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S.V. Luniov¹, P.P. Shygorin², B.Ya. Venhryn³

Electrical Properties of $Ge/Ge_{(x)}Si_{(1-x)}$ thin films on the boundary of semiconductor-dielectric transition

¹Lutsk National Technical University, Lutsk, Ukraine, <u>luniovser@ukr.net</u>

²Lesya Ukrainka Volyn National University, Lutsk, Ukraine, <u>shygorin.pavlo@vnu.edu.ua</u>

³Lviv Polytechnic National University, Lviv, Ukraine, <u>bohdan.y.venhryn@lpnu.ua</u>

Calculations of the dependencies of carrier concentration and specific electrical conductivity at room temperature for the undoped and doped germanium nanofilms, grown on the $Ge_{(x)}Si_{(1-x)}$ substrate with crystallographic orientation (001), on a film thickness and substrate composition, have been provided based on the theory of electrical conductivity for the two-dimensional semiconductor nanostructures. It was established that the dielectric-semiconductor transition for thin germanium films with a thickness of d < 7 nm can be achieved either by increasing the film thickness, which reduces the effectiveness of quantum size effects or by increasing the silicon content in the $Ge_{(x)}Si_{(1-x)}$ substrate. The latter increases the internal mechanical stress in the film and, consequently, the concentration of intrinsic current carriers. Doping such germanium film by the donor impurities with the ionization energy $E_d < 150$ meV also leads to the implementation of the dielectric-semiconductor transition. The presented calculations of the electrical properties of germanium thin films can be utilized in developing the scientific foundations for their synthesis and in designing channels of the n-MOSFET and n-MODFET transistors, lasers based on heterojunctions, and electro-optical modulators based on such films.

Keywords: quantum size effects, dielectric-semiconductor transition, internal mechanical strains, germanium thin films, intrinsic carrier concentration, specific electrical conductivity.

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Introduction

Silicon integrated circuit manufacturing technologies have reached a level where further performance improvements can no longer be achieved solely through geometric scaling [1]. Therefore, scientists have concluded that in many new electronic device structures, silicon can be replaced by germanium, which has higher mobility of current carriers and allows heterostructures of various compositions and practically arbitrary layer thicknesses to be obtained on silicon or silicon-germanium alloy substrates [2-5]. Significant internal mechanical strains exist in heterostructures obtained based on silicon and germanium, associated with the considerable difference in the lattice constants of these materials. This allows for the growth of very thin germanium films on Si or $Ge_{(x)}Si_{(1-x)}$ substrates, which can be used to create lasers, electro-optical modulators and MOSFET transistors [611]. The integrity, quality, and homogeneity of the electrical and optical properties of these germanium films are determined by their crystallinity and dislocation density [12-15]. The degree of crystallinity, dislocation density, and dislocation flow, as well as the magnitude of internal strains in the film, depend on the technological conditions of its growth (temperature and growth atmosphere, subsequent heat treatment, the presence of uncontrolled impurities and doping) [16-21]. In particular, studies [20, 21] demonstrated that additional doping of germanium films by the donor or acceptor impurities reduces the dislocation density, which also depends on the nature of the doping impurity. Therefore, selecting the optimal technology for producing germanium films can ensure high electrical performance. Another significant factor influencing the electrical properties of very thin germanium films is the presence of quantum size effects. In previous studies [22-24], it was established that the electrical conductivity of the germanium nanofilm with a thickness of d<7 nm, growing on the $Ge_{(x)}Si_{(1-x)}$ substrate with a crystallographic orientation of (001), strongly depends on quantum size effects. The efficiency of these effects is, in turn, a function of the degree of doping of the nanofilm by the donor impurities. The film's conductivity is also determined by the substrate composition. The magnitude of internal mechanical strains in the nanofilm increases with the increasing silicon content in the substrate, under the influence of which a deformational reconstruction of the nanofilm band structure occurs. In particular, $(L_1-\Delta_1)$ inversion of the absolute minimum type of the conduction band of the germanium nanofilm was obtained under the action of significant internal deformations. The mechanism of this inversion and its influence on the electrical properties of bulk germanium single crystals were extensively studied in [25-27]. In [23], the dielectric-semiconductor transition was first achieved in germanium nanofilms at sub-room temperatures. However, comprehensive studies on the impact of internal mechanical strains and the degree of doping with donor impurities with different ionization energies on the mechanisms and the possibility of implementing such a transition at room temperature have not been investigated.

