Surface photovoltage in a $p$-GaN(Cs) photocathode

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Abstract. Temperature and optical power density dependences of the photovoltage at a $p$-GaN(Cs) photocathode surface were measured in the temperature range 90–295 K. The study demonstrated that band bending at the $p$-GaN(Cs) photocathode surface can be reduced by $\sim 0.5$ eV without modifying the surface atomic structure. The surface photovoltage impact on the $p$-GaN(Cs) photocathode quantum efficiency and photoelectron energy distributions was analyzed.

1. Introduction
The study of low-energy photoelectron emission from $p$-GaN photocathodes with effective negative electron affinity (NEA) [1] is of practical and scientific interest. At a semiconductor surface with NEA, the vacuum level is located below the bottom of the conduction band in the bulk of the semiconductor (see figure 1). Photocathodes with NEA based on $p$-GaN are one of the key elements of the ultraviolet position-sensitive single-photon detectors [2, 3] and are promising candidates for electron sources in photoinjectors [4, 5]. Photoemission studies of GaN surfaces with NEA were used to obtain information about the energy spectrum of GaN [6, 7], elastic and inelastic scattering of photoelectrons during their emission from NEA semiconductors into vacuum [8–11].

Upon illumination, the surface photovoltage effect [12] may occur, which leads to a reduction of the surface charge in $p$-type semiconductors due to the charge of non-equilibrium photoelectrons (see figure 1). As a result, the surface band bending decreases and the semiconductor work function increases. The surface photovoltage leads to undesirable effects such as a decrease in the quantum efficiency ($QE$) of the semiconductor photoemitters [13–15] and a photoinduced shift of electronic spectra in photoemission spectroscopy of semiconductor surface states [16, 17]. At the same time, the surface photovoltage can be used as a tool to study the photoemission properties of the surface [14] and to determine the magnitude of surface band bending using photoreflectance spectroscopy [18].

Note that GaN is a wide-bandgap semiconductor ($\epsilon_g \approx 3.5$ eV), and the surface band bending on the $p$-GaN surface can reach $\sim 3$ eV [1]. Thus, the magnitude of the surface photovoltage on $p$-GaN can reach high values, especially at low temperatures [16]. In [19], it was shown that in ultraviolet and X-ray photoelectron spectroscopy studies of clean $p$-GaN surfaces the value of the surface photovoltage ($SPV$) can reach $\sim 1.5$ eV at low temperatures. Thus, it is possible to modify the value of surface band bending of a $p$-GaN photocathode through the surface photovoltage by varying the intensity of
illumination. The ability to modify surface band bending without changing the atomic structure of the surface can be useful in low-energy photoelectron spectroscopy [8-11].

In [19], the authors point out that it was difficult to describe the dependence of the surface photovoltage of a p-GaN surface on temperature by existing analytical models. They believe that this was due both to the inadequacy of the models themselves and to the presence of defects in the near-surface region of p-GaN, the concentration of which is poorly controlled. Indeed, heavily doped p-GaN epitaxial layers can have a rather high concentration of point defects [20], the value of which strongly depends on the growth technology of a GaN film. These defects can affect the magnitude of the surface photovoltage [12]. The surface photovoltage on clean p-GaN surfaces was studied previously [19]. The adsorption of alkali-metal atoms on the surface of semiconductors can significantly change the electronic structure of the surface and, accordingly, the surface photovoltage magnitude [13, 17, 18]. A detailed study of the surface photovoltage effect on a p-GaN surface with a NEA state created by the adsorption of alkali metal atoms has not previously been conducted.

![Figure 1. Energy diagram of a p-GaN(Cs) photocathode in the dark (dashed) and under band-to-band illumination (solid). The surface photovoltage SPV, the current of photoelectrons trapped at the surface \( J_{\text{sp}} \), the current of equilibrium holes \( J_{\text{h}} \), and the photocurrent \( J_{\text{ph}} \) are shown.](image)

In this work, we studied the surface photovoltage effect at the surface of a p-GaN(Cs) photocathode in the temperature range 90–295 K. The steady-state SPV is determined by measuring the contact potential difference (\( U_{\text{cpd}} \)) between a p-GaN(Cs) photocathode and a metal anode in a vacuum photodiode. It was shown that it is possible to reduce the band bending on the surface of a p-GaN(Cs) photocathode by \( \sim 0.5 \) eV without modifying the atomic structure of the surface. The surface photovoltage dependence on temperature was measured, and the mechanisms for the formation of the surface photovoltage on a p-GaN(Cs) surface are discussed. The dependence of the photoemission characteristics of a p-GaN(Cs) photocathode on SPV is analyzed.

