Surface Photovoltage-Induced Ultralow Work Function Material for Thermionic Energy Converters

Peter Schindler,*†‡△ Daniel C. Riley,¶§∥ Igor Bargatin,# Kunal Sahasrabuddhe,¶§∥ Jared W. Schwede,¶ Steven Sun, Piero Pianetta,¶ Zhi-Xun Shen,¶§∥ Roger T. Howe,† and Nicholas A. Melosh

†Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States
‡Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States
¶Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, United States
§Department of Applied Physics, Stanford University, Stanford, California 94305, United States
∥Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States
⊥Cyclotron Road, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
#Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6315, United States
∇Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

ABSTRACT: Low work function materials are essential for efficient thermionic energy converters (TECs), electronics, and electron emission devices. Much effort has been put into finding thermally stable material combinations that exhibit low work functions. Submonolayer coatings of alkali metals have proven to significantly reduce the work function; however, a work function less than 1 eV has not been reached. We report a record-low work function of 0.70 eV by inducing a surface photovoltage (SPV) in an n-type semiconductor with an alkali metal coating. Ultraviolet photoelectron spectroscopy indicates a work function of 1.06 eV for cesium/oxygen-activated GaAs consistent with density functional theory model predictions. By illuminating with a 532 nm laser we induce an additional shift down to 0.70 eV due to the SPV. Further, we apply the SPV to the collector of an experimental TEC and demonstrate an I–V curve shift consistent with the collector work function reduction. This method opens an avenue toward efficient TECs and next-generation electron emission devices.

The work function is a fundamental surface parameter of a material that determines how easily electrons can be extracted to a field-free region outside the surface; lower work functions facilitate electron emission at lower temperatures. Work functions play a key role in technologies that require precise control of contact barriers such as printed and organic electronics,1–3 electron emission devices (terahertz sources4,5 and fluorescent light bulbs6), electron sources for scientific instruments,7,8 and in thermionic energy converters (TECs).9,10 For TECs and photon-enhanced TECs (PETECs),11 discovery of thermally stable, ultralow work function materials (less than 1 eV) would allow thermionic conversion of heat (>500 °C) or solar radiation directly to electricity with efficiencies exceeding 50% (cf. Figure S1c).

The most commonly used materials for low work function applications that are chemically and thermally stable are compounds like lanthanum hexaboride12,13 and thoriated tungsten.14–17 However, their work functions (~2.5 eV) are not low enough for efficient collectors in thermionic...
converters. Instead, submonolayer coatings of alkali metals (most commonly cesium) on substrate surfaces result in work functions that are much lower than the work function of either substrate or coating individually. This effect is due to the partial transfer of electron charge from the adsorbate to the substrate and the resulting formation of surface dipoles that lower the vacuum energy level near the surface.26 Collector work functions of \( \sim 1.6 \text{ eV} \) have been achieved in TECs using cesiated metals,26 while coatings using both cesium and oxygen are well-known to achieve \( \sim 1 \text{ eV} \) work functions in photocathode applications, for instance on III–V semiconductors or silver.20,21 Diamondoids22 and phosphorus-doped diamond thin films have shown similarly low work functions.23 Our group has achieved a 1.0 eV work function by electrostatically gating cesium/oxygen covered graphene,24 which resulted in enhanced TEC efficiency.25 The lowest theoretically predicted value to date is 0.7–0.8 eV for potassium adsorbed on monolayers of MoTe2 or WTe2.26

Nearly all development of low work function surfaces for TECs has focused on metal electrodes. Despite the phenomenal progress in semiconductor technology over the last 50 years, semiconductor electrodes for TECs have hardly been explored.27 However, the photon-enhanced thermionic emission (PETE) concept, which uses a semiconductor emitting emitter, has been proposed and demonstrated.11,28

