Functional Materials 16, No.1 (2009)

Infrared spectroscopy and electroreflectance in the region of fundamental optical transition E_0 of heavily doped *n*-GaAs (100)

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Received October 1, 2008

Studied were the reflection spectra of dynamically chemically etched *n*-GaAs (100) single crystals with electron concentration of 10^{18} to $5{\cdot}10^{18}$ cm^{-3} in the 1.4–25 μm range as well as the electroreflection ones in 1.3–1.6 eV range using electrolytic method. The values of physical parameters and parameters in the space charge region of subsurface layer of the investigated material have been obtained: electron concentration N, plasma frequency ω_p, relaxation time of free carriers over the pulse τ_p, energies of optical transitions E_0 (Γ_{8v}–Γ_{6c}), electrooptical energy $\hbar\theta$, surface electric field F_S, phenomenological broadening parameter Γ, energy relaxation time τ, the wave function oscillation durability of quantum-mechanical particle λ_{KF} with the reduced effective mass μ at a given surface electric field F_S. The energy diagram of the chemico-dynamically etched *n*-GaAs (100) surface has been found to include an extreme. The presence of such extreme is explained by zero value of the electron wave function on the surface and/or the structure gettering of the free carriers.

Исследованы спектры отражения в диапазоне 1,4–25 мкм и спектры электроотражения с использованием электролитической методики в спектральном диапазоне 1,3–1,6 эВ монокристаллов *n*-GaAs (100) с концентрацией электронов 10^{18}–$5{\cdot}10^{18}$ $см^{-3}$ после химико-динамического травления. Получены значения физических параметров и параметров в области пространственного заряда приповерхностного слоя материала: концентрации электронов N, плазменные частоты ω_p, время релаксации свободных носителей по импульсу τ_p, энергии оптических переходов E_0 (Γ_{8v}–Γ_{6c}), электрооптической энергии $\hbar\theta$, поверхностного электрического поля F_S, феноменологического параметра уширения Γ, энергетического времени релаксации τ, протяженности осцилляции волновой функции квантово-механической частицы λ_{KF} с приведенной эффективной массой μ при данном поверхностном электрическом поле F_S. Выявлено, что энергетическая диаграмма химико-динамически травленой поверхности *n*-GaAs (100) имеет экстремум. Появление такого экстремума объяснено нулевым значением волновой функции электронов на поверхности и (или) со структурным геттерированием свободных носителей.

For the investigation of heavily-doped functional materials, it is reasonable to use a complex of methods. In heavily doped materials, such physical mechanisms are present as broadening of the impurity band, change of the state density, scattering of charge carriers on the charged impurities, on the inhomogeneities of doping over the sample volume, etc., that complicate the explanation of experimental results. Heavily doped gallium arsenide is a substance of importance for practical use in electronics as a substrate for the production of the modern high-frequency electronic devices,

nanostructures, radiation detectors, LEDs, photodiodes, etc., due to its optical and electrophysical properties. In this work, in order to obtain the values of the physical parameters for the subsurface layer of the heavily doped GaAs (100) crystals, the reflection spectra in the 1.4–25 μm wavelength range (a Fourier spectrometer) and electroreflection spectra in the region of the fundamental optical transition E_0 in 1.3–1.6 eV energy range (double monochromator DMR-4) were studied.

In Fig. 1, the reflection spectrum of a *n*-GaAs (100) single crystal of 300 μm thickness after dynamic chemical etching is shown. Basing on quantitative analysis of the reflectance spectrum in the specified wavelength range, using the position of the reflection minimum [1] the electron concentration N was obtained to be $2.9 \cdot 10^{18}$ cm^{-3}, and from this value, the plasma frequency was evaluated ($\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_\infty \varepsilon_0 m^*_{opt}}}$, $\varepsilon_\infty = 12$ [2], $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m) to be $0.993 \cdot 10^{14}$ s^{-1}.

According to the Drude model [3, 4], dielectric function ε in general case can be written as

$$\varepsilon = \varepsilon_\infty \left[1 - \frac{\omega_p^2}{\omega^2 + \frac{1}{\tau_p^2}} \left(1 - i \frac{\frac{1}{\tau_p}}{\omega} \right) \right], \qquad (1)$$

where τ_p is the relaxation time of free carriers over the pulse.