2. Experimental details

The measurements were performed with a homemade planar photodiode where a transmission-mode p-GaN(Cs) photocathode and a metallic anode were mounted parallel to each other in a hermetically sealed titanium-aluminum case. The diameters of the photocathode and anode were 18 mm. The distance between them was \( \sim 0.3 \) mm. The photocathode was fabricated from a p-GaN/AlN heterostructure grown on a (0001) sapphire substrate by MOCVD. The thickness of the wurtzite p-GaN layer of the photocathode was 170 nm, and the concentrations of magnesium and free holes (at 295 K) in this layer were \( 1 \times 10^{19} \) and \( \sim 2 \times 10^{17} \) cm\(^{-3} \), respectively. The methods of cleaning the p-GaN surface were described in [21]. Cesium was deposited on a clean p-GaN surface at room temperature in ultrahigh vacuum until the maximal \( QE \) was obtained. The photocathode \( QE \) at a wavelength of 350 nm was 6 %.

The measurements were performed using a setup consisting of a stabilized xenon lamp, a monochromator, quartz lenses, a liquid-nitrogen optical cryostat, a digital lock-in amplifier, several DAC–ADC units, and a computer. The system of lenses was used to homogeneously illuminate the photocathode center. A diaphragm with an aperture of 3 mm was installed in front of the photocathode. The maximal optical power density at the photocathode was \( P_{\text{om}} \approx 0.1 \) mW/cm\(^2\).
Calibrated neutral-density filters were used to attenuate the optical power density \( (P_o) \) by up to five orders of magnitude. In all experiments, the photon energy of light was \( h\omega \approx 3.65 \) eV. When measuring \( QE \), an accelerating voltage of 12 V was applied to the anode. When measuring the first and the second derivatives of photocurrent with respect to the voltage, a controlled DC voltage \( U \) and an AC voltage with an amplitude of 40 mV were simultaneously applied to the anode. The amplitudes of the first and second harmonics of the AC photocurrent component as a function of \( U \) were measured by a digital lock-in amplifier.

The photoemission was studied in the temperature range 90–295 K. The time to reach the steady-state \( \text{SPV} \) at a \( p \)-GaN surface can strongly depend on the temperature and optical power density [22]. In our experiments, the time to approach the steady-state photocurrent values reached several hours at the lowest temperatures and low optical power densities, which prevented the accurate measurement of the steady-state \( \text{SPV} \) under such experimental conditions.

### 3. Results and discussion

Figure 2 shows the photocurrent-voltage characteristics \( (J_{ph}(U)) \) of a vacuum photodiode with a \( p \)-GaN(Cs) photocathode, measured at two different values of \( P_o \) at room temperature. The curves are normalized to \( P_o \). At low voltages, the photocurrent is zero, since there is a contact potential difference between the photocathode and the anode. As the voltage increases, the photocurrent begins to increase rapidly. With a further increase in \( U \), the photocurrent grows and reaches saturation, since in this case an external acceleration voltage exceeding \( U_{cpd} \) is applied between the photocathode and the anode and now all photoelectrons can reach the anode. The voltage between the photocathode and the anode, at which the photocurrent reaches saturation, was designated as \( U_{sat} \). The value of \( U_{sat} \) was determined by the position of the peak in the second derivative of \( J_{ph}(U) \) with respect to \( U \) [23], which are shown in the inset in figure 2. It is seen from figure 2 that the photocurrent normalized to \( P_o \) decreases with an increase in \( P_o \) in the saturation region. Note that the photocurrent in the saturation region divided by \( P_o \) is proportional to the \( QE \) of the photocathode. Thus, the \( QE \) of the \( p \)-GaN(Cs) photocathode decreases with increasing light power density \( P_o \). As seen from figure 2, \( U_{sat} \) decreases with increasing \( P_o \). Since \( U_{sat} \) at low light power densities \( P_o \) is equal to \( U_{cpd} \), the change in \( U_{sat} \) is determined by the change in the work function of the \( p \)-GaN(Cs) photocathode. Thus, the work function of the \( p \)-GaN(Cs) photocathode decreases with increasing \( P_o \).
Figure 3. The saturation voltage of a $p$-GaN(Cs) photodiode versus the optical power density at 295 K (squares), 200 K (circles) and 90 K (triangles).

Figure 4. The quantum efficiency of a $p$-GaN(Cs) photocathode versus the optical power density at 295 K (squares), 200 K (circles) and 90 K (triangles).

