Photoemission from $p$-GaAs(Cs,O) under transition from negative to positive electron affinity

D E Protopopov$^{1,2}$, V S Khoroshilov$^{1,2}$, A G Zhuravlev$^{1,2}$, D M Kazantsev$^{1,2}$, V L Alperovich$^{1,2}$

$^1$Rzhanov Institute of Semiconductor Physics, 630090 Novosibirsk, Russia
$^2$Novosibirsk State University, 630090 Novosibirsk, Russia

E-mail: d.protopopov@g.nsu.ru

Abstract. The evolution of the electron escape probability from $p$-GaAs(Cs,O) to vacuum was measured under the transition from the state of negative to the state of positive electron affinity. The transition was induced by the deposition of excess cesium or oxygen on the $p$-GaAs(Cs,O) surface activated to the state of negative electron affinity. Under deposition of excess cesium, the escape probability was significantly lower as compared to excess oxygen, presumably, due to reflection and scattering of electrons on two-dimensional cesium metal clusters. Under Cs-induced transition, at positive values of affinity, a new peak was observed below the band gap in the photoemission quantum yield spectra. The peak stems presumably from: (i) the effective capture of sub-bandgap light in the structure, which consists of the heavily doped $p^+$-GaAs epilayer grown on the semi-insulating GaAs substrate, due to diffuse backside reflection from the rough back surface of the substrate; (ii) absorption of the captured light near the emitting $p^+$-GaAs surface due to the Franz-Keldysh effect in the strong surface electric field; (iii) emission of the electrons generated near the surface.

1. Introduction

The deposition of thin (subnanometer) layers of cesium and oxygen to the atomically clean $p$-GaAs surface leads to the reduction of the surface potential barrier for electron emission to vacuum and the formation of the state with negative effective electron affinity (NEA) $\chi^* \approx -0.2$ eV at which the vacuum level is below the bottom of the conduction band in the bulk of GaAs (figure 1(a)) [1]. Due to high values of photoemission quantum yield (up to ~ 50% [2]), NEA photocathodes based on $p$-GaAs(Cs,O) are widely used in various photoemission devices [1-4]. Interest in semiconductors with relatively small positive electron affinity (PEA) $\chi^* \approx 0.2$-0.4 eV (figure 1(b)) is due to the possibility of increasing the efficiency of solar energy conversion using photon-enhanced thermionic emission (PETE) [5-8]. Earlier, the transition from the state with PEA to the state with NEA and back, from NEA to PEA, was experimentally studied by means of photoemission quantum yield spectroscopy [9, 10]. A non-monotonic dependence of the escape probability of thermalized electrons to vacuum $P_t$ on the effective electron affinity $\chi^*$, with a deep minimum near $\chi^* \approx 0$, was observed. The minimum was explained by the change in the mechanism of emission at the transition from a positive to a negative affinity. Another observation consisted in the significant quantitative differences in the escape probability values obtained for the experiments with excess cesium and oxygen depositions. It was suggested that the difference was due to electron reflection or scattering at the two-dimensional cesium clusters that reduce the photoemission current at large Cs coverages. However, the
experimental data obtained in [10] were not sufficient to prove this hypothesis, because in that experiments the initial values of NEA $\chi^*$ differed significantly. The aim of the present study is to fill this gap by improving the photoemission quantum yield spectroscopy technique and performing additional experiments by depositing excess cesium and oxygen on optimally activated $p$-GaAs(Cs,O) surfaces with close initial values of quantum yield and affinity. The results support the hypothesis about the role of electron scattering on Cs clusters. Also, a substantial increase in the signal/noise ratio allowed us to resolve a new Cs-induced sub-bandgap peak in the photoemission quantum yield spectra. A qualitative explanation of the possible origin of this new peak is given.

![Figure 1](image)

**Figure 1.** Band diagrams of the $p$-GaAs(Cs,O) surface with negative (a) and positive (b) effective electron affinities. In (a), the emission from the bottom of the bulk conduction band (pathway 1) and through the states localized in the surface band bending region (pathway 2) are schematically illustrated by the dashed and solid horizontal arrows. In (b), the emission pathways for direct photoemission (3) and PETE (4) are shown by dark blue and red arrows, respectively.

