ELECTROREFLECTION MODULATION SPECTROSCOPY STUDIES OF A NEAR-SURFACE LAYER IN SEMICONDUCTORS AND SEMICONDUCTOR-BASED STRUCTURES

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The possibility for the electroreflection modulation spectroscopy to be applied for studying the electronic parameters of the surfaces of semiconductors and semiconductor-based structures, as well as the electrolyte—semiconductor and metal—semiconductor interfaces, has been demonstrated. Making use of the polarization (tensor) anisotropy of the electrooptical effect, the surface and bulk contributions to the electroreflection signal have been separated. The effectiveness of the separation method has been demonstrated for the analysis of the electroreflection spectra from the (110) surface of germanium with intrinsic conductivity measured for the E_1 and $E_1 + \Delta_1$ transitions (within the spectral range 1.9—2.5 eV) provided the directions of the light polarization vector $\mathbf{e} \parallel [001]$ and $\mathbf{e} \parallel [1\bar{1}0]$ and the temperature $T = 300$ K. The energy diagram of the etched surface of i-Ge has been revealed to involve an extremum. The occurrence of such an extremum has been attributed to the vanishing of the electron work function at the surface and/or to the influence of the specular image forces.

1. Introduction

In connection with the rapid development of nanophysics and nanoelectronics, the contemporary level of science and technique requires that the researches of the near-surface layers of solids be carried out. In comparison to the bulk of solids, such layers may be the regions, where electronic processes may undergo substantial variations owing to the variations of the electron band structure, the mobility of current carriers, the time of their energy relaxation, as well as to the availability of the surface potential. In comparison with the classical spectroscopy, when applied to investigating the peculiarities of the electron band structure of solids, the electroreflection one has higher resolution. The thickness of the layer, which forms an observed electroreflection signal in the range of direct interband transitions, is defined by the penetration depths of the electric field and light. Electroreflection spectroscopy makes it possible to investigate electronic effects in the near-surface layers and to draw conclusions concerning the structural perfection of the latter. Provided that the near-surface layers of semiconductor crystals are enriched with majority current carriers, such electronic effects as the quantizations of current carriers near the surface [1], the electrooptical band-population effect [2], and the variation of the potential barrier profile near the semiconductor surface manifest themselves. The analysis of the tensor anisotropy of the electrooptical effect provides new opportunities for the study of surfaces and phase interfaces. In doing so, one should use the experimental setup where the electric field applied to the specimen and the propagation direction of a light wave are oriented in parallel to each other and perpendicularly to the researched surface, because it is this configuration that makes the anisotropy of the electrooptical effect in the near-surface layer observable.

In this work, in order to study the shape of the near-surface potential barrier, we have considered the anisotropic spectra of electroreflection from the near-surface layer of a model semiconductor (germanium with intrinsic conductivity).

2. Phenomenological Description of Electroreflection

Let us consider a semiinfinite single-crystalline semiconductor with the complex index of refraction

$N = n + i\chi$. Here, χ is the extinction factor of the medium which is connected to the absorption factor α by the relation $\alpha = 4\pi\chi/\lambda$; λ is the light wavelength. The reflection factor of the external medium—semiconductor system, $\rho = r\exp(i\theta)$, looks like

$$\rho = \frac{n_0 - N}{n_0 + N}, \quad (1)$$

if light strikes the surface normally. Its relative modulation is

$$\frac{\Delta\rho}{\rho} = \frac{1}{2}\left(\frac{\Delta R}{R}\right) + i\Delta\theta, \quad (2)$$

where $R = |r|^2$ is the reflectance of the system, n_0 the index of refraction in the medium, and

$$\Delta\theta\,(\omega_0) = -\frac{\omega_0}{\pi}P\int\limits_0^\infty \left[\frac{\Delta R}{R}(\omega)\right](\omega^2 - \omega_0^2)^{-1}d\omega \quad (3)$$

is the modulation of the phase which is determined by the transformation of the electroreflection spectrum according to the Kramers—Kronig relations. Provided that a uniform electric field with the intensity F is applied to an isotropic medium, the complex index of refraction N would change by ΔN. Therefore, from relation (1), we obtain

