

UDC 621.315.592

Photoelectron transfer through *p*-GaAs(Cs, O)–vacuum interface with positive and negative electron affinity

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Received April 26, 2024

Revised April 27, 2024

Accepted April 27, 2024

The evolution of the energy distributions of electrons emitted from *p*-GaAs(Cs, O), during the transition from negative to positive effective electron affinity upon the deposition of excess cesium has been studied. It was found that during the deposition of excess cesium the evolution of energy distributions is caused not only by the increase in surface work function, but also by the decrease in the probability of electron escape into vacuum. The results are compared with the experiment on excess oxygen adsorption. Presumably, the changes in the escape probability are caused by electron scattering on two-dimensional cesium clusters with metallic excitation spectrum.

Keywords: photoemission, GaAs, negative electron affinity, electron escape probability into vacuum.

DOI: 10.61011/SC.2024.05.59167.6336H

1. Introduction

The study of photoelectron transport through the semiconductor-vacuum interface is of both, scientific and practical interest. Scientific interest is related to the mechanisms of transformation of a quasiparticle in a crystal into a free electron in a vacuum, as well as the scattering of energy, momentum and spin of photoelectrons at the interface. The clarification of these issues is of practical interest due to the use of photoemission as a method for studying the electronic structure of solids [1,2] and the physical basis of the operation of semiconductor photocathodes [3–6]. It is known that adsorption of cesium and oxygen on the surface of *p*-GaAs reduces the potential barrier for electrons to escape into vacuum to a state with negative effective electron affinity (NEA) $\chi^* \approx -0.2$ eV, at which the vacuum level lies below the bottom of the conduction band in semiconductor volume. This state ensures a high quantum yield of emission from NEA-photocathodes [3,4]. The surfaces *p*-GaAs with relatively small ($\chi^* \approx 0.2-0.4$ eV) positive electron affinity (PEA) are also of interest because of potential for solar energy transformation improvement as described in [7,8]. Though implementation of this potential in practice is doubtful because of low probability of electron escape from *p*-GaAs into vacuum [9], the study of transition between the states with NEA and PEA on the surface *p*-GaAs(Cs, O) turned out to be useful to figure out the mechanisms of photoemission [10–12].

In papers [10–12] transition between the states with NEA and PEA during cesium and oxygen adsorption on *p*-GaAs surface was examined by method of photo-

emission quantum yield spectroscopy. In PEA state two thresholds were observed in the photo-emission spectra. The high-energy threshold is associated with the direct photoemission of electrons excited in the conduction band with the energy above the vacuum level during inter-band optical transitions. The second threshold with photon energy equal to the band gap width is due to the so-called photon-enhanced thermionic emission (PETE) of electrons that are excited below the vacuum level and acquire the energy necessary for emission from the crystal lattice due to phonons absorption in the process of thermalization [7–9]. The effective electron affinity χ^* was defined basing on the position of direct photo-emission spectral threshold as described in [10–12]. The probabilities of emission of hot and thermalized electrons P_h and P_t were obtained by comparing the experimental spectra of quantum yield with the calculations and were considered as amplitudes of direct photo-emission and PETE contributions into the full photocurrent spectrum. It was found that escape probabilities P_h and P_t depend on the affinity χ^* in a complex way, varying from much lower than unity ($10^{-2}-10^{-1}$) in PEA region to 0.5 in NEA region. These results are consistent with the hypothesis on low probability of electrons escape into vacuum for a single collision with the surface [13,14]. At the same time, a relatively large quantum yield of photo-emission from *p*-GaAs(Cs, O) with NEA is provided by the capture of electrons to quantum-sized states localized in the area of surface band bending and „by multiple collisions“ with the surface during the lifetime on these states [5,6,12,14]. Another important fact is that experimental dependencies $P_{h,t}(\chi^*)$ turned out to

be multi-valued [10–12]. In particular, during the cesium deposition on clean surface p -GaAs(001) the values $P_{h,t}$ at Cs-coverages $\theta > 0.5$ monolayer (ML) appeared to be less than ones at the same values of χ^* in the area of $\theta < 0.5$ ML [10]. It was also found that during the adsorption of excessive cesium on p -GaAs(Cs,O) surface with NEA, causing the transition from NEA to PEA, the dependencies $P_{h,t}(\chi^*)$ lie below than ones obtained during the same transition caused by exposure in excessive oxygen [11,12]. These results demonstrate the cesium-induced effect of decrease in the probabilities of photoelectrons escape into vacuum.

