Transient surface photovoltage in n- and p-GaN as probed by x-ray photoelectron spectroscopy

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Transient surface photovoltage (SPV) of n and p-GaN was measured using x-ray photoelectron spectroscopy (XPS) with a time resolution of 0.1 s. The measured SPV transients for both n- and p-GaN are $\ll$0.1 s, and for the n-GaN they are not affected by flood-gun electrons. However, for the p-GaN, the transient character of the SPV is dramatically changed in the presence of flood-gun electrons. The combination of time-resolved XPS, flood gun, and laser illumination give us a new way to study the surface electronic structure and other surface properties of semiconducting materials in a chemically specific fashion. © *2011 American Institute of Physics*.
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Light impinging on surface structures of materials results in a number of photochemical processes which are exploited for a variety of applications. Basic understanding of these processes at the atomic and molecular levels is a must for intelligent use and design of numerous devices and surface photovoltage (SPV) is one of these processes frequently encountered and utilized.[1,2] Among the many techniques used for analyzing SPV is the Kelvin probe (KP), an optoelectronic measurement technique with no chemical specificity. X-ray photoelectron spectroscopy (XPS) is another commonly utilized technique with excellent chemical and surface specificity. XPS-based SPV measurements of semiconducting materials date back three decades using both synchrotron and laboratory-based equipment.[3–6] However, except for Si (Refs. 7 and 8) and GaAs,[9,10] no transient SPV measurements using XPS have been reported to date. The high photon density of commercial monochromatic x-ray sources allows for reasonably fast (subsecond) acquisition of XPS data of a narrow spectral region to be recorded in the snap-shot mode, which can reveal the transient behavior of a sample, in a chemically addressed fashion, when subjected to external stresses like light illumination, resulting in SPV. Measurements of transient SPV relate chemical information to surface band structure, as well as to electrical properties of surface moieties, and most importantly, to the nature and dynamics of surface defects. GaN is a wide-band-gap semiconductor heavily investigated for use in optoelectronic and other electronic devices, and its surface and defect structures determine many of device properties.[11] This work reports an initial attempt of measuring the SPV formation and decay by recording the binding energy (B.E.) of the Ga $2p_{3/2}$ XPS peak in the fast snap-shot mode for furthering our understanding of this important process at the atomic level.

The samples were grown on double polished c-plane sapphire by low-pressure MOCVD (AIX 200/4 RF-S). The Si doped n- and the Mg doped p-GaN had conductivities of 57.6 S^{-1} cm^{-1} and 0.79 S^{-1} cm^{-1}, respectively. A Thermo Fisher K-Alpha spectrometer with monochromatic Al $K\alpha$ x-rays was used for XPS analysis. Transient SPV measurements on both n- and p-GaN samples were performed using a 50 mW 405 nm laser (CrystaLaser) in cw mode as the excitation source. A shutter connected to a signal generator was used to turn the laser on and off. The sample surfaces were cleaned by low energy (200 eV) Ar^+ ions, till C 1*s* and O 1*s* peaks fell below detection limits. No annealing of the sample was performed after cleaning.

Figure 1 depicts the experimental set up and the Ga $2p_{3/2}$ peak recorded with and without illumination, yielding +0.15 eV and −0.39 eV binding energy shifts due to the SPV for the n- and p-GaN, respectively. The SPV measured on the n-GaN sample is smaller than the steady-state values measured by KP,[12,13] which can be estimated for 405 nm as 0.4 V for an intensity of 0.03 W/cm^2.[14] This is larger than our measured value, despite the much higher intensity of our excitation source. This difference in the measured values can be attributed in part to differences in the oxidation extent and cleanliness of the surface.[16] However, photovoltage creation by x-rays is also a possibility since earlier measurements have yielded differences in the measured band bending values, which were attributed to inadvertent creation of SPV by x-rays.[14,16] No previous SPV measurements on p-GaN have