2. **Experimental**

The experiments were done on epitaxial layers of heavily doped $p^+$-GaAs(001) with hole concentration of $\sim 7 \times 10^{18}$ cm$^{-3}$. Atomically clean GaAs(001) surfaces were prepared by removing oxides in a solution of HCl in isopropyl alcohol under the dry nitrogen atmosphere, transferring to an ultrahigh vacuum set-up without any air contact and subsequent heating in vacuum [11]. The photoemission measurements were done at room temperature $T = 300$ K. Cesium and oxygen were deposited from outgassed dispensers. The cesium coverage was determined by the calibration based on the results of X-ray photoelectron spectroscopy [12]. The oxygen exposure was estimated from the time dependence of the oxygen pressure.

The photoemission quantum yield spectra were measured under Cs or O$_2$ deposition on $p$-GaAs(Cs,O) surface preliminary activated to the state of NEA, using the technique adapted for systems with parameters varying in time [7, 13, 14]. This technique consists in the continuous measuring the photoemission current as a function of photon energy and time during the deposition of cesium and oxygen. The photoemission spectra corresponding to fixed time points and, thus, to fixed (Cs,O)-layer compositions were determined by the interpolation of the obtained data array [13, 14].

3. **Results and discussion**

At the first stage of the experiment, the atomically clean $p$-GaAs surface was activated to the state of NEA by codeposition of Cs and O$_2$ [3]. Then either an additional cesium overlayer was deposited on the thus prepared NEA surface, or the surface was exposed to excessive flux of oxygen. In both cases the exposure to excessive Cs or O$_2$ caused gradual increase of the effective affinity $\chi^*$ and, thus, the
transition from the state of NEA to PEA. Photoemission quantum yield spectra were measured during this transition. The evolution of the spectra measured under deposition of cesium and oxygen on the NEA p-GaAs(Cs,O) surface are shown in figures 2(a) and 2(b), respectively. The spectra evolve with increasing affinity from top to bottom. The spectra contain contributions from the direct photoemission of electrons photoexcited with energies above the vacuum level (pathway 3 in figure 1(b)) and the emission of electrons, which are excited below the vacuum level and acquire the additional energy required for emission to vacuum from phonons, by thermalization up in energy (photon-enhanced thermionic emission (PETE), illustrated by pathway 4 in figure 1(b)). For positive values of effective affinity \( \chi^* > 0 \), the spectra contain two thresholds: the high-energy threshold \( \varepsilon_t \) for direct photoemission, which increases with increasing \( \chi^* \), and the fixed low-energy threshold for PETE at the GaAs band gap \( \varepsilon_g \) [7]. For negative values of affinity \( \chi^* < 0 \), the spectra contain only one threshold at \( \varepsilon_g \).

The comparison of figures 2(a) and 2(b) shows that, for the deposition of Cs and O₂, the evolution of the above bandgap \( h\omega > \varepsilon_g \) spectral shapes are similar, while in the subbandgap region \( h\omega < \varepsilon_g \) the spectra are different. In particular, under Cs deposition, a pronounced additional peak below the band gap is observed for positive values of \( \chi^* \) (figure 2(a)), while under O₂ deposition only a weak shoulder is seen in this spectral region. This sub-bandgap peak was not observed earlier [10].

**Figure 2.** Photoemission quantum yield spectra at p-GaAs(Cs,O) surface under the deposition of excessive cesium (a) and oxygen (b). The spectra evolve from top to bottom, as indicated by the vertical arrows.

**Figure 3.** Zoomed images of the photoemission spectra in the near band gap region for the deposition of cesium (a) and oxygen (b). The vertical arrow indicates the spectral position of the sub-bandgap peak.
A more detailed comparison of the spectra in the near-bandgap spectral region can be done using zoomed images of this region, which are shown in figures 3(a) and 3(b) for the deposition of excessive Cs and O₂, respectively. It is seen that, at the initial stage of Cs deposition (three top spectra in figure 3(a)), a shoulder appears below the band gap. Under further Cs deposition, the shoulder develops into a pronounced peak (eight bottom spectra in figure 3(a)) with the spectral position at photon energy \( h\omega = 1.365 \text{ eV} \) and the width at half maximum of approximately 25 meV. On the contrary, as seen in figure 3(b), after moderate oxygen exposures, only a weak shoulder is observed in the spectra below the bandgap (see the spectra in the middle of figure 3(b)). The shoulder practically vanishes at larger O₂ exposures (see the spectra in the bottom of figure 3(b)).

