Photovoltage measurement by modulated photoemission on the \(p\)-GaAs surface with cesium overlayers

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Abstract. A contactless two-beam modulated photoemission technique for measuring the photovoltage on the surface of highly doped semiconductors is proposed and verified for the \(p^+\)-GaAs surface with adsorbed Cs. The surface photovoltage evolution under the Cs deposition on the highly doped \(p^+\)-GaAs surface is compared with that observed on Cs/UP\(^+\)-structures by the photoreflectance spectroscopy method. The pump intensity dependence of the photovoltage is measured. This allows us to determine the absolute photovoltage values.

1. Introduction
The photovoltage on a semiconductor surface consists in reducing the surface band bending due to the separation of photogenerated electrons and holes in a surface electric field and, as a consequence, to a partial screening of this field [1]. The photovoltage effect underlies the operation of photodetectors on Schottky barriers and should be taken into account when determining the band bending magnitude using optical and photoemission spectroscopies [2]. The photovoltage substantially affects the operation of GaAs(Cs,O) photocathodes with the negative effective electron affinity (NEA) [3]. In the NEA photocathodes, due to the activating (Cs,O) overlayer, the vacuum level is lower than the conduction band bottom in the semiconductor bulk (figure 1(a)). Therefore, the photoelectrons that have reached the emitting surface can escape into vacuum without additional energy consumption. This provides a high quantum yield of NEA photocathodes, which are widely used in photomultipliers and sources of ultra-cold and spin-polarized electrons [4, 5]. The NEA value \(\chi^* = \chi - \phi\) depends on the true affinity \(\chi\) (which remains positive on the GaAs(Cs,O) surface) and the band bending \(\phi\). Therefore, a decrease in \(\phi\) due to the photovoltage leads to a decrease in the absolute value of the effective affinity \(\chi^*\) and, as a consequence, to a decrease in the photoemission quantum yield. When a semiconductor NEA photocathode is illuminated with powerful laser pulses, an almost complete flattening of the surface band bending can occur during the pulse due to the photovoltage [6]. As a result, the transfer from a state with NEA to a state with close to zero or even positive electron affinity takes place, and the photoemission quantum yield decreases sharply. This limits the number of electrons emitted to vacuum during a single pulse (the so-called "charge limit problem"). The photovoltage magnitude contains information on the processes of photoelectron accumulation near the surface, their capture on surface states and subsequent recombination [1, 7, 8].

Earlier, the photovoltage evolution during the cesium and oxygen adsorption on the GaAs surface was studied by the non-contact photoreflectance technique, since the amplitude of the photoreflectance signal \(\Delta R/R\) is proportional to the photovoltage value [9–13]. These studies were carried out on \(p\)-GaAs epitaxial layers with a moderate doping level \(p \approx 3 \times 10^{17}\) cm\(^{-3}\) [9], as well as on special GaAs...
structural with a thin (≈ 10 nm) undoped layer grown on top of heavily doped $p^+$-GaAs [14–16].

It was shown in [13] that, during the cesium adsorption, the photovoltage sharply increases due to an increase in the band bending, saturates, and decreases by more than an order of magnitude when the cesium coverage exceeds 0.5 monolayer (ML) due to an increase in the local conductivity in the cesium overlayer during the formation of Cs clusters. Unfortunately, the photoreflectance technique does not allow one to determine the magnitude of band bending and photovoltage on the surface of heavily doped $p^+$-GaAs with hole concentrations $p > 5 \times 10^{18} \text{cm}^{-3}$ characteristic of the NEA photocathodes, since the photoreflectance signal for such high doping levels becomes immeasurably small. Therefore, the question about the photovoltage evolution on the surface of heavily doped $p^+$-GaAs with adsorbates remains open.

