Photoemission properties of flat and rough GaAs surfaces with cesium and oxygen layers

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Abstract. The evolution of surface band bending and the probabilities of electron emission in a vacuum are studied under cesium and oxygen deposition on atomically flat and rough As-rich and Ga-rich GaAs (001) surfaces by means of photoreflectance spectroscopy and photoemission quantum-yield spectroscopy. On the rough surface, as compared to the flat one, the suppression of non-monotonic Cs-induced band bending variations is observed, along with the overall band bending increase. Multiple repeated activations of the GaAs (001) surface by cesium and oxygen followed by vacuum anneals led to an increase in the root-mean-square roughness from $R_q \sim 0.1$-$0.2$ nm up to $\sim 3$ nm. As a result, the probability of electron escape into vacuum decreased by half.

1. Introduction

The $p$-GaAs surfaces with adsorbed cesium and oxygen layers are widely used to create photocathodes with a negative effective electron affinity (NEA) [1]. The surfaces of semiconductors with a relatively low (0.2 - 0.4 eV) positive affinity, such as $p$-GaAs with adsorbed cesium, have recently attracted attention due to the possibility of increasing the solar energy conversion efficiency using photon-enhanced thermionic emission [2, 3, 4]. The quantum yield and other photoemission parameters are determined by a set of electronic properties of Cs/GaAs and GaAs (Cs,O) interfaces, including band structure, kinetic and transport parameters, such as true and effective electron affinity, the magnitude and width of surface band bending, surface recombination rate, and the probability of electron escape into vacuum. It is reasonable to assume that these electronic properties should depend on the morphology of the initial GaAs surface and of the interfaces with the adsorbates [5], but the available experimental data on these dependences are scarce. One can start photoemission studies from a smooth GaAs surface with atomically flat terraces separated by monatomic steps. However, the chemical treatment and vacuum anneals aimed at preparing an atomically clean surface, cesium and oxygen deposition, and additional anneals in vacuum for the adsorbate layers removal may substantially change the surface morphology in the course of the two-stage activation procedure [1]. In particular, the chemical removal of oxides in the solution of HCl in isopropyl alcohol retains the overall step-terraced morphology of the GaAs (001) surface, but it leads to the appearance of small-scale roughness with a monolayer amplitude on terraces [6, 7]. Vacuum anneals also lead to the GaAs(001) surface roughening [8]. The literature does not offer sufficient data concerning the influence of cesium and oxygen deposition, as well as of subsequent vacuum anneals on the surface
morphology. In this work, we studied how the clean surface preparation, repeated cesium and oxygen depositions, and vacuum anneals, which are necessary for the fabrication of \( p \)-GaAs(Cs,O) photoemitters with the state of NEA, affected the surface morphology, as well as electronic properties such as surface band bending, electron affinity, and emission probability in vacuum for Cs/GaAs and GaAs(Cs,O) interfaces.

2. Experimental
The experiments were made on \( p \)-GaAs(001) epitaxial layers and "epi-ready" substrates. The morphology of the surfaces was studied \textit{ex-situ} by atomic force microscopy (AFM). The thermal smoothing of the GaAs(001) surface was performed in conditions close to equilibrium between the surface and Ga and As vapors. The equilibrium conditions during the thermal smoothing were provided by a saturated Ga-GaAs melt placed in a graphite container together with the GaAs sample intended for smoothing [7].

Atomically clean and structurally ordered As-rich and Ga-rich GaAs (001) surfaces were prepared by chemically removing oxides from the solution of HCl in isopropyl alcohol (HCl-iPA) in an inert nitrogen atmosphere, transferring to the ultra-high vacuum setup without air contact, and subsequent annealing in vacuum [9]. The As-rich GaAs surface was obtained by annealing in vacuum at \( T = 400 \) °C. To obtain the Ga-rich GaAs surface, we also used the effect of a Cs-induced decrease in temperature of the transition from an As-rich to Ga-rich surface at \( T = 500 \) °C [10]. Cesium and oxygen were deposited from the degassed dispensers.

The band-bending evolution was measured by means of photoreflectance spectroscopy, using the Fourier transform of Franz-Keldysh oscillations. To provide a uniform electric field near the surface, epitaxial UP\(^+\) structures with thin (~ 100 nm) undoped surface layers were used [11]. A modification of the photoreflectance spectroscopy technique to a "real-time" version allowed us to measure the band-bending evolution during the Cs deposition with high precision [12]. The photoemission was measured in the "reflection" geometry from the illuminated surface. The effective electron affinity and the probability of escape of "thermalized" and "hot" electrons into vacuum were determined from the photoemission quantum yield spectra according to the procedure described in [4].

