The increase in band bending at the p-GaN(Cs) – vacuum interface due to the photoemission from surface states

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Abstract. The photoelectron processes in a p-GaN(Cs) photocathode with the effective negative electron affinity were studied experimentally within the 90–295 K temperature range. It was found that the photocathode illumination at the photon energies, which are below the energy gap of the p-GaN layer, increases the band bending at a semiconductor surface due to the photoemission from surface states.

1. Introduction

The study of photoemission processes in p-GaN(Cs,O) photocathodes with the effective negative electron affinity (NEA) state leads to the improvement of ultraviolet (UV) position sensitive photodetectors and photoelectron source parameters [1–3] and contributes to a better understanding of the physics of electron transport through atomic interfaces. Several attempts have been made to study the inelastic scattering at the p-GaN(Cs,O) surface [4–6]. In [4] it was stressed out that the scattering to a side valley is the main mechanism of inelastic photoelectron scattering at the surface of a p-GaN(Cs,O) photocathode, while the position of the side valley in GaN is still a matter of debate [7–9]. Recently [5, 6], it has been experimentally established that the photoelectron escape into vacuum from the p-GaN(Cs,O) photocathode is accompanied by the optical phonon cascade emission at the surface, though the type of emitted optical phonons has not been determined. Since photoelectron scattering probabilities depend on the electron kinetic energy, it could be possible to determine the dominant type of optical phonons and to elucidate the role of side valley scattering by measuring emitted photoelectron energy distributions at different surface band bending values ($V_{bb}$).

The possibility of the modification of surface band bending on the p-GaN photocathode with the NEA state by the surface photovoltage effect using super-bandgap illumination (see process A in figure 1) has been recently demonstrated [10]. Such an approach has some serious drawbacks. In this approach, the photoemission properties are probed and the surface band bending is modified by the same light beam. Also, to significantly reduce $V_{bb}$, one needs to illuminate a photocathode with an intense light beam, which can create a lateral voltage drop across the semiconductor heterostructure [10] and produce a space charge in vacuum, both of which could prevent accurate measurements of photoelectrons energy distributions.

It is known [11] that the semiconductor surface illumination by sub-bandgap photons can modify the surface band bending (see process B in figure 1). As was shown earlier [12, 13], the quantum efficiency ($QE$) of the p-GaN(Cs,O) photocathode at sub-bandgap photon energies is many orders of
magnitude smaller than \(QE\) at super-bandgap photon energies. One can assume that the photocathode surface illumination by a sub-bandgap pump beam could significantly modify the surface band bending, while negligibly affecting photoemission measurements. The sub-bandgap surface photovoltage was studied earlier on the oxide covered the \(n\)-GaN surface [14], while the study of the sub-bandgap surface photovoltage on a \(p\)-GaN surface with the NEA state had not been previously reported. Also, since the surface photovoltage studies on the \(p\)-GaN surface with the NEA state could involve a substantial photoemission current into vacuum, one cannot discard the possibility of positive surface charging during the photoemission from surface states (see process C in figure 1).

In this work, the ability to control the \(p\)-GaN(Cs) photocathode surface band bending by the sub-bandgap illumination is experimentally studied and analyzed. It is found that \(V_{hh}\) can be increased at certain sub-bandgap photon energies, when a substantial number of photoelectrons are emitted into vacuum from surface states, in contrast with the super-bandgap illumination case, which was studied in our previous work [10]. The escape probability of photoelectrons from the conduction band into vacuum \((P_{esc})\) was shown to monotonically increase with an increase in the surface band bending value from \(\approx 2.1\) eV to \(\approx 3.2\) eV.

\[\text{Figure 1. Energy diagram of a } p\text{-GaN(Cs) – vacuum interface at the dark (dashed line) and under illumination (solid line). Processes A, B (C) are shown, leading to the photoinduced reduction (increase) in the surface band bending value.}\]

2. Experimental details

The measurements were performed with a homemade planar photodiode where a semitransparent \(p\)-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 concentrations of magnesium and free holes (at 295 K) in the wurtzite \(p\)-GaN layer were \(\sim 10^{19}\) and \(\sim 10^{17}\) cm\(^{-3}\), respectively. The \(p\)-GaN surface cleaning methods were described in [15]. Cesium was deposited on a clean \(p\)-GaN surface at room temperature in ultrahigh vacuum until the maximal \(QE\) was obtained. The photocathode \(QE\) was 6% at a wavelength of 350 nm.