The photoemission quantum yield spectroscopy allows to reliably determine the electron affinity χ^* and the probability of electrons escape into vacuum $P_{h,t}$ only for the PEA region due to the difference in spectral thresholds of direct photoemission and PETE. In NEA region because of thresholds coincidence it is impossible to directly find the value χ^* from the spectra, therefore, in studies [10–12] it was implicitly found from P_t/P_h ratio. Thus the separation of affinity and escape probabilities contributions to the evolution of photoemission quantum yield was complicated. The magnitude of the negative affinity can be determined directly by measuring the energy distributions of the emitted electrons [15,16]. The electron affinity can be determined by the width of the energy distribution, while its amplitude exhibits the electron escape probability. In addition, the measurement of energy distributions is a more „differential“ technique and allows us to study the electron escape probabilities depending on their energy, while parameters P_h and P_t , used for description of photoemission quantum yield spectra, corresponded to the escape probabilities averaged over the distribution functions of hot and thermalized electrons

In this study the effect of excessive cesium adsorption on p -GaAs(Cs,O) surface with NEA on the electron escape probability was analyzed by measuring the energy distributions. It has been established that during the adsorption of excess cesium, the evolution of energy distributions is due to both, an increase in the surface work function and a significant decrease in the probability of electrons escaping into vacuum. Possible microscopic reasons of the cesium-induced decrease in the escape probability are discussed.

2. Experimental method

Experiments were carried out on the layers of heavily doped p -GaAs(001) with holes density of $\sim 6 \cdot 10^{18} \text{ cm}^{-3}$, grown by method of metalorganic chemical vapour deposition. 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 heating in vacuum [17]. The experiment was carried out in a setup with separate positions for cesium deposition and for measuring the distributions of emitted electrons along

the longitudinal component of kinetic energy $N_e(\epsilon_{lon})$. The sample surface was illuminated with a laser of photon energy of $\hbar\omega = 1.9 \text{ eV}$ (wavelength 650 nm) exceeding the band gap width GaAs 1.42 eV. Prior to measuring the energy distributions the atomically clean surface p -GaAs was activated to a state with NEA by joint application of cesium and oxygen according to [15] until the photoemission quantum yield of $\sim 25\%$ was obtained. The distributions $N_e(\epsilon_{lon})$ were measured by method of retarding potential using a molybdenum mesh anode located $\sim 1 \text{ mm}$ away from the sample. The details of the activation procedure and energy distributions measurements are given in work [15].

3. Results

To study the effect of excess cesium on the probability of electron escape from p -GaAs(Cs,O), an experiment on the measurements of the distributions of emitted electrons along the longitudinal energy component $N_e(\epsilon_{lon})$ during the cesium-induced transition from NEA to PEA was performed. In the beginning of the experiment the atomically clean surface p -GaAs was first activated to a state with NEA, after that, excess cesium was deposited on the surface; the results are shown in Figure 1. The energy distributions $N_e(\epsilon_{lon})$ were measured on the surface in its state with NEA (curve 1) and after excess cesium deposition during surface relaxation (curves 2–5); no energy distributions were measured during cesium deposition. Electron energy in Figure 1 counts from the bottom of the