At the surface of a semiconductor, the Fermi level is usually pinned because of trap states. Fermi level pinning occurs near mid gap for many compound semiconductors, such as gallium arsenide (GaAs).29 For a doped material, the charged trap states are mirrored in a depletion (space charge) region, which causes band bending, as shown in Figure 1a. When a semiconductor is illuminated, photoexcited minority carriers gather at the surface because of the built-in potential in the surface depletion region. The charge build-up forms an internal dipole that opposes the dipole stemming from the trap states and flattens the bands, assuming the surface states do not change significantly upon illumination.30,31 (see Figure 1b). Therefore, the surface photovoltage (SPV) raises the Fermi level closer to the vacuum level in an n-type semiconductor and lowers the work function, \( \phi \). Conversely, the SPV effect will increase the work function in a p-type semiconductor. These shifts in work function have been observed extensively in the literature.32–34 Depending on surface properties and illumination conditions, it has been observed to influence the flux dependence of photoemission yields35 and to cause core-level shifts in photoemission spectroscopy measurements.36

In this Letter, we use the SPV effect for an n-type semiconductor to reduce the work function of its surface (with and without an alkali metal coating). Density functional theory and ultraviolet photoelectron spectroscopy using synchrotron radiation confirm a work function of 1.06 eV for cesium/oxygen-coated, n-type GaAs. We achieve a record-low work function of 0.70 eV by inducing an SPV by shining a 532 nm laser on the sample. This method is extendable across semiconductor material systems and can be applied to the collector of a TEC using an efficient laser diode, potentially increasing the efficiency of thermionic energy conversion dramatically. Further, we report the application of the SPV effect in a TEC, demonstrating the shift in the \( I–V \) curve due to the collector work function reduction. We observe a shift of 0.23 eV in the power consumption quadrant, and 0.28 eV in the power production quadrant, of the \( I–V \) curve. These results are consistent with the SPV induced work function shift.

The work functions of clean and cesium/oxygen-activated GaAs are modeled by ab initio density functional theory (DFT) and measured by ultraviolet photoelectron spectroscopy (UPS). To achieve an ultralow work function, we use a submonolayer coating of cesium in the presence of oxygen (Cs/O2). Predictions of electronic properties are obtained by gradient-corrected DFT. While it is known that DFT tends to underestimate semiconductor band gaps, the center of the gap (and hence the Fermi level) is predicted accurately.37 The unit cell for the calculation of the work function of clean GaAs comprised a slab (face centered cubic, 5 atomic layers in thickness, (100) oriented surface) with 10 Å of vacuum on either side to suppress interactions of periodic images of the slab. The calculation gives a work function of 4.52 eV for clean GaAs, which agrees well with literature reports for clean (100)-oriented GaAs.38 However, one should note that work functions reported in the literature often have a large range; in the case of (100)-oriented GaAs, it strongly depends on the fraction of Ga to As at the surface.39 Further, DFT yields insight into the effect of Cs/O2 coverage on the work function. The number of Cs/O2 dipoles per unit cell area determines the coverage (normalized to 1 Cs/O2 per 30 Å²). Figure 2a shows a plot of the calculated work functions at different Cs/O2 coverages where the minimum work function of 1.06 eV is obtained at a coverage of around half a monolayer of Cs/O2. This trend is consistent with other alkali-metal covered surfaces reported in the literature.40

The ionically relaxed unit cell is displayed from the side and top in Figure 2b for the case of optimal coverage for achieving minimal work function. The electrostatic potential calculated with respect to the Fermi level for both clean and optimally Cs/O2-coated GaAs is plotted in Figure S9. The work function is given by the difference of the electrostatic potential energy in the vacuum region, \( E_{\text{vac}} \) and the Fermi energy, \( E_F \). Convergence of the work function with respect to the vacuum layer thickness between slab and its periodic images is confirmed as shown in Figure S8.
To measure the work function $\phi$ we utilize UPS with the low-energy cutoff method facilitated by synchrotron radiation at the Stanford Synchrotron Radiation Light Source (SSRL) at the SLAC National Accelerator Laboratory.\textsuperscript{40} The photoemission low-energy cutoff (LEC) of the electron energy distribution curve (EDC) determines the work function by the following equation:

$$\phi = E_{\text{cutoff}} - q \cdot V_{\text{bias}} + \phi_{\text{analyzer}}$$  \hspace{1cm} (1)

where $\phi_{\text{analyzer}}$ is the work function of the hemispherical analyzer which is measured in reference to the Au 4$f_{5/2}$ core level, $V_{\text{bias}}$ is the negative bias applied to the sample, and $E_{\text{cutoff}}$ is the cutoff for the lowest kinetic energies and is calculated from the rising edge of the EDC by fitting a complementary error function,\textsuperscript{40} as described in Methods.