That is why the purpose of this work is to conduct such studies, as they are more practically relevant for modelling and developing various nanoelectronics elements based on germanium nanofilms, which primarily operate at temperatures near room temperature.

I. Theoretical calculations

The calculations of the band structure for both undoped and donor-doped germanium nanofilms, grown on the $Ge_{(x)}Si_{(1-x)}$ (001) substrate, were performed in works [22, 28]. According to [28], the expressions for the carrier concentration in the strained germanium nanofilm are given by:

$$n_{L_{1}} = \left(\frac{2}{d}\sum_{n=1}^{\infty}e^{-\frac{h^{2}n^{2}}{8m_{\parallel}^{L_{1}}kTd^{2}}}\right)\frac{2\pi m_{\perp}^{L_{1}}kT}{h^{2}} \cdot e^{\frac{E_{F}-E_{L_{1}}}{kT}}, \ n_{\Delta_{1}} = \left(\frac{2}{d}\sum_{n=1}^{\infty}e^{-\frac{h^{2}n^{2}}{8m_{\parallel}^{\Delta_{1}}kTd^{2}}}\right)\frac{2\pi m_{\perp}^{\Delta_{1}}kT}{h^{2}} \cdot e^{\frac{E_{F}-E_{\Delta_{1}}}{kT}}, \tag{1}$$

$$p_{1} = \left(\frac{2}{d}\sum_{n=1}^{\infty} e^{-\frac{h^{2}n^{2}}{8m_{1}kTd^{2}}}\right) \frac{2\pi m_{1}kT}{h^{2}} \cdot e^{-\frac{E_{F}-E_{V_{1}}}{kT}}, p_{2} = \left(\frac{2}{d}\sum_{n=1}^{\infty} e^{-\frac{h^{2}n^{2}}{8m_{2}kTd^{2}}}\right) \frac{2\pi m_{2}kT}{h^{2}} \cdot e^{-\frac{E_{F}-E_{V_{2}}}{kT}}.$$
 (2)

Here, n_{L_1} and n_{Δ_1} are the electron concentrations in the L_1 - and Δ_1 - conduction band minima of the Ge nanofilm; p_1 and p_2 are the concentrations of "light" and "heavy" holes for the valence band branches; d is the nanofilm thickness; $m_{\perp}^{L_1} = 0.082 m_0$, $m_{\parallel}^{L_1} = 1.58 m_0$, $m_{\perp}^{\Delta_1} = 0.32 m_0$, $m_{\parallel}^{\Delta_1} = 1.65 m_0$, $m_1 = 0.044 m_0$, $m_2 = 0.28 m_0$ are the effective masses of conduction in the L_1 -and Δ_1 - minima and for the "light" and "heavy" hole bands, respectively [29 – 31]; m_0 is the free electron mass; E_F is the Fermi energy; E_{L_1} , E_{Δ_1} , E_{V_1} , E_{V_2} are the energy positions of the corresponding conduction band minima and valence band branches in the strained germanium nanofilm.

The electron and hole concentrations of in the conduction and valence bands, as well as the intrinsic current carriers, are given by:

$$n = n_{L_1} + n_{\Delta_1}, p = p_1 + p_2, n_i(\varepsilon) = \sqrt{np}.$$
 (3)

The concentration of intrinsic current carriers in an unstrained germanium nanofilm is given by:

$$n_i(0) = \frac{4\pi kT}{h^2 d} \left(m_\perp^{L_1} m_p \right)^{1/2} \left[\sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_\parallel^{L_1} kT d^2}} \cdot \sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_p kT d^2}} \right]^{1/2} \cdot e^{-\frac{E_g(0)}{2kT}}.$$
(4)

Here $m_p = 0.193m_0$ is the effective mass of conductivity for holes, $E_q(0) = 0.66$ eV [29].

The specific conductivity for unstrained $\sigma(0)$ and strained $\sigma(\varepsilon)$ nanofilms is given by:

$$\sigma(0) = q n_i(0) (\mu_{L_1} + \mu_p),$$

$$\sigma(\varepsilon) = q n_i(\varepsilon) (\mu_n(\varepsilon) + \mu_p(\varepsilon)),$$
(5)

where μ_{L_1} , μ_p are the mobility in the unstrained nanofilm; $\mu_n(\varepsilon)$ and $\mu_p(\varepsilon)$ are the effective electron and hole mobility in the strained nanofilm.