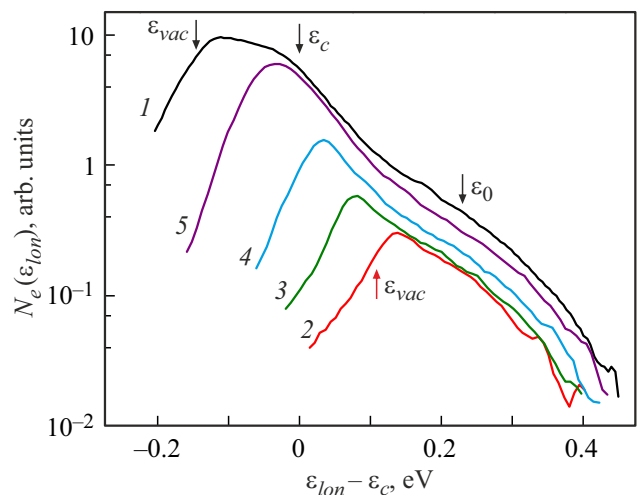


Figure 1. Distributions of emitted electrons along the longitudinal component of kinetic energy ϵ_{lon} in the experiment of p -GaAs(Cs,O) surface transition from NEA to PEA by applying excess cesium. Curve 1 was measured before the cesium deposition, curves 2–5 — after the cesium deposition during the relaxation of adsorbed layer. Arrows indicate position of the vacuum level ϵ_{vac} (for curves 1 and 2), bottom of conduction band in the bulk ϵ_c and initial energy of photoelectrons ϵ_0 . (A color version of the figure is provided in the online version of the paper).

conduction band ε_c in quasi-neutral GaAs bulk, the position of which was found from the initial distribution $N_e(\varepsilon_{lon})$ (curve 1). The value of ε_c and vacuum level ε_{vac} were defined from positions of characteristic points in $N_e(\varepsilon_{lon})$ distributions, where derivative $dN_e/d\varepsilon_{lon}$ has extremum values [18]. During measurements we also observed the changes in the anode work function which resulted in shift of ε_0 singularity, which looks as a weak arm in distributions $N_e(\varepsilon_{lon})$, associated with initial energy of photo-electrons in GaAs conduction band [19]. The singularity shift ε_0 was defined by combination of different curves $N_e(\varepsilon_{lon})$; this shift is taken into account in Figure 1. The amplitude of high-energy part of energy distributions A was defined in the energy range $\varepsilon_{lon} - \varepsilon_c = 0.2-0.3$ eV as an average ratio $N_e/N_{e(1)}$, where $N_{e(1)}$ — initial energy distribution before excess cesium deposition (curve 1). The amplitude of energy distribution A is supposed to be proportional to the escape probability of hot electrons P_h .

Figure 2 shows the change in the work function of surface p -GaAs(Cs,O) $\Delta\Phi_C$, work function of anode $\Delta\Phi_A$ and amplitude of energy distributions A in the experiment of excess cesium deposition. From comparison of curves 1 and 2 in Figure 1 it is seen that cesium deposition resulted in decrease of the distribution width $N_e(\varepsilon_{lon})$, which indicates the increase in work function of surface p -GaAs(Cs,O) and transition to a state with PEA. At the same time, the amplitude of energy distributions A has decreased by several times, which indicates a cesium-induced decrease in the probability of electron escape. During process of surface relaxation (curves 2–5 in Figure 1) the work function Φ_C and amplitude of energy distributions A changed towards initial values: Φ_C decreased, while A increased. At that, in Figure 2 we may see an initial site where the most intensive changes Φ_C and A occur, during which the work function of anode Φ_A was also reduced. It is reasonable to assume that this process is associated with partial desorption of cesium from the surface of p -GaAs(Cs,O) and its re-deposition on the surface of the anode. Further, as seen from Figure 2, the changes in Φ_A stopped, and more slow relaxational changes in Φ_C and A continued because of structural transformations in the adsorption layer on the surface p -GaAs(Cs,O) [10].