The photoemission was studied in the temperature range of 90–295 K. The vacuum photodiode was mounted in a liquid-nitrogen optical cryostat. A diaphragm with an aperture of 3 mm was installed in front of the photocathode center. The photocathode was illuminated through the diaphragm by probe and pump light beams to measure \(P_{esc}\) and to change \(V_{hh}\), respectively. A modulated light beam from a UV light-emitting diode (LED) passed through a monochromator was used as a probe beam. The laser with a wavelength of 532 nm and a UV LED with a central wavelength of 280 nm were used to create pump beams. The light intensities of pump beams were not modulated. The mean photon energies of the probe, pump sub-bandgap and pump super-bandgap beams were 3.59 eV, 2.33 eV and 4.4 eV, respectively. A set of neutral density filters was used to change the probe and pump beam light intensities. The vacuum photodiode current was measured by means of transimpedance amplifier. A
lock-in was used to measure the RMS value of the AC photocurrent created by the probe beam. To measure (to suppress) the photocurrent, an accelerating (retarding) voltage of 8 V (-8 V) was applied to the photodiode.

![Figure 2](image1.png)

**Figure 2.** Normalized photocurrent-voltage characteristics of the vacuum photodiode with a p-GaN(Cs) photocathode at two optical power density values of the sub-bandgap pump beam. Inset: second derivatives of photocurrent-voltage characteristics. $T = 295$ K.

![Figure 3](image2.png)

**Figure 3.** Saturation voltage of a p-GaN(Cs) photocathode versus the saturated photocurrent density of the sub-bandgap pump beam at 295 K (squares), 240 K (circles) and 160 K (triangles).

### 3. Results

The current-voltage characteristics of a vacuum photodiode with a p-GaN(Cs) photocathode illuminated by a sub-bandgap pump beam of different optical power densities ($P_{\text{opt}}$) are presented in figure 2. The curves are normalized by the saturated photocurrent density created by the sub-bandgap pump beam ($J_{\text{pump}}$). As can be seen, the photocurrent always increases with an increase in voltage and starts to saturate after a certain voltage. The saturation voltage ($U_{\text{sat}}$) was defined as the local minimum position of the second derivative of the photocurrent-voltage characteristic, as shown in the inset of figure 2 [10]. As can be seen in figure 2, the saturation voltage is increasing with an increase in $P_{\text{opt}}$ of the sub-bandgap pump beam and, consequently, with an increase in $J_{\text{pump}}$. This behaviour differs from the super-bandgap illumination case [10], where $U_{\text{sat}}$ is decreasing with an increase in $P_{\text{opt}}$ of the super-bandgap pump beam at low $P_{\text{opt}}$ and starts to increase at high $P_{\text{opt}}$. The dependence of $U_{\text{sat}}$ on $J_{\text{pump}}$ is shown in figure 3. At low temperatures, the $U_{\text{sat}}(0)$ was obtained by measuring nonstationary current-voltage characteristics after cooling the photocathode from room temperature to the designated temperature in the dark.