Figure 3 and figure 4 show the dependences of $U_{\text{sat}}$ and $QE$ on the optical power density for different temperatures. We first considered the dependence $U_{\text{sat}}(P_{\text{o}})$ at a temperature of 295 K. As can be seen from figure 3, $U_{\text{sat}}$ is practically independent of $P_{\text{o}}$ at low $P_{\text{o}}$. When a certain power density is exceeded ($\sim 10^6$ W/cm$^2$), $U_{\text{sat}}$ begins to decrease as a logarithm of $P_{\text{o}}$. As the temperature decreases to 200 K, the dependence $U_{\text{sat}}(P_{\text{o}})$ does not change but the decrease in $U_{\text{sat}}$ begins to occur at a much lower power ($\sim 10^4$ W/cm$^2$) and the rate of fall in $U_{\text{sat}}$ decreases with increasing $P_{\text{o}}$. At the maximum optical power density, the rate of fall in $U_{\text{sat}}$ slows down and $U_{\text{sat}}(P_{\text{o}})$ starts to deviate from the logarithmic dependence. At a temperature of 90 K, the initial part of $U_{\text{sat}}(P_{\text{o}})$ was not measured, since the time to approach the steady-state values of $U_{\text{sat}}$ reached several hours. At intermediate values of $P_{\text{o}}$, $U_{\text{sat}}$ decreases as a logarithm of $P_{\text{o}}$. At high optical power density, $U_{\text{sat}}$ begins to increase rapidly.

We then considered the dependences $QE(P_{\text{o}})$. As can be seen from figure 4, $QE$ is almost independent of the power density of light at 295 K and low $P_{\text{o}}$. When a certain power density is exceeded, $QE$ begins to decrease as a logarithm of the power density.

From a comparison of figure 3 and figure 4, it can be seen that the dependences $QE(P_{\text{o}})$ and $U_{\text{sat}}(P_{\text{o}})$ at 295 K and 200 K have almost the same form. As mentioned above, the decrease in $U_{\text{sat}}$ is determined by an increase in the work function of the $p$-GaN(Cs) photocathode. It is known that an increase in the work function leads to a decrease in $QE$ [13]. From this, we can conclude that the observed effects are a consequence of the surface photovoltage effect, which reduces the surface band bending and increases the work function of the photocathode by the same amount.

At 90K, $QE(P_{\text{o}})$ always decreases with increasing $P_{\text{o}}$, while $U_{\text{sat}}(P_{\text{o}})$ begins to increase after a certain power density. We believe that the variation in $U_{\text{sat}}$ in this power range is not equal to the variation in the contact potential difference $U_{\text{cpd}}$. Apparently, this behavior of $U_{\text{sat}}$ is associated with the voltage drop across the photocathode heterostructure due to the Ohms law. The acceptor binding energy in $p$-GaN:Mg is $\sim 0.2$ eV [20], and therefore the $p$-GaN layer has a high resistivity at low temperatures. The photocurrent flowing through the $p$-GaN heterostructure creates a voltage drop between the edge of the photocathode, where the electrical contact to the $p$-GaN layer is located, and the central region of the photocathode, from which the photoemission into a vacuum occurs. Therefore, in order to collect all the electrons from the photocathode, it is necessary to apply an additional voltage between the photocathode and the anode, so $U_{\text{sat}}$ increases.

Thus, with the exception of the region of very high $P_{\text{o}}$ and low temperatures, the change in $U_{\text{sat}}$ is equal to the value of the surface photovoltage:

$$U_{\text{sat}}(P_{\text{o}}) = U_{\text{sat}}(0) - SPV(P_{\text{o}}),$$

(1)
Figure 5 shows the dependences of the surface photovoltage on the optical power density, calculated from relation (1). The dependences obtained are well described by the function:

\[ SPV(P) = E_0 \ln(1 + P/P_{th}) , \]  

where \( E_0 \) and \( P_{th} \) are the coefficients characterizing the rate of photovoltage increase and the threshold power, respectively.