The Cs-induced sub-bandgap peak was reproducibly observed in all experiments performed in this study, although its amplitude varied by a factor of about 3 for various experimental runs. In figures 2(a) and 3(a) we presented the spectra of the run in which the peak was well-pronounced. The absence of a distinct sub-bandgap peak in [10] can be partly explained by lower signal-to-noise ratio in the earlier experiments; this follows from the comparison of the spectra in the subband region (figure 2 of [10] and figures 2 and 3 of the present work).

The origins of the Cs-induced sub-bandgap peak and of its amplitude variations, are not clear yet. A tentative explanation of the peak is based on the Franz-Keldysh effect in the surface electric field. The explanation is as follows. The light with photon energies \( h\omega < \varepsilon_g \) below the GaAs bandgap is effectively captured in the structure due to diffuse backside reflection from the rough back surface of the substrate and to the total internal reflection inside the sample. However, for photon energies \( h\omega \) sufficiently close to the bandgap \( \varepsilon_g \), the light can be absorbed in the near-surface band bending region due to the Franz-Keldysh effect in the surface electric field, which leads to the shift of the threshold of the interband optical transitions towards lower photon energies. Despite the small band bending region width (~ 10 nm), a significant part of the light intensity may be absorbed due to multiple light traverse through this region. The emission of electrons excited near the surface may contribute to the observed sub-bandgap photoemission. With increasing photon energy \( h\omega \) the absorption coefficient in the epilayer and substrate increases; consequently, the effects of backside reflection, light capture and, thus, multiple traversing through the band bending region vanish, and the respective sub-bandgap photoemission decreases. The observation of the peak under Cs deposition and its absence under O₂ exposure is consistent with the proposed explanation and earlier results on Cs-induced increase and O₂-induced decrease in the band bending and surface electric field [15, 16].

To determine the effective affinity \( \chi^* \) and the escape probabilities of hot \( (P_h) \) and thermalized \( (P_t) \) electrons to vacuum, the experimental spectra measured under the oxygen deposition were compared to the theory that takes into account the contributions of both direct photoemission and PETE [7]. The details of comparing the measured and calculated spectra and determination of the fitting parameters are described in [7, 10]. Thus, from the spectroscopic data we can obtain the evolution of the parameters \( \chi^* \), \( P_h \) and \( P_t \), along with the dependences \( P_h(\chi^*) \) and \( P_t(\chi^*) \) [9, 10]. It was shown in [10] that the \( P_t(\chi^*) \) function is a more sensitive characteristic of the energy dependence of escape probability as compared to \( P_h(\chi^*) \).

The dependences \( P_t(\chi^*) \) determined for O₂ and Cs depositions on the activated p-GaAs(Cs,O) surface with the state of NEA are shown in figure 4. For the spectra measured under Cs deposition and presented in figure 2(a), the comparison with theoretical calculations was hindered by the presence of the sub-bandgap peak, which was not accounted for by the model. Therefore, along with the data obtained from the "oxygen" experiment performed in this study and presented in figure 2(b), the data from the "cesium" experiment performed in [10] are shown in figure 4.

It is seen that the shape of both Cs and O₂ dependencies are qualitatively the same, with a deep minimum at \( \chi^* = 0 \) and a sharp decrease for positive \( \chi^* \geq 0.2 \text{ eV} \). The minimum was observed earlier and explained by the change of the emission mechanism under the transition from negative to positive effective affinity. The main point of this explanation is that at negative or near-zero effective affinity, the emission occurs mainly from the states localized in the band bending region to which electrons are effectively captured. Therefore, at near-zero affinity, when the localized states lie below the vacuum...
level, the electron escape probability is small because the emission requires additional thermal activation. The reason for the sharp decrease at $\chi^* \geq 0.2$ eV was tentatively explained by the electron capture in the side valleys of the conduction band from which the emission is hindered by the necessity to conserve the tangential component of the electron momentum [7, 10].