To compare the effect of cesium and oxygen adsorption on the electrons escape probability an experiment was carried out to measure the energy distributions $N_e(\varepsilon_{lon})$ under exposure of surface p -GaAs(Cs,O) with NEA in the excess oxygen. Unlike the experiment with excess cesium, in this experiment the sample was always in a position to measure energy distributions, which made it possible to study the evolution of these distributions directly during oxygen exposure. The results of measuring the distributions $N_e(\varepsilon_{lon})$ are given in Figure 3, and Figure 4 illustrates the changes in the work function $\Delta\Phi_C$ and amplitude of energy distributions A depending on oxygen dose. The work function of anode Φ_A in this experiment was constant with an accuracy of 5 meV. It can be seen from Figure 3 and Figure 4 that the effect of oxygen was mainly reduced to a decrease in the width of the energy distributions and an

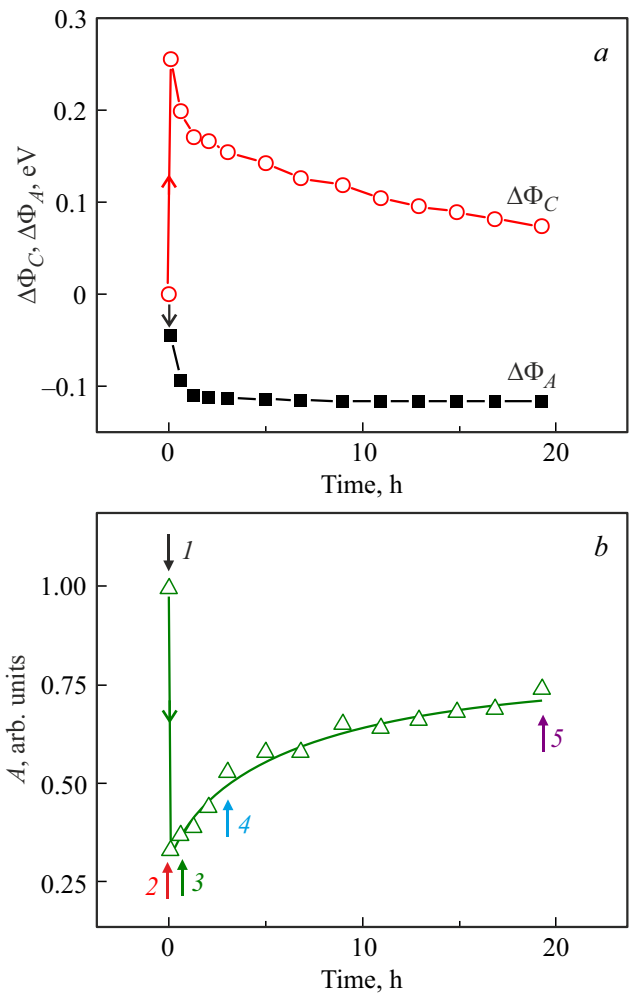


Figure 2. The change in the work function of surface p -GaAs(Cs,O) $\Delta\Phi_C$ (circles) and metallic anode $\Delta\Phi_A$ (squares) (a), and the amplitude of energy distributions A (b) in the experiment for Cs-induced transition from NEA to PEA. The initial point on the surface with NEA was measured before excess Cs deposition, other points — in the process of relaxation of surface after Cs deposition. The arrows indicate the points corresponding to the energy distributions 1–5 in Figure 1.

increase of the work function Φ_C , while the amplitude of energy distributions A varied slightly, which is consistent with the results of [16]. Unlike the experiment with cesium, the amplitude of energy distributions A did not decrease, but even slightly (by $\sim 20\%$) increased, which indicates a higher probability of electrons escaping into vacuum.