In this paper, we propose a method for measuring the surface photovoltage by modulating the photoemission current caused by a probe light beam from a monochromator using an additional modulated laser pump beam, which modulates the surface band bending by generating electron-hole pairs near the surface. This technique has been tested for the Cs/$p^+$-GaAs system. The photovoltage evolution with increasing Cs coverage is compared with the data previously obtained on GaAs UP$^+$-structures.

2. Experimental

The photoemission measurements were carried out on epitaxial $p^+$-GaAs(001) layers with a hole concentration $p \approx 7 \times 10^{18} \text{cm}^{-3}$. The photoreflectance spectra were measured on homoepitaxial undoped/$p^+$-doped (UP$^+$) GaAs structures [15]. The UP$^+$-structure consists of a highly doped $p^+$-GaAs buffer layer (with a thickness of $\approx 1 \mu \text{m}$ and an acceptor concentration of $\approx 10^{18} \text{cm}^{-3}$), which is grown on a semi-insulating GaAs(001) substrate, and of a thin (≈ 100 nm) undoped $i$-GaAs layer that is grown atop the buffer layer. 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 any air contact and subsequent heating in vacuum [17, 18]. The measurements were carried out at room temperature $T = 300 \text{K}$. Cesium was deposited from carefully outgassed dispensers filled with cesium chromate. The cesium coverage was determined by the calibration based on the results of X-ray photoelectron spectroscopy [19].

**Figure 1.** Band diagram of the GaAs(Cs,O) surface with negative effective electron affinity $\chi^* < 0$ (a) and positive effective electron affinity $\chi^* > 0$ (b). The arrows schematically show the interband optical transition of electrons from the valence band to the conduction band, thermalization and diffusion to the emitting surface. The band diagrams in the dark and under illumination, with an account of photovoltage $\Delta \phi$, are shown by solid and dashed lines, respectively.
In order to measure the photovoltage, a two-beam technique was used. Figure 2 shows a schematic diagram of the experimental setup. The GaAs surface was illuminated by two modulated beams: a high-intensity pump beam of a laser diode with $h\nu_{1} = 1.8$ eV and a low-intensity probe beam from a monochromator with a photon energy $h\nu_{2} = 2.5$ eV. The intensity modulation frequencies were $f_{1} = 1.31$ kHz and $f_{2} = 0.32$ kHz, respectively. The total laser power was 30 mW. The laser pump beam caused the modulation of the surface band bending and the work function with a frequency $f_{1}$ (figure 1(b)). The probe beam caused the photoemission which was modulated with a frequency $f_{2}$. As a result, the photoemission from Cs/GaAs was modulated by both frequencies $f_{1}$ and $f_{2}$. Therefore, the signals at the sum and difference frequencies were proportional to the photovoltage. By analogously multiplying the $f_{1}$ and $f_{2}$ reference signals and attenuating the difference frequency $f_{1} - f_{2}$ using a high-pass filter, the $f_{1} + f_{2}$ reference signal was obtained for the lock-in detection of the photoemission signal on the $f_{1} + f_{2}$ frequency. In order to subtract the spurious signals caused, in particular, by the laser pump-induced photoemission, we closed the monochromator probe beam every 20 seconds. As a result, the signal difference measured for the open and closed probe beam was taken as a useful signal $\Delta I$. This difference is proportional to the surface photovoltage magnitude. In addition to the signal $\Delta I$, the signal phase shift was also measured. As it was shown earlier [10, 13], the phase shift allows determining the photovoltage relaxation time.