The LEC measurements of the clean and Cs/O$\textsubscript{2}$-activated, highly n-doped GaAs sample are shown in Figure 2c. For clean GaAs, photoemission is stimulated by a 130 eV probe beam. The electron energy has been corrected to account for the sample bias ($V_{\text{bias}} = 9.93$ V) and the analyzer work function ($\phi_{\text{analyzer}} = 4.40$ eV) to yield the work function (eq 1). The measurement determines the baseline work function of clean GaAs to be 4.52 ± 0.1 eV. Then cesium and oxygen are codeposited to minimize the work function and maximize the photoemission current as described in Methods. After Cs/O$\textsubscript{2}$ activation, the work function is low enough that a very small amount of ambient light (leaking into the chamber through the laser viewport) can already stimulate photoemission. Therefore, the 130 eV probe beam is not required to induce photoemission. The work function measured for Cs/O$\textsubscript{2}$-activated GaAs is 1.06 ± 0.1 eV. For Cs/O$\textsubscript{2}$-coated surfaces, a slow decay in the work function is measured after a few minutes that can be attributed to poisoning of the alkaline coating commonly observed in cesium photocathode tests.\textsuperscript{41} In practice, this can be mitigated by lower vacuum pressures. Our UPS-measured work function of clean, n-doped GaAs agrees well with the DFT-predicted value. The good agreement of DFT and experiment, despite the calculation assuming GaAs to be intrinsic (undoped), is due to the Fermi level pinning for GaAs being close to midgap.\textsuperscript{29} Moreover, the predicted minimum work function of 1.06 eV agrees well with both the literature\textsuperscript{21,42} and our LEC measurements.

To further reduce the work function we induce an SPV in the sample by shining a 532 nm laser on both clean and Cs/O$\textsubscript{2}$-activated GaAs. The LEC measurements of the clean GaAs sample with and without the laser-induced SPV are shown in Figure 3a. The electron energy has been corrected as before to yield the work function. Photoemission in this measurement is

![Figure 2](image1.png)

**Figure 2.** (a) DFT calculated work functions versus Cs/O$\textsubscript{2}$ coverage (normalized to 1 Cs/O$\textsubscript{2}$ per 30 Å$^2$). The work functions of clean and optimally Cs/O$\textsubscript{2}$-coated GaAs are 4.52 and 1.06 eV, respectively. (b) Unit cell of the Cs/O$\textsubscript{2}$-coated GaAs slab (10 Å of vacuum on either side) as seen from the side and the top. (c) LEC values of clean and Cs/O$\textsubscript{2}$-coated GaAs are plotted and determine the work functions to be 4.52 and 1.06 eV, respectively.

![Figure 3](image2.png)

**Figure 3.** LEC method is used to determine the work function. Black and red curves correspond to the laser being turned off and on, respectively. (a) The work function of clean GaAs shifts from 4.52 to 4.32 eV because of the SPV effect induced by a 24 mW/cm$^2$ laser. (b) For Cs/O$\textsubscript{2}$-coated GaAs a shift from 1.06 to 0.70 eV is observed using a laser power of 10 mW/cm$^2$. \textsuperscript{474} DOI: 10.1021/acsomeglett.9b01214

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Figure 3b shows the LEC measurement of the GaAs sample (with and without SPV) after being activated with Cs/O2. With the laser illumination intensity limited to \( \sim 10 \text{ mW/cm}^2 \) to prevent saturation of the hemispherical analyzer measuring the EDC, the work function decreases from 1.06 to 0.70 eV. The shift for Cs/O2-coated GaAs is larger (0.36 eV at 10 mW/cm\(^2\)) than for clean GaAs (0.20 eV at 24 mW/cm\(^2\)). This difference can be explained by the strong dependence of the SPV effect on the density of surface trap states (affecting the Fermi level pinning) that is likely much lower for clean GaAs than for Cs/O2-coated GaAs.

