Relaxational kinetics of photoemission from Cs/GaAs and GaAs(Cs,O) surfaces at elevated temperatures

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Abstract. The relaxational kinetics of the photoemission from the Cs/GaAs and GaAs(Cs,O) surfaces at elevated temperatures is studied. It was found that heating to moderate temperatures of about 150°C leads to substantial changes in the amplitude and shape of the Cs coverage dependences of the photoemission current, along with the changes of its relaxational kinetics after the cesium deposition. After the oxygen exposure on the GaAs(Cs,O) surface, a photoemission relaxational increase is observed due to changes in the affinity. The temperature dependences of the amplitude and decay time of the relaxational kinetics on the Cs/GaAs and GaAs(Cs,O) surfaces were obtained.

1. Introduction

Gallium arsenide surfaces with adsorbed cesium overlayers have been used for several decades as a model system for studying the initial stages of metal-semiconductor interface formation and as a basis of $p$-GaAs(Cs,O) photocathodes with a negative effective electron affinity (NEA), at which the vacuum level is below the conduction band bottom in the GaAs bulk [1]. Due to high photoemission quantum yield values (up to ~ 50% [2]), $p$-GaAs(Cs,O) NEA photocathodes are widely used in photomultipliers and sources of ultra-cold and spin-polarized electrons [3].

Semiconductor surfaces with relatively small positive electron affinities have recently attracted attention again due to the opportunity for improving solar energy conversion efficiency using the photon-enhanced thermionic emission (PETE) [4, 5, 6]. Figure 1 shows the direct photoemission of hot electrons (path 1), which are excited by light above the vacuum level, and the PETE process (path 2) in which electrons are excited by light below the vacuum level, and acquire additional energy for emission from the heated lattice. Thus the PETE process involves harvesting both the energy of photons and thermal energy of a heated crystal lattice. It was shown theoretically [4, 5] that, for the optimally chosen bandgap, affinity, and temperature values, the use of PETE makes it possible to overcome the Shockley-Queisser limit for the single-bandgap photovoltaic solar cell efficiency [7]. The Cs/GaAs system seems suitable for PETE solar energy converters because the GaAs band gap is close to the optimal value and the effective affinity can be adjusted by the submonolayer Cs coverage deposition.

The problem of the Cs/GaAs system is the cesium overlayer instability at elevated temperatures [8]. Moreover, even at room temperature, the photoemission current kinetics reveals the nonequilibrium character of the Cs/GaAs surface [9, 10]. The solution for this problem may be the use of the GaAs surface with (Cs,O) layers. It is known that oxygen exposure leads to the increase in the
cesium binding energy [11]. In the present work, the photoemission kinetics after the deposition of cesium and oxygen on the GaAs(001) surface at elevated temperatures was investigated in order to study the thermal stability of the GaAs(Cs,O) surface. These experiments allowed us to determine the temperature dependence of the relaxation times and amplitudes of photoemission kinetics.

2. Experimental

The measurements were carried out on epitaxial $p$-GaAs(001) layers with a hole concentration $p = 7 \times 10^{18}$ cm$^{-3}$. Atomically clean GaAs(001) surfaces were prepared by removing oxides in a solution of HCl in isopropyl alcohol under dry nitrogen atmosphere, transferring to an ultrahigh vacuum set-up without air contact, and a subsequent heating in vacuum at a temperature $T \approx 540°C$ [12, 13]. In the experiments, the temperature was controlled by diffusive reflectance spectroscopy with an accuracy better than ± 7°C [14, 15, 16]. Cesium and oxygen were deposited from carefully outgassed dispensers filled with cesium chromate and barium peroxide, respectively. The cesium coverage $\theta$ was determined by the calibration based on the results of X-ray photoelectron spectroscopy [17]. The oxygen exposure was estimated from the time dependence of the oxygen pressure [18, 19].

To measure the photoemission current, the GaAs surface was illuminated by two monochromatic light beams with photon energies $\hbar \omega = 1.82$ eV and $\hbar \omega = 2.75$ eV. In order to extract the photocurrent corresponding to each light beam, the beams were modulated at different frequencies of 3 kHz and 220 Hz, respectively, and the photocurrents were measured by two lock-in-amplifiers. Each light beam intensity was calibrated, and the quantum yield $Y$ was determined from the photoemission current.