To find out the reasons of the $U_{\text{sat}}$ increase with increasing $P_{\text{opt}}$ of the sub-bandgap pump beam, the photocathode was simultaneously illuminated by the pump and probe beams at room temperature. The super-bandgap illumination-induced probe AC photocurrent ($I_{\text{probe}}$) is proportional to $P_{\text{opt}}$ and, consequently, to $QE$ at super-bandgap photon energies. As was shown in [10], $QE$ at super-bandgap photon energies is roughly proportional to $V_{\text{bb}}$. If the dependences of $I_{\text{probe}}$ on $U_{\text{sat}}$ obtained under illumination by both sub-bandgap and super-bandgap pump beams are of the same origin at low $P_{\text{opt}}$ of the pump beams, then the change in $U_{\text{sat}}$ upon sub-bandgap illumination is equal to the change in $V_{\text{bb}}$. The effect of sub-bandgap and super-bandgap pump beams on the $I_{\text{probe}}$ is demonstrated in figure 4, where the time dependences of $I_{\text{probe}}$ and pump beams illumination-induced DC photocurrents ($I_{\text{pump}}$) are shown. As can be seen, an additional illumination of the photocathode causes a decrease in $I_{\text{probe}}$ [10] in the case of the super-bandgap pump beam (blue curve) and an increase in $I_{\text{probe}}$ in the case of...
the sub-bandgap pump beam (red curve). The $I_{\text{probe}}$ dependences on $I_{\text{pump}}$ are shown in figure 5. In both cases, the logarithmic dependence is observed at high optical pump power levels. We increased the probe beam light intensity by one order of magnitude and did not observe any significant effect of the probe beam light intensity on relative modifications of the probe photocurrent by pump beams. To compare the effects of super-bandgap and sub-bandgap illuminations on the photoemission properties of the photocathode, the dependences of $I_{\text{probe}}$ on $U_{\text{sat}}$ are shown in figure 6. As can be seen in figure 6, the data obtained for each pump beam can be well fitted with the same linear dependence, which indicates that an increase in $U_{\text{sat}}$ is caused by an increase in $V_{\text{th}}$.

Figure 4. Kinetics of the AC probe photocurrent and DC pump photocurrents from the $p$-GaN(Cs) photocathode. The red (blue) curve corresponds to sub-bandgap (super-bandgap) pump beam illumination. $T = 295$ K.

Figure 5. AC probe photocurrent from the $p$-GaN(Cs) photocathode versus DC pump beam photocurrent created by sub-bandgap (squares) and super-bandgap (circles) illuminations. $T = 295$ K.

Figure 6. AC probe photocurrent from the $p$-GaN(Cs) photocathode versus the saturation voltage with additional sub-bandgap (squares) and super-bandgap (circles) illumination. $T = 295$ K.

Figure 7. Kinetics of the AC probe photocurrent from the $p$-GaN(Cs) photocathode. The arrows pointed downward (upward) indicate the time moment of retarding (accelerating) voltage application. The photocathode was illuminated by the sub-bandgap pump beam during the time interval indicated by the red zone. $T = 200$ K.
To check whether the increase in \( I_{\text{probe}} \) and \( U_{\text{sat}} \) by the sub-bandgap pump beam illumination was caused by the photoemission process itself, we conducted a separate experiment at a low temperature to reduce the surface band bending relaxation rate [10, 14]. The photocathode was illuminated at 200 K by a sub-bandgap pump beam, while the retarding voltage was applied to the vacuum photodiode so that the photocurrent created by the sub-bandgap pump beam was equal to zero. As shown in figure 7, the \( I_{\text{probe}} \) was additionally decreased immediately after cessation of the sub-bandgap illumination and the application of the accelerating voltage.

4. Discussion

It was demonstrated earlier [10] that \( U_{\text{sat}} \) and \( P_{\text{esc}} \) decrease upon super-bandgap illumination of the \( p\)-GaN(Cs) photocathode, which was explained by the \( V_{\text{bb}} \) decrease through the surface photovoltage effect [11]. Upon the photocathode sub-bandgap illumination, \( U_{\text{sat}} \) and \( P_{\text{esc}} \) increased simultaneously (see figure 3 and figure 5). As can be seen in figure 6, super-bandgap and sub-bandgap illuminations modify the photoemission properties of the photocathode in opposite directions. Therefore, we conclude that sub-bandgap illumination leads to an increase in the \( V_{\text{bb}} \) value of the \( p\)-GaN(Cs) photocathode. We also made the photoemission measurements of surface charging on the \( p\)-GaN(Cs,O) photocathode surface and observed a similar behavior of the surface band bending upon sub-bandgap illumination. The increase in \( V_{\text{sc}} \) can be caused by the photoemission process itself (see process C in figure 1). As was shown in figure 7, the photocathode surface illumination by the sub-bandgap probe beam in the external retarding electric field, which suppresses photocurrent, leads to a decrease in the initial value of the probe photocurrent and, consequently, leads to a decrease in \( V_{\text{bb}} \). Therefore, the increase in the surface band bending value observed in pump-probe experiments is caused by the sub-bandgap photoemission into the vacuum itself. The mechanism for an increase in the surface band bending induced by the photoemission from semiconductors into vacuum was discussed by Hecht [16]. He speculated that, in a moderately doped \( p\)-type semiconductor with alkali metal adsorbates at low temperatures, the electrons flow through a band bending region to the surface can be too low to compensate the photoemission current without a substantial increase in \( V_{\text{bb}} \). This mechanism can explain our observations.