Having the calculated values of actual ε_1 and imaginary ε_2 parts of the dielectric permeability and taking into account connection between optical constants ε_1, ε_2, n, χ:

$$\varepsilon_1 = n^2 - \chi^2, \qquad (2)$$

$$\varepsilon_2 = 2n\chi, \qquad (3)$$

the reflection index R is got:

$$R(n,\chi) = \frac{(n-1)^2 + \chi^2}{(n+1)^2 + \chi^2}. \qquad (4)$$

The theoretical curve is shown in Fig. 1 near an experimental curve, as calculated basing on the Drude model at parameters $\varepsilon_{inf} = 12$, $\omega_p = 0.993 \cdot 10^{14}$ s^{-1}, $\tau_p = 7.75 \cdot 10^{-14}$ s.

Thus, from the reflection spectrum in infrared region, the free carrier concentration N, plasma frequency ω_p, and relaxation time of free carriers over the pulse τ_p have been determined.

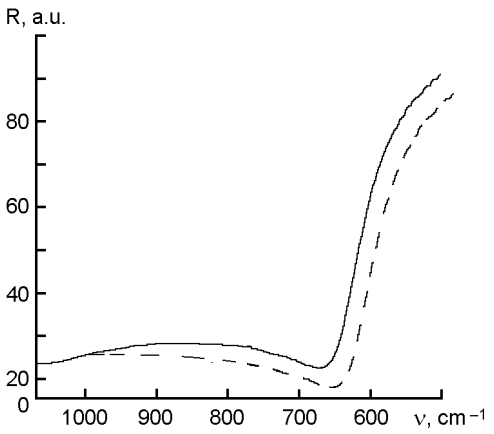

Fig. 1. IR reflectance spectrum of *n*-GaAs (100). Solid curve, experiment; dotted line, theoretical curve.

As the electron concentration in the investigated samples of *n*-GaAs (100) single crystals is within the $10^{18} \div 5 \cdot 10^{18}$ cm^{-3} range, the main mechanism of free charge carrier scattering is scattering on charged impurities. For *n*-GaAs (100) sample with the electron concentration of $2.9 \cdot 10^{18}$ cm^{-3}, the scattering time of on the charged impurities $\tau_i = m^*_e \mu_e / e$ has been estimated to be of $8.87 \cdot 10^{-14}$ s ($\mu_e = 2000$ cm^2/V·c [5], $m^*_e = 0.078 m_0$ [6]).

It is known that the subsurface layer thickness which forms the electroreflection signal that is observed in particular points of Brillouin zone is defined by the penetration depth of electric field (screening depth L_D or L_{TF}) and light (d). The ratio of those factors is of decisive importance for the obtaining of information on the material under study from the reflection spectra [3, 4]. The electroreflection modulation spectroscopy makes it possible to determine energy of optical transitions for the direct interband transitions (connected with the change of the material dielectric permeability ε ($E = \hbar\omega$, F)) in the conditions when the absorption coefficient α is too high to be determinable in the region of photon energies substantially exceeding that corresponding to the absorption edge. To measure the relative change of the material reflectance $\Delta R/R$ in the electric field F, where R is the reflection coefficient, it is enough to create the electrical field in the subsurface layer of semiconductor. Electrolytic method en-

ables to modulate the surface barrier field of the sample by applying ac voltage, while applying in addition a constant bias, it is possible to change the average field value. The use of the modulation electroreflection spectroscopy enables to make conclusions about the subsurface layer structural perfection of electronic materials and to reveal the influence of physicochemical treatments on the surface state. The geometrical sizes of the elements of modern electronic devices are such that surface (subsurface layer) is decisive in their operation.

In Fig. 2, electroreflection spectrum of n-GaAs (100) single crystal with the concentration of free electrons N = $2.9 \cdot 10^{18}$ cm^{-3} is shown. The measurements were carried out at room temperature using non-polarized light in the 1.3–1.6 eV energy range using electrolytic method (1-N. aqueous KCl as the electrolyte). The polarity of the electroreflection extremes and the dependence of their amplitude on the applied voltage show that a depleted layer is realized on the surface. The values of flat band potential, according to the electroreflection data, is $\varphi_{fb} = -2.02$ V (Fig. 3).