4. Discussion

The obtained results indicate that transition from NEA to PEA on the surface p -GaAs(Cs,O) occurs in significantly different way when excessive cesium and oxygen are deposited. The adsorption of excess oxygen leads mainly to higher work function of the surface; at the same time, the probability of electron escape varies slightly. On

the contrary, excess cesium not only increases the work function, but also significantly reduces the probability of electrons escaping into vacuum. This is consistent with findings in papers [10–12] obtained by method of photoemission quantum yield spectroscopy. In this study, the effect of a cesium-induced decrease in the escape probability is confirmed by measuring the energy distributions of emitted electrons, where changes in the work function in NEA area were determined directly by the width of the energy distributions. In addition, measurements of energy distributions complement the previously obtained results because it became possible to get data on dependence of the electron escape probability on their energy.

For light with photons energy of 1.9 eV the high-energy part of distributions $N_e(\epsilon_{lon})$ is defined by direct photoemission, therefore the amplitude of energy distributions A corresponds to the escape probability of hot electrons. As seen from Figure 1, when cesium is applied the form of curves $N_e(\epsilon_{lon})$ in the area of large energies $\epsilon_{lon} > \epsilon_{vac}$ remained practically unchanged. Hence, the effect of cesium-induced decrease in the escape probability $P_h(\epsilon_{lon})$ is slightly dependent on energy, and this is consistent with the use of the coefficient P_h (in describing the photoemission spectra) which is independent of energy and has a sense of escape probability averaged by the function of hot electrons distribution [10–12]. At the same time, as can be seen from Figure 3, when applying excess oxygen, the increase in the amplitude of distributions $N_e(\epsilon_{lon})$ is more pronounced for the near-vacuum electron energies, which may indicate that oxygen-induced increase of the escape probability is energy dependent.

The most likely cause of decrease in the escape probability during excess cesium deposition on surface p -GaAs(Cs,O) is reflection or scattering of the emitted

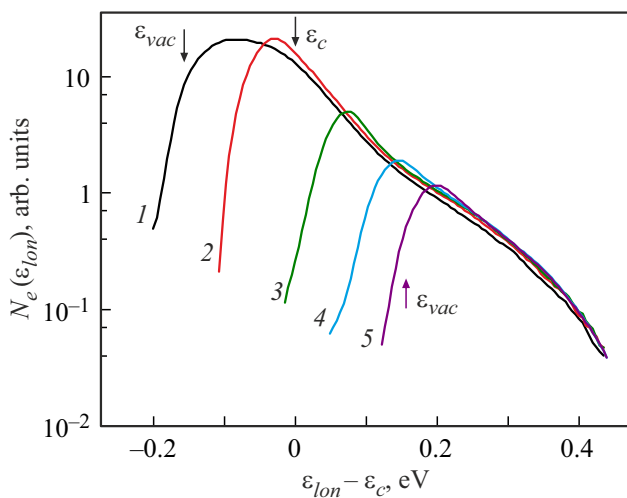


Figure 3. Distributions of emitted electrons along the energy longitudinal component ϵ_{lon} in the experiment of oxygen-induced transition of surface p -GaAs(Cs,O) from NEA to PEA. Curve 1 was measured before the exposure in oxygen, curves 2–5 — during the exposure in oxygen.