To our knowledge, our measurement of 0.70 eV is the lowest work function reported in the literature. We rely on synchrotron-based UPS with the LEC method because we believe this is the most reliable method for determining the work function of semiconductors. Another, direct way of measuring the work function is photoelectron yield spectroscopy (PYS) commonly used for metals. While PYS may also be used for semiconductors, the energy threshold obtained may not coincide with the Fermi level, making the determination of the work function more challenging. Importantly, for some materials, determining work functions by alternative methods such as field-emission characteristics or Kelvin-probe has resulted in different, much lower values compared to using UPS or PYS. For instance, electrode materials have been reported to have work functions as low as 0.6 eV when fitting field-emission plots while the work function is greater than 2 eV when UPS or PYS is employed. Kelvin-probe measured work functions for Cs/O2-coated silver have been reported to be \( \sim 0.6 \) eV, while work functions are \( \sim 1 \) eV when using PYS. These lower values, while tantalizing, are unfortunately not representative of the material in practical operation (e.g., as a photocathode or thermionic electrode).

Figure 4 shows the work function of Cs/O2-coated GaAs (as determined from the LEC shift) as a function of laser intensity. The dependence of the work function on the intensity is logarithmic, as expected. The full EDC curves are plotted in Figure S4.

The logarithmic behavior observed in Figure 4 is in agreement with an SPV model that is similar to a Schottky diode model:

\[
V_{SPV} = \eta k_B T_E \left( \frac{j_{ph}}{R_0} + 1 \right)
\]

where \( R_0 \) is the recombination rate of the surface in the dark and \( j_{ph} \) is the surface photocurrent which varies directly with the illumination intensity. While the SPV effect is very simple in principle, it is extremely difficult to model quantitatively. The recombination rate of carriers at the surface is dependent on numerous parameters, including the trap density, trap energies, sticking coefficient of the trap states, doping, and temperature. The nature of the trap states changes depending on the illumination level, because traps may become saturated.

The experimental results demonstrate that we can achieve an ultralow work function using the SPV effect. The LEC method relies on measuring the energy of emitted electrons to measure the work function. However, an electrode using the SPV effect in a TEC device will be used as an electron collector. Therefore, we measure the SPV effect in an electron collection mode in a TEC device-like environment.

A custom ultrahigh vacuum (UHV) chamber was built to observe how the \( I-V \) characteristics of a thermionic device change when the SPV is induced by a 650 nm laser with an output power of 200 mW. Details of the chamber and thermionic device are described in Methods, and a schematic of the experimental setup is shown in Figure S6.

Figure 5a shows the \( I-V_{bias} \) curve for a bare GaAs collector with and without laser exposure. The data is fit in the Boltzmann regime, where the current \( J \) rises exponentially with an increase in bias, using a modified Richardson–Dushman equation:

\[
J = A T_E^2 \exp \left( -\frac{\phi_C - q V_{bias}}{k_B T_E} \right)
\]

where \( V_{bias} \) is the applied bias voltage across the device (i.e., potential of collector with respect to the emitter), \( A \) the material-specific Richardson coefficient, \( k_B \) the Boltzmann constant, \( T_E \) the temperature of the emitter, and \( \phi_C \) the GaAs collector work function. In this regime, there is a potential barrier between the emitter and collector, because the collector vacuum level is above the emitter vacuum level. The current is determined by the fraction of electrons with enough energy to overcome the work function of the anode and the device bias. Therefore, we expect this region of the \( I-V_{bias} \) curve to shift with respect to \( V_{bias} \) if the collector work function, \( \phi_C \), changes.

Figure 5a demonstrates a clear shift in the \( I-V_{bias} \) curve when illuminated, corresponding to a work function reduction.
The shift in the $I-V_{bias}$ curve of the Ba-activated TEC-prototype device when illuminated (Figure 5b) demonstrates that the SPV effect may be used to reduce the work function of the collector of a thermionic device operating in a power production regime—a definitive proof-of-concept toward higher-efficiency thermionic energy conversion. Integrating a low-power light-emitting diode into the device architecture of a TEC would enable a sustained reduction of the collector work function and hence an increased efficiency.

