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Authors
Han, Kevin
Ahn, Geun Ho
Cho, Joy
et al.

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Bright electroluminescence in ambient conditions from WSe_2 p-n diodes using pulsed injection

Kevin Han[1], Geun Ho Ahn[1,2], Joy Cho[1,2], Der-Hsien Lien[1,2], Matin Amani[1,2], Sujay B. Desai[1,2], George Zhang[1,2], Hyungjin Kim[1,2], Niharika Gupta[1,2], Ali Javey[1,2], and Ming C. Wu[1]

[1]Electrical Engineering and Computer Sciences, University of California at Berkeley, Berkeley, CA 94720, United States
[2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

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Transition metal dichalcogenide (TMDC) monolayers are promising for next-generation nanoscale light emitters due to their direct band gap, high optical efficiency, and ease of top-down fabrication. In this work, we study the time-resolved electroluminescence of monolayer WSe_2 lateral p-n junctions in ambient conditions, and identify the decay in current over time as the main issue preventing stable device operation. We show that pulsed voltage bias overcomes this issue and results in bright electroluminescence in ambient conditions. This is achieved in a simple back-gated transistor structure, without the use of dual gates, heterostructures, contact optimization, or chemical doping methods. Internal quantum efficiency (IQE) of electroluminescence reaches ~1%, close to the photoluminescence quantum efficiency, indicating efficient exciton formation with injected carriers. Emission intensity is stable over

hours of device operation. Finally, our device exhibits ~15 ns rise and fall times, to our knowledge the fastest direct modulation speed reported for TMDC light-emitting diodes.

I. INTRODUCTION

Monolayer transition metal dichalcogenides (TMDCs) are a class of single-molecule-thick direct-bandgap semiconductors that show great potential for next-generation electronics[1–4] as well as optoelectronic devices such as light-emitting diodes (LEDs) and photodetectors[5–12]. One long-recognized challenge in TMDC electronics is the large hysteresis in TMDC field-effect transistors (FETs). The cause of this hysteresis has been studied extensively, with some results pointing to charge trapping caused by adsorption of water and oxygen on the monolayer surface[13–15], and others to intrinsic defects[15,16]. In electrically injected light-emitting devices, some form of electrostatic gating is typically needed as well to form a P-N junction, due to the difficulty of traditional doping techniques for monolayers, and so the same problem is encountered. In FETs, hysteresis manifests as a shift in the I_d-V_g curve as gate voltage is swept in opposite directions. At a constant gate bias, this is seen as a decay in current over time[14,15]. Although some past works on TMDC electroluminescence have shown high EL quantum efficiencies ~10^{-2}, these are reported only in high-vacuum conditions[5,6,17,18], where hysteresis is partially mitigated.

A simple alternative approach is pulsed voltage bias, which has been shown to yield hysteresis-free FET characteristics in 2D materials in ambient conditions[19–21]. In addition, bright electroluminescence has been observed from TMDC capacitors operated under fast pulsed bias[12]. In such two-terminal devices, electrons and holes are separately injected into the semiconductor in alternating cycles (unipolar injection). In this work, we show that pulsed injection is also effective for traditional bipolar injection TMDC LEDs, yielding stable EL from monolayer WSe_2 devices in ambient conditions. EL quantum efficiency is ~10^{-2}, close to that of photoluminescence (PL). This implies that EL efficiency in our devices is primarily limited not by charge carrier confinement but by intrinsic material quality.

II. Electroluminescence from WSe_2 P-N diodes

Our device design (Fig. 1a) is a back-gated WSe_2 FET structure operated as a p-n diode. The gate stack is either 50 nm SiO_2 on a p++ Si substrate, or 20 nm Al_2O_3 on a transparent ITO/glass substrate (see Methods). Devices on both substrates showed bright light emission. WSe_2 was chosen due to its ambipolar nature, required for bipolar carrier injection. In general, most devices were ambipolar or slightly p-type in their I_d-V_g characteristics (Supplementary Fig. S1, S7). Identical structures using monolayer MoS_2 showed only n-type I_d-V_g and no light emission (Supplementary Fig. S2). For diode operation, one contact is designated as the P contact with alternating voltage between V_p and V_g. The other (N) contact alternates between V_n and V_g, with $V_n < 0$ (Fig. 1b). Light is emitted only during the on period t_{on}. Fig. 1c shows the EL spectrum of the device overlaid with the photoluminescence (PL) spectrum of the same device. The clear peak at ~1.65 eV shows that EL and PL are both due to the usual recombination of A excitons, and confirms the monolayer nature of the flakes. PL quantum efficiency versus pump intensity shows a drop at high pump intensity due to exciton-exciton recombination, similar to past work[22] (Supplementary Fig. S3). Fig. 1d shows the light emission overlaid on an image of the device, confirming emission comes from the channel region.