$$\frac{\Delta\rho}{\rho} = -\frac{2n_0\Delta N}{n_0^2 - N^2}. \quad (4)$$

Passing to the consideration of the modulation of the dielectric permittivity ε of a semiconductor

$$\Delta\varepsilon = \Delta\varepsilon_1 + i\Delta\varepsilon_2 = 2N\Delta N, \quad (5)$$

where $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are, respectively, the variations of the real and imaginary parts of the dielectric permittivity of the isotropic medium and extracting the real part $\Delta R/R$ of relation (4), we obtain the relative variation of the specimen reflectance in the electric field:

$$\frac{\Delta R}{R}(E,F) = \frac{R(E,F) - R(E,0)}{R(E,0)} =$$

$$= \alpha(n_0,n,\chi)\Delta\varepsilon_1 + \beta(n_0,n,\chi)\Delta\varepsilon_2, \quad (6)$$

where $E = \hbar\omega$ is the energy of photons, α and β are the Seraphin partial coefficients [3–5], and $\hbar$ is the Planck's constant.

According to work [3], the variation of the imaginary part of the complex dielectric permittivity of a three-dimensional critical point of the 3DM_0 type in the case of the direct allowed transitions in the electric field F can be written down in the form

$$\Delta\varepsilon_2(\omega,\ F) = \varepsilon_2(\omega,\ F) - \varepsilon_2(\omega,\ 0) = \frac{B_j}{\omega^2}\,\theta^{1/2}F(\eta), \quad (7)$$

where $F(\eta)$ is the electrooptical function of the first kind, the argument of which is equal to

$$\eta = \frac{E_0 - \hbar\omega}{\hbar\theta}, \quad (8)$$

E_0 is the electron transition energy,

$$\hbar\theta = \left(\frac{e^2F^2\hbar^2}{2\mu}\right)^{1/3} \quad (9)$$

the characteristic parameter (electrooptical energy) of the Franz–Keldysh effect [3], e the electron charge, $\mu^{-1} = (m_c^*)^{-1} + (m_v^*)^{-1}$ the reduced effective mass for the optical transition concerned, and m_c^* and m_v^* are the effective masses of electrons and holes in the conduction and valence bands, respectively.

With the use of the Kramers—Kronig relations, one can find the variation of the real part of the complex dielectric permittivity in the electric field F:

$$\Delta\varepsilon_1(\omega,\ F) = \frac{B_j}{\omega^2}\,\theta^{1/2}G(\eta), \quad (10)$$

where $G(\eta)$ is the electrooptical function of the second kind.

The electrooptical functions of the first, $F(\eta)$, and second, $G(\eta)$, kinds can be expressed in terms of the Airy functions Ai(η) and Bi(η), and the Heaviside function $U(\eta)$ [3–5]. The Airy functions describe the one-dimensional motion of free carriers in the uniform external electric field and are independent solutions of the electron-hole pair equation in the vicinity of the optical transition in the effective mass approximation [4].

The electron transition E_0 is characterized by a broadening Γ. The value of the latter depends on the lifetime of free current carriers which, in its turn, is governed by the processes of current carrier scattering by lattice vibrations, impurities, and surface defects, because the electroreflection signal is formed in the space-charge region (SCR). Taking Γ into account, we get

$$\eta = \frac{E_0 - \hbar\omega + i\Gamma}{\hbar\theta} = \frac{E_0 - E + i\Gamma}{\hbar\theta}. \quad (11)$$

Expression (11) means that the complex frequency

$$\omega' = \omega - i\omega_1 \quad (12)$$

is introduced in the calculation of the electrooptical effect. Really,

$$\eta = \frac{E_0 - \hbar\omega'}{\hbar\theta} = \frac{E_0 - \hbar\omega + i\hbar\omega_1}{\hbar\theta} = \frac{E_0 - \hbar\omega + i\Gamma}{\hbar\theta}, \quad (13)$$

where $\hbar\omega_1 = \Gamma$.

It should be noted that the Kramers—Kronig relations (the Hilbert transformation) are extremely important when analyzing the spectra of ordinary reflection and electroreflection. According to those relations, the real part of the function can be expressed in terms of its imaginary part. This means, that the real and imaginary parts of both the complex index of refraction $N(\omega) = n(\omega) + i\chi(\omega)$ and the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ satisfy those dispersion relations.