It is seen in figure 4 that, unlike figure 5(b) in [10], the initial values of the affinity and escape probability in the "oxygen" experiment are approximately the same as in the "cesium" one. Still, $P_t$ values in the "cesium" experiment are considerably (by 3-5 times) lower than in the "oxygen" experiment. This difference is an additional proof of the hypothesis proposed in [10] that the reflection and scattering of emitted electrons on two-dimensional cesium clusters plays a significant role in the reduction of the escape probability and photoemission quantum yield.

![Figure 4](image_url)

**Figure 4.** Electron escape probability $P_t$ versus $\chi^*$ measured for the excess oxygen (circles, this work) and cesium (triangles, taken from [10]) deposition on the activated $p$-GaAs(Cs,O) surface with the state of NEA.

4. Conclusions
In conclusion, by means of photoemission quantum yield spectroscopy, the evolution of the electron escape probability to vacuum was measured at the $p$-GaAs(Cs,O) surface under the transition from the state of negative electron affinity to the state of positive electron affinity. The transition was caused by the deposition of excessive cesium or oxygen on the $p$-GaAs(Cs,O) surfaces activated to the state of NEA with close values of the effective affinity and photoemission quantum yield. A new peak was observed below the GaAs band gap in the photoemission quantum yield spectra. The peak may stem from the sub-bandgap absorption in the band bending region due to Franz-Keldysh effect in the surface electric field. Under the transition from negative to positive electron affinity by the deposition of excess cesium on the GaAs(Cs,O) surface, the escape probability to vacuum was lower by a factor of 3-5 as compared to the transition performed by excess oxygen. The obtained results are in agreement with the hypothesis that electron reflection or scattering on cesium clusters, which are formed under deposition of excessive Cs, significantly contribute to the reduction of the electron escape probability to vacuum.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (grant 20-02-00355 A).

References
[1] Bell R L 1973 Negative Electron Affinity Devices (Oxford: Clarendon)
[2] Siegmund O H W, Tremsin A S, Vallerga J V 2003 Nucl. Instrum. Methods Phys. Res. A **510** 185
[3] Bakin V V, Pakhnevich A A, Zhuravlev A G, Shornikov A N, Akhundov I O, Tereshechenko O E, Alperovich V L, Scheibler H E, Terekhov A S 2007 e-J. Surf. Sci. Nanotechnol. 5 80

[4] Karkare S, Dimitrov D, Schaff W, Cultrera L, Bartnik A, Liu X, Sawyer E, Esposito T, Bazarov I 2013 J. Appl. Phys. 113 104904

[5] Schwede J W, Bargatin I, Riley D C, Hardin B E, Rosenthal S J, Sun Y, Schmitt F, Pianetta P, Howe R T, Shen Z-X, Melosh N A 2010 Nat. Mater. 9 762

[6] Schwede J W, Sarmiento T, Narasimhan V K, Rosenthal S J, Riley D C, Schmitt F, Bargatin I, Sahasrabuddhe K, Howe R T, Harris J S, Melosh N A, Shen Z-X 2013 Nat. Commun. 4 157

[7] Zhuravlev A G, Romanov A S, Alperovich V L 2014 Appl. Phys. Lett. 105 251602

[8] Kribus A, Segev G 2016 J. Opt. 18 073001

[9] Zhuravlev A G, Khoroshilov V S, Alperovich V L 2017 JETP Lett. 105 686

[10] Zhuravlev A G, Khoroshilov V S, Alperovich V L 2019 Appl. Surf. Sci. 483 895

[11] Alperovich V L, Tereshchenko O E, Rudaya N S, Sheglov D V, Latyshev A V, Terekhov A S 2004 Appl. Surf. Sci. 235 249

[12] Tereshchenko O E, Alperovich V L, Terekhov A S 2004 JETP Lett. 79 131

[13] Zhuravlev A G, Scheibler H E, Jaroshevich A S, Alperovich V L 2010 J. Phys.: Condens. Matter 22 1858015

[14] Zhuravlev A G, Alperovich V L 2018 Appl. Surf. Sci. 461 10

[15] Alperovich V L, Paulish A G, Terekhov A S 1994 Phys. Rev. B 50 5480

[16] Alperovich V L, Paulish A G, Terekhov A S 1995 Surf. Sci. 331 1250