To illustrate the need for pulsed bias, we measure EL versus time and current versus time for both DC (step) voltage and pulsed voltage at 5 kHz. Bright emission is observed under both DC and pulsed bias. Note that the emission mechanism in our devices is clearly distinct from the pulsed light-emitting capacitor reported previously[12], since continuous light emission is seen on a scale of ~seconds, as opposed to the ~10 ns pulses that only occur during voltage transitions. However, under DC bias, both emission and current rapidly decay by orders of magnitude within a few seconds (Fig. 2a,b). Past reports on current decay in MoS_2 FETs show roughly comparable time constants ~10 s[14,15]. The ratio of light emission to current, which is proportional to the efficiency, remains roughly constant over time, showing that the decay in current is responsible for the decay in light emission. In contrast, pulsed bias yields extremely stable light emission and current over >1000s (Fig. 2c,d). Most devices under pulsed bias showed no decrease or small decrease (<2x) in light emission in the first few minutes, then stayed stable for the remaining duration of the applied bias, with the longest test performed being >3 hours (Supplementary Fig. 4). The frequency response is shown in Fig. 2e. Here, emission intensity is defined as the average intensity over 10s, starting 5s after the pulsed bias is applied. Above ~1 kHz, emission intensity is relatively stable with frequency, while below ~1 kHz, current decay causes EL to drop very quickly. However, note that the stability also depends on duty cycle, which is fixed at 50% here. For very low duty cycle (long t_{off}), emission intensity can still be stable at low frequencies ~1 Hz (Supplementary Info).

Next, we study the emission characteristics under varying bias to extract the optimal bias condition. The relative injection level of electrons and holes, and thus the exciton formation efficiency, depends on the voltages $(V_p - V_g)$ and $(V_n - V_g)$ applied to the contacts. If $\left|V_p - V_g\right| \gg \vee V_n - V_g \vee$¿, holes will be predominantly injected and will simply diffuse across the channel to the opposite contact without forming excitons, and vice versa for $\left|V_p - V_g\right| \ll \vee V_n - V_g \vee$¿ (Fig. 3a). We determine the optimal bias condition by keeping $(V_p - V_n)$ constant and sweeping V_g from V_n to V_p while tracking the EL and current. Fig. 3b shows the EL intensity versus gate voltage, where V_p and V_n are fixed at $V_p = 5V$ and $V_n = -5V$, along with the current and EL efficiency. Each point corresponds to one on period $t_{on} = 0.5s$, and current and emission intensity are defined as the time-average during the on period. An off time of t_{off} = 10s is used to recover the device between pulses (Supplementary Info). The brightest emission occurs near V_g = 0, where both holes and electrons are injected. The minimum current point at $V_g \cong 1.8$V corresponds to the most bipolar injection, and coincides with the highest internal quantum efficiency (IQE) 1%. $\left|V_p - V_g\right| < ¿ V_n - V_g \vee ¿$ at this point, indicating slightly p-type characteristics typical of monolayer WSe_2. We obtain an L-I curve at optimal bias conditions by first setting $V_g = 1.25$ V, approximately the point of maximum efficiency above, where current is also not too low. Then we increase the source-drain bias while keeping $¿ V_p - V_g \vee ¿ \vee V_n - V_g \vee ¿$ constant at ~0.6. For comparison, we also take an L-I curve with V_g = 0 (i.e. equal $¿ V_p - V_g \vee ¿$ and $¿ V_n - V_g \vee ¿$). L-I and IQE are plotted in Fig. 3c, along with the corresponding PL L-L curves. PL shows a roughly constant IQE of ~1.6%, while EL at optimal bias shows a peak of ~1.3% at low current and decreases slightly at higher currents, possibly due to variation in optimal bias condition with voltage. In contrast, EL at equal P and N bias is low (~0.3%) at low current and stays below ~0.8% throughout.

