Study of surface influence on the n-Ge(110) electroreflectance spectra and their polarization spectroscopy

O.I.Vlasenko, P.O.Gentsar, A.V.Stronski

V.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine

The contribution of the real (preliminary chemically etched) (110) surface of n-Ge into electroreflectance effect (energy range 1.9–2.6 eV) basing on polarization anisotropy of electrooptical effect has been separated under assumption that the surface electroreflectance component is isotropic while the bulk component of electroreflectance is anisotropic with respect to the light polarization vector orientation. The influence of the surface state on the anisotropic electroreflectance spectra, form changes of the subsurface potential barrier and internal mechanical stresses after mechanical polishing have been considered. Electron parameters of the n-Ge(110) subsurface layer are determined.

Разделен вклад реальной (предварительно химически травленной) поверхности n-Ge (110) в эффект электроотражения (энергетический диапазон 1,9–2,6 эВ) с использованием поляризационной (тензорной) анизотропии электрооптического эффекта в предположении, что поверхностная составляющая электроотражения изотропна, а объемная составляющая электроотражения анизотропна относительно ориентации вектора поляризации световой волны. Проанализировано влияние состояния поверхности на анизотропные спектры электроотражения, изменение формы приповерхностного потенциального барьера и внутренних механических напряжений после механической полировки. Определены электронные параметры приповерхностного слоя n-Ge(110).

The thickness of layer which forms the electroreflection signal (observed in singular points of Brillouin zone) is defined by the penetration depth of electric field and light. The use of electroreflectance modulation spectroscopy enables to study the electron phenomena in subsurface layers and to judge their structural perfection. Recently, a great attention is given to of the surface characteristic investigations of semiconductors and semiconductor structures [1, 2]. This is connected with the fact that geometry of the elements of modern electronic devices is such that the surface (surface layers) and interfaces (metal-semiconductor, semiconductor-semiconductor, etc.) play a decisive role in their performance. The functional possibilities of the electronic devices are defined also by the internal mechanical stresses in crystals. Additional data on surface are provided by the electroreflection anisotropy measurements which enable to separate the surface and bulk contributions into electroreflection signal [3, 4]. This work presents the results of such separation taking the real (preliminary chemically etched) surface of n-Ge(110) as an example. The work purpose is to study the changes in the subsurface layer of n-Ge during structural disordering, and also accompanying peculiarities in electromodulation spectra.

The electroreflectance spectra of the chemically etched and mechanically polished surface of n-Ge(110) with electron concentration 10^{18} cm^{-3} were measured using the electrolytic method at the first modulation harmonic frequency $f = 2.2$ kHz at room
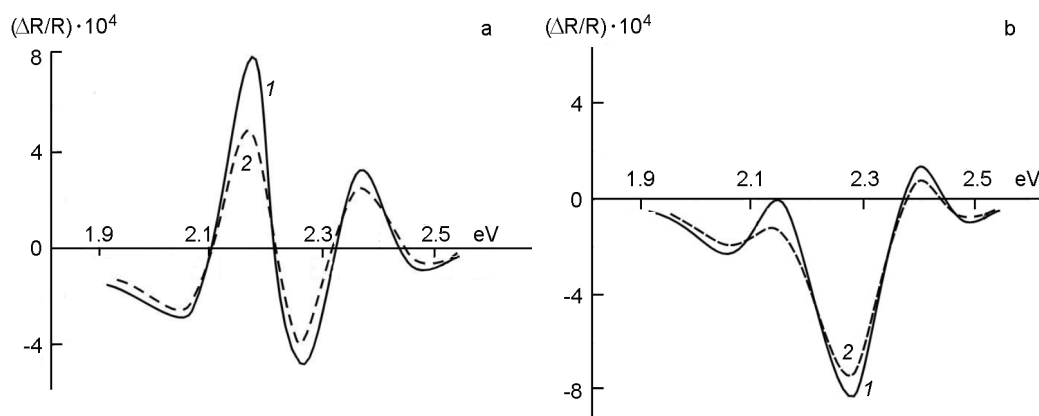
Fig. 1. Electroreflectance spectra (*1*, *2*) for etched (a) and mechanically polished (b) *n*-Ge(110) surface with concentration $n = 10^{18}$ cm^{-3}. Constant bias -0.3 V. Modulation 15 mV (a), 300 mV (b). Polarization vector $e \parallel [001]$ (curve *1*), $e \parallel [1\bar{1}0]$ (curve *2*).

