Tunneling-injection in vertical quasi-2D heterojunctions enabled efficient and adjustable optoelectronic conversion

Wei-Chun Tan1, Chia-Wei Chiang1, Mario Hofmann2 & Yang-Fang Chen1

The advent of 2D materials integration has enabled novel heterojunctions where carrier transport proceeds through different ultrathin layers. We here demonstrate the potential of such heterojunctions on a graphene/dielectric/semiconductor vertical stack that combines several enabling features for optoelectronic devices. Efficient and stable light emission was achieved through carrier tunneling from the graphene injector into prominent states of a luminescent material. Graphene’s unique properties enable fine control of the band alignment in the heterojunction. This advantage was used to produce vertical tunneling-injection light-emitting transistors (VtLET) where gating allows adjustment of the light emission intensity independent of applied bias. This device was shown to simultaneously act as a light detecting transistor with a linear and gate tunable sensitivity. The presented development of an electronically controllable multifunctional light emitter, light detector and transistor open up a new route for future optoelectronics.

The discovery of graphene and other 2D materials has led to the emergence of a new class of hybrid materials that derive their properties from interfaces between layers of dissimilar materials1–4. Carrier transport in such heterojunctions is commonly proceeds by tunneling and thermionic emission current which is fundamentally different from traditional diffusion-based charge transport and makes these structures especially promising for optoelectronic devices5–11. Conversion between electrical and optical signals is required in a large variety of applications ranging from solid state lighting, ubiquitous information displays, light-based wireless communication and optical computing12–16. Future development in these areas relies on improvements in several areas.

A wide range of accessible wavelengths, for example, is required for lighting applications as well as wide-bandwidth optical communication. Furthermore, the increasing resolution of displays will necessitate high integration densities of emitters17–20. Finally, optical computing applications will require multifunctional devices that allow efficient coupling between electronic and optical functionalities. All of these advances will have to be compatible with increased scale and ease of fabrication.

Current light emitters have severe limitations that prevent them from supporting these developments. While crystalline semiconductors exhibit composition-dependent emission properties, fabrication challenges arise for each new material combination21. Furthermore, emission characteristics are deteriorated by large bias currents and inevitable defects22. While organic semiconductors promise low cost production and access to different emission profiles their intrinsically slow carrier transport limits the efficiency of those emitters23–25. Finally, future requirements for higher device integration density, e.g. in monolithically integrated light emitting diode (LED) arrays and on-chip optical communication, cannot be satisfied with current configurations where each light emitter is driven by a dedicated transistor26.

We here demonstrate the potential of metal/insulator/semiconductor heterojunctions between 2D and thin film materials as a composited architecture for efficient and multifunctional optoelectronic devices as shown in Fig. 1(a). The tunneling-based carrier transport produces efficient and color stable light emission. The operation mechanism was elucidated to be a gate-tunable and energy-selective carrier tunneling process, which is different from previously reported graphene-based Schottky-barrier devices27 and represents an operation mechanism that
is compatible with many different luminescent materials. In the case of GaN selective injection in states close to the band edge results in a narrow emission peak at 400 nm. The demonstrated electrostatic control over the emission intensity through gating yields three-terminal vertical tunneling-injection light emitting transistors (VtiLET) with high efficiency. Our architecture furthermore enables the application of such light emitters as a photodetector with linear and tunable sensitivity. Finally, the employed self-aligned vertical architecture significantly reduces fabrication complexity and is suitable for a wide range of morphologies and nanostructures.