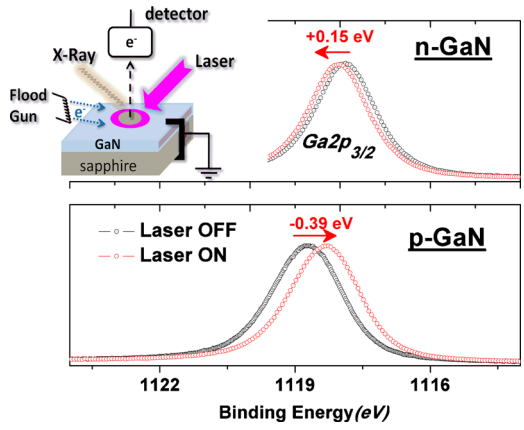

FIG. 1. (Color online) The Ga $2p_{3/2}$ region for the n- and p-GaN samples without and under illumination with a 50 mW 405 nm laser. The experimental set-up is shown as an inset.

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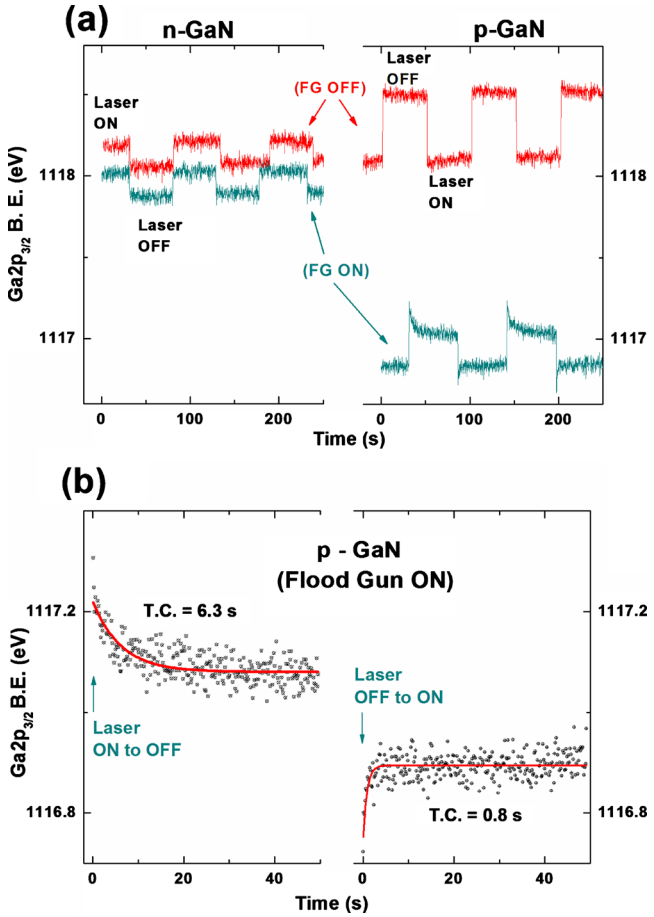

FIG. 2. (Color online) (a) The Ga $2p_{3/2}$ B.E. changes recorded in the transient mode with 0.1 s intervals, as the laser is turned ON and OFF at 0.01 Hz frequency, with the flood-gun turned-off (red, upper) and turned-on (cyan, lower). (b) Exponential fits to the laser ON and OFF time-windows for the p-GaN with flood-gun electrons.

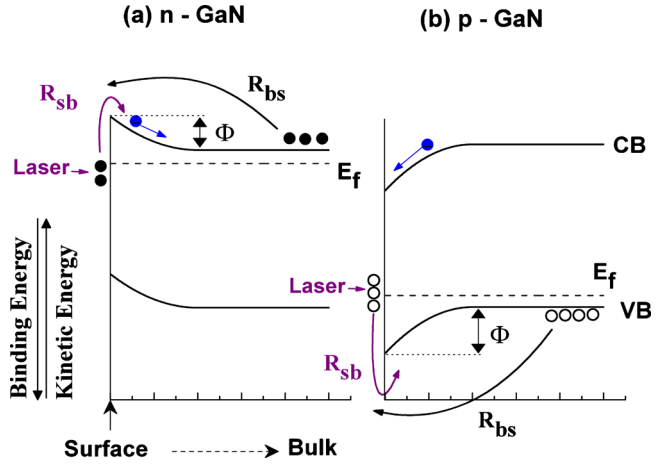

FIG. 3. (Color online) Mechanisms involved in n-GaN (a) and p-GaN (b) with illumination. SPV is generated by excitation of electrons or holes out of surface states by subbandgap illumination at a rate of R_{sb}. SPV decays under dark conditions by thermal excitation of electrons or holes over the surface barrier Φ at a rate of R_{bs}. Flood-gun electrons (indicated by blue dots) are swept to the bulk for n-GaN, and to the surface for p-GaN.

