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Light trapping and subbandgap maximum in photoemission quantum yield spectra of p-GaAs(Cs,O)

© V.S. Khoroshilov[1,2], D.E. Protopopov[1,2], D.M. Kazantsev[1,2], H.E. Scheibler[1,2], V.L. Alperovich[1,2]

[1] Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
[2] Novosibirsk State University, Novosibirsk, Russia
E-mail: alper_v@mail.ru

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In the spectra of the photoemission quantum yield of p-GaAs(Cs,O) measured in the reflection geometry, a peak was found at a photon energy lower than the band gap of GaAs. It is shown that the appearance of the peak is due to the trapping of weakly absorbed radiation, which scatters diffusely on the rough back face of the epitaxial structure. Possible microscopic mechanisms of the appearance of the peak are discussed: the Franz-Keldysh effect in the surface electric field and adsorption-modified optical transitions in cesium adatoms.

Keywords: photoemission, GaAs, negative electron affinity, quantum yield spectra.

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The deposition of subnanometer cesium and oxygen layers onto an atomically clean p-GaAs surface lowers the potential barrier for electron escape into vacuum to a state with negative effective electron affinity (NEA) $\chi^* \approx -0.2$ eV. Owing to their high photoemission quantum yield, NEA photocathodes based on p-GaAs(Cs,O) are used widely in photomultipliers and electron sources [1]. The interest in surfaces with small positive electron affinity (PEA) $\chi^* \approx 0.2-0.4$ eV stems from the potential to raise the efficiency of solar energy conversion [2]. The transition between p-GaAs(Cs,O) surfaces with NEA and PEA was examined in [3,4] using the photoemission quantum yield (PEQY) spectroscopy technique under illumination from the side of the emitting surface („reflection"geometry). Only a monotonic PEQY growth with an increase in photon energy, which is attributable to an enhancement of the absorption coefficient in the region of interband transitions [1], has been observed earlier in this geometry. In the present study, features in the form of a step or peak at a subbandgap (smaller than bandgap width $\varepsilon_g = 1.43$ eV of GaAs) photon energy have been detected for the first time in PEQY spectra of p-GaAs(Cs,O) surfaces.

Experiments were performed using p-GaAs(001) with thickness $d_p = 4\,\mu$m and a hole density of $6 \cdot 10^{18}$ cm^{-3} grown by metalorganic vapor-phase epitaxy on semi-insulating i-GaAs substrates with thickness $d_i = 400\,\mu$m and a rough (matte) back face. Atomically clean surfaces were prepared by removing oxides with a solution of HCl in isopropyl alcohol in dry nitrogen atmosphere with subsequent transfer into a high-vacuum setup (without contact with air) and annealing in vacuum at a temperature of 750 K [5]. The surface was activated to a state with NEA by depositing cesium and oxygen onto it. Excess oxygen or cesium were then deposited onto the activated surface. This induced a transition from NEA to PEA and suppressed the photoemission current [3,4]. PEQY spectra were measured in the refection geometry during photocurrent degradation. The sample temperature was maintained at 295 K during cesium and oxygen deposition and measurement of the spectra.

Solid curves in Fig. 1, *a* represent PEQY spectra measured in the process of deposition of excess oxygen onto the p-GaAs(Cs,O) surface that was activated to a state with NEA in advance. Higher spectrum numbers correspond to higher oxygen doses (in langmuirs, L): *1* — 0 L, *2* — 0.04 L, *3* — 0.08 L, *4* — 0.12 L, *5* — 0.16 L, *6* — 0.20 L, *7* — 0.25 L. Although the quantum yield in these spectra increases monotonically with photon energy $\hbar\omega$, a pronounced „step" at $\hbar\omega = 1.365 \pm 0.003$ eV is seen in the subbandgap region. Following annealing and another activation, the experiment on deposition of excess cesium was performed (Fig. 1, *b*). The spectra in Fig. 1, *b* correspond to the following Cs doses (in monolayers, ML): *1* — 0 ML, *2* — 0.26 ML, *3* — 0.36 ML, *4* — 0.43 ML, *5* — 0.49 ML, *6* — 0.52 ML, *7* — 0.57 ML. It can be seen that the evolution of spectra in the course of cesium-induced degradation differs from the one induced by oxygen: as the excess cesium dose increases, the subbandgap step turns into a peak.

