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1 **Measuring the Surface Photovoltage of a Schottky Barrier under**
2 **Intense Light Conditions: Zn/p-Si(100) by Laser Time-Resolved**
3 **Extreme Ultraviolet Photoelectron Spectroscopy**

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13

14**Abstract**

15 The addition of a metal overlayer to a semiconductor photocatalyst is a
16frequently used synthetic route to passivate the surface and, via the
17formation of a Schottky barrier, to enhance catalytic activity of the
18photocatalyst material. While it is known that Schottky junctions decrease
19recombination by charge separation, measurements of the depletion region
20dynamics have remained elusive. Here, we use ultrafast pump-probe
21transient photoelectron spectroscopy to measure material-specific dynamics
22of the Zn/n-GaP(100) system. Through photoemission measurements the
23Schottky barrier height is determined to be 2.1 ± 0.1 eV at 10 monolayers of
24total Zn deposition. Transient photoemission measurements utilizing a 400
25nm pump pulse show that, after excitation, holes are transferred from n-
26GaP(100) to the Zn overlayer within a few ps, as evidenced by shifts of the
27Zn 3d and Ga 3d core levels to higher binding energies. Within the timescale
28of the experiment (130 ps) no carrier recombination is observed in the
29junction. Furthermore, a long-lived surface photovoltage signal is observed
30at times > 1 ms after photoexcitation. This work further exemplifies the

31potential of transient XUV-PES as a material-specific technique for the study
32of heterojunctions.

33 **I. Introduction**

34 Gallium phosphide, a semiconducting material with an indirect band
35gap of 2.26 eV, has received much attention for its potential applications in
36optics, electronics, and photocatalysis.¹ Of particular importance for
37photocatalysis is the ability of GaP to retain its original surface structure and
38electronic properties while operating in an aqueous solution. While the basic
39photocatalytic activity of untreated GaP is established, the already promising
40efficiency and stability of GaP can be improved through the use of coatings
41of metals or semiconductors.² In the earliest work, Au and Ag films were
42deposited onto n- and p-type GaP wafers and the electrical properties were
43characterized in the presence and absence of illumination with light.³ The
44experiments showed a marked increase in photocurrent in these samples, as
45well as an increased resistance to corrosion in solution when compared to
46untreated GaP samples. Subsequent work focused on nanostructured GaP
47with a variety of dopant atoms, metals, and semiconductor materials on the
48surface, leading to further improvements in catalytic efficiency and stability.^{2,}
49⁴⁻⁶

50 To understand the effect of surface treatments on the carrier lifetime
51and behavior in the depletion region of GaP junctions with other materials,
52the work here explores the Zn/n-GaP system using a high harmonic
53generation (HHG) based extreme ultraviolet photoelectron spectroscopy

54(XUV-PES) technique.⁷ In addition to the element, oxidation state, and
55surface sensitivity afforded by the photoemission method, time dependent
56dynamics are obtained by incorporation of a time-delayed UV/Vis laser pulse
57in conjunction with the XUV probe pulse. This technique has been previously
58used to observe the dynamics of electron transport in defect rich and defect
59poor TiO₂ films on p-Si(100)⁸ as well as Zn layers on p-Si(100).⁹ Now, using
60the same technique, the dynamics of surface charging by hole transport from
61n-GaP to Zn are observed. Observation of the Ga 3d and Zn 3d core levels
62allows for the characterization of dynamics in both the GaP and Zn of the
63heterojunction in real-time.

64 In this work the barrier height as a function of Zn coverage is
65determined by monitoring the binding energy shift of the substrate Ga 3d as
66observed via XUV-PES. Then, through the use of transient XUV-PES, material-
67specific changes in the surface photovoltage of the Zn/n-GaP(100) system
68are observed in the overlayer (substrate) through energy shifts in the
69position of the Zn 3d (Ga 3d). The electronic properties, such as Fermi level
70pinning and carrier transport, which are observed and discussed in the
71transient XUV-PES measurements, serve to further the understanding of
72carrier dynamics within the depletion region of metal-semiconductor
73heterojunction photocatalytic systems.