Within the single electron theory, the change of the real dielectric permeability part is

$$\Delta\varepsilon_1(E,F) = \varepsilon_1(E,F) - \varepsilon_1(E,0), \qquad (5)$$

which is defined by the electric field F; for three-dimensional critical point of $3DM_0$ type, it is

$$\Delta\varepsilon_1(E,F) = \frac{C(\hbar\theta)^{1/2}}{E^2} G(\eta), \qquad (6)$$

where C is a constant; $E = \hbar\omega$, the photon energy; $G(\eta)$, the electrooptical function of 2nd type which is expressed through Airy function describing one-dimensional motion of free charge carriers in a homogeneous external electrical field.

$$\eta = \frac{E_0 - \hbar\omega + i\Gamma}{\hbar\theta}, \qquad (7)$$

where E_0 is the optical transition energy; Γ, phenomenological parameter of broadening; $\hbar\theta = (e^2F^2\hbar^2/2\mu)^{1/3}$, characteristic parameter of the Franz-Keldysh effect theory (electrooptical energy); $\mu^{-1} = (m_e^*)^{-1} + (m_p^*)^{-1}$, reverse reduced effective mass; (m_e^*) and (m_p^*), effective masses of electrons and holes, respectively, involved in the considered optical transition.

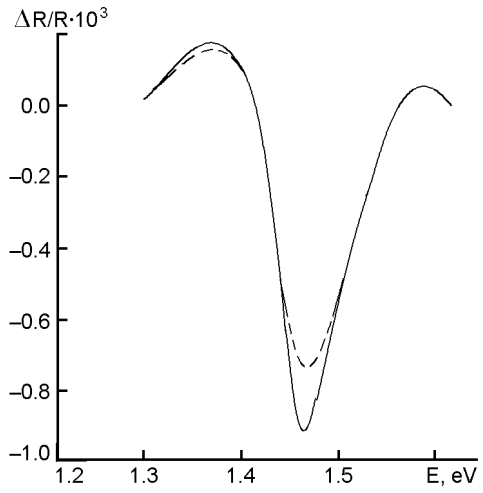

Fig. 2. Electroreflectance spectrum of *n*-GaAs (100) single crystal with the free electron concentration $N = 2.9 \cdot 10^{18} cm^{-3}$. Solid curve, experiment. Dotted line, theoretical curve for $E_0 = 1.422$ eV; $\hbar\theta = 0.063$ eV; $\Gamma = 0.080$ eV.

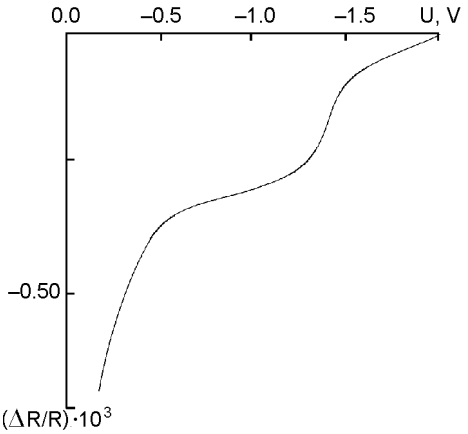

Fig. 3. Dependence of the electroreflectance signal $\Delta R/R$ on potential V enriching the surface of *n*-GaAs (100) with electrons at the dominating extreme energy $E = 1.472$ eV (Fermi level E_F is positioned in the conductance band, $2kT$ above the bottom).

Assuming that all donor impurities are ionized, the surface electric field F_S is given by [7]

$$F_S = \frac{eN}{\varepsilon_0\varepsilon_\infty} L_{TF}, \qquad (8)$$

where ε is dielectric permeability of the material; L_{TF}, the electric field penetration depth (screening depth

$$L_{TF} = \left(\frac{\varepsilon_\infty \varepsilon_0 kTF_{1/2}(\mu^*)}{e^2 N F_{-1/2}(\mu^*)} \right)^{1/2},$$

designations are generally accepted). For $\mu^*\left(\mu^* = E_F/kT\right) = 2$; $N = 2.9 \cdot 10^{18}$ cm^{-3}; $\varepsilon_\infty = 12$, we have $L_{TF} = 11.74$ nm; $F_S = 2.09 \cdot 10^5$ V/cm.

According to the above, the characteristic parameter of Franz-Keldysh effect $\hbar\theta$ for $m_e^* = 0.078 m_0$, $m_p^* = 0.5 m_0$ [6] equals 0.063 eV.

