Evolution of photoemission properties on Cs/GaAs and GaAs(Cs,O) surfaces under thermal cycling

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Abstract. The photoemission properties on Cs/GaAs and GaAs(Cs,O) surfaces prepared at room temperature were studied under thermal cycling. The evolution of electron affinity and escape probability to vacuum was measured using photoemission quantum yield spectroscopy for the surfaces with various Cs-O overlayer compositions. It was found that an increase in the oxygen exposure led to the improvement in the thermal stability of electron affinity.

1. Introduction

The non-equilibrium processes, which are associated with the adatom adsorption (sticking, diffusion and accommodation) on semiconductor surfaces, are of scientific and practical interest. The observation of non-monotonic cesium dose dependence and relaxational kinetics of photoemission current on the Cs/GaAs surface [1, 2] proves that the non-equilibrium processes play a significant role at room temperature (RT), at which p-GaAs(Cs,O) photocathodes with the state of negative electron affinity are prepared [3]. These photocathodes are widely used in photomultipliers and sources of ultra-cold and spin-polarized electrons [4]. So, the temporal and thermal instabilities of their photoemission properties are a problem that hinders these practical applications. Surfaces with relatively small positive electron affinities also attract attention in relation with the opportunity to increase the efficiency of solar energy converters by using the photon-enhanced thermionic emission (PETE) [5, 6, 7]. The direct photoemission and PETE are illustrated by the pathway 1 and pathway 2 in figure 1, respectively. According to theoretical estimations [5, 6], the working temperature of PETE converters should be relatively high, exceeding 200°C. Thus, for these converters, the issue of the thermal stability of emission properties is highly relevant.

The temperature influence on the Cs/GaAs surface photoemission properties was experimentally studied earlier [8, 9]. In Reference [8], two types of experiments were carried out. First, it was found that the Cs deposition on the p-GaAs surface heated to a moderate temperature (T ~ 100°C) leads to substantial qualitative changes in the shape of Cs coverage dependences of photoemission current and surface band bending, along with the changes of relaxational kinetics after the Cs deposition. Second, the photoemission thermal stability was studied by preparing Cs/GaAs surfaces at room temperature followed by measuring photoemission quantum yield spectra under the heating from RT up to T ~ 100°C and a subsequent cooling down to RT. Substantial irreversible variations in the effective affinity and escape probabilities were observed under such thermal cycling. A possible way to increase the thermal stability of Cs/GaAs photoemission properties consists in adding some oxygen to the
adsorption layer and, thus, forming a GaAs(Cs,O) surface. It is known from the results of the thermal desorption experiments that an oxygen exposure leads to an increase of the cesium binding energy on the GaAs surface [10]. It was proved earlier that the codeposition of Cs and O₂ on the p-GaAs surface at elevated temperatures qualitatively changed the shape of the photoemission current relaxational kinetics and substantially reduced its amplitude [9]. However, the question about the oxygen influence on the photoemission stability of the GaAs(Cs,O) surface prepared at RT under subsequent thermal cycling remained open. The present paper is aimed at answering this question experimentally. It is shown that the increase of the oxygen dose leads to the overall improvement of the p-GaAs(Cs,O) photoemission stability under thermal cycling, as compared to the Cs/GaAs surface without oxygen.

Figure 1. Band diagram of the GaAs(Cs,O) surface with positive effective electron affinity \( \chi^* > 0 \). Thermalization, diffusion, and emission pathways are shown schematically by the stepwise arrows for the direct photoemission (1) and PETE (2).

Figure 2. Photoemission quantum yield spectra measured at the GaAs(Cs,O) surface under heating (curves 1–4) and cooling (curves 4–6). Curve (1) \( T = 20^\circ \text{C} \); (2) \( 40^\circ \text{C} \); (3) \( 60^\circ \text{C} \); (4) \( 80^\circ \text{C} \); (5) \( 40^\circ \text{C} \); (6) \( 20^\circ \text{C} \). Dashed lines indicate the evolution of the thresholds at \( \epsilon_g \) and \( \epsilon_t \).