temperature ($T = 300$ K) and transitions E_1, $E_1 + \Delta_1$ (in the 1.9–2.6 eV spectral range) at the directions of the light polarization vector $\hat{e} \parallel [001]$ and $\hat{e} \parallel [1\bar{1}0]$. The electric field applied to the single crystal and incident light were mutually parallel and directed perpendicular to the (110) surface. As an electrolyte, the buffer solution 0.1 M K$_2$SO$_4$:0.025 M Na$_2$HPO$_4$:0.025 M KH$_2$PO$_4$ was used. To slow down the electrochemical reaction rates at the Ge electrolyte surface, low potentials enriching the surface in electrons were applied to the sample. The constant bias applied to the sample was controlled against the reference saturated calomel electrode. The threshold sensitivity of the measurements consisted $5 \cdot 10^{-6}$, and spectral resolution $3 \cdot 10^{-3}$ eV. The mechanical polishing was carried out using fine-grained diamond paste.

In Fig. 1, presented are the electroreflectance spectra obtained for the etched (Fig. 1a) and mechanically polished (Fig. 1b) surface of *n*-Ge(110) with donor concentration $n = 10^{18}$ cm^{-3} with bands bending which enrich surface in electrons and directions of light polarization $\hat{e} \parallel [001]$ (curve *1*) and $\hat{e} \parallel [1\bar{1}0]$ (curve *2*). In electroreflection spectra of etched *n*-Ge surfaces, each critical point in doublet E_1, $E_1 + \Delta_1$ correspond to the two opposite in sign extrema (Fig. 1a). Mechanical polishing of the *n*-Ge surface results in unipolar spectra with weakened extrema anisotropy (Fig. 1b).

Electroreflection signals for chemically etched as well as for mechanically polished *n*-Ge(110) surface of with concentration $n = 10^{18}$ cm^{-3} have approximately equal amplitudes (with respect to zero), but spec-

tra for the mechanically polished surface were obtained at modulation 20 times bigger than that used for chemically etched surface. As is known, the peak amplitude must increase at increasing modulation voltage [5]. Thus, this experiment shows an essential influence of the long-range order on the formation of critical points in the reduced state density of germanium.

By using the polarization (tensor) dependence of the electrooptical effect it is possible to separate the contribution of the surface and volume to the electroreflectance signal in the supposition that the surface contribution of the electromodulation $(\Delta R/R)_S$ is isotropic with respect to the light polarization vector, while the volume component $(\Delta R/R)_V$ is anisotropic. This is realized if the linear electrooptical effect in center-symmetrical cubic crystal is present [6], at amorphization of the subsurface layer and for some other cases. With such assumptions, we have for light polarization $\hat{e} \parallel [1\bar{1}0]$

$$\frac{\Delta R}{R} = \sum_{i=1}^{2}(A_i\Delta\varepsilon_{is} + B_i\Delta\varepsilon_{iv}) = \left(\frac{\Delta R}{R}\right)_S + \left(\frac{\Delta R}{R}\right)_V. \quad (1)$$

Thus, for the light polarization vector direction $\hat{e} \parallel [001]$, it is possible to write:

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

$$= \left(\frac{\Delta R}{R}\right)_S + S_0\left(\frac{\Delta R}{R}\right)_V, \quad (2)$$

where S_0 is the polarization anisotropy coefficient of the volume component of elec-
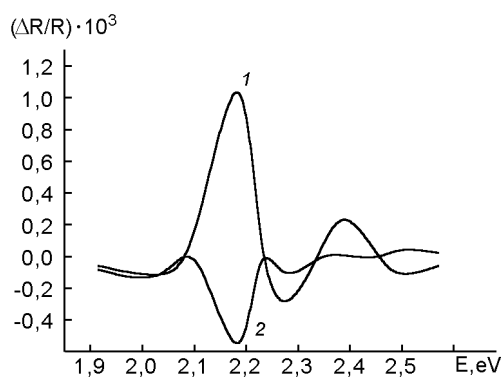
Fig. 2. Bulk electroreflectance component $(\Delta R/R)_V$ (Keldysh-Franz effect) (curve *1*) and surface electroreflectance component $(\Delta R/R)_S$ (curve *2*) for *n*-Ge(110) with concentration of electrons $n = 10^{18}$ cm^{-3}. Dependences were obtained using the polarization (tenzor) dependence of the electrooptical effect.
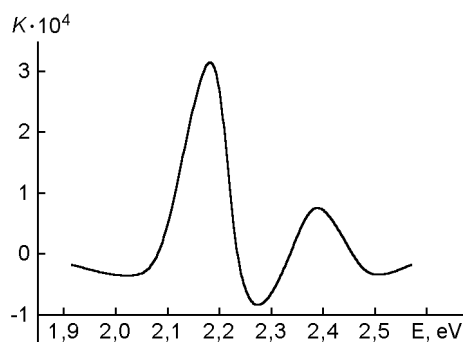

Fig. 3. Difference electroreflectance spectra $K = (\Delta R/R)\hat{e} \parallel [001] - (\Delta R/R)\hat{e} \parallel [1\bar{1}0]$ for two directions of light polarization vector: $\hat{e} \parallel [001]$ and $\hat{e} \parallel [1\bar{1}0]$ for *n*-Ge(110) with the electron concentration $n = 10^{18}$ cm^{-3} obtained using experimental results presented in Fig. 1a.

trooptical effect for which the Keldysh-Frantz effect is responsible. Let the the weak field criterium be assumed to be realized [7] due to screening action of the sub-surface layer in the bulk, thus, the S_0 is constant over the whole spectrum and is the same for real and imaginary parts of $\Delta\varepsilon_V$ [8]. From (1–2) relations, we get

$$\left(\frac{\Delta R}{R}\right)_S = \frac{S_0 - S}{S_0 - 1}\frac{\Delta R}{R}, \qquad (3)$$

$$\left(\frac{\Delta R}{R}\right)_V = \frac{S - 1}{S_0 - 1}\frac{\Delta R}{R}. \qquad (4)$$

The polarization anisotropy coefficient for the volume component of electrooptical effect S_0 is

$$S_0 = \frac{2}{3}\frac{m_t + 2m_l}{m_t + m_l}. \qquad (5)$$

For germanium, $m_l = 1.58$ m_0; $m_t = 0.082$ m_0 [9], thus, S_0 is 1.3.

In this work, the separation method of surface and volume electroreflection components is applied to the real (preliminary etched) *n*-Ge(110) surface. In Fig. 2, the separation results of the electroreflection surface component (curve *2*) and bulk component (curve *1*) for chemically etched surface.

Results concerning separation of the surface and bulk components of the electroreflectance for real (preliminary chemically etched) *n*-Ge(110) surface (Fig. 2) have shown that the electroreflectance bulk component of $(\Delta R/R)_V$ agrees well in shape and

energy positions of peaks with dependence of $(\Delta R/R)\hat{e} \parallel [001] - (\Delta R/R)\hat{e} \parallel [1\bar{1}0]$ on photon energies $E = \hbar\omega$ (Fig. 3) and with measured electroreflectance spectra in the region of weak enrichment of the *n*-Ge(110) surface in electrons at the specified directions of light polarization vector (Fig. 1a). This result supports the legitimacy of the used model for the separation of surface electroreflectance component $(\Delta R/R)_S$ and the bulk one $(\Delta R/R)_V$.