**Figure 5.** The surface photovoltage of a p-GaN(Cs) photocathode versus the optical power density at 90–295 K.

The steady-state \( SPV \) at the p-GaN(Cs) photocathode surface is determined by the balance of the fluxes of non-equilibrium photoelectrons and equilibrium holes moving from the photocathode bulk to the surface (see figure 1). The current of photoelectrons trapped at the surface \( (J_{rec}) \) is proportional to the \( P_o \). The current of holes \( (J_h) \), which try to restore equilibrium at the surface, depends on many parameters [13, 22], such as the acceptor concentration, the surface band bending value, and the density of surface states. The expression for the flux of holes coincides with the expression for the current of a non-ideal diode [13, 22]. Thus, we can write the equation of the balance between photoelectron and hole currents:

\[ aP_o = J_h \exp((eSPV)/(nkT)) - 1 , \]  

where \( a \) is the proportionality coefficient, \( J_h \) is the restoring current density [13], \( e \) is the elementary charge, \( n \) is the ideality factor, \( k \) is the Boltzmann constant and \( T \) is the temperature. Comparing equations (2) and (3), we can obtain a connection between the parameters determined from the experiment with the physical parameters of the p-GaN(Cs) surface:

\[ n = eE_0 / kT , \]  

\[ J_h = aP_o . \]  

**Figure 6.** The temperature dependence of the restoring current density (squares) and the ideality factor (circles) of the p-GaN(Cs) photocathode surface.

The temperature dependences of the ideality factor \( n \) and the restoring current density \( J_h \) are shown in figure 6. It can be seen that \( n = 2 \) at room temperature, and a twofold increase in \( n \) is observed with decreasing temperature to 90 K. An increase in the ideality factor with decreasing temperature may indicate a significant contribution of hole tunneling through the potential barrier at the photocathode surface at low temperatures [14]. The value of the ideality factor equal to 2 at high temperatures indicates the significance of the recombination of non-equilibrium photoelectrons through defects located in the middle of the band gap in the surface band bending region [22].
From figure 6, it can be seen that the restoring current density $J_{he}$ strongly depends on temperature. When the temperature decreases from 295 K to 90 K, the hole current decreases by 7 orders of magnitude. We believe that the main reason for the decrease in the hole current is a decrease in the concentration of free holes in $p$-GaN with decreasing temperature, since the acceptor binding energy in $p$-GaN:Mg is $\sim 0.2$ eV [20]. Note that the probability of transmission through the potential barrier on the surface is higher for holes with high kinetic energy. As the temperature decreases, the proportion of high-energy holes also decreases, which leads to an additional decrease in the restoring hole current.

Small values of the restoring current densities at low temperatures allow changing the surface band bending of the $p$-GaN(Cs) photocathode by $\sim 0.5$ eV without modifying the atomic structure of the surface. This makes it possible to investigate the influence of the magnitude of the surface band bending on the photoemission properties of a $p$-GaN(Cs) photocathode. Figure 7 shows the dependence of the QE of the $p$-GaN(Cs) photocathode on the magnitude of the surface photovoltage. The data was obtained by combining the data from figure 4 and figure 5. It can be seen from figure 7 that, $QE$ monotonously decreases with an increase in the surface photovoltage magnitude. The resulting dependence of $QE$ on $SPV$ is close to linear. Information on the causes of $QE$ reduction can be obtained from an analysis of the longitudinal energy distribution of photoelectrons emitted by a $p$-GaN(Cs) photocathode ($n_e(\varepsilon_{on})$ distributions) [23]. Figure 8 shows $n_e(\varepsilon_{on})$ distributions at different values of $SPV$. The curves are normalized to $P_e$. From figure 8, it can be seen that with decreasing surface band bending of the $p$-GaN(Cs) photocathode, the width of the $n_e(\varepsilon_{on})$ distribution decreases by the amount of $SPV$, and the amplitude of the energy distribution remains almost unchanged.

![Figure 7](image1.png)  
**Figure 7.** The quantum efficiency versus the surface photovoltage of a $p$-GaN(Cs) photocathode at 295 K (squares), 200 K (circles) and 90 K (triangles). The photon energy was 3.65 eV.

![Figure 8](image2.png)  
**Figure 8.** The curves of the longitudinal energy distribution of photoelectrons emitted from the $p$-GaN(Cs) photocathode at different $SPV$s. The photon energy was 3.65 eV. $T = 240$ K.

4. Summary
The surface photovoltage at a $p$-GaN(Cs) photocathode surface was measured in the temperature range 90–295 K. The dependence of the surface photovoltage on temperature is analyzed and the mechanisms of the photovoltage formation on a $p$-GaN(Cs) surface are discussed. It has been shown that the surface band bending in a $p$-GaN(Cs) photocathode can be reduced by $\sim 0.5$ eV by using surface photovoltage effect without alteration of the surface atomic structure. This can be useful for studying the photoemission of low-energy electrons from a $p$-GaN NEA photocathode into a vacuum. The dependence of the photoemission properties of a $p$-GaN(Cs) photocathode on the surface band bending value is analyzed.
Acknowledgements
We are grateful to V.V. Lundin (Ioffe Institute, Russian Academy of Sciences) for providing heterostructures for fabricating photocathodes.

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