3. Results and discussion

In order to compare the thermal stability of Cs/GaAs and GaAs(Cs,O) surfaces, we measured the photoemission quantum yield under the cesium and oxygen deposition at elevated temperatures and during a subsequent relaxation on the GaAs surface. Figure 2 shows the photoemission quantum yield evolutions at two photon energies under the cesium adsorption of $\theta \approx 0.7$ monolayer (ML) and oxygen exposure of $\approx 0.05$ Langmuir (L), and the subsequent relaxation on the GaAs surface at various temperatures in the range of 20°C – 150°C.

At room temperature, a pronounced leading peak at $t = 18$ min ($\theta \approx 0.45$ ML) is observed in the cesium dose dependence. The leading peak evolves into a plateau starting from $T \approx 80°C$. The heights of the peak and plateau gradually decrease with increasing temperature due to an increase in the effective electron affinity. The temperature increase also causes changes in the shape of the oxygen dose dependence. The maximum of oxygen dose dependence was observed at room temperature. At elevated temperatures this maximum shifts to low oxygen doses, and disappears at $T \approx 80°C$. 

![Figure 1. Band diagram of the Cs/GaAs 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).](image-url)
After switching off the cesium and oxygen sources, the relaxational kinetics of the photoemission quantum yield \(Y(t)\) is observed. It was shown earlier [8] that, after switching the Cs source off at room temperature, the relaxational decrease and increase of the photoemission current are observed for small \((\theta \leq 0.4 \text{ ML})\) and large \((\theta > 0.5 \text{ ML})\) Cs coverages, respectively. For intermediate coverages \((0.4 \text{ ML} < \theta \leq 0.5 \text{ ML})\), the photoemission current was relatively stable after switching off the Cs source, with virtually no relaxational kinetics. It was proved that the relaxational decrease in \(Y\) at small coverages is due to the relaxational decrease in the band bending [10]. The band bending relaxation is virtually absent at large coverages \((\theta > 0.5 \text{ ML})\), when two-dimensional Cs clusters with a metallic spectrum of electronic excitations are formed on the Cs/GaAs surface [14]. Therefore, the relaxational increase in \(Y\) is due to decrease in the true affinity, caused by the rearrangement of cesium-induced surface microdipoles in the Cs overlayer. Similar photoemission quantum yield kinetics was also observed under the cesium relaxation on the GaN surface [20].

As seen in figure 2, the dose dependences and relaxational kinetics of the photocurrent, corresponding to different photon energies, are qualitatively similar. However, some additional kinks in the relaxational kinetics at \(\hbar\omega = 1.82 \text{ eV}\) are observed after the cesium adsorption. These kinks may be caused by the nonmonotonic dependence of the thermalized electron escape probability on the affinity [21]. The photon energy increase of up to \(\hbar\omega = 2.75 \text{ eV}\) leads to the emission of hot electrons, which have their monotonic escape probability dependence on the affinity. As a result, the photocurrent features in the dose dependences and relaxational kinetics at \(\hbar\omega = 2.75 \text{ eV}\) are caused by the changes in the effective electron affinity. For this reason, below we analyze the \(Y(t)\) dependences at \(\hbar\omega = 2.75 \text{ eV}\) to elucidate possible microscopic reasons for the relaxational kinetics of the photoemission current.

Figure 3 shows the normalized quantum yield kinetics under the cesium (a) and oxygen (b) relaxations. As seen in figure 3(a), the relaxational increase and decrease in the quantum yield is observed for low \((T \leq 60^\circ\text{C})\) and high \((T \geq 150^\circ\text{C})\) temperatures, respectively. For intermediate temperature, the quantum yield relaxational kinetics is nonmonotonic and has a maximum. This maximum shifts to small times under the temperature increase. The appearance of the maximum may be caused by the changes of the relaxation mechanism. At room temperature, the relaxational decrease in the true electron affinity \(\chi\) causes the photocurrent increase. At higher temperatures, the relaxational decrease in the band bending \(\varphi_S\) was observed [8]. As a result, the domination of the band bending
relaxation at elevated temperatures causes the change of relaxation in $\chi^* = \chi - \varphi_S$ from falling to growing. The nonmonotonic quantum yield kinetics is observed because of the different characteristic relaxation times of $\chi(t)$ and $\varphi_S(t)$ kinetics, which also depend on temperature.

As seen in figure 3(b), after the switching off the oxygen source, the quantum yield increase under relaxation was observed for all temperatures. It is known that oxygen exposure on the Cs/GaAs surface leads to the decrease in the band bending due to the reduction in the density of the Cs-induced surface states [22]. Therefore, the band bending relaxation is virtually absent, and the true affinity relaxational decrease leads to the quantum yield increase.