In the case of small variations $\Delta\theta$ of the phase angle, the real and imaginary components of the dielectric permittivity can be written down in the form

$$\Delta\varepsilon_1 = \frac{1}{2}\gamma\frac{\Delta R}{R} - \delta\Delta\theta, \quad (14)$$

$$\Delta\varepsilon_2 = \frac{1}{2}\delta\frac{\Delta R}{R} + \gamma\Delta\theta, \quad (15)$$

where

$$\gamma = \frac{n}{n_0}\left(n^2 - 3x^2 - n_0^2\right), \quad (16)$$

$$\delta = \frac{x}{n_0}\left(3n^2 - x^2 - n_0^2\right). \quad (17)$$

Therefore, the relative variation $\frac{\Delta R}{R}(E,F)$ of the reflectance of the researched specimen in the electric field F can be expressed in terms of the variations of the real, $\Delta\varepsilon_1$, and imaginary, $\Delta\varepsilon_2$, parts of the dielectric permittivity. The latter are expressed analytically in terms of the electrooptical functions of the first, $F(\eta)$, and second, $G(\eta)$, kinds [3–5], the arguments of which are of form (13).

The thickness of the layer that is involved in the formation of an electroreflection signal is defined by the penetration depths of the electric field and light. Therefore, the electroreflection method is very sensitive to the structure of the thin near-surface layer of thickness d (the light penetration depth),

$$d = \frac{\lambda}{4\pi N}. \quad (18)$$

Lately, the intensive researches of nanostructures – such as quantum wells, quantum wires, quantum dots, and multilayer systems – have been carried out [5–7].

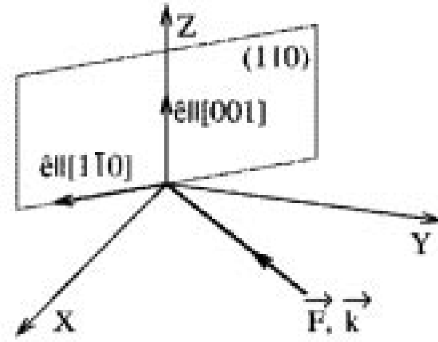

Fig. 1. Orientations of the researched i-Ge(110) surface, the vector of the applied electric field **F**, the direction of light propagation **k**, and the light polarization vectors **e**'s

3. Experimental Method

The electroreflection spectra of the chemically etched (110) surface of i-Ge with a current carrier concentration of 2×10^{19} m^{-3} were measured following the electrolytic method. The measurements were performed for the transitions E_1 and $E_1 + \Delta_1$ (within the spectral range $1.9 - 2.5$ eV) at the frequency of the first modulation harmonics $f = 2.2$ kHz, at room temperature $T = 300$ K, and provided the $\mathbf{e} \parallel [001]$ or $\mathbf{e} \parallel [1\bar{1}0]$ directions of the light polarization vector. The electric field applied to the researched single crystal and the propagation direction of incident light were parallel to each other and directed perpendicularly to the surface (Fig. 1). The buffer solution 0.1M K_2SO_4: 0.025M Na_2HPO_4: 0.025M KH_2PO_4 was used as electrolyte. In order to slow down the rates of electrochemical reactions at the Ge—electrolyte interface, the specimens were electrically biased by small values of applied potentials which enriched the researched surface with electrons. The constant bias applied to the specimens was monitored with respect to a saturated calomel reference electrode. The threshold sensitivity of measurements was 5×10^{-6} and the spectral resolution 3×10^{-3} eV.

4. Results and Their Discussion

In Fig. 2, the electroreflection spectra of the etched i-Ge(110) surface enriched with electrons are depicted. The spectra were measured using two main directions of the polarization vector: $\mathbf{e} \parallel [001]$ (curve *1*) and $\mathbf{e} \parallel [1\bar{1}0]$ (curve *2*).