The obtained experimental electroreflectance spectra for the *n*-Ge(110) samples with the electron concentration $n = 10^{18}$ cm^{-3} in the region of weak enrichment in electrons correspond in shape and alternation order of the dominating extrema to the situation when energy bands in the direction are sloped down towards to the surface. This means that surface layers of GeO$_2$ or GeO do not cause any structural gettering and that the electron wave function on the surface $\psi(z)$, which is equal to zero is not pronounced in the experiment conditions.

It is to note that the electroreflectance spectra for the mechanically polished surface is mainly positioned in the negative part with respect to zero, that is, the relative change of the reflectance ability of the *n*-Ge(110) single crystal in electric field $(\Delta R/R)$ $(E,F)\leq 0$, except for the high energy region. Such behavior of the electroreflectance spectra can be explained by the presence of the extremum in the electrostatic potential ψ dependence on coordinate z. In such case, the electroreflectance signals formed at different sides of extremum are

opposite in phase, the electroreflectance signal phase being defined by the phase of the largest of those signals. This can be considered as an evidence of donor gettering near the polished n-Ge(110) surface. Let be noted that the effect of the electroreflectance signals formed at both sides from extremum on the $\psi(z)$ dependence shows that redundantly doped layer formed during polishing does not exceed in thickness the volume screening depth. The redundant donor concentration near the polished n-Ge(110) surface is estimated from Poisson equation, taking into account that the Fermi level in the region of extremum moves into c-band and values $d^2\psi(z)/dz^2 < 0$. Using this procedure for the sample with $n = 10^{18}$ cm^{-3}, $\Delta N_d \geq 5 \cdot 10^{19}$ cm^{-3} was found. The accumulation of donors near the polished n-Ge(110) surface explains the electrooptical effect of band filling (electric analog of Burstein-Moss effect), which operates in parallel with the effect of interband tunneling (Keldysh-Franz effect).

The light penetration depth in the 1.9–2.6 eV energy region changes from 9.4 nm (for $E = 2.6$ eV) to 12.9 nm (for $E = 1.9$ eV). The electric field penetration depth of the can be estimated according to [10] using expression $L_D = (\varepsilon\varepsilon_0 kT/e^2 n)^{1/2}$. In our case, L_D is 4.73 nm ($\varepsilon = 16.2$; $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m). Thus, electric field along z coordinate being perpendicular to the surface and extending into the sample depth is non-uniform. According to the theory, when we operate in the region of the surface layer enrichment in the majority charge carriers, the electric field is changing according to the exponential law $F = F_s \exp(-LD/z)$. By considering the experimental electroreflectance spectra for the chemically etched n-Ge(110) surface (Fig. 1a) using Eure functions of complex variable, which take into account the optical spectra broadening (dependence of argument η on the phenomenological broadening parameter Γ) connected with the time of charge carriers energy relaxation τ as well as the non-uniformity of the modulation field F, the electron parameters for n-Ge were found to be $E_1 = 2.11$ eV; $E_1 + \Delta_1 = 2.31$ eV; $\hbar\theta = 36.41 \cdot 10^{-3}$ eV; $\Gamma = 0.067$ eV.

It is to note that the enriched layer (space charge region) thickness is defined by the effective screening length L that in the case of enriching band bending may differ from screening length L_D. That is, in the case of the subsurface layer enrichment in majority charge carriers, the volume charge is concentrated just in the subsurface layer, because in this case, the screening is povided by the majority charge carriers, that is, electrons. The classical thickness of enriched layer can be found using expression $L = 2kT/eF$ [5]. The electric field can be found using Poisson equation under assumption that all donor impurities are ionized [5, 10, 11]

$$\frac{d^2\psi(z)}{dz^2} = \frac{eN_D}{\varepsilon_0\varepsilon}, \tag{6}$$

where z is the coordinate perpendicular to the electrolyte-semiconductor interface; ε, Ge dielectric constant; N_D, concentration of the ionized impurities;

$$F = \int_z^{L_D} \frac{eN_D}{\varepsilon_0\varepsilon} dz = \frac{eN_D}{\varepsilon_0\varepsilon}(L_D - z)$$

and this implies that the surface field F_s equals $F_s = F_{z=0} = (eN_D/\varepsilon_0\varepsilon)L_D$.