2. Experimental

The measurements were carried out on the epitaxial p-GaAs(001) layers with hole concentration \( p \approx 7 \times 10^{18} \text{ cm}^{-3} \). Atomically clean GaAs(001) surfaces were prepared by removing oxides in the solution of HCl in isopropyl alcohol under dry nitrogen atmosphere, transferring to an ultrahigh vacuum set-up without air contact, and a subsequent heating in vacuum at \( T \approx 540^\circ \text{C} \) [11, 12, 13]. In the experiments, the temperature was controlled by diffusive reflectance spectroscopy with an accuracy better than ±5°C [11, 14, 15]. Cesium and oxygen were deposited from carefully outgassed dispensers filled with cesium chromate and barium peroxide, respectively. The cesium coverage was determined by the calibration based on the results of X-ray photoelectron spectroscopy [16]. The oxygen exposure was estimated from the time dependence of the oxygen pressure [17, 18].

The evolution of photoemission properties was studied using photoemission quantum yield spectroscopy. To record the photoemission quantum yield spectra, the surface was illuminated by a monochromatic light beam, and the photocurrent was measured. The quantum yield values were obtained after the photocurrent normalization by the incident light intensity. Effective electron affinity \( \chi^* \) and the probability of electron escape to vacuum were determined from the comparison of experimental and calculated quantum yield spectra, as described in References [19, 20].
3. Results and discussion

In order to study the thermal stability of electron affinity and electron escape probability on the GaAs surface with cesium and oxygen overlayers, we measured the quantum yield spectra under thermal cycling. The initial GaAs(Cs,O) surface was prepared at room temperature by the deposition of 0.7 monolayer (ML) of cesium and 0.02 Langmuir (L) of oxygen on the atomically clean GaAs surface. After cesium and oxygen deposions, the surface was kept at room temperature for one hour to complete the major relaxation processes [1, 2, 9]. Then the photoemission quantum yield spectra were measured at elevated temperatures. The average rate of heating and cooling was 10°C every 10 minutes. Figure 2 shows the photoemission quantum yield spectra measured at various temperatures increasing stepwise from \( T = 20°C \) up to 80°C (lines 1-4) and then decreasing from 80°C down to 20°C (lines 4-6). In this experiment the electron affinity on the GaAs(Cs,O) surface remains positive (\( \chi^* > 0 \)). Therefore, two thresholds are observed in the quantum yield spectra [19, 20]. The high energy threshold \( \varepsilon_1 \) corresponds to the onset of the emission of “hot” photoelectrons light-excited with the initial energy above the vacuum level (pathway 1 in figure 1). The low energy threshold at the GaAs band gap \( \varepsilon_g \) corresponds to the emission from the “Maxwellian tail” of the energy distribution of photoelectrons that are excited by light below the vacuum level near the bottom of the conduction band and are thermalized upward in energy owing to the interaction with phonons (pathway 2 in figure 1). Thermal cycling leads to the reversible variations in threshold \( \varepsilon_1 \) caused by the temperature dependence of the GaAs band gap, and to the irreversible variations in threshold \( \varepsilon_g \) caused by the change in the work function on the GaAs(Cs,O) surface due to the thermally stimulated structural relaxation or partial desorption of the Cs-O layer.

Figure 3 shows the evolution of the electron affinity (a) and the escape probability (b) on the GaAs(Cs,O) surfaces under the thermal cycling, which were obtained from the measured spectra. For comparison, in figure 3, the temperature dependences of electron affinity and escape probability on the Cs/GaAs surface from Reference [8] are also shown. As seen in figure 3(a), on the Cs/GaAs surface, effective affinity \( \chi^* \) increased during both heating and cooling. So, the final value of \( \chi^* \) was \( \sim 100 \) meV higher than the initial value. The electron escape probability decreases by an order of magnitude during heating and subsequent cooling (figure 3(b), squares). It is seen that the oxygen deposition on the Cs/GaAs surface leads to the increased stability of electron affinity and escape probability. The electron affinity \( \chi^* \) on the GaAs(Cs,O) surface decreased by only \( \sim 20 \) meV and \( \sim 10 \) meV under heating and cooling, respectively. The observed affinity variations can be caused by the irreversible restructuring of Cs-O overlayer (diffusion, accommodation or, maybe, partial desorption). At the same time, the electron escape probability does not change significantly. Thus, the photoemission properties of the GaAs(Cs,O) surface are more stable under thermal cycling, in comparison with the Cs/GaAs surface.