74 **II. Experimental Setup**

75 The experimental apparatus used in these experiments has been
76previously described in detail.⁷ Briefly, the apparatus consists of a surface

77science chamber coupled to a laser and monochromator system that
78provides narrow band XUV femtosecond pulses for photoemission electron
79time-of-flight measurements. Ultrafast pulses are produced by a Spectra-
80Physics Spitfire amplifier producing 2.7 W average power of 35 fs pulses
81centered at 800 nm and 1 kHz repetition rate. The amplifier is seeded by a
82Spectra Physics Tsunami oscillator pumped by a 5 W frequency-doubled
83Nd:YVO₄ continuous laser. The pulses from the amplifier are split into a
84probe beam, used to generate the XUV radiation, and a pump beam that is
85frequency doubled to 400 nm for excitation of the GaP semiconductor
86material.

87 The 800 nm probe pulses are focused into a semi-infinite gas cell at an
88intensity of 10^{14} - 10^{15} W cm⁻². The cell is filled with Ar gas at approximately 25
89Torr pressure. Under these conditions harmonics of the fundamental 800 nm
90light are produced from the 7th to 29th order, corresponding to 11 eV to 45 eV
91photon energy. These photon energies are sufficient to bring about
92photoemission from the 3d core levels of both Zn and Ga. The harmonics and
93residual 800 nm radiation impinge upon a plane grating after the gas cell
94where they are separated. By changing the angle of the grating, a single
95harmonic is selected to probe the sample. The selected harmonic is reflected
96by a cylindrical and toroidal mirror, resulting in a focused beam with a
97diameter of 0.2 mm. Any additional harmonics or the 800 nm fundamental
98are blocked by a slit at the entrance to the sample chamber.

99 The pump arm is directed to a variable delay stage after being split
100 from the probe pulse to allow for time-resolved measurements. The 800 nm
101 beam is passed through a beta-barium borate (BBO) crystal to produce 400
102 nm radiation by second harmonic generation. The resulting light is reflected
103 from two 400 nm high reflector optics, removing the residual 800 nm
104 radiation. The remaining light is focused by a lens and reflected onto the
105 sample by a silver mirror located slightly above the XUV beam immediately
106 before the sample chamber, resulting in a pump spot with 1 mm diameter at
107 the sample.

108 The UHV end chamber is equipped with tools for preparation and
109 characterization of surfaces. Among these are an Ar⁺ ion gun, used to clean
110 the GaP(100) sample, a Zn oven, used to deposit the Zn film onto the GaP,
111 and an Auger spectrometer for characterizing surface composition and
112 coverage. Photoelectrons are collected and analyzed by a time-of-flight
113 photoelectron spectrometer (TOF-PES) with a 1 m long double-walled μ -metal
114 inner tube and a microchannel plate (MCP) detector at the end of the drift
115 region. The signal is then acquired via a 5 GHz multichannel scaler unit.

116 The n-GaP(100) crystal used in this study is a bulk single crystal,
117 grown by the Czochralski method, that was purchased from MTI corporation.
118 Before Zn deposition, the n-GaP(100) film was cleaned using the argon gun
119 with a filament emission current of 20 mA and a beam voltage of 3 kV for 10
120 min. Rounds of cleaning were repeated until an Auger electron spectroscopy
121 spectrum of the bare n-GaP film presented only phosphorus and gallium

122peaks. Through atomic force microscopy imaging (SI Fig. **S1**) the RMS
123roughness value was found to be 0.95 nm and 1.6 nm for an unsputtered
124and sputtered sample, respectively. The Zn films were grown by evaporation
125of zinc metal from a homebuilt evaporator. Briefly, the evaporator consists of
126a 4 cm long, 0.5 mm in diameter Ta filament wrapped around a piece of Zn
127metal. A current of approximately 2.80 A is applied to the Ta filament, which
128results in resistive heating of the filament and heating of the zinc. Due to the
129difference in Ta and Zn evaporation temperatures no Ta is observed on the
130sample after Zn deposition. Under these deposition conditions the Zn is
131found to deposit at a rate of 1.4 minutes/monolayer (See SI figures 2 and 3).
132In this work no attempt is made at determination of the growth mechanism.
133Photoemission spectroscopy measurements of the junction system were
134recorded with the sample at a nominal temperature of 25 °C.