In order to compare the thermal stability of the Cs/GaAs and GaAs(Cs,O) surfaces, we have plotted the normalized kinetics amplitude versus temperature under the cesium (figure 4(a)) and oxygen (figure 4(b)) relaxations. As seen in figure 4(a), the kinetics amplitude monotonically decreases from 60% to -60% under the temperature increase. As noted above, the decrease in the cesium kinetics amplitude does not indicate the increase in the thermal stability of the Cs/GaAs surface, but is caused by the compensation of the multidirectional $\chi(t)$ and $\varphi_S(t)$ kinetics. The dependence of the kinetics amplitude on temperature under the oxygen relaxation is nonmonotonic, but it does not exceed 25%. Thus, the GaAs(Cs,O) surface is more thermally stable than the Cs/GaAs surface due to the increase in the binding energy of cesium adatoms [8]. However, the electron emission thermal stability of Cs/GaAs or GaAs(Cs,O) systems should be substantially increased for the PETE applications.

The nonmonotonic dependence of the kinetics amplitude on temperature (figure 4(b)) is possibly caused by a contribution of several relaxation processes on the GaAs(Cs,O) surface. In order to determine the quantity and decay times of these contributions, we have plotted the normalized difference between the photoemission quantum yield and the corresponding quantum yield saturation.

![Figure 3. Relaxational kinetics of the photoemission quantum yield after the cesium (a) and oxygen (b) depositions on the GaAs(001) surface at various temperatures. The dependences are normalized by the values measured at the moment of switching off the cesium and oxygen sources (at $t = 0$).](image1)

![Figure 4. Temperature dependence of the normalized kinetics amplitude $(Y_\infty - Y_0)/Y_\infty$ after the cesium (a) and oxygen (b) depositions on the GaAs(001) surface.](image2)
\[ Y_s = \frac{(Y(t) - Y_\infty)}{(Y_0 - Y_\infty)} \] under the cesium (figure 5(a)) and oxygen (figure 5(b)) relaxations. As seen in figure 5, the kinetics at \( t > 10 \) min is well described by an exponent with a decay time \( t_1 \approx 20 \) min. The deviations from this exponent at \( t < 10 \) min, after switching off the cesium and oxygen sources, are accurately described by at least two additional exponents with decay times \( t_2 \approx 3 \) min and \( t_3 \approx 0.5 \) min.

Figure 5. Semi-log plot of the photoemission relaxation kinetics at \( \hbar\omega = 2.75 \) eV after the cesium (a) and oxygen (b) depositions on the GaAs(001) surface at various temperatures.

Figure 6. Temperature dependences of decay times for the partial contributions to the photoemission quantum yield kinetics after the cesium (a) and oxygen (b) depositions on the GaAs(001) surface.

Figures 6(a) and 6(b) show the temperature dependences of the decay time for relaxation after the cesium and oxygen depositions, respectively. As seen in figure 6(a) and figure 6(b), the decay times substantially decrease at elevated temperatures due to the acceleration of the relaxation process. Apparently, each decay time corresponds to a specific energy barrier, which is overcome during relaxation. At the same time, the nonmonotonic temperature dependences of the decay time which are observed under the oxygen relaxation may be caused by a complex distribution of energy barriers. Unfortunately, we cannot exactly specify which relaxation processes correspond to these decay times. Although they are complicated, the temperature dependences of the decay time confirm that the relaxational kinetics of photoemission on the Cs/GaAs and GaAs(Cs,O) surfaces reflect a complex restructuring in the adsorption layer, i.e. diffusion, accommodation or possibly partial desorption of cesium and oxygen adatoms.

4. Summary
To summarize, in this paper we have experimentally studied the quantum yield evolution under the cesium and oxygen adsorptions, and the subsequent relaxation on the GaAs surface at elevated temperatures. Substantial changes in the cesium relaxational kinetics are observed in the relatively narrow temperature range of 20°C – 150°C. Presumably, this observation indicates that new relaxation channels are activated in the non-equilibrium Cs/GaAs system at elevated temperatures. Under the oxygen relaxation the photoemission quantum yield increase is observed for the entire temperature
range. The temperature dependence of the amplitude and decay time of the photoemission kinetics on the GaAs surface under cesium and oxygen overlayers relaxation was obtained. The photocurrent relaxational kinetics on the GaAs(Cs,O) system does not exceed 25%, which confirms the higher GaAs(Cs,O) surface thermal stability, as compared to the Cs/GaAs surface. However, for the PETE application, the electron emission thermal stability of the GaAs(Cs,O) system should be substantially increased.

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