been reported in literature, except for band-bending using KP and XPS techniques. However, the available data are scattered, pointing to a downward surface band-bending of 0.8,[16] 1.1 to 1.6,[15] and 2.6 eV.[13] In the absence of other measurements for p-GaN, an expected value for subbandgap excitation SPV cannot be specified. But, it should be noted that our measured value of 0.39 V is within the range made possible by the band-bending of p-GaN, and is larger than that of the n-GaN sample, as expected due to the larger band-bending.

Additional information can be derived from the transient measurements of the position of the Ga $2p_{3/2}$ peak when recorded at 0.1 s intervals, with the laser illumination being turned on and off with a period of 100 s, as shown in Fig. 2(a). The red curves depict transient SPV observed when the flood-gun is turned off. With the laser, both the ON-to-OFF and OFF-to-ON transients in n-GaN and p-GaN are fast ($\ll$0.1 s). The fast OFF-to-ON transient is consistent with the earlier results and the excitation mechanism involved, from which a slope can be estimated as 1–2 V/s for the wavelength and intensity of excitation source that is used in our study,[13] which is below the detection limit of our equipment. Since a similar mechanism is probably involved, a fast OFF-to-ON transient for the p-GaN is also expected due to our intense SPV excitation source.

Previous reports on the transient characteristics of SPV measured on n-GaN using the KP method have identified the mechanisms responsible for the observed SPV and the transients.[12,13] The subbandgap excitation utilized in the present work implies that the mechanism responsible is the resonant excitation of electrons from surface states into the bulk, as shown in Fig. 3(a).[13] Similarly, it is assumed that in p-GaN the SPV is created by resonant excitation of holes from surface states into the bulk as shown in Fig. 3(b). For the assumed SPV mechanisms, the OFF-to-ON transient is caused by the time it takes for the electrons in n-GaN (or holes in p-GaN) to be excited out of surface traps. The ON-to-OFF transient is then caused by the time it takes for charge carriers to return back over the surface barriers. Usually, thermal excitation is the mechanism with which the carriers are excited over the surface barrier but, for the case of XPS, the possibility of charge carriers being excited by x-rays may also need to be considered. The high excitation intensity utilized in our experiments is not expected to influence the ON-to-OFF transient rate and, based on earlier reports, a logarithmic decay that should extend over hundreds of seconds should be expected.[13] Accordingly, the fast ON-to-OFF transients observed in this work need further explanation. We suggest reduced band-bending due to x-ray induced photovoltage and excitation of charge carriers over the surface potential barrier by absorbed x-rays as possible mechanisms that can explain the fast ON-to-OFF transients. The fast transients and the possible involvement of the x-rays in the OFF-to-ON transient warrants further investigation of the processes involved.

The low-energy electron flood-gun facility of the XPS system, which is commonly employed to neutralize charging and the associated binding energy shift(s) on less conducting surfaces, was utilized to gain further information about the nature of the SPV transients. In Fig. 2(a), the cyan curves (lower) plot the transient SPV acquired under exposure to the flood-gun with a nominal current rating of 100 μA, leading to a small charging shift of $\sim$0.2 eV for the n-, and a relatively higher $\sim$1.5eV for the p-GaN sample, due to the higher resistivity of the latter. For the SPV transient the effect of the flood-gun is very informative, as seen from Fig. 2(a) and in further detail in Fig. 2(b). When the flood-gun

was turned on, the transient photovoltage measured from p-GaN showed features that have never been reported previously. In contrast, the use of the flood-gun did not affect the transient SPV of the n-GaN sample.