In summary, we demonstrate for the first time a material with an ultralow work function of 0.70 eV by illuminating Cs/O₂-coated, n-type GaAs with a 532 nm laser to induce an SPV. UPS confirms a work function shift from 4.52 to 4.32 eV for clean GaAs and from 1.06 to 0.70 eV for Cs/O₂-coated GaAs caused by the SPV. Further, we verify that the SPV method is applicable to the collector of a thermionic converter operating in a power production regime.

The magnitude of the band bending at the surface (cf. Figure 1) poses an upper limit for the SPV. An increase in doping concentration shifts the Fermi level closer to the band edge, resulting in an increased band bending and thus higher SPV. However, this effect levels off logarithmically, and for highly doped (nondegenerate) semiconductors, the Fermi level position converges toward the band edge. Therefore, wider band gap materials (e.g., GaN, AlN) would be of greater interest for future work as the effect of doping on the band bending tends to be more pronounced the wider the gap.⁵⁰ This could potentially lead to even larger SPV-induced work function shifts. As this method is extendable across several semiconductors, it can facilitate the development of highly efficient thermionic converters and electron emission devices.

## METHODS

Self-consistent, periodic, total energy calculations based on gradient-corrected DFT were performed using Quantum ESPRESSO.⁵¹ Ultrasoft Vanderbilt pseudopotentials were used to describe core electron interactions.⁵² The Kohn–Sham one-electron valence states were expanded in a plane wave basis set with a kinetic energy cutoff of 600 eV. The electron density of 0.23 ± 0.08 eV due to the SPV effect. The static parameters of the fit for the data in the Boltzmann regime are $A = 70$ A/(cm²K²)⁴⁹ and an area of 9.1 mm². With the laser on, the fit gives the temperature $T_E = 816 ± 16 °C$ and the work function $\phi_C = 4.57 ± 0.07$ eV. With the laser on, the temperature and work function are $T_E = 800 ± 11 °C$ and $\phi_C = 4.33 ± 0.05$ eV. The work function shift determined by the fits is consistent with the shift measured by the LEC method. The given errors are based on linearly fitting (on a logarithmic plot) the Boltzmann regime by picking the same current threshold for both laser conditions. While these fitting errors appear to be smaller than the errors in the LEC measurements (~100 meV), there is additional uncertainty in the absolute values depending on the selection of the current threshold. However, as long as the same threshold is chosen for both laser conditions, the relative work function shift is accurate and its error is based on the fitting errors of the individual laser conditions. To confirm that the SPV effect is indeed observed only on the semiconductor, the laser is on/off cycled on GaAs and a tungsten control sample, as shown in Figure S3.

For the case of no alkali metal coverage, the work function is too large for the device to be operating in power production mode. To shift the $I-V_{bias}$ curve into the power producing quadrant we use a GaAs sample activated with a low work function barium coating. The low work function coating is produced by raising the dispenser cathode emitter to a high enough temperature for it to evaporate barium onto the collector. The measured $I-V_{bias}$ curves are shown in Figure 5b, and again a clear shift is observed when illuminated, corresponding to a work function reduction of 0.28 ± 0.06 eV. With the laser off, the fit gives an emitter temperature $T_E = 645 ± 11 °C$ and collector work function $\phi_C = 2.08 ± 0.03$ eV. The DFT-calculated work function for optimally Ba-covered GaAs is 2.06 eV (cf. Figure S10), which agrees well with the fitted collector work function. With the laser on, the emitter temperature and collector work function are $T_E = 615 ± 22 °C$ and $\phi_C = 1.80 ± 0.05$ eV. Interestingly, the work function shift observed for Ba-activated GaAs is roughly 0.1 eV less than that for Cs/O₂-activated GaAs (Figure 3b). This is likely due to differences in the surface state distributions that arise from the two distinct alkali metal coatings.