Results

The electro-luminescence and I-V characteristics of VtiLET device. The fabricated vertical tunneling-injection light emitting transistor on sapphire substrate with the structure shown in Fig. 1(a) was characterized using Raman spectra to reveal the signals of p-GaN and graphene separately in Fig. 1(b). The top layer of graphene plays a role of gate electrode. Meanwhile, the middle layer of graphene is the source terminal and the drain terminal belongs to p-GaN. In order to demonstrate the importance of the thin 10 nm SiO2 layer in the emission process, we first compare the result for both samples of graphene/SiO2/p-GaN and graphene/p-GaN. Figure 2(a) shows the electroluminescence (EL) spectra of the graphene/SiO2/p-GaN and graphene/p-GaN devices under forward source-drain-bias (which was defined $V_{SD} > 0$ V, $V_S = 0$ V, and then $V_{SD} > 0$ V here). The emission peak of graphene/SiO2/p-GaN device around 400 nm can be attributed to the transition from states near the conduction band to acceptor impurity states caused by interstitial Mg atoms near the valence band28. A small shoulder at around 387 nm originates from p-GaN band edge emission around 3.2 eV29. The emission behavior is different from commonly observed emission in metal/insulator/semiconductor devices that operate through impact ionization and avalanche multiplication and require large reverse-bias voltages30–32. Furthermore, the emission spectrum in graphene/p-GaN heterojunctions (without thin SiO2) is characterized by a broad band emission as shown in Fig. 2(a).

Figure 1. (a) Schematic of the vertical tunneling injection light emitting transistor (VtiLET) (b) Micro-Raman spectra for graphene on p-GaN and SiO2 substrates with the indication of p-GaN and graphene characteristic peaks.

Figure 2. (a) Electroluminescence (EL) spectra of graphene/thin SiO2/p-GaN device under forward bias ($V_{SD} > 0$ V) of 12 V. (b) Simmons plot of current measurement and the measured data were fitted to equation (1). (inset) Energy level diagram of the graphene/thin SiO2/p-GaN device under forward bias ($V_{SD} > 0$ V).

The difference in emission characteristics can be explained when considering the added oxide layer. Without the oxide layer, the applied voltage will mainly drop in the GaN film, which can induce a large band bending near the Schottky interface and cause a broad emission and red shift. However, with the addition of the oxide layer, the
highest potential drop will occur at the tunneling interface and minimal band bending within the p-GaN. Under an applied forward bias ($V_{SD} > 0$ V), the bands of p-GaN at the interface near the thin SiO$_2$ are bent upwards and the work function of graphene changes to smaller values (inset of Figure 2(b)). Due to the large voltage drop across the thin SiO$_2$ insulating layer, the applied bias induces an accumulation layer of holes near the SiO$_2$/p-GaN interface. The injected electrons can then recombine radiatively with holes in p-GaN near the interface and generate the UV emission, which will reduce the linewidth and cause the blue shift compared with the sample without thin SiO$_2$ layer.

In the tunneling regime, the Simon's approximation describes the current-voltage diagram. In the applicable limit of large applied bias, the dependence equation of $I_{SD}$ versus $V_{SD}$ can be written as:

$$I_{SD} \propto V_{SD}^2 \exp \left( \frac{-4d \sqrt{2m_e \varphi}}{3eV} \right).$$

(1)

Here $d$ is the barrier width, $m_e$ is the electron effective mass and $\varphi$ is the tunneling barrier height. The good agreement with the model is demonstrated in Fig. 2(b), where we plot the natural logarithm of the source-drain current divided by $V_{SD}$ as a function of $I_{SD}$. As expected, the plot exhibits a linear dependence which is commonly known as a Fowler–Nordheim tunneling. As shown in Fig. 2(b), the field emission goes through a triangular barrier under a large voltage.

The observed mechanism is fundamentally different from the traditional operation of an LED. While conventional LEDs operate through minority carrier conduction and recombination, our tunneling-LEDs work by injecting carriers directly into prominent states by tunneling without the need for efficient carrier transport. Therefore tunneling-LEDs are compatible with a wide range of luminescent materials that do not exhibit high carrier conductivities. Furthermore, the large potential drop across the oxide barrier minimizes the band bending within the p-GaN which reduces the effect of impact ionization that usually broadens the spectrum. Consequently, a 13% narrowing full width at half maximum (FWHM) and 5.4 nm blue shift of the p-GaN emission spectrum can be observed (Fig. 2(a)).