The relative change in the electrical conductivity of the strained germanium nanofilm can be represented as follows [23]:

$$\frac{\sigma(\varepsilon)}{\sigma(0)} = \frac{n_i(\varepsilon)}{n_i(0)} \frac{b_4(1+B) + b_5B + b_6}{(1+B)(1+b_7)}.$$
 (6)

The designations for the quantities B, b_4 , b_5 , b_6 , b_7 in expression (6), as well as detailed calculations, are presented in [23]. The electron concentration in the doped germanium nanofilm by the donor impurity is determined by the expression [26]:

$$n(\varepsilon) = ax. \tag{7}$$

Here $x = e^{\frac{E_F}{kT}}$ is the solution of the next equation:

$$2x^3 + cx^2 - \frac{N_d c + 2b}{a}x - \frac{bc}{a} = 0,$$
 (8) with

$$a = \frac{4\pi kT}{h^2 d} \left(m_{\perp}^{L_1} \sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_{\parallel}^{L_1} kT d^2}} \cdot e^{-\frac{E_{L_1}}{kT}} + m_{\perp}^{\Delta_1} \sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_{\parallel}^{\Delta_1} kT d^2}} \cdot e^{-\frac{E_{\Delta_1}}{kT}} \right), \tag{9}$$

$$b = \frac{4\pi kT}{h^2 d} \left(m_1 \sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_1 kT d^2}} \cdot e^{\frac{E_{V_1}}{kT}} + m_2 \sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_2 kT d^2}} \cdot e^{\frac{E_{V_2}}{kT}} \right), \ c = e^{\frac{E_d}{kT}},$$

and N_d is the concentration of the donor impurity, E_d is the energy of their ionization.

Expression (6) for the case of a doped germanium nanofilm can be represented as follows:

$$\frac{\sigma(\varepsilon)}{\sigma(0)} = \frac{n(\varepsilon)\mu_n(\varepsilon) + p(\varepsilon)\mu_p(\varepsilon)}{n(0)\mu_{L_1} + p(0)\mu_p(0)}.$$
 (10)

According to [23],

$$\mu_n(\varepsilon) = \frac{\mu_{L_1} A + \mu_{\Delta_1}}{1 + A}, \quad \mu_p(\varepsilon) = \frac{\mu_1 B + \mu_2}{1 + B}, \quad (11)$$

with

$$A = \frac{n_{L_1}}{n_{\Delta_1}} = \frac{\sum_{n=1}^{\infty} e^{-\frac{h^2 n^2}{8m_{\parallel}^{L_1}kTd^2}}}{\frac{-\frac{h^2 n^2}{8m_{\parallel}^{\Delta_1}kTd^2}}{m_{\perp}^{2m_{\perp}}}} \left(\frac{m_{\perp}^{L_1}}{m_{\perp}^{\Delta_1}}\right) e^{\frac{E_{\Delta_1} - E_{L_1}}{kT}}.$$

Then, considering expressions (3) and (10), the relative change in the specific electrical conductivity of the strained germanium nanofilm, doped by the donor impurity, is given by:

$$\frac{\sigma(\varepsilon)}{\sigma(0)} = \frac{n(\varepsilon)\frac{\mu_{L_1}A + \mu_{\Delta_1}}{1 + A} + \frac{n_i^2(\varepsilon)}{n(\varepsilon)} \frac{\mu_1 B + \mu_2}{1 + B}}{n(0)\mu_{L_1} + \frac{n_i^2(0)}{n(0)}\mu_P(0)},$$
(12)

where μ_{L_1} and μ_{Δ_1} are the electron mobilities in the L₁ and Δ_1 -valleys of the conduction band, μ_1 and μ_2 are the mobilities of "light" and "heavy" holes, and $\mu_P(0)$ is the hole mobility in the unstrained nanofilm. Expressions for calculating these mobilities under conditions of electron and hole scattering by acoustic phonons are provided in [23]. The energy position E_d of the donor impurity in the strained germanium nanofilm was determined using the solutions to the electroneutrality equation obtained in [28].

II. Results and discussion

Fig 1 shows the dependencies of the intrinsic carrier and electron concentration on the thickness of undoped and doped by the shallow donor impurity germanium nanofilm, respectively. The calculations were performed at T=300 K and for the case of nanofilm growth on a $Ge_{(x)}Si_{(1-x)}$ substrate with crystallographic orientation (001). As previously established in our studies [22-24], for such nanofilms with a thickness d<7 nm, quantum size effects become significant, strongly influencing the carrier concentration and electrical conductivity.

