13.1;13.2

Surface photovoltage in heavily doped p^+-GaAs with adsorbed cesium and oxygen overlayers

© V.S. Khoroshilov[1,2], D.M. Kazantsev[1,2], S.A. Rozhkov[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

Received August 7, 2023
Revised September 15, 2023
Accepted September 15, 2023

A new method for measuring the surface photovoltage based on the dependence of photoemission quantum yield on the band bending has been developed. Using this technique, the evolution of photovoltage in heavily doped p^+-GaAs ($6 \cdot 10^{18}\,\mathrm{cm}^{-3}$) under cesium and oxygen adsorption is studied. Reversible changes in photovoltage, which differ qualitatively from those observed earlier on lightly doped p-GaAs, are presented. The observed behavior is explained by the variations in surface recombination velocity during the formation and decay of two-dimensional cesium clusters.

Keywords: photoemission, surface photovoltage, GaAs, photoluminescence, negative electron affinity.

DOI: 10.61011/TPL.2023.11.57192.19703

It is known that the adsorption of cesium and oxygen on the surface of heavily doped p^+-GaAs is a possible way to reach a state with an effective negative electron affinity (NEA) $\chi^* = \chi - \varphi_S \approx -0.2\,\mathrm{eV}$, where χ is the affinity and φ_S is the surface band bending. This state ensures a high quantum yield of photoemission from p^+-GaAs(Cs,O) photocathodes [1]. The trapping of photoelectrons at surface states leads to the emergence of photovoltage V (i.e., to a reduction in band bending due to partial screening of the surface electric field [2]). The photovoltage raises effective affinity χ^* and, consequently, reduces the quantum yield of NEA photocathodes (especially under irradiation with high-intensity laser pulses [3]). In view of this, the measurement of surface photovoltage of p^+-GaAs(Cs,O) is of interest for examining the effects of surface trapping and recombination of electrons on photoemission.

The evolution of photovoltage upon adsorption of cesium and oxygen on the surface of p-GaAs has been examined earlier via photoreflectance spectroscopy for samples with moderate doping ($p \approx 1.5 \cdot 10^{17}\,\mathrm{cm}^{-3}$) and special UP$^+$ structures with a thin (30−100 nm) undoped surface layer [4,5]. It was found that when Cs and O_2 layers are deposited sequentially, photovoltage V increases as a result of adsorption of Cs and decreases following O_2 adsorption. This behavior was attributed to exponential dependence $V(\varphi_S)$ [6] and adatom-induced variations of the band bending: φ_S increases due to the formation and charging of Cs-induced surface states after the deposition of Cs and decreases due to the „passivation“ of these states when O_2 is deposited. The sensitivity of photoreflectance spectroscopy turned out to be insufficient for examination of the surface of heavily doped p^+-GaAs(Cs,O) with a doping level of $p \geq 5 \cdot 10^{18}\,\mathrm{cm}^{-3}$ typical of NEA photocathodes [6]; therefore, the issue of evolution of photovoltage upon adsorption of cesium and oxygen on such surfaces remained open. A novel and more sensitive technique for photovoltage measurement based on the dependence of the quantum yield of photoemission on the band bending was developed in the present study in order to clarify this issue. The behavior of photovoltage revealed with the use of this technique differs qualitatively from the one observed earlier.

The samples of p^+-GaAs(001) for experiments were grown by liquid-phase epitaxy and doped with zinc to a level of $p \approx 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$. Atomically clean Ga-rich surfaces were prepared by chemical removal of oxides in the atmosphere of nitrogen and heating in vacuum at 760 K [7]. The deposition of Cs and O_2 and all measurements were performed at room temperature ($T = 295\,\mathrm{K}$) in a vacuum chamber with a base pressure of 10^{-8} Pa (Fig. 1). The surface of a sample was irradiated with two light beams *1* and *2* with the same wavelength $\lambda_1 = \lambda_2 = 850\,\mathrm{nm}$ and intensities $P_1 \approx 0.1\,\mathrm{mW/cm^2}$ and $P_2 \approx 1\,\mathrm{mW/cm^2}$ modulated at frequencies $f_1 = 80\,\mathrm{Hz}$ and $f_2 = 1030\,\mathrm{Hz}$. Each beam generated photoemission current $J_{1,2}$ and surface photovoltage $V_{1,2}$. The influence of photovoltage on effective affinity χ^* and, consequently, on the quantum yield of photoemission resulted in the emergence of photovoltage-induced photocurrent $\mathbf{\Delta J}$ at summary and difference frequencies $f_2 \pm f_1$. Amplitude ΔJ and phase φ of this current were measured by sequential lock-in detection of signals at frequencies f_2 and f_1.

