Romano, S. A. Mulenko, Y. V. Kudryavtsev, T. Gorbachuk, C. Fotakis, E. L. Papadopoulou, and R. Klini, *Appl. Surf. Science*, **254**: 1288 (2007).
7. L. Doolittle, *RUMP RBS Simulation Program* (Ithaca, N.Y.: Computer Graphics Service, Ltd., 1993).
8. C. W. Wert and R. M. Thomson, *Physics of Solids* (New York: McGraw-Hill Book Company: 1964).
9. A. P. Caricato, G. Leggieri, A. Luches, F. Romano, G. Barucca, P. Mengucci, and S. A. Mulenko, *Appl. Surf. Science*, **254**: 1224 (2007).
10. H. S. Nalwa, *Handbook of Nanostructured Materials and Nanotechnology* (San Diego: Academic Press: 2000), vols. **1–5**.
11. A. Ishida, D. Cao, S. Morioka, Y. Inoue, and T. Kita, *J. of Electronic Materials*, **38**: 940 (2009).
12. K. V. Shalimova, *Fizika Poluprovodnikov* (Moscow: Ehnergoatomizdat: 1985) (in Russian).