Except for the region of very high pump optical powers at low temperatures [10], the change in \( U_{\text{sat}} \) is equal to the variation in surface band bending (\( \Delta V_{\text{bb}} \)):

\[ U_{\text{sat}}(J_{\text{pump}}) = U_{\text{sat}}(0) + \Delta V_{\text{bb}}(J_{\text{pump}}). \]  

The dependences of the variation in surface band bending on the sub-bandgap illumination-induced photocurrent density calculated from relation (1) are shown in figure 8. The obtained dependences are surprisingly well described by the conventional diode relation:

\[ \Delta V_{\text{bb}}(J_{\text{pump}}) = n k T \ln(1 + J_{\text{pump}}/J_0), \]  

where \( n \) is the “ideality factor” and \( J_0 \) is the “saturation current density”, which are the analogs of the ideality factor and saturation current density of a diode.

The temperature dependences of \( n \) and \( J_0 \) are shown in figure 9. The \( J_0 \) exponentially decreases by 5 orders of magnitude with a temperature decrease from 295 K to 90 K. The \( n \) value is substantially larger than 1 and increases with an increase in temperature in the studied temperature range. Following Hecht [16], a semiconductor surface with adsorbates charged by photoemission can be treated as a reverse biased Schottky diode. It follows from equation (2) that the restoring current density exponentially depends on \( V_{\text{bb}} \), which indicates [17] that thermo-field emission through a surface band bending region could play a substantial role in the surface charging of the \( p\)-GaN(Cs) – vacuum interface. As was seen in figure 7, the analysis of (2) is further complicated by the sub-bandgap photovoltaic effect (see processes B in figure 1), which reduces the positive surface charge by additional transitions at the surface.
Figure 8. Surface band bending variation at a p-GaN(Cs)–vacuum interface versus the photocurrent density induced by sub-bandgap illumination.

Figure 9. Temperature dependence of the “saturation current density” (squares) and “ideality factor” (circles) of the p-GaN(Cs)–vacuum interface.

Since the value of the sub-bandgap illumination-induced photoemission current depends on the voltage between a photocathode and an anode (see figure 2), the method for the photoemission-induced band bending modification is not compatible with longitudinal energy spectroscopy [5–6]. However, it can be used to measure the photocathode integral photoemission characteristics such as $P_{\text{esc}}$. The $P_{\text{esc}}$ dependence on $\Delta V_{bb}$ of the p-GaN(Cs)–vacuum interface, measured at two temperatures is presented in figure 10. In our previous work [10], it was shown that the band bending of the p-GaN(Cs) photocathode can be decreased by $\approx 0.4$ eV by super-bandgap illumination. In our current work, we were able to increase it by $\approx 0.8$ eV by photoemission from surface states induced by sub-bandgap illumination. As we can see, the escape probability monotonically rises with an increase in the band bending value. Following [12] we calculated $V_{bb}$ in the dark of our photocathode to be $\approx 2.4$ eV. Therefore, we can change the photoelectron energies at the surface in the interval from $\approx 2.1$ eV to $\approx 3.2$ eV. Presumably [8], the side valley bottom energy lies in this region. The monotonic dependence of $P_{\text{esc}}$ in the investigated energy range indicates that the side valley scattering is not the main mechanism of photoelectron inelastic scattering at the p-GaN(Cs)–vacuum interface.

Figure 10. The escape probability of photoelectrons from the conduction band of a p-GaN(Cs) photocathode into vacuum versus the variation in surface band bending.
5. Summary
The sub-bandgap illumination-induced surface charging was studied for the first time at the p-GaN(Cs) – vacuum interface. The photovoltaic surface band bending reduction and the photoemission-induced surface band bending increase were observed and analyzed. The surface band bending modification by the sub-bandgap and super-bandgap illuminations allowed us to obtain the dependence of the escape probability of photoelectrons from the conduction band into vacuum on the surface bend bending value.

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