Next, we study the modulation speed of the device by performing time-resolved measurements using time-correlated single-photon counting (TCSPC). Supplementary Fig. S5 shows the measurement setup, and Fig. 4 shows time-resolved electroluminescence at 1 MHz, together with the P and N voltage pulses measured on an oscilloscope. Emission only occurs when both P and N voltage are applied, confirming bipolar carrier injection. The emission intensity is nearly constant during the entire P/N voltage overlap period. The rise and fall times shown in the inset are ~12 ns and ~18 ns respectively. We note that this rise/fall time is ~20x faster than monolayer LEDs using vertical tunnel injection heterostructures[24], which is likely due to the lower capacitance of the lateral injection scheme used here. To our knowledge, this is the fastest direct modulation speed reported for TMDC LEDs.

I. CONCLUSION

In this work, we have shown that the hysteresis and current decay commonly seen in TMDC transistors also play an important role in light-emitting diodes. Pulsed injection is an effective way to circumvent this issue, yielding bright and stable EL using a simple back-gated FET structure, with efficiency near that of PL. We show how to extract the optimal bias condition for efficient bipolar injection, and study the high frequency behavior of light emission. A fast ~15 ns rise/fall time is observed, indicating strong potential for high speed light modulation. Pulsed emission is stable over hours of operation. Further improvements in efficiency will come from contact optimization to enable lower voltage operation, as well as advances in CVD growth to improve intrinsic material quality. Higher speed can be obtained by coupling to an optical cavity to enhance spontaneous emission rate[24–27].

II. METHODS

Device fabrication for SiO_2/Si substrates begins with a p++ Si substrate with 50 nm thermal oxide (Silicon Valley Microelectronics), with alignment marks (5/60 nm Ti/Au) deposited by electron beam evaporation. Monolayer WSe_2 flakes are grown on quartz using chemical vapor deposition (CVD) using similar conditions as in Ahn *et al*[28]. Flakes ~100 μm in size are transferred onto the gate oxide using a pick-and-place method, and source/drain contacts are patterned using e-beam lithography (EBL) followed by thermal evaporation (15 nm Ni) and liftoff in acetone for 30 min. Devices on transparent substrate use ITO (280 nm)/glass (Thin Film Devices) with 20 nm Al_2O_3 deposited by atomic layer deposition. Before contact deposition, flakes are patterned with EBL and etched in XeF_2 (3T XeF_2, 4T N_2, 30 s/cycle, 3 cycles).

Electroluminescence measurements are carried out with a low-frequency probe setup using two Keithley 2401 SourceMeters for quasi-DC measurements, or two synchronized HP33120A function generators for TCSPC and frequency response. For quasi-DC and frequency response measurements, light is collected from the top through a 20x objective and focused onto either a grating for spectral measurement, or mirror for spatial measurement, then onto a Si CCD. For TCSPC measurements, light is collected through the backside with a 20x objective and focused onto a Si avalanche photodiode (Micro Photon Devices) synchronized with a trigger pulse from a DG535 pulse generator (Stanford Research Systems). Photoluminescence measurements are taken using the same microscope setup as the quasi-DC tests, with a 532 nm pump laser focused onto the flake using a 50x objective.

Electrical measurements are done using an Agilent B1500 parameter analyzer or a HP4145b parameter analyzer. Vacuum measurements are done using a Lakeshore TTPX probe station. Gas response measurements are done using a home built gas sensing chamber.

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IV. Author contributions

K.H. and M.C.W. designed the study. K.H. performed the measurements and analysis, and wrote the manuscript. G.H.A., J.C., and G.Z. performed the CVD growth. M.A. helped with electrical measurements. D.-H.L. and S.B.D. provided helpful discussion. H.K. helped with MoS_2 exfoliation. N.G. helped with gas sensing measurements. A.J. advised on the experiments and manuscript.

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Figure Captions

Figure 1. Light emission from pulsed WSe_2 p-n diodes. (**a**) Device schematic. Contact/gate oxide/gate stack is either Ni (15 nm)/SiO_2 (50 nm)/Si or Ni (15 nm)/Al_2O_3 (20 nm)/ITO. (**b**) Schematic of voltage pulsing. Light is emitted when both $V_p > V_g$ and $V_n < V_g$, while during the off state $V_p = V_n = V_g$. (**c**) EL and PL spectra taken on same device. (**d**) Spatial map of emission from an etched device. Left: optical micrograph. Scale bar is 5 μm. Middle: emission intensity during pulsed injection, overlaid on CCD image. Emission occurs in the channel region between the two contacts. Right: device in off state with no bias applied.