As illustrated in Fig. 1a, an unstrained germanium nanofilm (x = 1) with a thickness of d = 2 nm exhibits dielectric properties. Increasing its thickness to 7 nm induces a dielectric-to-semiconductor transition. This transition can also be achieved by increasing the silicon content in the substrate, which in turn elevates the internal mechanical strains in the nanofilm. These strains reduce the band gap width of the nanofilm, leading to a rise in the concentration of intrinsic current carriers [22, 23]. Another method to implement the semiconductor transition in a germanium nanofilm is doping by the donor impurities. As shown in Figs. 1b, 1c, and 1d increasing the concentration of dopants raises the electron concentration in the conduction band of the nanofilm due to the complete ionization of shallow donors at room temperature. Notably, for silicon contents of 100% and 75% in the Ge(x)Si(1-x) substrate, the doping level (ranging from 10¹¹ to 10¹³ cm⁻³) has a minimal impact on the dielectric-to-semiconductor transition. In these cases, the primary driver of the transition is the significant internal mechanical strains in the germanium nanofilm, which drastically increase the concentration of intrinsic current carriers, which is many times greater than the concentration of the doping impurity. Therefore, to impart semiconductor properties to germanium nanofilms grown on a germanium substrate (unstrained nanofilm) or substrates with lower silicon content (and correspondingly lower internal strains), it is necessary to dope the nanofilm with donor impurities at concentrations across a broader range of $Ge_{(x)}Si_{(1-x)}$ (001) substrate compositions. As noted in [23], increasing the silicon content in the substrate slightly reduces the carrier mobility relative to the corresponding changes in their concentration. Thus, the qualitative and quantitative dependencies of the specific electrical conductivity of the germanium nanofilm on its thickness will primarily be determined by changes in carrier concentration and the efficiency of quantum size effects. According to Fig. 2, the relative specific electrical conductivity of undoped germanium nanofilms decreases with increasing thickness, whereas that of doped nanofilms increases. This can be explained by the fact that in undoped and unstrained nanofilms, as shown in Fig. 1a, quantum size effects are most pronounced, which lead to a significant change in the concentration of intrinsic current carriers (by nearly four orders of magnitude) when the film thickness varies from 2 nm to 7 nm. In strained nanofilms, with a higher intrinsic carrier concentration, the efficiency of quantum size effects is lower. Accordingly, the specific electrical conductivity of strained nanofilms $\sigma(\varepsilon)$ decreases less significantly with increasing thickness than that of unstrained films $\sigma(0)$.

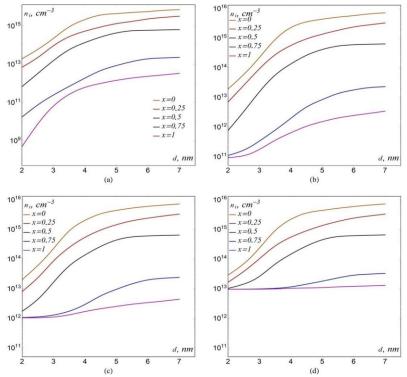


Fig. 1. The dependencies of the intrinsic carrier concentration and electron concentration for the undoped and doped by the shallow donor impurity germanium nanofilm grown on a $Ge_{(x)}Si_{(1-x)}$ (001) substrate on its thickness: (a) is undoped nanofilm; (b), (c), (d) is doped nanofilm with concentrations $N_d = 10^{11}$ cm⁻³, 10^{12} cm⁻³, 10^{13} cm⁻³, respectively.

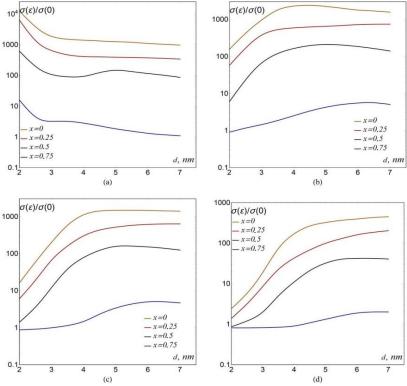


Fig. 2. Dependencies of the relative change in specific electrical conductivity for the undoped and doped germanium nanofilm by the shallow donor impurity, grown on a $Ge_{(x)}Si_{(1-x)}$ (001) substrate on its thickness: (a) undoped nanofilm; (b), (c), (d) is doped nanofilm with concentrations $N_d = 10^{11}$ cm⁻³, $N_d = 10^{12}$ cm⁻³, $N_d = 10^{13}$ cm⁻³, respectively.