3. Results and discussion

In order to verify the proposed modulated photoemission technique, we measured the dose dependence of the surface photovoltage during the cesium deposition on the $p'$-GaAs(001) surface. Figure 3(a) shows the dependences of photocurrents caused by the pump and test beams, which are measured at frequencies $f_{1}$ and $f_{2}$ under the Cs deposition. As can be seen in figure 3(a), at the cesium adsorption, the photocurrent increases, goes through a maximum and then decreases. This maximum is due to the nonmonotonic behavior of the effective electron affinity during the Cs adsorption on the GaAs(001) surface [20, 21]. In the cesium adsorption process, the electron affinity decreases at small Cs coverages ($\theta < 0.45$ ML), reaches a minimum at $\theta \approx 0.45$ ML, increases by $\sim 0.1$ eV and saturates at $\theta \geq 0.7$ ML. Meanwhile, the electron effective affinity remains positive for all cesium coverages (figure 1(b)). As seen in figure 3(a), an increase in the photon energy leads to a shift in the photoemission maximum towards smaller cesium coverages. The dependence of the photoemission maximum position on the photon energy was observed earlier and can be associated with a nonmonotonic and different dependence of the probability of escape of hot and thermalized electrons into vacuum during the cesium adsorption [20–23].

The dependence of the photoemission signal measured at the sum frequency, normalized to the photoemission current for the photon energy $h\nu_{2} = 2.5$ eV is shown in figure 3b (the left scale). For comparison, the dependence of the photoreflectance amplitude $AR/R$, measured on the GaAs UP*-structure, as described in [24], is also shown in figure 3(b) (the right scale). As shown in [9–13], the photoreflectance signal is proportional to the surface photovoltage. It is seen in figure 3(b) that, despite the obvious difference in the shapes, both photovoltage curves increase at small Cs coverages $\theta$, go through a maximum at $\theta \approx 0.35$ ML and sharply decrease at $\theta > 0.4$ ML. Also, an additional

Figure 2. The schematic diagram of the experimental setup. On the right panel: time profiles of the pump $f_{1}$ and probe $f_{2}$ light intensities and photocurrent.
maximum at a small coverage $\theta \approx 0.07$ ML is observed at the GaAs UP$^+$-structure, which is revealed as a weaker shoulder at the $p^+$-GaAs surface at $\theta \approx 0.1$ ML.

A sharp increase in the surface photovoltage at small Cs coverages was explained by a sharp increase in the band bending due to the formation of adatom-induced surface states and by the effective capture of photoelectrons by these positively charged donor-like states [13, 24]. The non-monotonic evolution of the photovoltage with more than one maximum correlates with the non-monotonic behavior of the band bending on the Cs/UP$^+$ GaAs structure. A much sharper initial increase in the surface band bending and photovoltage observed on the UP$^+$-structure is due to a much lower concentration of positively charged surface states (and, thus, Cs adatoms) needed to cause a certain band bending at the UP$^+$-structure with a much larger width of the surface electric field region ($\approx 100$ nm), as compared to $p^+$-GaAs ($\approx 10$ nm). A sharp drop in the photovoltage at large coverages $\theta > 0.4$ ML, which is observed on both structures, is caused, presumably, by the formation of cesium clusters on the GaAs surface, which leads to an increase in the local surface conductivity and an increase in the surface recombination rate. As a result, the photovoltage on the Cs/GaAs surface decreases.

By measuring the $\Delta I$ signal by the lock-in amplifier at the sum of modulation frequencies, we also detected a phase shift of the signal which is determined by the photovoltage relaxation time (not shown). However, we could not calculate the relaxation time from the obtained phase shift values, because it was difficult to determine accurately the initial (reference) phase shift of our signal $\Delta I/I$. We are going to overcome this difficulty by experimentally determining the initial phase in experiments with semiconductor photodiodes, where the photovoltage relaxation time should be much shorter than on the semiconductor surface.

Figure 3. Dose dependence of the photocurrent of the photon energy $h\omega_1 = 1.8$ eV (line 1) and $h\omega_2 = 2.5$ eV (line 2) (a) and photovoltage measured by the modulated photoemission (left scale, squares) and photoreflectance (right scale, triangles) methods (b).