The surface electric field F_s calculated for the sample with concentration 10^{18} cm^{-3} is $5.28 \cdot 10^6$ V/m. Thus, the classical thickness of enriched layer L is 9.47 nm. Knowing the values of surface electric field and electrooptical energy, it is possible to estimate the values of the reduced effective mass μ for the specified optical transitions. In our case, $\mu = 0.022\ m_0$. Let us determine characteristic for the Keldysh-Franz effect parameter λ_{KF} ($\lambda_{KF} = \hbar\theta/eF_s$) with the length defining the extent of wave function oscillations at the reduced mass μ in the uniform electric field F_s (wavelength of electron with $\hbar\theta$ energy). That parameter is $6.9 \cdot 10^{-9}$ m.

The mechanical polishing by the fine-grained diamond pastes results in the change of n-Ge electron parameters: $E_1 = 2.15$ eV; $E_1 + \Delta_1 = 2.35$ eV; $\Gamma = 0.107$ eV. Using the Heisenberg uncertainty principle for energy E and time t ($\Delta E \cdot \Delta t \geq \hbar$), the relaxation effects during light absorption in crystals are described [5] by phenomenological parameter of broadening Γ, which is connected with energy relaxation time τ of the photogenerated charge carriers by relation $\Gamma = \hbar/\tau$. This expression enables to estimate τ values for the respective electronic transitions using the optical electroreflection method. For n-Ge(110) with the concentration $n =$

10^{18} cm^{-3}, for optical transitions E_1 and $E_1 + \Delta_1 \tau = \hbar/\Gamma = 9.82 \cdot 10^{-15}$ s (for etched surface) and $\tau = 6.15 \cdot 10^{-15}$ s (for mechanically polished one). Let us evaluate de Broglie wavelength λ_{DB} of electron with the effective mass equal to $m^*_n = 1.58\ m_0$ [12] and energy kT using the expression $\lambda_{DB} = \dfrac{2\pi}{\left(2m^*_n kT/\hbar^2\right)^{1/2}}$. In our case, $\lambda_{DB} = 6.15$ nm. It is possible to conclude that de Broglie wavelength λ_{DB} is exceeds the screening length L_D but is smaller that the the enriched layer thickness L.

Proceeding from the results obtained, let the internal mechanical stresses be estimated which arise during mechanical polishing of the specified crystals. At hydrostatic pressure P, the electron transition energy change $\Delta E_1 = (a_C - a_V)\Delta V/V$ [10], where a_C and a_V are deformation potentials of the conduction and valence bands, respectively; $\Delta V/V$, the relative volume change which can be written as $\Delta V/V = -3\Delta P(S_{11} + 2S_{12})$, where S_{11} and $2S_{12}$ are the elasticity tensor components related to those of rigidity tensor C_{11} and C_{12} as $(S_{11}+2S_{12})^{-1} = C_{11}+2C_{12}$. Using the above expressions, we obtain

$$\frac{\Delta E_1}{\Delta P} = \frac{-3(a_C - a_V)}{(C_{11} + 2C_{12})}. \qquad (7)$$

For Ge, $(a_C - a_V) = -12$ eV; $C_{11} = 1.285 \cdot 10^{11}$ Pa; $C_{12} = 0.483 \cdot 10^{11}$ Pa [10]. Using these values, we obtain the value of transition energy change coefficient of for Ge at hydrostatic pressure $\Delta E_1/\Delta P = 1.599 \cdot 10^{-10} eV/Pa$. The estimation of the change of internal mechanical stresses in n-Ge at $\Delta E_1 = 0.04$ eV gives value of $\Delta P = 2.5 \cdot 10^8$ Pa.