By their shape and the order of the appearance of extrema, the obtained spectra correspond to the case where the energy bands are bent upwards if one goes

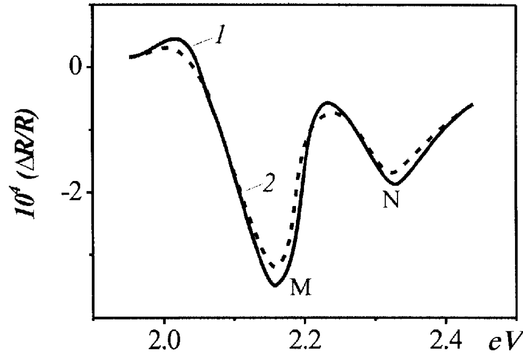

Fig. 2. Electroreflection spectra from the chemically etched i-Ge(110) surface for the light polarization directions $\mathbf{e} \parallel [001]$ (*1*) and $\mathbf{e} \parallel [1\bar{1}0]$ (*2*). The applied bias voltage is −0.2 V, and the modulation is 0.2 V

towards the surface. Under conditions that the near-surface layer of i-Ge was enriched with electrons, i.e. the surface was biased positively, such a situation would emerge if there were an extremum in the dependence of the electrostatic potential of the semiconductor φ on the z coordinate. In this case, the electroreflection signals that would be formed on the different sides of the extremum would have the opposite phases, with the phase of the spectrum being determined by the phase of the largest signals.

In order to determine the coordinate dependence of the electrostatic potential near the surface of a semiinfinite crystal under stationary conditions, it is necessary to solve the Poisson equation which looks in the homogeneous case like

$$\frac{d^2\varphi(z)}{dz^2} = -\frac{4\pi\rho(z)}{\varepsilon\varepsilon_0}, \tag{19}$$

where ε_0 is the dielectric permittivity of vacuum, and $\rho(z)$ is the density of the space charge at a distance z from the surface. That is, the z axis is directed in parallel to both the electric field applied to the surface and the propagation direction of the incident light. Since the surface has been etched (surface charges are absent), the charge density $\rho(z)$ in our case equals

$$\rho(z) = e[p(z) - n(z)], \tag{20}$$

where the nonequilibrium concentrations of holes, $p(z)$, and electrons, $n(z)$, in the SCR look like

$$p(z) = n_i \exp\left(\frac{-e\varphi(z)}{kT}\right), \tag{21}$$

$$n(z) = n_i \exp\left(\frac{e\varphi(z)}{kT}\right), \tag{22}$$

n_i being the bulk concentration of electrons (or holes) in the region beneath the SCR. Substituting Eqs. (20)—(22) into Eq. (19), we find

$$\frac{d^2\varphi(z)}{dz^2} = \frac{4\pi e n_i}{\varepsilon\varepsilon_0}\mathrm{sh}\left(\frac{e\varphi(z)}{kT}\right). \tag{23}$$

If $e\varphi(z) \ll kT$ and provided the boundary conditions

$$\varphi(z) = 0, \quad z \to \infty \tag{24}$$

$$F = -\varepsilon\frac{d\varphi(z)}{dz}, \quad z = 0, \tag{25}$$

the shape of the potential barrier near the surface is described by the exponential law, and the analytical expression for it looks like [3]

$$\varphi(z) = \frac{FL_\mathrm{D}}{\varepsilon}\exp\left(-z/L_\mathrm{D}\right), \tag{26}$$

where

$$L_\mathrm{D} = \left(\frac{\varepsilon\varepsilon_0 kT}{8\pi e^2 n_i}\right)^{1/2} \tag{27}$$

is the Debye screening length. The electric fields, at which the electroreflection spectra were being measured, were of the order of $10^6 - 10^8$ V/m; therefore, this case is not actual.

The surface concentration of the majority current carriers n (in our case, electrons) equals

$$n = \int\limits_0^\infty [n(z) - p(z)]dz \tag{28}$$

at a positive band bending. Let the value of F be supposed constant, so that the potential profile $\varphi(x)$ may be approximated by two linear sections

$$\varphi(z) = \begin{cases} \varphi_s - Fz, & 0 \le \mathrm{z} \le \varphi_s/F, \\ 0, & z \ge \varphi_s/F, \end{cases} . \tag{29}$$