Figure 5. TEC prototype device $I-V_{bias}$ curves with and without laser illumination are plotted. Fitting the data in the Boltzmann regime (shaded in gray) determines the work function shift between the not illuminated (black) and illuminated (red) cases. (a) GaAs anode without Ba coating shows a clear shift in the $I-V_{bias}$ curve corresponding to a change of 0.23 eV in work function (in power consumption mode). (b) With Ba coating, an $I-V_{bias}$ curve shift corresponding to a change of 0.28 eV in work function is observed (in power production mode).
holding valence electrons to improve convergence. The generalized gradient approximation with the parametrization of Perdew–Burke–Ernzerhof (PBE) was used for the exchange–correlation functional.\textsuperscript{53}

The unit cell for bulk GaAs had face-centered cubic symmetry repeated in a super cell geometry. The first Brillouin zone was sampled by a \((10 \times 10 \times 10)\) \(k\)-point mesh. The lattice constant of the relaxed unit cell was 5.739 Å, which is within ~1.5\% deviation from the experimental value.\textsuperscript{54} Convergence was ensured with respect to plane wave cutoff and number of \(k\) points.

The slab geometry described in the main text was formed on the basis of the relaxed bulk unit cell with 10 Å of vacuum on either side. The Cs/O\textsubscript{2} adsorbates were placed using the atomic simulation environment (ASE)\textsuperscript{55} and relaxed quasi-Newtonian with convergence set to a force of 0.05 eV/Å. The three lowermost atomic layers (total slab thickness was 5 atomic layers) were fixed during relaxation to facilitate convergence, which has shown to give accurate work functions for other materials.\textsuperscript{56} To obtain accurate work functions we mirrored the unit cell in the \(z\) direction instead of using the built-in dipole correction available in Quantum Espresso. This procedure is illustrated in Figure S7. For the slab, the first Brillouin zone was sampled by a \((5 \times 5 \times 1)\) \(k\)-point mesh.

The work function was measured by UPS using synchrotron radiation and the LEC method at SSRL, SLAC National Accelerator Laboratory.\textsuperscript{50} The setup is illustrated in Figure S5. The GaAs sample was a 0.5 mm thick wafer with (100) orientation and n-type Si doping \((1.0 \times 10^{18} \text{ to } 1.2 \times 10^{18} \text{ cm}^{-2})\), grown by MTI Corporation using the vertical gradient freeze method. The sample was dipped in 10\% HCl for 1 min, followed by two 1 min rinses in deionized water. An electron beam evaporation system was used to deposit 100 nm of nickel, then 20 nm of platinum onto the entire underside of the sample for electrical contact. It was then affixed to a molybdenum sample holder using molybdenum clips and mounted on a transfer arm inside the load lock (pumped to 10\(^{-8}\) Torr). After the sample was transferred into an UHV chamber (base pressure of 3 \times 10\(^{-10}\) Torr), it was annealed at approximately 400 °C to remove surface oxides, carbon, and other impurities. Cleaning was verified via the As 3d core level. Prior to annealing, a small photoemission peak corresponding to arsenic oxide was observed 2.8 eV below the kinetic energy of the bulk As 3d peak. This peak was not present after the sample had been annealed, confirming the oxide removal. This method of cleaning in HCl and annealing has been shown to be effective at removing carbon contamination on the surface as well.\textsuperscript{57} For the clean GaAs sample, photoemission was stimulated by a probe beam with a photon energy of 130 eV.

Cesium was deposited onto the sample with a degassed getter (SAES Getters S.p.A.) to lower the sample work function. While the Cs was deposited, ambient light was allowed to enter the chamber, which was sufficient to induce photoemission. The sample was biased negatively with a 9 V battery to drive photoemission current from the sample surface to the surrounding grounded chamber. Once the photoemission current was maximized, O\textsubscript{2} was administered into the chamber at a pressure of approximately \(2 \times 10^{-9}\) Torr with a leak valve. The Cs and O\textsubscript{2} were codeposited and adjusted to increase the photoemission current until it was again maximized, a method based on typical semiconductor photocathode surface preparation.\textsuperscript{58,59}

The sample was illuminated at an angle of 45° with a 532 nm laser and a beam diameter of approximately 6 mm to induce the SPV. The sample bias (9.9 V DC) was used to accelerate electrons toward the multichannel plate of the energy analyzer. The EDC was measured with a PHI 10-360 hemispherical analyzer with a resolution of approximately 100 meV.