For uniaxial contraction in [111] direction,

$$\frac{\Delta E_1}{P} = -\frac{1}{\sqrt{3}}\, dS_{44} = -\frac{1}{\sqrt{3}}\, d\, \frac{1}{C_{44}}, \qquad (8)$$

where d is deformation shear potential of shift; C_{44}, rigidity modulus ($d = -5$ eV; $C_{44} = 0.68 \cdot 10^{11}$ Pa for Ge [10]). In this case, $\Delta E_1/\Delta P = 0.425 \cdot 10^{-10} eV/Pa$, and the change of the internal mechanical stresses during mechanical polishing at $\Delta E_1 = 0.04$ eV is $9.41 \cdot 10^8$ Pa. Thus, as a result of mechanical polishing of n-Ge(110) samples, the mechanical stresses in n-Ge(110) are changed by the mean value between $2.5 \cdot 10^8$ Pa (hydrostatic pressure) and $9.41 \cdot 10^8$ Pa (uniaxial pressure for [111] direction), that is by $5.95 \cdot 10^8$ Pa.

References

1. A.O.Volkov, O.A.Ryabushkin, *Devices and Experimental Technique*, **5**, 121 (2001).
2. A.A.Gerasimovich, S.V.Zhokhovets, G.Gobsh, D.S.Domanevsky, *Fiz. Tekh. Polupr.*, **39**, 729 (2005).
3. A.M.Evstigneev, O.V.Snitko, L.V.Artamonov et al., *Ukr. Fiz..Zh.*, **5**, 756 (1986).
4. P.A.Gentsar, L.A.Matveeva, A.A.Kudryavtsev, E.F.Venger, *Sem. Phys., Quant. Elec.& Optoelec.*, **6**, 141 (2003).
5. V.A.Tyagai, O.V.Snitko, Light Electroreflectance in Semiconductors, Naukova Dumka, Kiev (1980) [in Russian].
6. R.Del Sole, D.E.Aspnes, *Phys. Rev. B.*, **17**, 3310 (1978).
7. D.E.Aspnes, *Surface Science*, **37**, 418 (1973).
8. K.Kondo, A.Moritani, *Phys. Rev. B*, **14**, 1577 (1976).
9. Physico-Chemical Properties of Semiconductor Substances: A Reference Book, ed. by A.V.Novoselova, V.B.Lazarev, Nauka, Moscow (1979) [in Russian].
10. P.Yu, M.Cardona, Fundamentals of Semiconductors, 3rd Ed., Springer-Verlag (2001).
11. P.O.Gentsar, L.O.Matveeva, L.A.Demchina, E.F.Venger, *Fiz. Khim. Tverd. Tela*, **5**, 237 (2003).
12. A.I.Anselm, Introduction to Theory of Semiconductors, Nauka, Moscow (1978) [in Russian].

Дослідження впливу поверхні
на спектри електровідбивання n-Ge(110)
та їх поляризаційну анізотропію

О.І.Власенко, П.О.Генцарь, О.В.Стронський

Відокремлено внесок реальної (попередньо хімічно травленої) поверхні n-Ge(110) в ефект електровідбивання (енергетичний діапазон 1,9–2,6 еВ) на основі поляризаційної (тензорної) анізотропії електрооптичного ефекту у припущенні, що поверхнева складова електровідбивання $(\Delta R/R)_S$ (за яку несе відповідальність лінійний електрооптичний ефект, що пов'язаний з поверхнею n-Ge(110))-ізотропна, а об'ємна складова електровідбивання (за яку несе відповідальність ефект Келдиша-Франца) – анізотропна відносно орієнтації вектора поляризації світлової хвилі. Проаналізовано вплив стану поверхні на анізотропні спектри електровідбивання, зміну форми приповерхневого потенціального бар'єру та внутрішніх механічних напружень після механічної поліровки. Визначено електронні параметри приповерхневого шару n-Ge(110).