Figure 4. Dependence of the photovoltage (a) and phase shift (b) on the laser intensity at the photon energy of the probe beam $h\omega_2 = 2.5$ eV (circles) and $h\omega_2 = 1.47$ eV (triangles).
To further test the method, the photovoltage dependence on the laser pump power was measured. Figures 4(a) and 4(b) show by circles the dependence of the $\Delta I/I$ signal and the phase shift of the signal on the laser pump intensity. These dependences were measured at a Cs coverage $\theta \approx 0.25$ ML. After the cesium deposition, the Cs/GaAs surface was kept at room temperature for 20 minutes to complete the major relaxation processes [20, 25, 26]. The laser pump intensity was controlled by neutral filters. In the measured dependences, two regions I and II can be distinguished, corresponding to low and high laser intensities. In region II, an increase in the pump intensity leads to an increase in the photovoltage. As seen in Figure 4a, the photovoltage dependence is a power law. The approximation of this dependence by a power function $\Delta I/I = P^\beta$ made it possible to determine the exponent $\beta = 0.84 \pm 0.05$. The difference between the exponent $\beta = 0.84$ and unity can be caused by saturating the photovoltage at a high pump intensity. As a result, we observe the initial stage of this saturation which causes a decrease in $\beta$.

A decrease in the laser pump intensity leads to a decrease in the photovoltage and, in region I, the photovoltage does not depend on the laser pump intensity. In this region, the laser-generated photovoltage magnitude becomes smaller than the photovoltage from the monochromator. Therefore, the saturation of the photovoltage signal is caused by the photovoltage from the monochromator beam. Since the photovoltages from the laser and the monochromator are generated at different frequencies $f_1$ and $f_2$, this leads to the corresponding phase shift in the recorded signal $\Delta I/I$. As a result, an increase in the laser pump intensity causes an increase in the phase shift (see figure 4 b). It should be noted that, in this case, the phase shift is changed by more than 90 degrees. This large phase shift is not clear and can be caused by phase shifts in electrical components when the photovoltage generation frequency is changed.

In order to determine the photovoltage magnitude, an experiment was also carried out for the probe monochromator beam with a photon energy $\hbar \omega = 1.47$ eV, which is near the GaAs band gap (figure 4(a) and 4(b), triangles). This photon energy is larger than that of the GaAs band gap $\varepsilon_g = 1.42$ eV, but smaller than the threefold of direct photoemission $\varepsilon_f = 1.7 - 2.1$ eV on the Cs/GaAs surface. As was shown earlier [21, 27], in this case, the electrons emit to vacuum from the Maxwell tail of the distribution function. As a result, the photocurrent of such electrons is proportional to $I \approx \exp(-\varepsilon_f/\kappa T)$. Then, the modulation of photoemission due to the photovoltage is $\Delta I/I \approx \Delta \chi^*/kT$. Thus, by measuring the signal for the photon energy of 1.47 eV, we can determine the absolute (in meV) photovoltage value. However, the decrease in the photon energy causes a dramatic decrease in the quantum yield and photocurrent. Therefore, we can obtain a useful photovoltage signal only for a high laser intensity. Since, the photovoltage in region II is determined mainly by the laser intensity, we believe that the photovoltage value does not depend on the photon energy of the probe beam. Therefore, the photovoltage dependences on the laser intensity for different photon energies of the probe beam were equated.

4. Summary

In summary, in this paper, a method for photovoltage measurement on highly doped semiconductors was tested. The photovoltage on the GaAs surface, which is generated by a laser beam, modulated the work function and photoemission current. We determined the photovoltage by the modulated photocurrent. In this work, we compared the photovoltage dependences on the highly doped $p^+$-GaAs surface and the surface of the GaAs UP$^*$-structure. A decrease in the photovoltage at a Cs coverage $\theta > 0.4$ ML is observed on both surfaces. The pump intensity dependence of the photovoltage was measured. The two regions with the photovoltage generation from the laser and probe beams were observed. The absolute photovoltage values were determined in the experiment with the photon energy of the probe beam near the GaAs band gap.
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