3. Results and discussion
To study the relation between the GaAs(001) surface morphology and the electronic states at the Cs/GaAs(100) interface, we measured the band-bending evolution under the Cs deposition on the smooth step-terraced as-grown \( p \)-GaAs(001) structures with the root-mean-square \( R_q \sim 0.2 \) nm (figure 1(a)), on the same epitaxial surfaces subjected to annealing in equilibrium conditions (figure 1(b)), and on the rough surface of the epitaxial structure obtained by annealing in non-equilibrium conditions (figure 1(c)). It is seen in figure 1(a) that the as-grown GaAs surface has a step-terraced morphology with flat terraces separated by monatomic steps, although the steps have a strongly jagged shape, presumably due to the kinetic instabilities during their growth. As seen in figure 1(b) the thermal smoothing in

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equilibrium conditions led to a notable improvement of the step-terraced morphology, in particular, to less jagged steps, although the root-mean-square roughness remained practically the same at $R_q \sim 0.2$ nm. Annealing in non-equilibrium conditions led to the destruction of the step-terraced morphology, the formation of a rough relief with dips and hills, and a roughness increase up to $R_q \sim 1$ nm (figure 1(c)).

The evolutions of band-bending $\phi_S$ are shown in figure 2 for the Cs deposition on As-rich (a) and Ga-rich (b) GaAs(001) surfaces. It is seen that the shape of $\phi_S(\theta)$ is different for the As-rich and Ga-rich surfaces [10, 12]. On the As-rich surface, $\phi_S$ increased steeply at small Cs coverages ($\theta \sim 0.1$ monolayer (ML)) and went through a maximum at larger coverages, while on the Ga-rich surface, several distinct maxima and minima ("fine structure") were reproducibly observed [12]. It is seen that the shape of $\phi_S(\theta)$ was similar for the as-grown sample and for the sample annealed in equilibrium, which is in agreement with the fact that both samples were atomically smooth with their qualitatively similar step-terraced morphology. Thus, the difference in the size and shape of monatomic islands and steps on the initial step-terraced GaAs surfaces did not substantially affect the dose dependences of the band bending. On the contrary, on the rough surface, the shape of $\phi_S(\theta)$ was distinctly different, with a substantially higher value of $\phi_S$ on the clean surface and a reduced amplitude of $\phi_S$ variations with the Cs coverage, including a less pronounced "fine structure". A possible reason for the distinction is a much higher defect-induced density of the surface states in the middle of the band gap on the rough surface. These states cause the initial band bending and restrict its variations under the Cs deposition.

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**Figure 2.** Evolution of the band bending $\phi_S$ under the Cs deposition on the as-grown GaAs(001) UP$^+$ structures (circles), on the structures annealed in equilibrium conditions (triangles), and on the rough (squares) As-rich (a) and Ga-rich (b) GaAs(001) surfaces.

It should be noted that cesium and oxygen deposition followed by annealing in vacuum may cause substantial changes in the GaAs surface relief. These changes should be taken into account when analyzing the relations between the surface morphology and electronic properties of Cs/GaAs and GaAs(Cs,O) interfaces. Figure 3(a) shows the AFM image of the initial as-grown step-terraced surface of an epitaxial $p$-GaAs layer. After removing oxides in HCl-iPA followed by annealing in vacuum at 400 °C, which yields a clean As-rich GaAs(001) surface, 0.5 ML of Cs was deposited; the second
anneal was made at 400 °C, after which the sample was retrieved from the vacuum setup and the AFM image shown in figure 3(b) was taken in the air. The image shown in figure 3(c) was obtained on a similar sample by means of the same procedure, except for that both anneals were made at 500 °C, which corresponds to the Ga-rich surface formation [10]. As seen in figure 3(b), the cesium adsorption on the As-rich surface and annealing in vacuum at $T = 400 \, ^\circ\mathrm{C}$ led to a deterioration in the step-terraced morphology, although the monatomic steps are still visible. A similar procedure with the anneals at a higher temperature $T = 500 \, ^\circ\mathrm{C}$ led to the appearance of "islands" with diameters of ~50 - 70 nm, heights of ~1 - 3 nm and a density of ~10 $\mu\text{m}^{-2}$. On the surface areas between the islands, the step-terraced morphology disappeared, and the root-mean-square roughness increased from $R_q \sim 0.12$ nm on the initial surface up to $R_q \sim 0.22$ nm.