As far as we know, subbandgap features in the form of a step and a peak have not been observed earlier. We believe that these features are associated with „trapping" of weakly absorbed radiation in an epitaxial structure. Owing to diffuse scattering by a matte back face and the smallness of the angle of total internal reflection from a specular front face (16°), this radiation may pass multiple times through the structure, producing a contribution to photoemission at each passage through the p-layer. The quantum yield is then roughly proportional to $N\alpha_p d_p$, where N is the characteristic number of passes and α_p is the absorption

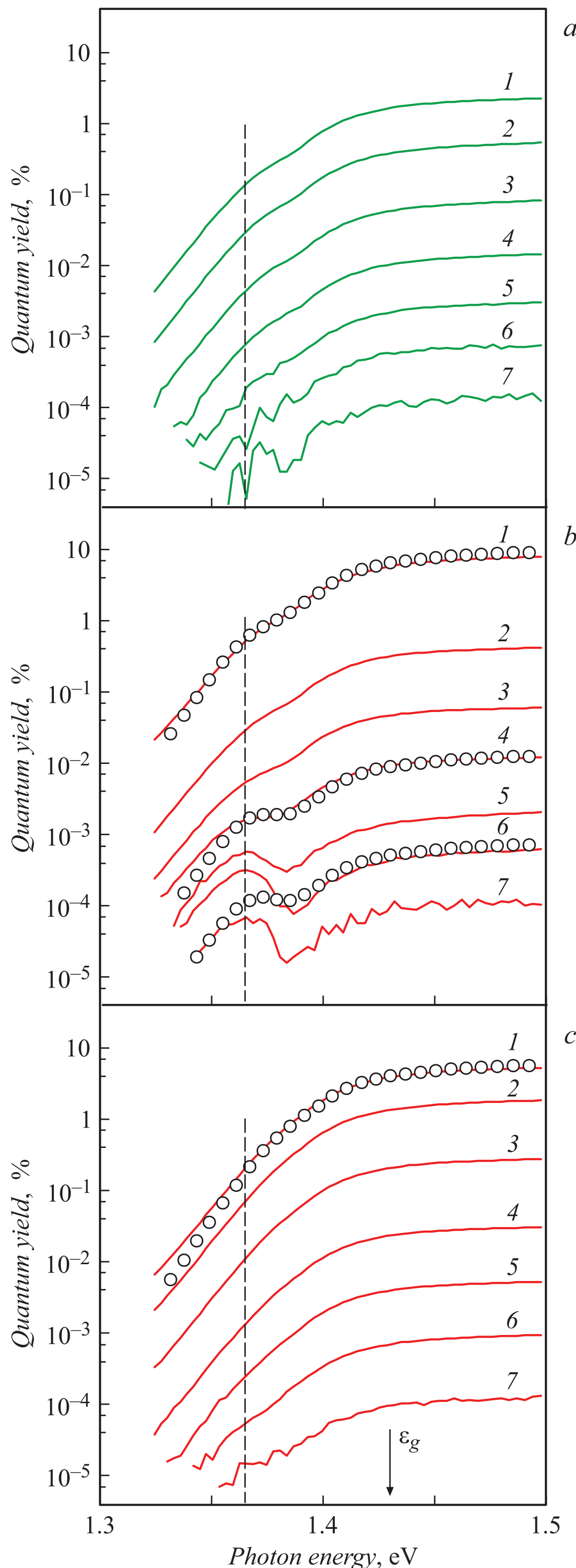

Figure 1. Evolution of PEQY spectra in the process of deposition of excess oxygen (a) and cesium (b, c) onto p-GaAs(Cs,O) surfaces activated to a state with NEA. a, b — Spectra of the sample with a matte back face, c — spectra measured after polishing of the back face. Dots correspond to calculated spectra with different S_d and R_d parameters (see text).