Photocurrent $\mathbf{\Delta J}$ is a sum of two components corresponding to the mutual influence of beams *1* and *2*: modulation of photoemission current J_1 by photovoltage V_2 and modulation of J_2 by V_1. An exponential dependence of quantum yield Y on electron affinity χ^*, which holds true for photon-enhanced emission of thermalized electrons from p^+-GaAs with a positive electron affinity (PEA) at

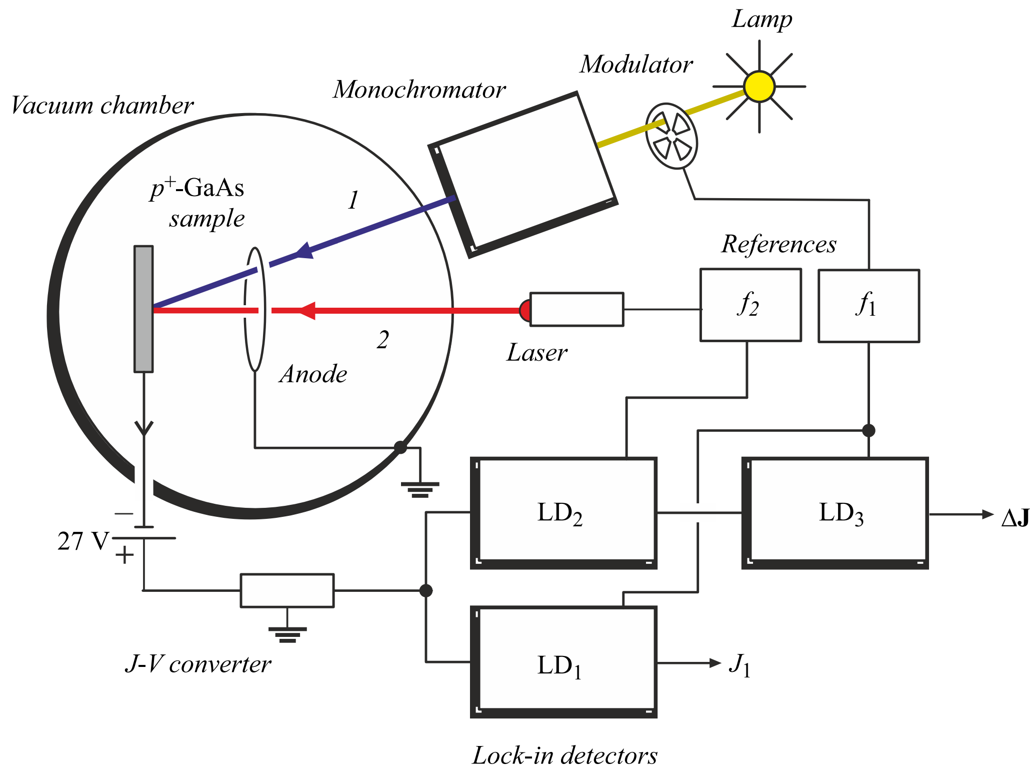

Figure 1. Diagram of the setup. *1, 2* — Light beams with their intensities modulated by frequencies $f_{1,2}$. Photoemission current J_1 and photovoltage-induced photocurrent $\mathbf{\Delta J}$ are measured by the system of lock-in detectors LD$_{1-3}$.