135 The sample is typically positioned 5 mm away from the entrance of the
136TOF-PES with the sample-surface-normal parallel to the spectrometer axis.
137This results in a laser beam incidence angle of 45° with respect to the
138surface normal. The sample position can be reproduced with an accuracy of
1390.02 mm and 0.5°. The base pressure of the chamber is typically 2×10^{-10}
140Torr and rises to 7×10^{-10} Torr when the sample chamber is opened to the
141beamline, due to residual Ar gas from the HHG cell. The calibration of the
142energy scale of the TOF-PES is checked by acquiring photoelectron spectra at
1433 adjacent harmonics, which are known to be spaced by 3.1 eV. Thus, the
144features in each PES are expected to also be spaced by 3.1 eV, giving an

145 internal calibration standard. The angular acceptance of electrons in the TOF
146 is 4 degrees to either side of the surface normal, giving a total acceptance of
147 8 degrees. Typical static photoemission spectra consist of an average of the
148 collected photoemission spectra of 500,000 laser pulses. To efficiently
149 acquire time-resolved data, each spectrum acquired in a transient
150 measurement is composed of 180,000 laser pulses. In a transient PES
151 experiment, time points between -5 to 5 ps are collected with 1 ps steps,
152 while points outside this region are collected with approximately 20 ps steps.
153 Cross correlation measurements of the pump and probe pulses by the laser
154 assisted photoelectric effect (LAPE) gave an instrument response function of
155 80 fs for this experiment.

156

157 **III. Schottky Junction: Barrier Height Characterization**

158 The photoemission spectrum of clean n-GaP, recorded using the 27th
159 harmonic of the nominal 800 nm fundamental from the Ti:Sapphire laser
160 (41.9 eV photon energy), is shown in figure 1a. To avoid any effects due to
161 the generation of excited carriers by ambient light, all light sources in the
162 chamber were turned off and all chamber viewports were covered during
163 acquisition. All binding energies discussed herein are referenced to the
164 center of a Fermi-Dirac distribution,^{9, 10} which is fit to a spectrum of the
165 tantalum clips holding the sample in place. For the Fermi-Dirac fit, the
166 distribution is convoluted with a Gaussian function to account for
167 instrumental broadening. The width of this Gaussian is only dependent on

the instrument, and it was determined to be 0.5 eV by previous work in our group for this instrument.⁹

The n-GaP photoemission spectrum shows two distinct features (Fig. 11a). The first, a broad and multi-peaked feature appears between -0.7 eV and -13.5 eV binding energy. The observed features are in good agreement with the previously calculated density of states for intrinsic GaP.¹¹ The onset of this band, at 0.7 ± 0.1 eV below the Fermi level of the sample, indicates that the conduction band minimum is located 1.5 ± 0.1 eV above the Fermi level. This value is obtained by fitting to the zero-background rise of the valence band edge, with the error bars representing a single standard deviation. The onset of the valence band was found by a linear fit of the valence band edge. The value of the valence band offset is where the linear fit intercepts the x-axis (see figure 1C). The second feature of interest, located at -20.7 ± 0.1 eV binding energy, corresponds to the Ga 3d core level. For this feature, the Ga 3d core level was fit with a Voigt line shape, with the error bars denoting one standard deviation. This peak location is in agreement with previous measurements of n-type GaP and other semiconductors incorporating Ga.¹²⁻¹⁴

The spectrum of 10 ML Zn deposited onto n-GaP is shown in figure 1b. Deposition of Zn induces several changes in the observed photoemission spectrum, with the foremost being the new, intense Zn 3d photoemission feature occurring at -10.6 ± 0.1 eV binding energy, as found by Voigt fitting. This feature is assigned to the 3d core level of the deposited Zn overlayer, as

discussed in previous work from our group and others.^{9, 15} While the Zn 3d core orbital of bulk Zn is composed of two spin-orbit split components of -10.2 and -10.3 eV, the resolution in our experiment is insufficient to observe this splitting. Finally, it is clear upon comparison of the clean n-GaP spectrum and the 10 ML Zn/n-GaP spectrum that the binding energy of the Ga 3d peak shifts from -20.6 ± 0.1 eV to -20.1 ± 0.1 eV. While the coverage of Zn greatly diminishes the Ga 3d signal due to the short mean free path of the Ga 3d electrons the peak is still visible. In a study of Zn deposition onto the GaP substrate (see SI) it was observed that after forming a monolayer the Zn atoms form particles. Thus, the coverage is not uniform over the entire surface, allowing Ga 3d electrons to escape despite their short mean free path.