coefficient of the p-layer. An increase in $\hbar\omega$ first leads to an enhancement of quantum yield, since α_p grows, while N remains virtually unchanged. As absorption in the p-layer and the substrate increases further, number of passes N decreases, thus leading to a slowdown in the growth or to a decrease in the quantum yield. A step or a peak emerge in PEQY spectra in these respective cases. When absorption becomes so strong that light gets absorbed completely in the first passage through the structure, the quantum yield increases again with $\hbar\omega$ due to the growth of α_p.

In order to verify this hypothesis, we polished the back face of the sample and repeated the experiment on cesium-induced degradation of the activated surface. Figure 1, c shows the PEQY spectra measured in this experiment at the same doses of excess cesium (within the accuracy of dose determination, which was $\sim 20\%$) that were used in the first experiment. It can be seen that these spectra exhibit an exponential tail, which corresponds to the interband absorption edge in p-GaAs [6], in the subbandgap region ($\hbar\omega < \varepsilon_g$), while step- and peak-shaped features are lacking completely. This confirms that subbandgap features are associated with light trapping due to diffuse scattering by a rough back face of an epitaxial structure.

A numerical calculation of PEQY spectra was performed with account for multiple reflections of light from front and back faces of the structure to establish a quantitative basis for the above hypothesis. The coefficients of light absorption in the p-layer [6] and the substrate [7] are shown in Fig. 2. The photocurrent was calculated in accordance with well-known formulae [1] for each passage of light through the structure; here, only the interband absorption was considered. In the calculations of light attenuation, absorption by free holes in the p-layer was also taken into account. The intensity of light reflected from the back face was a combination of diffuse and specular components at a ratio of $S_d/(1-S_d)$. Reflection coefficient R_d of the diffuse component was another parameter used alongside with S_d. The diffuse component had a Lambert angular distribution (i.e., its intensity was proportional to the cosine of the reflection angle).

The calculated data (dots) are compared with typical experimental spectra *1*, *4*, and *6* in Fig. 1, b and *1* in Fig. 1, c). It can be seen that the calculation with specular reflection from the back face ($S_d = R_d = 0$) provides a fine description of spectra of the sample with a polished back face (Fig. 1, c). The calculation with mixed diffuse–specular reflection ($S_d = 0.2$, $R_d = 0.95$) reproduces the step in spectrum *1* of the sample with a matte back face (Fig. 1, b). Spectrum *4* with a moderate subbbandgap peak is fitted well by the calculation with $S_d = 0.75$ and $R_d = 1$. Spectrum *6*, which corresponds to high cesium doses, is compared with the results of calculations for purely diffuse reflection ($S_d = R_d = 1$). It can be seen that the amplitude of the peak in experimental spectrum *6* is significantly higher than in the calculated one. In addition, it is clear that the deposition of cesium onto the front face of the structure cannot affect the parameters of light reflection from the