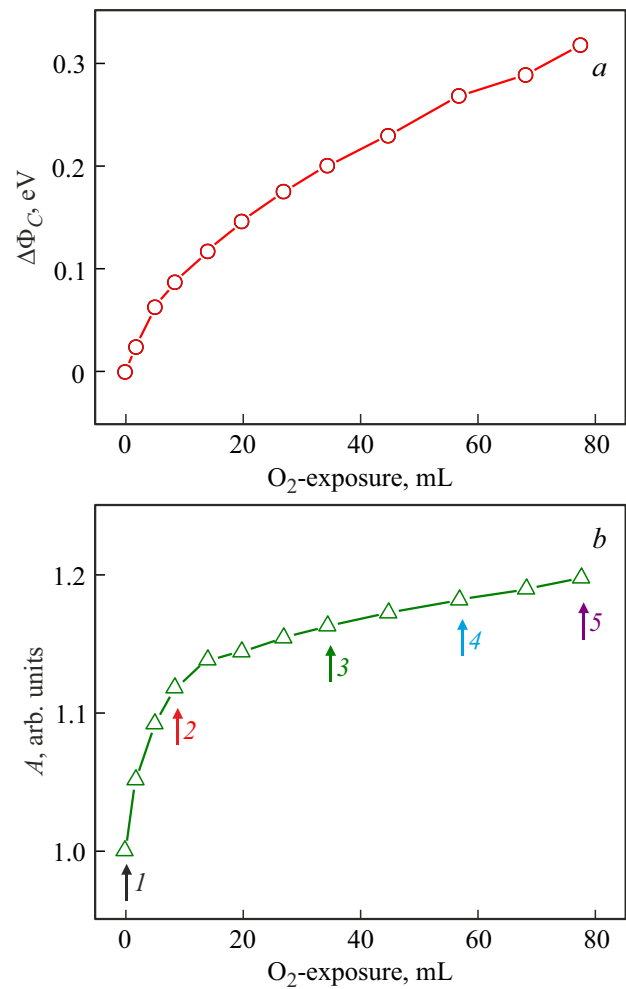


Figure 4. The change in the work function of surface p -GaAs(Cs,O) $\Delta\Phi_C$ (a), and the amplitude of energy distributions A (b) depending on the dose of excess oxygen (in millilangmuirs, mL) in the experiment on transition from NEA to PEA. The arrows indicate the points corresponding to the energy distributions 1–5 in Figure 3.

electrons on 2D „metallic“ cesium clusters which were earlier observed to form on surface Cs/GaAs [20,21]. An increase in the escape probability during the relaxation of cesium layer, as well as during oxygen adsorption, can be explained by the destruction of cesium clusters. The formation of two-dimensional cesium clusters was observed by scanning tunneling microscopy on surface Cs/GaAs(110) [20]. The adsorption of cesium on this surface also led to the appearance of peaks in the electron energy loss spectra (EELS) caused by excitation of local plasmons in Cs clusters [21]. Similar plasmon peaks were observed during the adsorption of cesium on GaAs surfaces with different crystallographic orientations and reconstructions, which indicates the universality of formation pattern for Cs clusters with metallic spectrum of electronic excitations [22]. The exposure of Cs/GaAs(110) surface in oxygen resulted in the disappearance of plasmon

satellites of photoemission spectroscopy lines [23], which is probably related to decay of cesium metallic clusters. The reversible variations in the surface photovoltage and photoluminescence intensity observed in the study [24] upon alternate deposition of cesium and oxygen on the surface of a strongly doped p^+ -GaAs(001) can also be explained by the formation and decay of cesium metal clusters. The microscopic mechanisms of the effect of these clusters on the probability of electrons escaping into vacuum are unclear. Possible mechanisms may consist in an increase in the reflection coefficient of electrons from the adsorbed cesium layer, as well as in diffuse scattering by collective (plasmon) or single-particle excitations of the electron gas in cesium clusters. The blurring of the low-energy electron diffraction pattern on Cs/GaAs(001) surface with large cesium coverages $\theta > 0.5$ ML [25], as well as effect of decrease in photoluminescence intensity [24] support the hypothesis of diffuse electron scattering on cesium clusters.

5. Conclusion

On the surface of p -GaAs(Cs,O) with negative effective electron affinity, the evolution of the energy distributions of emitted electrons during the transition from negative to positive affinity during excess cesium and oxygen deposition was measured. It has been established that the cesium-induced transition from NEA to PEA is accompanied by both, an increase in the surface work function and a significant decrease in the probability of electrons escaping into vacuum. On the contrary, with a similar transition caused by exposure to excess oxygen, the probability of electron escape remains almost unchanged. The possible reason for the effect of cesium on the probability of electrons escape is the reflection or scattering of electrons on two-dimensional clusters of cesium.

Funding

The 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.

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Translated by T.Zorina