This explains the relative decrease in the specific electrical conductivity $\sigma(\varepsilon)/\sigma(0)$ of undoped germanium nanofilms (Fig. 2a). Doping germanium nanofilms by the donor impurities reduces the role of quantum size effects on their electrical properties [24]. In this case, the character of the dependences of the specific electrical conductivity, both for an unstrained and strained nanofilm, on its thickness will be different and, as a result, the relative value of the specific electrical conductivity $\sigma(\varepsilon)/\sigma(0)$ will increase with increasing nanofilm thickness (Fig. 2 b, 2 c, 2 d). Calculations show that these results are valid for donor impurities with ionization energies of E_d < 150 meV, which are fully ionized at room temperature in both unstrained and strained germanium nanofilms. At higher ionization energies, the donor energy levels are not fully ionized, leading to a reduction in electron concentration in the conduction band [24]. Moreover, increasing the silicon content in the substrate, and hence the internal mechanical strains in the nanofilm, further increases the ionization energy of the donor impurities.

Figure 3 presents the dependencies of electron concentration on the thickness of a germanium nanofilm doped by the deep donor impurity at a concentration of $N_d = 10^{13}$ cm⁻³ at T = 300 K. The calculations were performed for donor impurity ionization energies $E_d = 150$ meV, $E_d = 250$ meV and $E_d = 300$ meV. As follows from the presented figures, increasing the ionization energy of the donor impurity from 150 to 300 meV leads to a decrease in the electron concentration in the conduction band of the unstrained germanium nanofilm. This is explained by an increase in the degree of deionization of the donor level. Additionally, unlike the case of a shallow donor impurity, for a germanium

nanofilm with a thickness of d < 3 nm, an increase in silicon content in the $Ge_{(x)}Si_{(1-x)}$ substrate to 50%, and the corresponding increase in internal mechanical strains, results in a reduction of electron concentration in the conduction band of the strained nanofilm compared to the unstrained one. In this case, changes in the electron concentration within the nanofilm are determined by two mechanisms: 1) an increase in the concentration of free current carriers, and 2) a decrease in the electron concentration in the conduction band due to an increase in the ionization energy of the donor impurity under the deformation, which leads to an increase in the degree of filling of the donor level by electrons.

The second mechanism is dominant for the strained germanium nanofilm with the thickness of d < 3 nm with the silicon content in the $Ge_{(x)}Si_{(1-x)}$ substrate of up to 50%, and for a silicon content of more than 50%, the first. Qualitatively similar dependences of the relative changes in the specific electrical conductivity $\sigma(\varepsilon)/\sigma(0)$ on the thickness of the germanium nanofilm were also obtained for the case of its doping by the deep donor impurity (Fig. 4).

The increase in the relative specific electrical conductivity with a higher silicon content in the $Ge_{(x)}Si_{(1-x)}$ substrate is explained by the increase in the concentration of intrinsic current carriers. Impurity energy levels with the ionization energy $E_d > 350$ meV will be filled by the electrons, and, accordingly, doping will not be affected on the dependencies of electron concentration or relative specific electrical conductivity on the thickness of the nanofilm. In this case, the mechanisms of quantum size effects will operate in the same manner as in undoped germanium nanofilm.

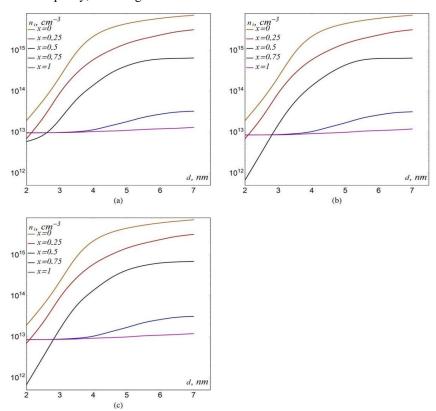


Fig. 3. Dependencies of electron concentration on the thickness of germanium nanofilm, doped by the deep donor impurity, for different ionization energies E_d of the doping impurity (in meV): (a) – 150, (b) – 250, (c) – 300.

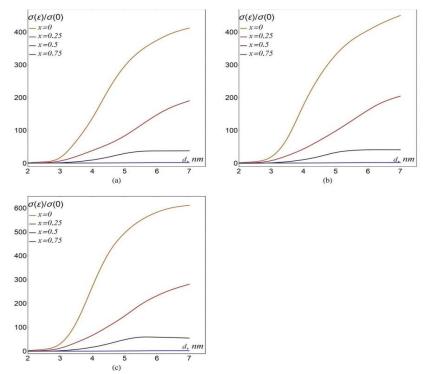


Fig. 4. Dependencies of the relative change in specific electrical conductivity on the thickness of germanium nanofilm, doped by the deep donor impurity, for different ionization energies E_d of the doping impurity (in meV): (a) -150, (b) -250, (c) -300.