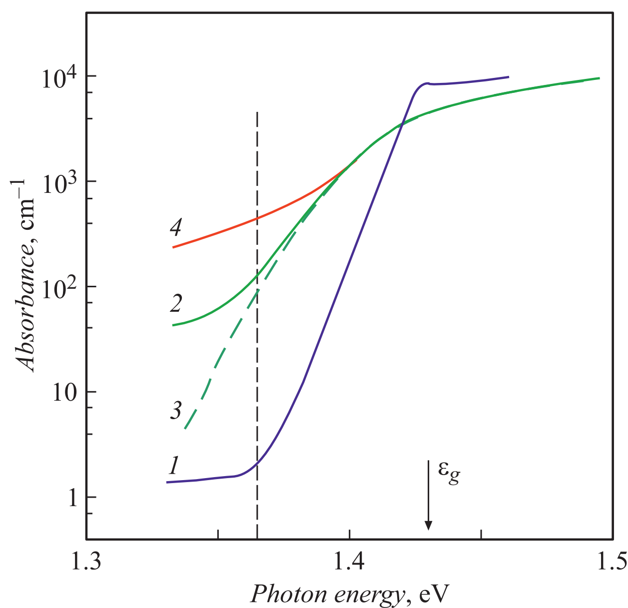

Figure 2. Spectra of the absorption coefficient of the i-GaAs substrate [7] (*1*), the p-GaAs layer [6] (*2*), and the surface electric field region [8] (*4*). Curve *3* represents the absorption coefficient of p-GaAs with just the interband transitions taken into account. The vertical line denotes the subbandgap peak position.

back face. Thus, the proposed model does not explain the evolution of the subbandgap peak in the experiment on cesium-induced degradation.

The Franz–Keldysh effect in the surface field region (SFR) is one of the probable reasons behind the emergence of the subbandgap peak. It is known that the deposition of cesium onto the surface of p-GaAs leads to a sharp increase in the surface field due to ionization of Cs-induced surface states [5]. The absorption coefficient calculated with account for the Franz–Keldysh effect in the surface field at a band bending of 0.7 eV and an SFR width of 10 nm (curve *4* in Fig. 2 [8]) is much higher than the coefficient with zero field. However, the results of calculations demonstrated that, owing to the SFR thinness, the relative contribution of the Franz–Keldysh effect to the PEQY spectrum is smaller than 1.5% and cannot explain the observed growth of the subbandgap peak in the process of cesium deposition.

Another possible explanation for the emergence of the subbandgap peak involves optical transitions in the cesium adsorption layer. Transitions $6s \to 6p_{1/2}$ and $6s \to 6p_{3/2}$ in isolated cesium atoms occur at energies of 1.39 and 1.45 eV, which are close to the bandgap width of GaAs, with oscillator strengths of 0.35 and 0.72, respectively [9]. It is fair to assume that these transitions (shifted and broadened due to the interaction with GaAs) may produce a significant contribution to subbandgap features of PEQY spectra. Since the energy of the ground (filled) state lies near the middle of the band gap of GaAs [5,10], excited electrons enter the conduction band and may escape into vacuum. Relying on the transition half-width derived from the measured peak shape ($\sim$ 20 meV), we estimated cross section $\sigma_0 \sim 6 \cdot 10^{-16}$ cm^2 [11] at the absorption band maximum. This value corresponds to a considerable probability of photon absorption in a single passage through a cesium monolayer: $P = \sigma_0 N_{\mathrm{Cs}} \sim 0.4$, where $N_{\mathrm{Cs}} \sim 7 \cdot 10^{14}$ cm^{-2} is the adatom density [5]. Thus, the estimate does not contradict our hypothesis regarding the nature of the peak. However, this is likely to be an upper-bound estimate, since the absorption band half-width may reach several tenths (rather than several hundredths) of an electronvolt [12], and the subbandgap peak may be formed by the low-energy tail of the band instead of its maximum.

We note in conclusion that features in the form of a step and a peak at a photon energy smaller than the bandgap width of GaAs were detected in spectra of the photoemission quantum yield of p-GaAs(Cs,O) in the reflection geometry. It was demonstrated experimentally that these features are caused by the diffuse reflection of light from a matte back face of the epitaxial structure. The results of calculations confirm that such features originate from the light trapping effect. Estimates contradict the hypothesis that the Franz–Keldysh effect is the microscopic cause of emergence of the peak, but are consistent with the assumption that the peak is induced by optical transitions in cesium adatoms, which are shifted in energy and broadened due to the interaction with GaAs.

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Conflict of interest

The authors declare that they have no conflict of interest.

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