Then, substituting Eqs. (21), (22), and (29) into Eq. (28), we obtain

$$n = 2n_i \int\limits_0^{\varphi_s/F} \left[\mathrm{sh}\frac{e(\varphi_s - Fz)}{kT}\right]dz =$$

$$= \frac{n_i kT}{eF}\left[\exp\left(\frac{e\varphi_s}{kT}\right) + \exp\left(-\frac{e\varphi_s}{kT}\right) - 2\right]. \tag{30}$$

According to the boundary conditions, the electric field equals

$$F = \frac{4\pi e n}{\varepsilon\varepsilon_0}. \tag{31}$$

Relations (30) and (31) result in the following expression for the electric field in the near-surface layer of the intrinsic semiconductor, provided that its surface is enriched with electrons [8]:

$$F = \frac{kT}{eL_D}\left[\exp\left(\frac{e\varphi_s}{kT}\right) + \exp\left(-\frac{e\varphi_s}{kT}\right) - 2\right]^{1/2}. \qquad (32)$$

Here, the screening length L_D equals

$$L_D = \left(\frac{\varepsilon\varepsilon_0 kT}{4\pi e^2 n_i}\right)^{1/2}. \qquad (33)$$

Having introduced the notation $y_s = e\varphi_s/kT$ for the dimensionless bending of energy bands (in our case, $y_s > 0$, because the bands are bent downwards), the analytical expression for the determination of the electric field value can be written down in the form

$$F = \frac{kT}{eL_D}[\exp y_s + \exp(-y_s) - 2]^{1/2}. \qquad (34)$$

The obtained experimental spectra of electroreflection were unipolar (Fig. 2). Therefore, the energies of electron transitions $E_1 = 2.18$ eV and $E_1 + \Delta_1 = 2.35$ eV were determined according to the energy position of the dominating extrema M and N, respectively. This implies that the value of the spin-orbit splitting $\Delta_1 = 0.17$ eV. The polarization (tensor) anisotropy coefficient of the electrooptical effect is defined as the ratio between the electroreflection signals measured at the given directions of the light wave polarization vectors:

$$S = \frac{(\Delta R/R)\,\mathbf{e} \parallel [001]}{(\Delta R/R)\,\mathbf{e} \parallel [1\bar{1}0]}. \qquad (35)$$

It should be noted that the polarization anisotropy coefficient depends on the energy of photons. For example, $S = 1.08$ and 1.1, respectively, in the vicinity of the dominating extrema M and N. In view of the polarization (tensor) dependence of the electrooptical effect, we separate the surface and bulk contributions to the electroreflection signal. In doing so, we assume that the surface component of electromodulation $(\Delta R/R)_s$ is isotropic with respect to the light polarization vector, and the bulk component $(\Delta R/R)_v$ is anisotropic. It is true for the surface-related linear electrooptical effect in a centrosymmetric cubic crystal [9], in the case of the near-surface layer amorphism, and in a number of other cases. For the light polarization $\mathbf{e} \parallel [1\bar{1}0]$, provided that the assumption made is valid, we have

$$\frac{\Delta R}{R} = \sum_{i=1}^{2}(A_i\Delta\varepsilon_{is} + B_i\Delta\varepsilon_{iv}) = \left(\frac{\Delta R}{R}\right)_s + \left(\frac{\Delta R}{R}\right)_v. \qquad (36)$$

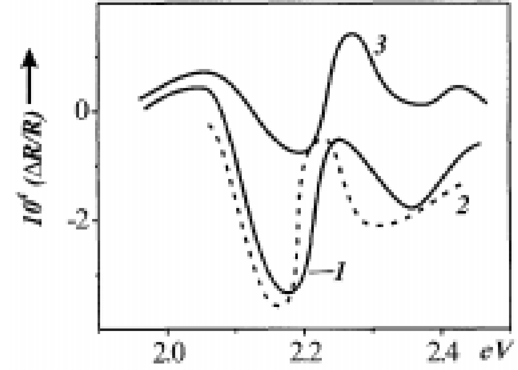

Fig. 3. Electroreflection spectrum from the chemically etched i-Ge(110) surface for the light polarization direction $\mathbf{e} \parallel [001]$ (*1*) and its isotropic (*2*) and anisotropic (*3*) components