The relaxation effects in the light absorption by a crystal are described by the phenomenological parameter of broadening Γ connected with the energy relaxation time of the photogenerated charge carriers by the relation $\Gamma = \hbar/\tau$. This enables to estimate τ values for the respective optical transitions using optical electroreflectance method. The τ value is defined by the interaction of electrons with the lattice vibrations, impurities, surface defects (because the electroreflectance signal is formed in the space charge region).

Our experiments have shown that the electroreflectance spectrum shape is varied depending on the voltage applied to the sample. The distance between zeros is increased as the depletion rises and the Franz-Keldysh oscillations are absent in the high-energy part of spectrum. This means that the intermediate case is realized when the additional energy obtained by a quantum-mechanical particle with the reduced mass μ in the considered optical transition $\hbar\theta$ and the broadening parameter Γ of the electron transition e_0 are comparable (the weak field condition of measurement mode for heavily doped *n*-GaAs (100) is not realized).

In the intermediate field region, the change of the dielectric permeability $\Delta\varepsilon = \varepsilon(E = \hbar\omega, F) - \varepsilon(E, 0)$ as a function of the electric field F is approximately linear. Moreover, the thickness of the depleted layer near the semiconductor surface is much smaller than the light penetration depth $d = \lambda/4\pi n$ at wavelength λ. Under the phenomenological approach [8, 9], the broadening parameter Γ estimated from the halfwidth of the dominating extreme in the electroreflectance spectrum (Fig. 2), is 0.080 eV. In Fig. 2, besides of the experimental electroreflectance curve (solid curve), theoretical curve (dotted line) for

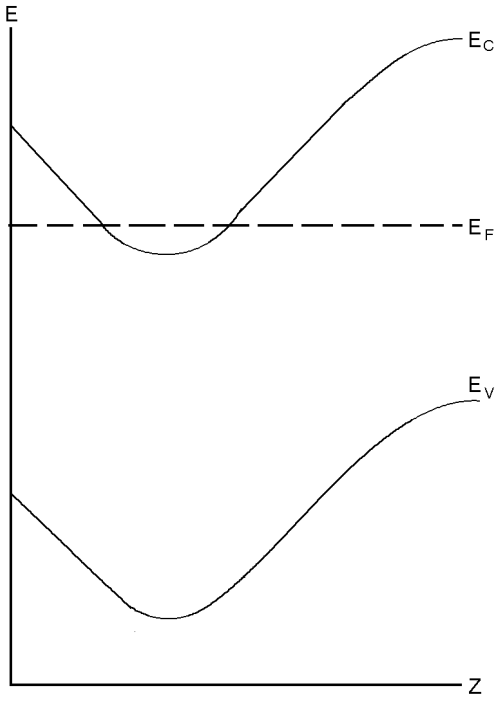

Fig. 4. Energy diagram of the real (chemico-dynamically etched) surface of *n*-GaAs (100).

parameters $E_0 = 1.422$ eV; $\hbar\theta = 0.063$ eV; $\Gamma = 0.080$ eV is presented.

Let us determine the energy relaxation time τ of the photogenerated charge carriers. Taking into account that the broadening parameter $\Gamma = 0.080$ eV (Fig. 2), we obtain $\tau = \hbar/\Gamma = 8.228 \cdot 10^{-15}$ s.

The parameter λ_{KF} characteristic for the Franz-Keldysh effect which defines the extent of wavefunction oscillations of a quantum-mechanical particle with the reduced mass μ in electric field F_S, that is, the wavelength of electron with energy $\hbar\theta$, can be found using expression $\lambda_{KF} = \hbar\theta/eF_S$. The parameter λ_{KF} is 3 nm. It is to note that the classical thickness of the enriched layer $L = 2kT/eF_S$ in our case is 2.4 nm.

The light penetration depth in the energy range 1.3 to 1.6 eV is changed from $d =$ 17.81 nm (for $E = 1.6$ eV) up to $d =$ 21.92 nm (for $E = 1.3$ eV). It is known that the information depth of the material under study is defined by the smallest from two quantities: light penetration depth and electric field penetration depth. Thus, the conclusion can be made that the "information" depth for *n*-GaAs (100) single crystal is defined by the screening depth L_{TF}.