The shift of the Ga 3d core level is related to the change in band bending upon deposition of Zn and can be used to assess the Schottky barrier height, as outlined in several previous studies.^{12, 16, 17} Briefly, the energy difference between the valence band maximum of GaP and the Ga 3d core level is a constant value that is intrinsic to the semiconductor (denoted as E_{c-v} in figure 1a and 1b). The Ga 3d binding energy, referenced to the Fermi level of the system, is known to shift with the bending of the valence and conduction bands. Since the Ga 3d shifts with the valence band, the changing position of the Ga 3d relative to the Fermi level, in conjunction with the known E_{c-v} value, gives the energetic separation of the valence band and the Fermi level. By subtracting this value from the band gap of GaP (2.26

214eV),¹⁸ the separation of the Fermi level and conduction band can be found,
215thus giving the Schottky barrier height. The band diagrams for n-GaP(100)
216and 10 ML Zn/n-GaP(100) are shown in figure 1a and 1b.

217 In figure 1d the measured Schottky barrier height as a function of Zn
218coverage is displayed. For these measurements photoelectron spectra were
219recorded sequentially at differing Zn coverages, followed by fitting as
220described above. At 0 ML of Zn, the barrier height of 1.5 ± 0.1 eV
221corresponds to the native n-GaP surface barrier to electron flow. As the
222coverage is increased, there is a clear shift of the barrier height to lower
223values, followed by a rise of the value with increasing Zn coverage. Such
224behavior has been previously observed for photoemission measurements of
225other metal-GaP contacts using synchrotron radiation, and it is explained by
226non-equilibrium effects that arise from the measurement techniques.^{9, 13, 19}
227Specifically, electron hole pairs are generated by interactions with
228photoelectrons leaving the material or by direct excitation of the substrate
229by the XUV radiation, which then segregate based upon the electric field
230present in the depletion region of the semiconductor. In this case, this means
231that holes are shuttled to the semiconductor surface, where they induce a
232long-lived photovoltage due to their slow recombination. The result is an
233initial shift of the Fermi level to higher binding energies at low surface
234coverages of Zn, giving a lower apparent barrier. This effect is also
235manifested as a shift of the Fermi level to a lower than expected value when
236compared to the reference (Ta sample holder) Fermi level. Such

237 nonequilibrium effects are removed as the metal thickness on the
238 semiconductor is increased, typically becoming negligible around 2 nm metal
239 thickness.¹³ It should be noted that while this effect is similar to the
240 phenomenon of surface charging in photoemission in non-metallic samples
241 this effect arises purely from excitations of electron hole pairs during
242 photoemission. In the case of these experiments, the measured barrier
243 height at 10 ML (~ 2.8 nm) of Zn coverage is used. This barrier height is
244 found to be 2.1 ± 0.1 eV, indicating that Zn deposition induces a further 0.5
245 eV band bending in the n-GaP substrate, which is consistent with the
246 formation of a Schottky barrier in this system.

247 The noise observed in these measurements is attributed to the
248 relatively small signal of both the Ga 3d core level upon Zn deposition as
249 well as the small signal of the Fermi level. The fits to these small features
250 lead to increased errors in the fits used, thus giving the large error bars.
251 Furthermore, while the position of the sample can be well reproduced, errors
252 in the measured quantities may result from slight differences in the position
253 or angle of the sample relative to the spectrometer.

254 **IV. Transient XUV-PES**

255 To assess the behavior of Zn/n-GaP junction under 400 nm
256 illumination, transient XUV-PES spectra are recorded for a series of pump-
257 probe time delays. A negative time delay indicates that the probe beam
258 precedes the 400 nm pump beam, while a positive time delay corresponds to
259 excitation with the 400 nm pump beam before the XUV probe beam induces

260photoemission. The spectra of 10 ML Zn/n-GaP with XUV only, at -18 ps and
261+130 ps time delays are shown in figure 2 for a 400 nm excitation density of
2622.5 mJ cm⁻² (4.4×10^{20} carriers cm⁻³).²⁰ While the carrier density was
263calculated assuming no attenuation by the 400 nm beam by the metal
264overlayer, studies have shown that as few as 10 nm layers of transition
265metals can attenuate the incoming radiation by 50%.^{21, 22} This effect is
266dependent upon the metal geometry on the surface as well as the metal
267identity.²² However, even in the 50% attenuation case the number of carriers
268excited by the 400 nm radiation is still much larger than the doping
269concentration (10^{18} cm⁻³) of the substrate.