Then, for the light polarization vector $\mathbf{e} \parallel [001]$, we can write down that

$$S\left(\frac{\Delta R}{R}\right) = \sum_{i=1}^{2}(A_i\Delta\varepsilon_{is} + S_0 B_i\Delta\varepsilon_{iv}) =$$

$$= \left(\frac{\Delta R}{R}\right)_s + S_0\left(\frac{\Delta R}{R}\right)_v, \qquad (37)$$

where S_0 is the polarization anisotropy coefficient of the bulk component of the electrooptical effect connected to the Franz—Keldysh effect. Let us assume further that, owing to the screening effect of the near-surface layer, the criterion of a weak field is fulfilled in the specimen's volume, so that the coefficient S_0 is constant over the spectrum and amounts to about 1.3 [10]. Then, from relations (36) and (37), we obtain

$$\left(\frac{\Delta R}{R}\right)_s = \frac{S_0 - S}{S_0 - 1}\frac{\Delta R}{R}, \qquad (38)$$

$$\left(\frac{\Delta R}{R}\right)_v = \frac{S - 1}{S_0 - 1}\frac{\Delta R}{R}. \qquad (39)$$

In Fig. 3, the results of the separation of the experimental electroreflection spectrum, which is measured at the $\mathbf{e} \parallel [001]$ polarization of a light wave, into the surface (isotropic, curve *2*) and bulk (anisotropic, curve *3*) components are depicted. By its shape and the order of appearance of the dominating extrema, the bulk component corresponds to the case where the energy bands are bent upwards if one goes towards the surface.

Values of the phenomenological parameter of broadening Γ for the E_1 and $E_1 + \Delta_1$ transitions

were found from the halfwidth of the bands in the vicinity to the M or N extremum, respectively. In our case, $\Gamma = 0.1015$ eV for the transition E_1 and $\Gamma = 0.13$ eV for the transition $E_1 + \Delta_1$. The intensity of the electric field $F = 2.2 \times 10^7$ V/m, at which the experimental electroreflection spectra were measured for two different directions of the light polarization vector, was evaluated from the measurements of the capacitance of the electrolyte—germanium system. The value of the electrooptical energy $\hbar\theta \approx 0.095$ eV was found by analyzing the experimental spectra (Fig. 2) on the basis of the Aspnes extended electrooptical functions. The absence of the Franz—Keldysh oscillations means that we have an intermediate case where the electrooptical energy is comparable with the phenomenological parameter of broadening Γ. Substituting the values of the electric field intensity F and the electrooptical energy $\hbar\theta$ quoted above into formula (9), we calculated the reduced effective mass $\mu \approx 0.022m_0$ for the considered optical transitions.

The Debye screening length $L_{\rm D}$ calculated by formula (33) was equal to 2.97×10^{-7} m ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, $\varepsilon = 16$, and $kT = 0.025$ eV). The light penetration depth calculated by formula (18) is varied from 9.8 to 13 nm in the spectral range $1.9 - 2.5$ eV. This testifies to that the electric field can be regarded constant across the thickness of the reflecting layer of the crystal. It should be noted that the thickness of the accumulation layer (the thickness of SCR) is governed by the effective screening length L^* which can be much less than the screening length $L_{\rm D}$ provided that the band bending is substantial. That is, if the near-surface layer is enriched with majority current carriers, the volume charge is concentrated just in the near-surface layer, because the screening is performed in this case by its majority carriers, i.e. by electrons (the band bending, being resulted from the application of strong electric fields to the surface of i-Ge, leads to the conductivity of the n-type in the near-surface layer). The classical value for the thickness of the accumulation layer can be found by the formula [3]

$$L^* = \frac{2kT}{eF}. \tag{40}$$

In our case, $L^* = 2.25$ nm.

Basing upon the Heisenberg uncertainty principle for the energy E and the time t ($\Delta E \Delta t \geq \hbar$) [11–13], the relaxational effects of the light absorption by a crystal can be described [3] by introducing the phenomenological parameter of broadening Γ, which is connected to the time of energy relaxation of photoinduced current carriers τ by the relation $\Gamma = \hbar/\tau$. This relation allows the values of τ for the corresponding electron transitions to be estimated making use of the optical electroreflection method. For example, for the i-Ge(110) surface with the concentration $n_i = 2 \times 10^{19}$ m^{-3}, $\tau_1 = \hbar/\Gamma_1 \approx 6.48 \times 10^{-15}$ s for the optical transition E_1, and $\tau_2 = \hbar/\Gamma_2 \approx 5.06 \times 10^{-15}$ s for the optical transition $E_1 + \Delta_1$.