The different responses of the SPV measured on n- and p-GaN to flood-gun electrons can be understood in terms of the band-diagrams shown in Fig. 3. It is known that low energy electrons can penetrate to a significant depth and some of them can be incorporated to the conduction band near the surface. For n-GaN the incorporated electrons will be swept away to the bulk and, consequently, to ground. Thus, for n-GaN, the flood-gun electrons will not significantly affect the measured band-shifts or the transients. For p-GaN, the incorporated electrons will be swept to the surface where they will form a sheet to shield the positive charge of the surface, or will fill the surface hole-traps and eliminate the positive charge. In either case, the result will be a flattening and reduction in the band-bending.

The SPV transients measured on the p-GaN sample with the flood-gun show that the transitions are nearly instantaneous when the laser is turned ON or OFF and are equal to 0.4 V, the same value of the SPV measured without the flood-gun. Accordingly, a question arises as to the contribution of the flood-gun electrons to the dynamics of the SPV transients. Since in our experimental set-up, the flood-gun electrons cannot be turned on or off as fast as the light source, we have performed an additional experiment where the sample is subjected to square-wave (SQW) pulses with 10 V amplitude while the XPS snap-shots are recorded. As described in our earlier work, this procedure results in shifting the position of the peaks by +10.00 eV and −10.00 eV, respectively, and at the same time enabling the sample to completely pull (in the +10 V cycle), or completely repel (in the −10 V cycle) the flood-gun electrons.[17] The results are shown in Fig. 4 for the resistive p-GaN sample. Whereas the position of the Ga $2p_{3/2}$ peak is shifted by exactly 10.00 eV in the "+" cycle (no charging), the corresponding shift is only 7.70 eV in the "−" cycle, revealing a charging shift of 2.30 eV due to repelling of the low energy electrons, which sets in with a much faster time constant ($\ll$0.1 s). Comparing these results with the laser excitation (reproduced in the same figure) assures us that the flood-gun electrons do not have any effect on the rise of the SPV transients. However, in the presence of the flood-gun electrons, the transients observed after the OFF-to-ON and the ON-to-OFF transitions are shielded severely, and decay with different time constants, as shown in Fig. 2(b) due to the differences in the nature of the transients. The decay after the ON-to-OFF transition has a time constant of 6.3 s, during which the flood-gun electrons accumulate on the surface and gradually eliminate the band-bending, thus decreasing the binding energy. The accumulation rate of the electrons on the surface governs the decay time-constant. At the beginning of the transient after the OFF-to-ON transition, the surface has accumulated a number of electrons that are initially held at the surface by the positive charges that cause the changes in band-bending, but are then swept away much faster ($<$1 s) into the bulk where they recombine with the holes.

The consistency of the flood-gun effects with the expected band-structure near the surface supports the observations and the measurements made and opens up the possibility to extend the use of XPS in new ways for taping many surface, dopant, defect, impurity, etc., related information of semiconducting materials.

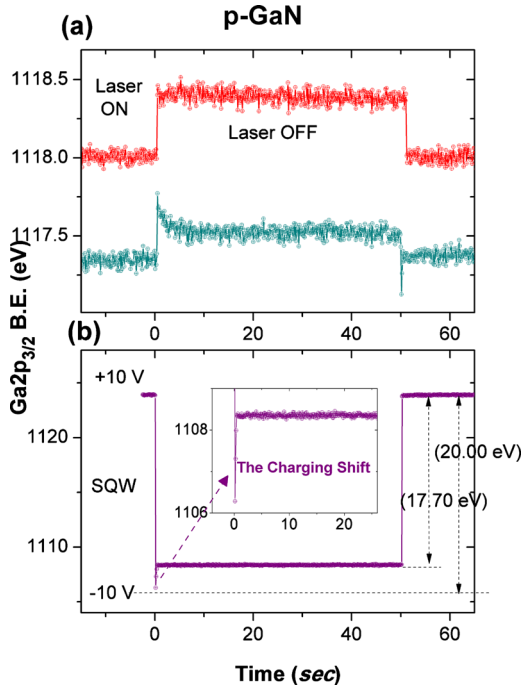

FIG. 4. (Color online) (a) The same data as presented in Fig. 2(a) for the p-GaN. (b) The Ga $2p_{3/2}$ B.E. changes recorded in the transient mode with 0.1 s intervals, as the sample is subjected to SQW electrical pulses with 10 V amplitude and 0.01 Hz frequency and with the flood-gun turned-on. The inset shows the expanded version of the data.

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