**The electric field effect performance of VtiLET device.** The single layer graphene serves in a two-fold role in our architecture. First, its very small effective electron mass improves the efficiency of tunneling injection. Furthermore, graphene acts as a transparent electrode that allows 3x more efficient emission of the UV light compared to common ITO electrodes (see Figure S1 for more details). Another feature of graphene is subsequently exploited to enhance the functionality of the emitter. Graphene’s work function can be widely tuned by injecting carriers directly into prominent states by tunneling without the need for efficient carrier transport. Therefore tunneling-LEDs are compatible with a wide range of luminescent materials that do not exhibit high carrier conductivities.

In the tunneling regime, the Simon’s approximation describes the current-voltage diagram. In the applicable limit of large applied bias, the dependence equation of $I_{SD}$ versus $V_{SD}$ can be written as:

$$I_{SD} \propto V_{SD}^2 \exp \left( \frac{-4d \sqrt{2m_e \varphi}}{3eV} \right).$$

The simplicity of the model is demonstrated in Fig. 2(b), where we plot the natural logarithm of the source-drain current divided by $V_{SD}$ as a function of $I_{SD}$. As expected, the plot exhibits a linear dependence which is commonly known as a Fowler–Nordheim tunneling. As shown in Fig. 2(b), the field emission goes through a triangular barrier under a large voltage.

The observed mechanism is fundamentally different from the traditional operation of an LED. While conventional LEDs operate through minority carrier conduction and recombination, our tunneling-LEDs work by injecting carriers directly into prominent states by tunneling without the need for efficient carrier transport. Therefore tunneling-LEDs are compatible with a wide range of luminescent materials that do not exhibit high carrier conductivities. Furthermore, the large potential drop across the oxide barrier minimizes the band bending within the p-GaN which reduces the effect of impact ionization that usually broadens the spectrum. Consequently, a 13% narrowing full width at half maximum (FWHM) and 5.4 nm blue shift of the p-GaN emission spectrum can be observed (Fig. 2(a)).

**The comparison of VtiLET between optics and electronics.** The light emitting transistor structure employed here was found to improve the performance of light emitters. Commercially available LEDs based on multiple GaN/InGaN/GaN quantum wells exhibit a turn on voltage around 2.75 V, which necessitates high operating voltages and increases power consumption. In our device, applying a gate voltage decreases the turn on voltage to 1 V under positive gate voltage and increases it to 12 V for under negative gate voltage. Application of a gate thus increases the efficiency by ~200% compared to un gated conductions. This novel operating mechanism
yields unoptimized emission efficiencies of ~50% of commercial multiple quantum well light emitting diodes (MQW-LEDs) (Fig. 4(a)), which could in the future be further enhanced through optimization of the graphene conductivity and the barrier thickness.

In addition to an enhanced emission, electrostatically controlled tunneling promises faster and more efficient transition between on- and off-states than conventional transistor operation mechanisms. This behavior makes it ideally suited for high speed connection between optics and electronics. To take full advantage of this linkage, conversion between light and current should proceed in both directions and a receiver is needed. We here demonstrate that our graphene/oxide/semiconductor structure can not only emit but also detect light. This dual role can improve the integration density of optical communication devices and enable on-chip optical computing.

Figure 4(b) shows the emission current under time-varying illumination with a 325 nm laser. The underlying band bending mechanism results in a much faster response and higher sensitivity than normal GaN-based devices. The response time to achieve saturation is below 0.5 seconds regardless of the light excitation while traditional devices require minutes to reach saturation. The photodetection mechanism was investigated by using different excitation sources. Figure S3 shows that the device has the largest photoresponse under 325 nm while 514 nm and 1064 nm show a much smaller response. In the case of the 1064 nm excitation, heating effects were identified as the origin of the response. We therefore conclude that excitation across the GaN band gap is responsible for the photoresponse. The small photoresponse of the 514 nm excitation source is attributed to contributions from defect transition. Photogeneration of electron-hole-pairs is followed by separation of the carriers within the p-GaN region near the surface where the bands are bent. This mechanism was confirmed by comparing the sensitivity under forward (VSD > 0 V) and reverse bias (VSD < 0 V) (Fig. 4(c)). We observe that the reverse bias has a larger photocurrent signal ratio than forward bias due to the asymmetric band brought about by the opposing internal and external fields under forward bias.