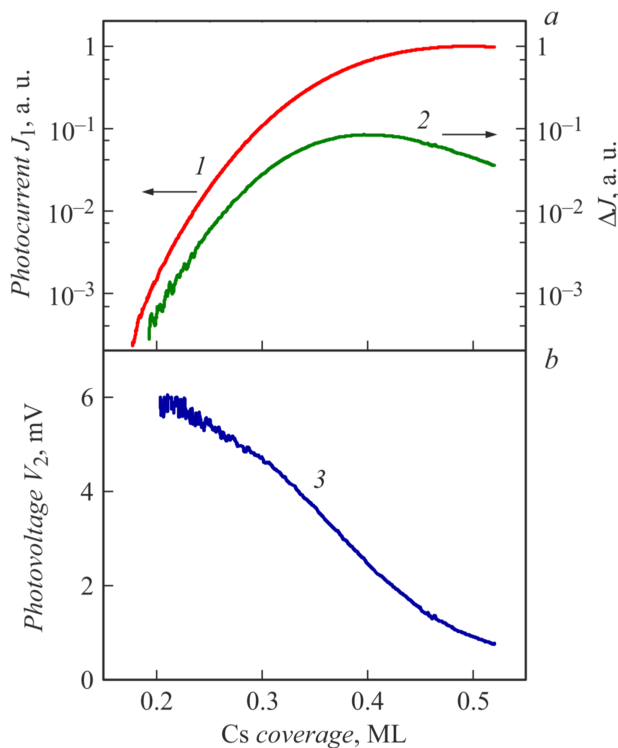

Figure 2. Evolution of photoemission current J_1 (*1*), photovoltage-induced photocurrent ΔJ (*2*), and surface photovoltage V_2 (*3*) upon adsorption of cesium on a clean p^+-GaAs surface. The radiation wavelength is 850 nm.

$\lambda_1 = \lambda_2 = 850$ nm [8], was used to calculate the photovoltage: $Y \propto \exp(-\chi^*/kT)$, where k is the Boltzmann constant. It was also assumed that the photovoltage is low ($V_{1,2} \ll kT/e$, where e is the electron charge) and thus depends linearly on intensity $P_{1,2}$ [6]. The choice of equal wavelengths $\lambda_1 = \lambda_2$ then ensured the equality of effects of mutual influence of beams *1* and *2*, since the magnitudes of these effects are proportional to products J_1V_2 and J_2V_1, and each of these products is specified by the product of intensities P_1P_2. Thus, photovoltage V_2 was calculated as

$$V_2 = \frac{kT}{e}\frac{\Delta J}{J_1}\frac{\pi}{4\cos\varphi}. \quad (1)$$

Characteristic photovoltage relaxation time τ was determined in accordance with the following relation: $\tan 2\varphi = 2\pi f_2 \tau$.

Figure 2, *a* presents the dependences of photoemission current J_1 and photovoltage-induced photocurrent ΔJ on cesium coverage θ (in monolayers, ML) upon adsorption on the surface of p^+-GaAs. Photocurrent J_1 increases with θ and, as is known, reaches its maximum at $\theta = 0.5$ ML when affinity χ^* is at its minimum [1,8]. The maximum of ΔJ is observed at lower θ and is specified by dependence $V_2(\theta)$. Photovoltage V_2 (Fig. 2, *b*) was calculated by inserting ratio $\Delta J/J_1$ into formula (1). It is evident that V_2 decreases monotonically as the Cs coverage increases. The phase of signal $\mathbf{\Delta J}$ was $\varphi \approx 7°$ within the entire