Let us evaluate the de Broglie wavelength $\lambda_{\rm dB}$ of an electron with the effective mass $m_n^* = 1.58m_0$ [14] and the energy kT by the formula

$$\lambda_{\rm dB} = \frac{2\pi}{\sqrt{m_n^* kT/\hbar^2}}. \tag{41}$$

In our case, $\lambda_{\rm dB} = 6.15$ nm. From here, one can draw conclusion that the de Broglie wavelength was comparable (being longer) with the thickness L^* of the accumulation region. Therefore, the sequence order of the extrema that was observed experimentally should represent the manifestation of quantum effects. There was an extremum in the dependence of the electrostatic potential φ of the semiconductor on the coordinate z, at a distance of about L^*. The results of the separation of the surface and bulk components of electroreflection obtained with the use of the polarization (tensor) anisotropy of the electrooptical effect (Fig. 3), also evidence for that. This extremum stemmed from the zero value of the wave function of electrons at the surface and/or from the action of the specular image forces.

The first reason is clear: we dealt with the accumulation region, so that the de Broglie wavelength of a quantum-mechanical particle that participated in the optical transition was longer than the dimension of SCR. The complex index of refraction $N = n + i\chi$, which is responsible for the parameters of the electroreflection signal and is defined by the nonequilibrium concentration of current carriers, varied within the near-surface layer under the given circumstances. Therefore, the requirement for the wave function of electrons to vanish at the surface (the concentration of current carriers is defined, according to quantum mechanics, as the square of the electron wave function $\psi(z)$) results in the energy diagram of the etched surface of i-Ge that is displayed in Fig. 4.

In work [15], the influence of the specular image forces on the profile of the electrostatic potential $\varphi(z)$ was considered. The formulae, which give the value of the image force potentials in a three-layer system (semiconductor—oxide—electrolyte, semiconductor—insulator—semiconductor, an so on; see

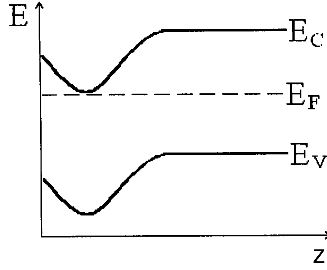

Fig. 4. Schematic energy diagram of the etched i-Ge surface

Fig. 5), where calculated. They look like

$$\varphi_1 = \frac{q}{\varepsilon_1}\frac{1}{z} + \frac{q}{\varepsilon_1}\left[\tilde{\varepsilon}_{12}\sum_{n=0}^{\infty}\frac{(\tilde{\varepsilon}_{21}\tilde{\varepsilon}_{23})^n}{[2a+2nc-z]} + \right.$$

$$\left. +\tilde{\varepsilon}_{23}\sum_{n=0}^{\infty}\frac{(\tilde{\varepsilon}_{21}\tilde{\varepsilon}_{23})^n}{[2a+2(n+1)c-z]}\right], \quad (42)$$

$$\varphi_2 = \frac{2q}{(\varepsilon_1+\varepsilon_2)}\left\{\sum_{n=0}^{\infty}\frac{(\tilde{\varepsilon}_{21}\tilde{\varepsilon}_{23})^n}{[2nc+z]} + \right.$$

$$\left. +\tilde{\varepsilon}_{23}\sum_{n=0}^{\infty}\frac{(\tilde{\varepsilon}_{21}\tilde{\varepsilon}_{23})^n}{[2a+2(n+1)c-z]}\right\}, \quad (43)$$

and

$$\varphi_3 = \frac{4q\varepsilon_2}{(\varepsilon_1+\varepsilon_2)(\varepsilon_2+\varepsilon_3)}\sum_{n=0}^{\infty}\frac{(\tilde{\varepsilon}_{21}\tilde{\varepsilon}_{23})^n}{[2nc+z]}, \quad (44)$$