Figure 2. Light emission and current for DC and pulsed bias. (**a**) Schematic of DC voltage bias. (**b**) Light emission and current over time for DC voltage of $V_p = -V_n = 4V$, with $V_g = 0V$. (**c**) Schematic of pulsed voltage bias, using a square wave with 50% duty cycle. (**d**) Light emission and current over time for pulsed voltage with $V_p = -V_n = 4V$, with $V_g = 0V$. Note the different time scale for (b) and (d). (**e**) Frequency response with $V_p = -V_n = 4.5$ V, taken with a different device from (b, d).

Figure 3. L-I-V characteristics and optimal bias condition. (**a**) Schematic of carrier injection regimes with varying gate voltage and fixed V_p and V_n. (**b**) EL

intensity, current, and EL IQE versus gate voltage V_g, for constant V_p = -V_n = 5 V. (**c**) Output power and IQE vs carrier injection rate for PL and EL. EL is taken at near-optimal bias condition extracted from V_g sweep (V_g = 1.25 V), as well as V_g = 0 V for comparison.

Figure 4. Time-resolved light emission. Top panel: Voltage pulses measured on an oscilloscope. Bottom panel: Time-resolved EL. Left inset: close-up of EL rise time. Right inset: close-up of EL fall time.

Supplementary Info

Causes of current decay in ambient conditions

To investigate the cause of the current decay, we studied the device in vacuum ($3x10^{-5}$ Torr) and after annealing at 140 C for 2 hours to remove adsorbates, followed by cooling back to room temperature. The current under electron injection (V_{ds} = 1V, V_g = 8V) becomes highly stable while the hole current (V_{ds} = 1V, V_g = -10V) still decays (Supplementary Fig. 6a). In ambient conditions for the same device, both electron and hole currents decay similarly (Supplementary Fig. 6b). In addition, the I_d/V_g curve shows decreased hysteresis in vacuum, and a shift in threshold voltage for electrons but not for holes (Supplementary Fig. 7). Therefore, we attribute the current decay in ambient to both adsorbed molecules on the surface of the monolayer, as well as additional hole traps that remain after removing adsorbates, possibly due to interface traps or intrinsic defects[16,23]. This shows that pulsing is still necessary in vacuum to obtain stable bipolar current injection. In air, H_2O and O_2 are the primary constituents possibly responsible for current decay[13]. To test the relative contributions of H_2O and O_2 on the device, we measured hysteresis in ambient air, dry air (21% O_2, 79% N_2), and pure N_2 (Supplementary Fig. 8). The hysteresis for both electrons and holes is higher in ambient than the other cases, while almost identical for dry air and pure N_2. Therefore, adsorbed water is likely the primary factor affecting the device in ambient conditions, similar to MoS_2 FETs[13,14].

Calculation of internal quantum efficiency (IQE)

For electroluminescence, IQE is determined by the formula $\eta_{EL}=\frac{P}{\eta_{setup}\eta_{extr}I}$, where P is the output photons/s collected, I is the input carriers/sec, η_{setup} is the efficiency of the optical setup, including objective, focusing optics, spectrometer, and CCD, and η_{extr} is the extraction efficiency from the substrate. η_{setup} is measured using a 532 nm laser incident on a spectralon sample to simulate an ideal Lambertian emitter, which then goes through the same optics as the EL measurement. This gives the absolute setup efficiency at 532 nm. Then, a blackbody source with known spectrum is shone on the sample and used to find the relative spectral efficiency, in particular the efficiency at 750 nm, the wavelength of EL. We obtain $\eta_{setup}=4.3\times10^{-3}$. η_{extr} is estimated from FDTD simulation of monolayer WSe_2 on SiO_2/Si substrate to be ~0.1. For photoluminescence, the efficiency is also divided by the absorbance A of WSe_2 at 532 nm. This is estimated from FDTD simulation to be 13.7% on SiO_2/Si.

Emission decay for varying off periods

For quasi-DC measurements with on period of 0.5s, the off period should be sufficiently long to avoid current decay between pulses. Off periods between 0.2s and 10s were tested with a sequence of 10 pulses for each off period. The device was rested for 30s after each 10 pulse sequence. Emission intensity is plotted in Supplementary Fig. S9. For pulse periods below ~0.5s, a clear decay is seen, while with the 10s rest period used for the V_g sweep measurements, the intensity fluctuates but there is no decay trend.