Figure 4(d) demonstrates the ability to electrostatically tune the detectors sensitivity independent of applied bias. The mechanism of the electrostatically tunable sensitivity is illustrated in the inset of Fig. 4(d). When the gate voltage (VG) increases, the decrease of the work function of graphene will induce larger band bending of p-GaN. Due to the larger bending the excited electron and holes could be separated much easier and generate a higher photoresponse. The observed linearity in sensitivity with gate voltages improves the accuracy of the sensor compared to traditional photosensors which exhibit an exponential characteristic. The different dependences of photosensitivity on gate voltage (VG) and source-drain bias (VSD) could enable sensors that are adaptable to widely different illumination conditions (through control of VSD) while retaining ultrahigh sensitivity (by modifying
VG). Compared with published reports of GaN based photodetectors, the photoresponse shown here is more than a factor of 10 times higher.

Conclusion

In conclusion, we have utilized a heterojunction of 2D materials and ultrathin films in a novel and multifunctional device that serves as light emitter, light detector and transistor. The integration of these unique properties requires less complex fabrication and lend themselves to new applications. It was observed that carrier injection from graphene into a luminescent material created emission from well-defined states and its intensity could be controlled by a gate. The mechanism was found to be based on tunneling through a barrier that could be modified by changing the graphene work function. The application of a gate was shown to enhance the emission efficiency and the performance of the emitter and also enabled multifunctional devices. The presented gate controlled carrier injection mechanism enabled fine control of the device operation, such as tunable detection sensitivity. Finally, the universal applicability of the underlying quantum tunneling mechanism is compatible with a wide range of 2D and quasi-2D materials which enables tailoring of device properties for a bright future for optoelectronics.

Methods

Device fabrication and characterization measurements. Figure 1(a) shows the structure of the proposed tunneling injector structure. Mg doped GaN \( (n_p = 3 \times 10^{17} \text{cm}^{-3} \text{determined by Hall measurement}) \) on sapphire acts as the luminescent material and the substrate which was grown by metal organic chemical vapor deposition. Before fabrication it was cleaned following established procedures.

A 10 nm thin SiO₂ film was deposited on the p-GaN surface as a tunneling barrier via radio frequency (RF) sputtering. Finally, graphene grown by chemical vapor deposition on copper foil was transferred onto the SiO₂ with the aid of polymethylmethacrylate (PMMA) following previous reports. The quality and thickness of the transferred graphene were verified by Raman spectroscopy (Jobin Yvon T64000) (Fig. 1(b)) and the Raman signal of graphene on p-GaN shows additional strong peaks at 573 cm⁻¹ which is the characteristic phonon frequency of the GaN and at 737 cm⁻¹ which was previously found to originate from Mg⁺⁺ dopants. Finally, the broad background is due to the photoluminescence (PL) effect from p-GaN. A solid gate dielectric layer was deposited on top of the graphene. To avoid damage to the graphene, we first used electron beam evaporation to obtain a 30 nm thin SiO₂ film that protects the graphene and then sputtered 300 nm thick SiO₂ film by RF sputtering. To keep...
the quality of this stacking structure without the damage from one more water transfer of graphene, dry transfer process of graphene onto the thick SiO2, as a transparent top-gate electrode which was followed with previous report. After that, Au/Ni for probe contacts which were subsequently deposited by electron beam evaporation at a pressure of ~6 × 10⁻⁷ Torr and at a constant sample rotation rate. To improve the deposited electrode's contact resistance, annealing was carried out in a furnace at 400 °C for 20 minutes.