270 For all the following discussion the features are fit as described in
271section III. The difference between the -10 ps time delay and XUV only
272spectra are found to show a slight shift, indicating that the effect of the
273probe is minimal at negative (probe before pump) time delays. The origin of
274this shift is discussed in further detail below. However, at +130 ps there is a
275clear shift of the spectrum to higher binding energies. In the spectra there
276are three features of interest: the Zn 3d core level, Ga 3d core level, and the
277Fermi level, which consists of electrons from the Zn overlayer. For all three of
278these components a shift to higher binding energy is observed. The binding
279energy shift of these features as a function of the pump-probe time delay is
280shown in figure 3. A figure with additional negative timepoints is included in
281the SI.

282 In figure 3a the transient behavior of the Zn 3d core level (red) and
283 Fermi level (black) are shown. The Zn 3d and Ga 3d core levels were fit with
284 a Voigt lineshape, while the Fermi level position was found by fitting with a
285 Fermi-Dirac distribution.^{9, 10} While the intensity of the Ga 3d peak is
286 diminished under the conditions of the transient experiment the peak is still
287 able to be observed and fit by a Voigt line shape. Examination of the data
288 shows that the time scale of excitation is quite similar for both features. In
289 addition to the similar time-scales, the absolute magnitudes of the Zn 3d and
290 Fermi level shifts for both features are similar, with a shift of approximately
291 0.6 eV towards higher binding energy compared to the static XUV only
292 spectrum. In figure 3b the transient behavior of the Ga 3d (blue) is shown in
293 comparison to the Zn 3d (red). The Ga 3d core level shifts with a similar
294 magnitude and time to that of the Zn 3d core level and the Fermi level. This
295 indicates the dominant dynamic processes within the Zn overlayer and
296 depletion region within GaP are similar. In work performed by Kamada and
297 coworkers on a Cs/p-GaAs junction under continuous illumination, a similar
298 trend was observed, with both Cs and Ga core levels shifting by a similar
299 magnitude and sign compared to the unilluminated case.²³

300 To understand the processes responsible for the observed shifts, the
301 behavior of the Zn 3d and Ga 3d core levels will be considered first. It is clear
302 from the similarity of their dynamics that the process that modulates the Zn
303 3d binding energy is also most likely responsible for the Ga 3d shift. The
304 space charge region of the material is negatively charged due to the n-type

doping of the substrate. Thus, holes are drawn towards the surface while electrons are shuttled into the bulk of the sample. The net result is a lowering of the electron quasi-fermi level in the Zn film and depletion region of n-GaP, which also reduces the band bending in n-GaP. While electron accumulation occurs in the bulk of n-GaP, the probe depth of XUV-PES is only a few nanometers, meaning that the results are mainly sensitive to the depletion region of n-GaP. Thus, the dynamics observed are assigned to the trapping of holes in the Zn layer, which also screens the electric field in the n-GaP depletion region, decreasing the band bending. A schematic picture of this process is shown in figure 4.

In the case of carrier transport from the semiconductor to the surface layer it is expected that the Zn 3d and Zn Fermi level should show similar dynamics, as observed in a transient XUV-PES experiment from this laboratory on a 3.5 ML Zn/p-Si(100) junction.⁹ It was observed in that work that for excitation densities in which band bending in p-Si(100) was the limiting factor, the Zn 3d and Fermi level shifted by a similar magnitude, while for higher excitation densities the Zn 3d showed a larger shift than the Fermi level. In both cases, the two features showed a similar time dependence. With this knowledge, along with the 0.6 eV shift in binding energy, which is well below the calculated band bending of 1.2 eV in the Zn/n-GaP junction, the dynamics observed here support the assignment of the dynamics as being induced by the transport of holes to the Zn layer after excitation, followed by a reduction in band bending throughout the junction.

328 It is clear from the collected data that the SPV signal shows no change
329 through the end of the delay ranged scanned, and thus no attempt is made
330 to assign a timescale for recombination. While a transient rise is observed
331 around time zero there is a 0.2 eV background shift when compared to an
332 unpumped photoelectron spectrum. Due to this background, which is
333 discussed below, the timescale for this initial rise is not assigned.