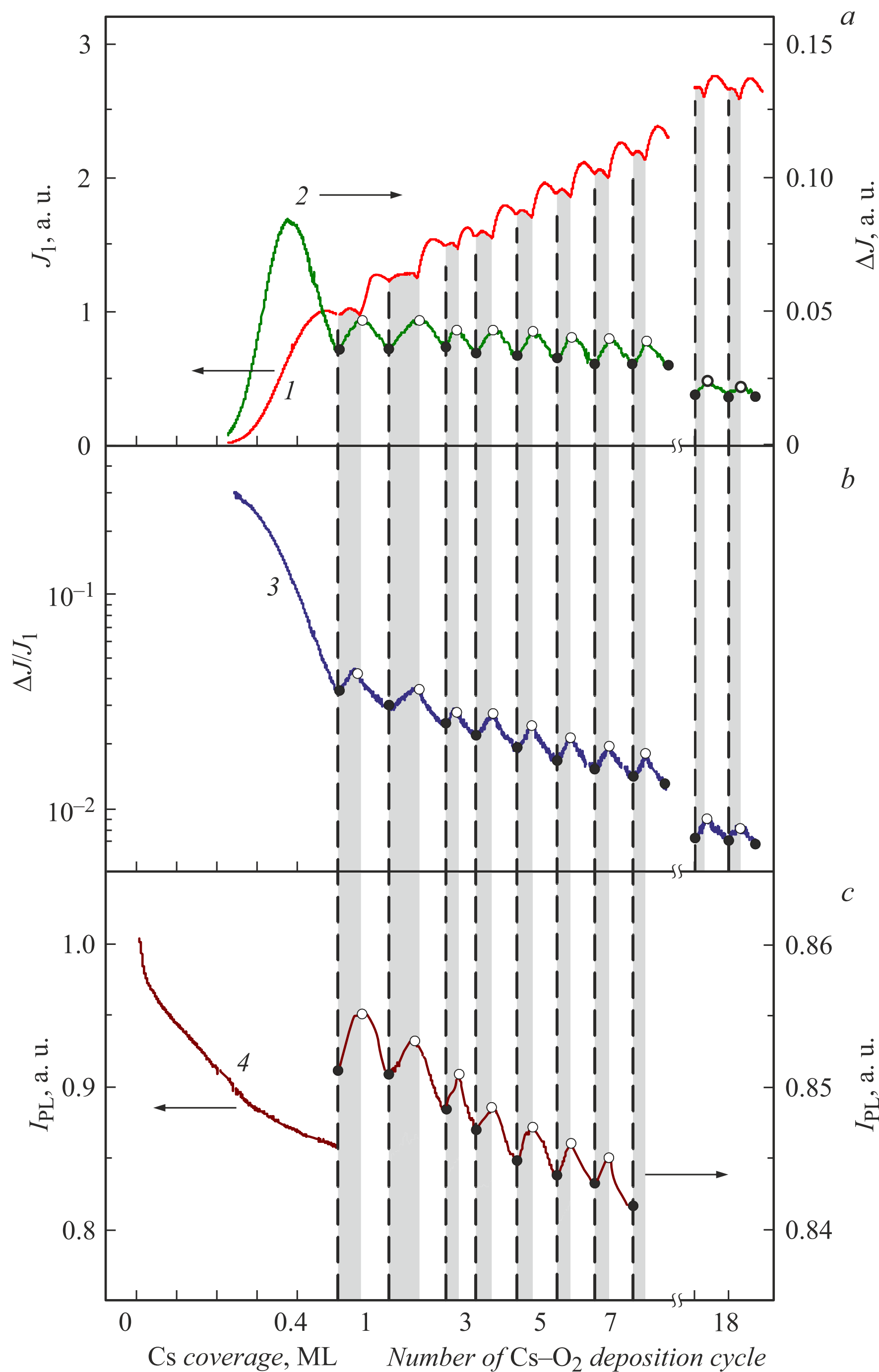

Figure 3. Evolution of photoemission current J_1 (*1*), photovoltage-induced photocurrent ΔJ (*2*), their ratio $\Delta J/J_1$ (*3*), and photoluminescence intensity I_{PL} (*4*) upon deposition of cesium and oxygen on the surface of p^+-GaAs. The regions of oxygen deposition are greyed out. Filled and open circles denote the moments when oxygen was „switched on" and „switched off," respectively.

range of $\theta = 0.2-0.5$ ML. This corresponds to photovoltage relaxation time $\tau \approx 40\,\mu$s.

The deposition of cesium was continued after $\theta = 0.5$ ML and combined with additional periodic oxygen deposition [1,5] (Fig. 3). It follows from Fig. 3, *a* that photoemission current J_1 varies nonmonotonically in each cycle of Cs and O_2 deposition, but increases in general due to a reduction in the effective electron affinity down to the state with a NEA [1]. The evolution of photovoltage-induced photocurrent is also non-monotonic: ΔJ decreases after cesium deposition and increases after oxygen deposition. Formula (1) is inapplicable in the determination of magnitude of photovoltage V_2 in the NEA case, since exponential dependence $Y(\chi^*)$ gives way to a linear one in the PEA–NEA transition [9]. However, ratio $\Delta J/J_1$ remains proportional to V_2 at low photovoltages $V_2 \ll kT/e$;

therefore, the evolution of $\Delta J/J_1$ shown in Fig. 3, b reproduces relative photovoltage variations. It can be seen that the photovoltage decreases after cesium deposition and increases after oxygen deposition.

This pattern differs qualitatively from the one observed earlier for moderately doped samples [4] and UP^+ structures [4,5] where the photovoltage was instead maximized after cesium deposition. This difference may be attributed to the formation of two-dimensional metallic cesium clusters on the surface of GaAs [10] that raise the rate of surface recombination and, consequently, reduce the photoinduced surface charge density and the photovoltage [2]. At the same time, the deposition of oxygen results in destruction of Cs clusters [10] and enhances the photovoltage. Note, however, that the direction and magnitude of photovoltage variations depended on the previous treatment of the p-GaAs(Cs,O) surface. The data presented in Figs. 2 and 3 were obtained after multiple cycles of deposition and thermal desorption of a (Cs,O) coverage; notably, the photovoltage increased with the number of cycles. The reasons for this remain unclear and may be associated with the GaAs surface oxidation or incomplete thermal removal of (Cs,O) layers.