where the subscript $i = 1, 2, 3$ denotes the layer; q is the charge which is located in the semiconductor at a distance a from the semiconductor–insulator interface (it is known that there exists an own oxide on the surface of a chemically etched semiconductor; for Ge, it can be GeO_2 or GeO, i.e. insulator); c is the thickness of the insulator interlayer; ε_i is the dielectric permittivity of the i-th layer medium;

$$\tilde{\varepsilon}_{12} = \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2} = -\tilde{\varepsilon}_{21}, \quad \tilde{\varepsilon}_{21} = \frac{\varepsilon_2-\varepsilon_1}{\varepsilon_1+\varepsilon_2},$$

$$\tilde{\varepsilon}_{23} = \frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3} = -\tilde{\varepsilon}_{32}, \quad \tilde{\varepsilon}_{32} = \frac{\varepsilon_3-\varepsilon_2}{\varepsilon_2+\varepsilon_3}.$$

The z axis is directed perpendicularly to the surface. Therefore, the coordinates of the medium 1 — medium 2 and medium 2 — medium 3 interfaces are $z = a$ and $z = a + c$, respectively.

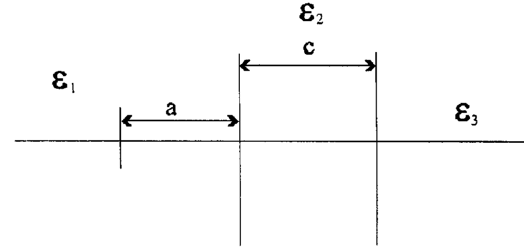

Fig. 5. Semiconductor—oxide—electrolyte system. The dielectric permittivities of the media equal ε_1, ε_2, and ε_3, respectively

5. Conclusions

On the basis of the quantitative analysis of the electroreflection spectra of light waves with two different polarizations **e** ∥ [001] and **e** ∥ [1$\bar{1}$0] from the chemically etched i-Ge (110) surface with a current carrier concentration of 2×10^{19} m^{-3}, as well as from the capacitance measurements of the Ge—electrolyte system, the energies of the electron transitions E_1 and $E_1 + \Delta_1$, the amplitude of the spin-orbit splitting Δ_1, the values of the near-surface electric field F_s, the electrooptical energy $\hbar\theta$, the reduced effective mass μ, the phenomenological parameters of broadening Γ_1 and Γ_2 for the considered optical transitions, the corresponding times of current carrier energy relaxation τ_1 and τ_2, and the classical thickness of the accumulation layer L^* have been determined. The conclusion concerning the uniformity of the electric field across the thickness of the reflecting layer of the crystal has been made. The energy diagram of the etched i-Ge surface has been revealed to contain an extremum. The emergence of such an extremum has been attributed to the zeroing of the electron wave function at the surface and/or to the influence of specular image forces.

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ДОСЛІДЖЕННЯ ПРИПОВЕРХНЕВОГО ШАРУ НАПІВПРОВІДНИКІВ ТА СТРУКТУР НА ЇХ ОСНОВІ МЕТОДОМ МОДУЛЯЦІЙНОЇ СПЕКТРОСКОПІЇ ЕЛЕКТРОВІДБИТТЯ

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Р е з ю м е

Показано можливості використання модуляційної спектроскопії електровідбиття для дослідження електронних параметрів поверхні напівпровідників та структур на їх основі, а також меж поділу фаз електроліт—напівпровідник, метал—напівпровідник. З використанням поляризаційної (тензорної) анізотропії електрооптичного ефекту розділено внески поверхні і об'єму в сигнал електровідбиття. Дію методики відокремлення продемонстровано на прикладі спектрів електровідбиття германію з власною провідністю i-Ge(110), отриманих на переходах E_1, $E_1 + \Delta_1$ (в спектральному діапазоні 1,9—2,5 еВ) при напрямках вектора поляризації світла $\mathbf{e} \parallel [001]$ і $\mathbf{e} \parallel [1\bar{1}0]$ та температурі $T = 300$ К. Виявлено, що енергетична діаграма травленої поверхні i-Ge містить екстремум. Появу такого екстремуму пояснено нульовим значенням хвильової функції електронів на поверхні і (чи) дією сил дзеркального відображення.