The thermal cycling experiments presented in figure 3 were performed up to 80°C, while the proposed PETE devices should operate at higher temperatures \( T \geq 200°C \) [5, 6]. The increase of the oxygen dose in the Cs-O overlayer enabled us to increase the maximal temperature in our further studying the thermal stability of emission properties of the GaAs(Cs,O) surface. In these experiments, prior to each heating, 0.75 ML of cesium was deposited on the clean GaAs surface, and then the Cs/GaAs surfaces were exposed to various oxygen doses at room temperature. Figure 4 shows the evolutions of electron affinity and electron escape probability of the GaAs(Cs,O) surfaces with various oxygen concentrations under heating up to \( T \sim 160°C \). The average heating rates were 10°C and 20°C every 10 minutes for opened and closed symbols, respectively. As shown earlier in Reference [19], under the oxygen adsorption on the Cs/GaAs surface, the electron affinity decreases, becomes negative, passes through the minimum at an oxygen dose of about 5 mL, and then increases back to the state of positive effective electron affinity. Therefore, as seen in figure 4(a), the initial value of affinity at room temperature increases with the increasing oxygen doses from 0.01 to 0.04 L.

Although the average heating rates of the GaAs(Cs,O) surfaces with various oxygen exposure values were different, it is seen that, for the low-temperature region \( (20°C < T < 100°C) \), the increase in the oxygen dose leads to a higher thermal stability of the effective affinity. At high temperatures \( T > \)
100°C we observed the increase in the electron affinity even for the highest oxygen dose. This increase can be caused by the onset of a significant desorption of the Cs-O overlayer [10]. It should be noted that, at elevated temperatures, the photoemission quantum yield dramatically decreases, and the interpretation of affinity evolution under cooling these surfaces was complicated by the high noise level in the measured photoemission spectra. Therefore, the cooling stage of the thermal cycle is not shown in figure 4.

As seen in figure 4(b), at elevated temperatures, large variations of the electron escape probability for all oxygen doses were observed. Apparently, the amplitude of these variations is determined by the universal affinity dependence of the escape probability, which consists in a sharp decrease of the escape probability with the increasing affinity above \( \chi^* > 0.2 \) eV \[19, 20\].

It should be noted that the decrease in the escape probability and, hence, photoemission quantum yield \( Y \) at high \( \chi^* \) did not allow us to investigate the thermal stability of the photoemission properties for oxygen doses over 0.04 L. Earlier, in Reference \[10\], the increase in the bond energy of cesium adatoms was observed for the oxygen doses from 0.2 L up to 10 L. In this work it was found that the

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**Figure 3.** Temperature dependences of effective electron affinity \( \chi^* \) (a) and electron escape probability (b) under the heating (empty symbols) and subsequent cooling (filled symbols) of the Cs/GaAs (squares, [8]) and GaAs(Cs,O) (triangles) surfaces. The lines are visual guides. The arrows on the lines show the heating and cooling direction.

**Figure 4.** Temperature dependences of effective electron affinity \( \chi^* \) (a) and escape probability (b) under the heating of the GaAs(Cs,O) surfaces with various oxygen doses. The lines with empty symbols, being obtained at a different heating rate, were copied from figure 3.
increase in the thermal stability of photoemission properties occurs at much smaller doses. However, increasing oxygen doses causes an increase in the electron affinity and a decrease in the escape probability [19]. For possible PETE applications, it is still necessary to find a compromise between the electron affinity, escape probability and thermal stability of photoemission properties.

4. Summary
In summary, in this paper, we experimentally studied the evolution of electron affinity and electron escape probabilities on the GaAs(Cs,O) surface at elevated temperatures. It was shown that, due to oxygen exposure, the photoemission properties of the GaAs(Cs,O) surface are more stable under thermal cycling, in comparison with the Cs/GaAs surface. Furthermore, the affinity evolution was studied under heating GaAs(Cs,O) surfaces with various doses of deposited oxygen, and it was found that the increase in the oxygen dose leads to a further improvement of the thermal stability. However, the obtained GaAs(Cs,O) surfaces are still unstable at high temperatures $T > 100^\circ$C. Therefore, for the possible practical PETE applications of these surfaces, their thermal stability should be substantially increased.

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