The photoemission current from the sample was monitored to ensure that internal resistivity does not affect the work function measurements. For Cs/O\textsubscript{2}-activated GaAs, the photoemission currents were 2.3 μA and 0.01 nA with the laser turned on (10 mW/cm\(^2\)) and off, respectively. The contact resistance of the Ni/Pt contacts on GaAs (after annealing) was ~15 Ω. Hence, the currents were low enough to render any resistance drops within the sample negligible.

The cutoff energy \(E_{\text{cutoff}}\) in eq 1 was calculated by fitting a complementary error function

\[
I(E) = A \cdot \text{erfc} \left( \frac{E_{\text{cutoff}} - E}{\sqrt{2} \sigma} \right) + I_{\text{min}}
\]

where \(I(E)\) is the intensity of the EDC as a function of energy and \(A, \sigma\) and \(I_{\text{min}}\) are free fitting parameters.\textsuperscript{60} Simultaneously with the EDC, the Ga 3d core level peak position was also measured.

For the TEC device measurements, a custom UHV chamber was built, a schematic of which is shown in Figure S6. The UHV chamber for this measurement was pumped by a turbomolecular pump and was able to reach pressures of \(4.5 \times 10^{-10}\) Torr when baked. There were several viewports for optical access. The sample mounting stage was a HeatWave Laboratories 101491-01 UHV heater stage with shielding. The stage was electrically isolated from the body of the chamber and the heater electrical leads, so that the sample could be biased and its collection current could be measured.

Suspended above the sample holder was a degassed 0.134 in. diameter HeatWave Laboratories 101101 barium tungsten dispenser cathode, which was heated to generate thermionic current.

The sample composition and preparation was identical to that used in the LEC experiment, except the second HCl cleaning performed immediately before loading into the vacuum chamber was done in air.

For the \(I-V\) bias measurement the sample heater stage (with mounted GaAs sample) was grounded through a Keithley 6485 current meter to measure the sample collection current. The emitter was biased relative to ground using a Keithley 6487 source meter, which measured the emitter emission current. The sample surface was illuminated with a 650 nm laser with an output power of 200 mW. The laser was incident at approximately 20° in reflection mode and was operated for at least 10 min before the measurement to stabilize it.

The bias voltage of the emitter was swept in 0.1 V steps over a wide enough range to map the entire \(I-V\) bias curve, and the current was measured at each step. The \(I-V\) bias curves were measured repeatedly with the laser blocked and exposed to establish repeatability and reversibility.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energylett.9b01214.
Illustration of TEC architecture, band diagram, and conversion efficiency. Ga 3d core-level shift plot; laser on/off cycling control measurements; full EDC curves of the LEC measurements; LEC measurement and thermionic device test setups; illustration of procedure to calculate the electrostatic potential by DFT; work function plotted versus vacuum layer thickness between slabs; comparison of electrostatic potentials for clean and optimally Ca/O₃-coated GaAs; DFT-calculated work function plot as a function of Ba coverage (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: pschind@stanford.edu. Phone: +1 650 248-1066. Fax: +1 650 725-3383.

ORCID
Peter Schindler: 0000-0002-1319-6570

Author Contributions
△P.S. and D.C.R. contributed equally to this work. I.B., D.C.R., and J.W.S. designed the experimental setup. D.C.R., K.S., J.W.S., and S.S. carried out sample preparation and performed sample characterization. D.C.R. and K.S. made photoelectron spectra measurements. D.C.R. constructed the TEC prototype and performed $I−V_{\text{bias}}$ measurements. D.C.R. and P.S. modeled the fit for the photoelectron spectra measurements and TEC device $I−V_{\text{bias}}$ curves. P.S. carried out DFT simulations and theoretical modeling for the material work functions. N.A.M, Z.-X.S, R.T.H., and P.P. supervised the project. P.S. and D.C.R. wrote the Letter with editing from J.W.S, K.S., and R.T.H.

Notes
The authors declare no competing financial interest.

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