Changes in the surface recombination rate induced by the formation and destruction of Cs- clusters may be detected by measuring photoluminescence intensity I_{PL} [11]. Figure 3, c presents the evolution of I_{PL} in a separate experiment with the p^+-GaAs surface irradiated with a laser operating at a wavelength of 650 nm. It is evident that I_{PL} decreases when cesium is deposited. This is indicative of an increase in the surface recombination rate and agrees qualitatively with the proposed explanation. Note that the magnitude of I_{PL} variations ($\sim 1\%$) is significantly lower than the one for $\Delta J/J_1$ ($\sim 25\%$). This is apparently attributable to the dominant influence of bulk recombination (compared to the surface one) on the photoluminescence intensity.

In our view, the direction of observed photovoltage variations is reversed relative to those reported earlier [4,5] due to the presence of two competing mechanisms affecting the photovoltage induced by cesium and oxygen adsorption: variations of the band bending and the surface recombination rate. Band bending variations $\Delta\varphi_S$ depend on the doping level via width w of the surface field region: $\Delta\varphi_S \propto w\Delta Q_S$, where ΔQ_S is the adatom-induced variation of the surface charge. With ΔQ_S being fixed, $\Delta\varphi_S$ in p^+-GaAs samples ($p \approx 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$, $w \approx 10\,\mathrm{nm}$) is several times lower than in moderately doped samples ($p \approx 1.5 \cdot 10^{17}\,\mathrm{cm}^{-3}$, $w \approx 60\,\mathrm{nm}$) [4] and UP^+ structures ($w \approx 30-100\,\mathrm{nm}$) [5]. Therefore, with band bending variations on the p^+-GaAs surface being suppressed, the surface recombination rate may exert a dominant influence on the photovoltage.

We note in conclusion that a new method based on the dependence of photoemission current on the band bending was used to examine the evolution of photovoltage on the surface of heavily doped p^+-GaAs ($6 \cdot 10^{18}\,\mathrm{cm}^{-3}$) upon adsorption of cesium and oxygen. Reversible variations in photovoltage between a low value after cesium adsorption and a high value after oxygen adsorption were observed. These photovoltage variations are reversed relative to those reported earlier for structures with a lower doping level and are attributable to changes in the surface recombination rate, which are presumably associated with the formation and decay of cesium clusters.

Funding

This study was supported by the Russian Science Foundation, grant No. 23-72-30003, https://rscf.ru/en/project/23-72-30003/.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R.L. Bell, *Negative electron affinity devices* (Clarendon, Oxford, 1973), p. 65–76.
[2] L. Kronik, Y. Shapira, Surf. Sci. Rep., **37**, 1 (1999). DOI: 10.1016/S0167-5729(99)00002-3
[3] A. Herrera-Gómez, G. Vergara, W.E. Spicer, J. Appl. Phys., **79**, 7318 (1996). DOI: 10.1063/1.361448
[4] V.L. Alperovich, A.G. Paulish, A.S. Terekhov, Phys. Rev. B, **50**, 5480 (1994). DOI: 10.1103/PhysRevB.50.5480
[5] V.L. Alperovich, A.G. Paulish, H.E. Scheibler, A.S. Terekhov, Appl. Phys. Lett., **66**, 2122 (1995). DOI: 10.1063/1.113923
[6] H. Shen, M. Dutta, J. Appl. Phys., **78**, 2151 (1995). DOI: 10.1063/1.360131
[7] O.E. Tereshchenko, V.L. Alperovich, A.G. Zhuravlev, A.S. Terekhov, D. Paget, Phys. Rev. B, **71**, 155315 (2005). DOI: 10.1103/PhysRevB.71.155315
[8] A.G. Zhuravlev, A.S. Romanov, V.L. Alperovich, Appl. Phys. Lett., **105**, 251602 (2014). DOI: 10.1063/1.4904986
[9] L.B. Jones, H.E. Scheibler, S.N. Kosolobov, A.S. Terekhov, B.L. Militsyn, T.C.Q. Noakes, J. Phys. D: Appl. Phys., **54**, 205301 (2021). DOI: 10.1088/1361-6463/abe1e9
[10] C. Laubschat, M. Prietsch, M. Domke, E. Weschke, E. Remmers, T. Mandel, E. Ortega, G. Kaindl, Phys. Rev. Lett., **62**, 1306 (1989). DOI: 10.1103/PhysRevLett.62.1306
[11] T. Kanata, M. Matsunaga, H. Takakura, Y. Hamakawa, T. Nishino, J. Appl. Phys., **68**, 5309 (1990). DOI: 10.1063/1.347023

Translated by D.Safin