References

1. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
2. Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. Nature 438, 197–200 (2005).
3. Chen, C. C. et al. Graphene-Silicon Schottky Diodes. Nano Letters 11, 1863–1867 (2011).
4. Kvak, J. Y. et al. Electrical Characteristics of Multilayer MoS2, FET's with MoS2/Graphene Heterojunction Contacts. Nano Letters 14, 4511–4516 (2014).
5. Young, A. F. & Kim, P. Quantum interference and Klein tunnelling in graphene heterojunctions. Nature Physics 5, 222–226 (2009).
6. Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. Graphene photonics and optoelectronics. Nat Photonics 4, 611–622 (2010).
7. Britnell, L. et al. Field-Effect Tunneling Transistor Based on Vertical Graphene Heterostructures. Science 335, 947–950 (2012).
8. Vaziri, S. et al. A Graphene-Based Hot Electron Transistor. Nano Letters 13, 1435–1439 (2013).
9. Kim, C. O. et al. High-performance graphene-quantum-dot photodetectors. Sci Rep 4, 6 (2014).
10. Chang, C. W. et al. Graphene/SiO2/p-GaN Diodes: An Advanced Economical Alternative for Electrically Tunable Light Emitters. Adv Funct Mater 23, 4043–4048 (2013).
11. Di Bartolomeo, A. Graphene Schottky diodes: An experimental review of the rectifying graphene/semiconductor heterojunction. Physics Reports-Review Section of Physics Letters 606, 1–58 (2016).
12. Schubert, E. F. & Kim, J. K. Solid-state light sources getting smart. Nature 488, 107–117 (2012).
13. Krames, M. R. et al. Status and future of high-power light-emitting diodes for solid-state lighting. J Displ Technol 3, 160–175 (2007).
14. Zeludev, N. The life and times of the LED - A 100-year history. Nature Photonics 1, 189–192 (2007).
15. Woods, D. & Naughton, T. J. Optical computing photonic neural networks. Nature Physics 8, 257–259 (2012).
16. Zima, Z. et al. LiF: Line-Of-Sight identification with WiFI. In: INFOCOM, 2014 Proceedings IEEE 2688–2696 (2014).
17. Walser, P. et al. Nitride semiconductors free of electrostatic fields for efficient white light-emitting diodes. Nature 406, 865–868 (2000).
18. Zhang, X.-M. et al. Fabrication of a High-Brightness Blue-Light-Emitting Diode Using a ZnO-Nanowire Array Grown on p-GaN Thin Film. Adv Mater 21, 2767–2770 (2009).
19. Cao, H. T. et al. An orange iridium(III) complex with wide-bandwidth in electroluminescence for fabrication of high-quality white organic light-emitting diodes. Journal of Materials Chemistry C 1, 7371–7379 (2013).
20. Ju, Z. G. et al. Advantages of the Blue InGaN/GaN Light-Emitting Diodes with an AlGaN/GaN/AlGaN Quantum Well Structured Electron Blocking Layer. Adv Optics 1, 377–381 (2014).
21. David, A. et al. Carrier distribution in (0001)InGaN/GaN multiple quantum well light-emitting diodes. Appl Phys Lett 92, 3 (2008).
22. Ji, Y. et al. Comparative study of field-dependent carrier dynamics and emission kinetics of InGaN/GaN light-emitting diodes grown on (1120)over-bar2) semipolar versus (0001) polar planes. Appl Phys Lett 104, 5 (2014).
23. Burroughes, J. H. et al. Light-emitting diodes based on conjugated polymers (vol 347, pg 539 1990). Nature 348, 352–352 (1990).
24. Sajjad, M. T. et al. Novel Fast Color-Converter for Visible Light Communication Using a Blend of Conjugated Polymers. Adv Materials 2, 194–199 (2015).
25. Gomez, E. F. & Steckl, A. J. Improved Performance of OLEDs on Cellulose/Epoxy Substrate Using Adenine as a Hole Injection Layer. Adv Optics 2, 439–445 (2015).
26. Liu, B. et al. Carbon-Nanotube-Enabled Vertical Field Effect and Light-Emitting Transistors. Adv Mater 20, 3605–3609 (2008).