334 It is important to note that the *pump*-induced SPV discussed above is
335 fundamentally the same as the previous discussed *probe*-induced SPV which
336 influences the observed Schottky barrier heights (section III). However,
337 probe-induced SPV is only observed in the case in which the substrate is
338 strongly excited by the probe radiation. Here, the thickness of the Zn
339 overlayer was chosen to minimize this effect in our experiments as discussed
340 in section III.

341 Finally, as noted above, there is a clear offset of the photoemission
342 spectrum at negative time delays relative to the XUV only spectrum of
343 approximately 0.25 eV for all features. There are two possible explanations
344 for this behavior: pump space-charge effects and long-lived states excited by
345 the 400 nm pump beam. Pump space charge effects can arise from the
346 interaction of photoelectrons induced by multiphoton absorption of the 400
347 nm pump beam and the XUV probe induced photoelectrons.^{24, 25} In these
348 experiments, the total number of photoelectrons induced by the 400 nm
349 pump beam is kept below 0.05 electrons per pulse through the time of flight
350 to avoid these effects. For reference, the number of photoelectrons induced

351by the XUV beam, which is the lowest stable number of counts that can be
352obtained using this HHG source, is on the order of 0.2 electrons per pulse.
353Although the number of observed electrons originating from the pump beam
354is 0.05 per pulse, the lowest energy electrons may not be observed at the
355detector due to stray electric fields, which can influence their flight.

356 While pump-induced space charge effects can have a strong influence
357on the observed transient spectrum, at negative times it is expected that the
358photoemission spectrum would shift to *lower* binding energies in the
359presence of space charge.²⁴ The observed shift in this experiment at
360negative times is to higher binding energy, thus pump-induced space charge
361effects are not consistent with the observed data. Furthermore, it is expected
362that pump-induced space charge effects will lead to a rising increase in the
363surface photovoltage shift before time zero over a period of 100 ps. In these
364experiments the surface photovoltage before time zero is essentially
365constant over this time frame, again indicating that pump-induced space
366charge effects are not influencing the phenomena observed here.

367 The second possibility, a long-lived surface photovoltage resulting from
368the 400 nm pump beam, is the more likely cause of this persistent shift, as
369explained next. In our experiment, we observe that the SPV persists between
370probe pulses, which are spaced 1 ms apart at a 1kHz repetition rate,
371implying a multiple millisecond decay of the SPV in the Zn/n-GaP system.
372While previous studies of GaAs semiconductors^{23, 26} and p-Si(100) junctions
373suggest that surface photovoltage decays in these systems on the

374picosecond timescale, it is valuable to consider the difference in band gaps
375between the different materials to get a clearer picture of the dynamics
376occurring. For example, in the case of Zn on p-Si(100), the band gap of
377silicon is 1.12 eV, and the Schottky barrier height was found to be 0.725 eV.
378However, n-GaP has a band gap of 2.26 eV, and the Zn/n-GaP barrier height
379is 2.1 eV. It is known that recombination in Schottky junction systems is
380governed by a modified thermionic emission law known as the Schottky
381formalism:

382
$$J = AT^2 e^{-\beta(\phi - SPV)}$$

383where A is the Richardson constant, β is $1/k_B T$, ϕ is the Schottky barrier
384height, and SPV is the measured surface photovoltage.²⁷ For similar
385Richardson constants and temperatures, it is clear that the main factor
386determining the recombination rate is the barrier height. Since a wide band
387gap semiconductor will likely have a higher barrier,¹⁷ it is then inferred that
388the recombination rate should be significantly decreased for systems in
389which the semiconductor has a wide band gap. For the wide band gap
390semiconductors ZnO and TiO₂, surface photovoltages have been observed to
391persist for milliseconds to seconds, depending on surface conditions.²⁸⁻³⁰ It
392should also be noted that as the SPV decays, the difference between
393Schottky barrier height and SPV becomes larger, resulting in a lowering of
394the recombination rate over the barrier, limiting the decay rate. This is
395suggested as the origin of the long-lived SPV observed in these experiments.