Figure 3. 1×1 $\mu\text{m}^2$ AFM images of the as-grown GaAs (001) surface (a), after the Cs deposition and annealing in vacuum at $T = 400 \, ^\circ\mathrm{C}$ (b) and $T = 500 \, ^\circ\mathrm{C}$ (c).

Figure 4 shows the AFM images of an "epi-ready" p-GaAs substrate, which was first brought to the step-terraced morphology by thermal smoothing in equilibrium conditions at $T = 650 \, ^\circ\mathrm{C}$ (a, d), activation by cesium and oxygen to the state of NEA and annealing in vacuum at $T = 500 \, ^\circ\mathrm{C}$ (b, e), and subsequent etching in HCl-iPA (c, f).

Figure 4 shows the AFM images of an "epi-ready" p-GaAs substrate, which was first brought to the step-terraced morphology by thermal smoothing in equilibrium conditions (figure 4(a)), and then activated to the state of NEA by cesium and oxygen deposition followed by annealing in vacuum at

Figure 3. 1×1 $\mu\text{m}^2$ AFM images of the as-grown GaAs (001) surface (a), after the Cs deposition and annealing in vacuum at $T = 400 \, ^\circ\mathrm{C}$ (b) and $T = 500 \, ^\circ\mathrm{C}$ (c).

Figure 4 shows the AFM images of an "epi-ready" p-GaAs substrate, which was first brought to the step-terraced morphology by thermal smoothing in equilibrium conditions (figure 4(a)), and then activated to the state of NEA by cesium and oxygen deposition followed by annealing in vacuum at
$T = 500 \, ^\circ C$ (figure 4(b)). The comparison of figures 3(c) and 4(b) shows that similar islands appeared on the surface, although with a larger concentration in the latter case. One can presume that these islands are gallium droplets [13], although we did not determine the chemical composition of the islands directly in this work. Figure 4(c) shows the image of the same sample after treatment in HCl-iPA. Instead of islands, pits of about the same sizes and concentration are seen in the image. This change in the morphology can be interpreted as a result of etching off the Ga droplets and, thus, it supports the assumption about the nature of the droplets.

The results of photoemission studies on the GaAs(Cs,O) surfaces with various morphologies are summarized in figure 5. The measured probabilities of electron escape in vacuum for "thermalized" $P_t$ (a) and "hot" $P_h$ (b) photoelectrons versus the effective affinity $\chi^*$ are shown here. These dependences were measured under an additional "excessive" oxygen exposure of the GaAs(Cs,O) surfaces "optimally" activated to the state of NEA. The minimum in $P_t$ near $\chi^* \approx 0$ was explained in [14] by the changeover in the emission mechanism under the transition from the positive to the negative effective affinity. It is seen in figure 5 that, for the rough surface with $R_q \approx 3 \, \text{nm}$ formed due to multiple cycles of activation and annealing, the escape probabilities are systematically lower than those measured on a smoother surface during the first activation cycle (by a factor of 1.3-2). According to figure 5, the photoemission quantum efficiency of the GaAs(Cs,O) surfaces activated to the state of NEA affinity decreases from 25% at a relatively flat surface to 12% at a rough surface. This decrease is partly due to a smaller absolute value of $\chi^*$ (by 15 meV), and partly due to a smaller electron escape probability. In its turn, the decrease in the escape probabilities can presumably be associated with the electron scattering on the rough surface.

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**Figure 5.** Escape probabilities for thermalized (a) and hot (b) electrons from the GaAs(Cs,O) surface versus the effective electron affinity under the oxygen deposition at the surface with $R_q\sim0.5 \, \text{nm}$ (triangles) and $R_q\sim3 \, \text{nm}$ (circles).

4. Summary

In conclusion, this work presents experimental evidence of the complex spectra of adatom- and defect-induced surface states on the Cs/GaAs (001) surface. The comparison of the band bending behavior under the Cs deposition on atomically flat and rough surfaces proves that surface roughness produces the defect-induced surface states which restrict the adatom-induced band bending variations. The initial as-grown GaAs surface morphology evolution upon annealing in vacuum and cesium adsorption were studied. It is shown that the surface became rough after annealing in vacuum at $T = 500 \, ^\circ C$, and...
islands of up to 3 nm in height appeared. The surface roughening under repeated activation by cesium and oxygen and annealing in vacuum led to an increase in the root-mean-square roughness by an order of magnitude up to $R_q \approx 3$ nm. As a result, the electron escape probability and photoemission quantum yield decrease by factors of 1.3 - 2.

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