27. Yang, H. et al. Graphene Barristor, a Triode Device with a Gate-Controlled Schottky Barrier. Adv Mater 20, 1140–1143 (2012).
28. Smith, M. et al. Mechanisms of band-edge emission in Mg-doped p-type GaN. Appl Phys Lett 68, 1883–1885 (1996).
29. Suzuki, M., Uemiyama, T. & Yanase, A. First-principles calculations of effective-mass parameters of AlN and GaN (vol 32, pg 8132, 1995). Phys Rev B 58, 10064–10064 (1998).
30. Alivov, Y. I. et al. Fabrication of ZnO-based metal-insulator-semiconductor diodes by ion implantation. Solid-State Electronics 48, 2343–2346 (2004).
31. Hwang, D. K. et al. ZnO-based light-emitting metal-insulator-semiconductor diodes. Appl Phys Lett 91, 121113 (2007).
32. Pankove, J. I. Optical processes in semiconducting thin-films. Thin Solid Films 96, 172–172 (1982).
33. Depas, M. et al. Determination of tunneling parameters in ultra-thin oxide layer poly-Si/SiO2/Si structures. Solid-State Electronics 38, 1465–1471 (1995).
34. Simmons, J. G. Generalized formula or electric tunnel effect between similar electrodes separated by a thin insulating film. J Appl Phys 34, 1793 (1963).
35. Schuegraf, K. F. & Hu, C. M. Metal-oxide-semiconductor field-effect-transistor substrate current during Fowler-Nordheim tunneling stress and silicon dioxide reliability. J Appl Phys 76, 3695–3700 (1994).
36. Allan, P. E. & Fuchs, J. N. Klein tunneling in graphene: optics with massless electrons. Eur Phys J B 83, 301–317 (2011).
37. Das, A. et al. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. Nat Nanotechnol 3, 210–215 (2008).
38. McCarthy, M. A. et al. Low-Voltage, Low-Power, Organic Light-Emitting Transistors for Active Matrix Displays. Science 332, 570–573 (2011).
39. Chen, C. H. et al. Novel fabrication of UV photodetector based on ZnO nanowire/p-GaN heterojunction. Chem Phys Lett 476, 69–72 (2009).
40. Li, D. B. et al. Influence of threading dislocations on GaN-based metal-semiconductor-metal ultraviolet photodetectors. Appl Phys Lett 98, 3 (2011).
41. Gu, F. X. et al. Large defect-induced sub-bandgap photoresponse in semiconductor nanowires via waveguiding excitation. Nanotechnology 22, 425201 (2011).
42. Li, X. S. et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. Science 324, 1312–1314 (2009).
43. Reina, A. et al. Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. Nano Letters 9, 30–35 (2009).
44. Calizo, I. et al. Temperature dependence of the Raman spectra of graphene and graphene multilayers. Nano Letters 7, 2645–2649 (2007).
45. Ferrari, A. C. et al. Raman spectrum of graphene and graphene layers. Phys Rev Lett 97, 187401 (2006).
46. Mahalingam, V. et al. Optical and structural characterization of blue-emitting Mg2+- and Zn2+-doped GaN nanoparticles. J Mater Chem 19, 3889–3894 (2009).
47. Feng, Y. & Chen, K. Dry transfer of chemical-vapor-deposition-grown graphene onto liquid-sensitive surfaces for tunnel junction applications. Nanotechnology 26, 035302 (2015).
Acknowledgements
This work was supported by the Ministry of Science and Technology and the Ministry of Education of the Republic of China.

Author Contributions
Y.-F.C., M.H. and W.-C.T. conceived the idea and designed the experiments. W.-C.T. and C.-W.C. fabricated and measured the samples. All the authors were involved in analyzing the data and writing the manuscript.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Tan, W.-C. et al. Tunneling-injection in vertical quasi-2D heterojunctions enabled efficient and adjustable optoelectronic conversion. Sci. Rep. 6, 31475; doi: 10.1038/srep31475 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2016