396 It should be noted that previous studies have indicated that the
397 interaction between an electron leaving the surface and the electric field
398 generated by SPV may have an effect on the observed transient spectra.³¹
399 Specifically, the observed dynamics may show a SPV present at negative
400 time delays, as observed in the data here. However, this effect will also
401 cause a slow rise of the photovoltage shift at negative time delays, which
402 does not occur in the data. Thus, it is unlikely that a time-evolving electric
403 field effect in the sample is the origin of the observed shift. The
404 characterized transients relative to this shift are the only processes reported
405 here.

406 **Conclusions**

407 In this work the photoexcitation dynamics of a 10 ML Zn/n-GaP(100)
408 system were measured using a HHG based transient XUV-PES technique.
409 XUV-PES spectra reveal that deposition of Zn results in an additional 0.5 eV
410 of band bending from the clean n-GaP surface, giving a Schottky barrier
411 height of 2.1 eV and showed a 1.5 eV surface barrier height in clean n-GaP.
412 Transient photoemission measurements, using 400 nm pump pulses, show
413 that the Zn and Ga 3d core levels and Zn Fermi level shift by approximately
414 0.6 eV to higher binding energy and display similar dynamics. Such results
415 are indicative of hole transport from n-GaP into the Zn overlayer, resulting in
416 a reduction in band bending at the interface and a shift of the electron quasi-
417 Fermi level to lower energy. These findings contrast with the results obtained
418 for studies of p-type Si with Zn in our group, in which electron transport to

419the Zn layer was the dominant process.⁹ The observed dynamics also
420indicate that there is a long-lived population of holes in the Zn overlayer,
421persisting for over 1 ms after the initial excitation. This population is
422attributed to the slowing of the thermionic emission process as the Schottky
423barrier is recovered after excitation. Here, element-specific photoelectron
424signals are derived not only from the deposited surface material, but also
425from the underlying semiconductor elements in the junction. Therefore, this
426work shows the powerful possibilities for element and material-specific XUV-
427PES measurements at junctions, providing for future measurement of a wide
428number of heterojunction systems with photoelectron spectroscopy on
429femtosecond and picosecond timescales.

430 Finally, the results of this study show both the promise and problems
431with time-resolved photoemission at short timescales. While it is clear that
432the electronic structure of the sample can be probed in great detail using
433XUV photoemission, and that short timescale dynamics are well captured,
434the long timescales associated with electron-hole recombination in this
435junction (and likely in other wide-bandgap semiconductor-metal junctions)
436are not adequately measured. This issue is due to the repetition rate of the
437laser, which in this experiment is 1 kHz, although it can be much higher in
438other tabletop laser-based experiments, and due to the physical limitations
439of delay stages. While femtosecond experiments have had success with
440narrow bandgap semiconductor systems, it is clear that approaches with
441longer timescales, such as synchrotron-based experiments, may be

442beneficial for systems with much longer lifetimes. Experiments with
443nanosecond laser systems with repetition rates of 10-20 Hz may also prove
444useful when coupled to an XUV source such as a helium lamp

445

446**Supplementary Material**

447The supplemental material contains AFM images of the sputtered and
448unsputtered surface and Auger Electron Spectroscopy data for the GaP/Zn
449depositions. An extended transient showing negative time points is also
450included.

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454**Figures**

Figure 1. A. Photoemission spectrum and band structure of n-GaP(100). **B.** Photoemission spectrum and band structure of 10 ML Zn/n-GaP(100). **C.** Measured barrier height as a function of Zn coverage.

459
 460 **Figure 2.** XUV only spectrum (red) compared to -18 ps (blue) and +132 ps
 461 (black) time delays for 10 ML Zn/n-GaP. The inset is an enlarged view of the
 462 Fermi level region of each trace.

463
 464 **Figure 3.** **A:** Transient traces for the binding energy shift of the Zn 3d core
 465 level (red) and Fermi level (black). **B:** Transient traces for the binding energy
 466 of the Zn 3d (red) and Ga 3d (blue) core levels.

467
 468 **Figure 4.** Band diagram of 10 ML Zn/n-GaP in the absence (solid lines) and
 469 presence (dotted lines) of the 400 nm pump beam. Photoexcited electrons
 470 are given as filled circles, while photogenerated holes are represented by
 471 empty circles. Hole transport to the surface results in an apparent increase in
 472 electron binding energy. Electron energy denotes the energy of electrons in
 473 the junction.

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