Experimental results have shown (Fig. 2) a non-monotonous dependence of the semiconductor electrostatic potential on the coordinate z. That is, energy diagram of the real surface of n-GaAs (100) (pre-treated by chemical-dynamic etching) has an extreme (Fig. 4). The obtained electroreflectance spectra of n-GaAs (100) testify that within the order of extreme alternation in the spectrum, energy bends are inclined up in the direction towards surface. Because the surface is etched (no surface charges), the appearance of such extreme can be connected with the fact that electron wave function $\psi(z)$ on the surface is zero. We work in the enriching region, so the de Broglie wavelength ($\lambda_{dB} = \frac{2\pi}{\sqrt{\frac{2m_e^* kT}{\hbar^2}}}$) for GaAs is $m_e^* = 0.078m_0$, thus $\lambda_{dB} = 27.76$ nm) of a quantum-mechanical particle involved in optical transition is higher that the space charge region.

In our case, changed is the complex refractive index $N = n + i\chi$ of the subsurface layer (which is responsible for the electroreflection signal which is defined by the nonequilibrium concentration of charge carriers. Zero value of electron wavefunction on the surface (according to the quantum mechanics, the concentration of charge carriers is defined by square of electron wave function $\psi(z)$) results in that the energy diagram of the real surface (preliminary chemico-dynamically etched) has an extreme. Other reason for the appearance of such extreme may be connected with the structure gettering, that is absorption, that is caused by the presence of the areas of GaAs (100) with defect structure which are able to absorb actively the point defects and bind impurities.

Thus, basing on quantitative analysis of the electroreflectance spectrum, the physical parameters and parameters of the space charge region of the subsurface layer (light penetration depth $d = \lambda/4\pi n$) have been determined in the region of fundamental optical transition E_0: energy of optical transition E_0, electrooptical energy $\hbar\theta$, phenomenological parameter of broadening Γ, surface electrical field F_S, relaxation time of charge carriers τ, Franz-Keldysh characteristic parameter λ_{KF}. Consideration of the n-GaAs (100) electroreflectance spectrum (Fig. 2) has shown a non-monotonous behavior of the semiconductor electrostatic potential as a function of coordinate z (de Broglie wavelength of quantum-mechanical particle is exceeds the thickness of the space charge region).

Thus, optical investigation results of heavily doped n-GaAs(100), namely, reflectance spectra in the wavelength region 1.4–25 μm, and electroreflectance spectra in the energy range 1.3–1.6 eV enable to obtain physical parameters of the investigated samples: electron concentration N, plasma frequency ω_p, relaxation time of free carriers over the pulse τ_p, energies of electron optical transitions E_0 and parameters of the space charge region $\hbar\theta$, Γ, F_S, τ, λ_{KF}, and using those data, to analyze the physical processes, mechanisms, and nature of the electron and optical phenomena in the subsurface layers and in the volume of the heavily doped material.

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Інфрачервона спектроскопія та електровідбивання в області фундаментального оптичного переходу E_0 сильнолегованого *n*-GaAs (100)

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Досліджено спектри відбивання у діапазоні 1,4–25 мкм та спектри електровідбивання з використанням електролітичної методики у спектральному діапазоні 1,3–1,6 еВ монокристалів *n*-GaAs (100) після хіміко-динамічного травлення з концентрацією електронів 10^{18}–$5\cdot10^{18}$ см$^{-3}$. Отримано значення фізичних параметрів та параметрів в області просторового заряду приповерхневого шару матеріалу: концентрації електронів N, плазмові частоти ω_p, час релаксації вільних носіїв за імпульсом τ_p, енергії оптичних переходів E_0 (Γ_{8v}–Γ_{6c}), електрооптичної енергії $\hbar\theta$, поверхневого електричного поля F_S, феноменологічного параметра уширення Г, енергетичного часу релаксації τ, протяжності осциляції хвильової функції квантово-механічної частинки λ_{KF} із приведеною ефективною масою μ при даному поверхневому електричному полі F_S. Виявлено, що енергетична діаграма хіміко-динамічно травленої поверхні *n*-GaAs (100) містить екстремум. Появу такого екстремума пояснено нульовим значенням хвильової функції електронів на поверхні і (або) зі структурним гетеруванням вільних носіїв.