Conclusions

The dielectric-semiconductor transition for undoped germanium nanofilms can be achieved through two methods: 1) by increasing the film thickness from 2 nm to 7 nm, which significantly weakens the role of quantum size effects; 2) by increasing the silicon content in the Ge(x)Si(1-x) substrate, which leads to an increase in the magnitude of internal mechanical strains in the nanofilm and, accordingly, the concentration of intrinsic current carriers in it. For doped germanium nanofilms, this transition can be realized by doping it with both shallow and deep donor impurities. At ionization energies of the donor impurity $E_d > 150$ meV, its deionization will occur, which leads to a decrease in the electron concentration in the conduction band of the nanofilm and, accordingly, the influence of the role of doping on the dielectricsemiconductor transition. Therefore, such transition is more effective when doping by the deep donor impurities at a concentration of $N_d > 10^{13} \text{ cm}^{-3}$. The dielectricsemiconductor transition mechanisms for the germanium nanofilm, doped by the donor impurity with the ionization energy $E_d > 350$ meV will be the same as for an undoped nanofilm, and doping by such impurities in this regard loses any meaning.

The presented calculations of the electrical properties of thin unstrained and strained germanium nanofilms must be taken into account in their synthesis, as well as in the development of various nanoelectronic elements based on them, in particular, the channels of n-MOSFET and n-MODFET transistor, heterojunction lasers, electro-optic modulators. In this case, first of all, the resistivity (specific electrical conductivity) of the raw material is important in the design of such elements, which justifies the practical significance of the obtained results.

Luniov S.V. – Doctor of Physical and Mathematical Sciences, Professor, Professor of the Department of Physics and Higher Mathematics, Lutsk National Technical University:

Shygorin P.P. – Candidate of Physical and Mathematical Sciences, Associate Professor, Associate Professor of the Department of Theoretical and Computational Physics named after A.V. Svidzinsky, Lesya Ukrainka Volyn National University;

Venhryn B. Ya. – Candidate of Physical and Mathematical Sciences, Associate Professor, Associate Professor of the Department of Applied Physics and Nanomaterials Science, Lviv Polytechnic National University.

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С.В. Луньов¹, П.П. Шигорін², Б.Я. Венгрин³

Електричні властивості тонких плівок Ge/Ge_(x)Si_(1-x) на межі переходу напівпровідник-діелектрик

¹Луцький національний технічний університет, м. Луцьк, Україна, <u>luniovser@ukr.net;</u>
²Волинський національний університет імені Лесі Українки, м. Луцьк, Україна, <u>shygorin.pavlo@vnu.edu.ua;</u>
³Національний університет «Львівська політехніка», м. Львів, Україна, <u>bohdan.y.venhryn@lpnu.ua</u>

На основі теорії електропровідності двовимірних напівпровідникових наноструктур проведено розрахунки залежностей концентрації носіїв струму та питомої електропровідності при кімнатній температурі для нелегованої та легованої наноплівки германію, вирощеної на підкладці $Ge_{(x)}Si_{(1-x)}$ з кристалографічною орієнтацією (001), від її товщини та складу підкладки. Було встановлено, що перехід дієлектрик-напівпровідник для тонких плівок германію товщиною d<7 нм можна реалізувати за рахунок збільшення її товщини, що пов'язано зі зменшення ефективності квантово-розмірних ефектів, або вмісту кремнію в підкладці $Ge_{(x)}Si_{(1-x)}$, внаслідок чого відбувається зростання величини внутрішніх механічних напружень в плівці та, відповідно, концентрації власних носіїв струму. Легування такої плівки германію донорною домішкою з енергією іонізації Ed<150 меВ також призводить до реалізації переходу дієлектрикнапівпровідник. Представлені розрахунки електричних властивостей тонких плівок германію можуть бути використані при розробці наукових основ їхнього синтезу та при конструюванні на основі таких плівок каналів n-MOSFET та n-MODFET транзисторів, лазерів на гетеропереходах та електрооптичних модуляторів.

Ключові слова: ефекти розмірного квантування, перехід діелектрик-напівпровідник внутрішні механічні напруження, тонкі плівки германію, концентрація власних носіїв струму, питома електропровідність.