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Novel Electrical and Optical Gas Sensors

By

Niharika Gupta

A dissertation submitted in partial satisfaction of the
requirements of the degree of

Doctor of Philosophy

in

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in the

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of the University of California, Berkeley

Committee in charge:

Professor Ali Javey, Chair

Professor Roya Maboudian

Professor Mary Cooper Scott

Fall 2022

Abstract

Novel Electrical and Optical Gas Sensors

by

Niharika Gupta

Doctor of Philosophy in Applied Science and Technology

University of California, Berkeley

Professor Ali Javey, Chair

Gas detection has wide-ranging applications, from industrial process control and greenhouse gas monitoring to disease diagnosis and pollution tracking, which are vital to support out civil life in many respects. To meet the needs of these applications, gas sensor technologies should enable scalable production and high performance. The current dominant technology is the micro-hotplate-based resistive ceramic sensor which suffers from high power consumption and poor selectivity. One of promising sensor technology, the chemical-sensitive field-effect transistors (CS-FET) have the advantage of miniature size, low-power consumption, and scalability. In order to improve the applicability of CS-FET sensors for real-world scenario, it is imperative to solve the problem of its response to ambient humidity. This can be achieved using integrated microheaters to locally heat the sensor, and evaporate the adsorbed water molecules.

Another challenge for CS-FET devices is they cannot be made sensitive to gases such as methane, CO₂, *etc.* at room temperature. Optical gas sensors are useful for these applications because their sensing mode does not depend on the interaction of the gas with the active material. However, optical sensors need high-performance infrared light emitters to detect gases at low concentrations. Black phosphorus (bP) has proven its ability to outperform the state-of-the-art compound semiconductors with its high photoluminescence quantum yield. Non-dispersive infrared (NDIR) gas sensors with LEDs based on bP are documented which can detect trace concentrations of greenhouse gases. However, optoelectronics based on bP have scalability issues due to its current deposition and processing methods. An ink-based approach to make uniform bP films by spin-coating has been demonstrated, which is then used to fabricate LEDs and photodetectors with high performance.

To my parents and partner

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1 Introduction

1.1 Need for gas sensors

Gas sensors are devices which can be used to qualitatively or/and quantitatively determine the presence of gases. They have long been integral to the safety of people in varied environments. For example, CO₂ and smoke sensors are critical to detect gas leaks, or for checking the operation of an air purifier in homes. In the industrial settings, NH₃, NO₂, CO₂ sensors, etc. are widely to detect presence of certain harmful gases. The presence of ethylene to check the freshness of perishable food like meat is essential in the food industry. Hydrogen and oxygen gas sensors are used to monitor the exhaust gas in the automobile industry for checking thermal runaway of batteries, preventing fires. In the field of environmental monitoring, detection of greenhouse gases like CO₂, ozone, freon, methane helps evaluate the accumulation of these gases in the atmosphere, which allows scientists to estimate their impact on future climate.

1.2 Figures of merit

Development of a gas sensor with good figures of merit is essential for these applications. It is not only important that the sensor has low cost, small form factor, simple design and room temperature operation but that it is highly sensitive and selective to the target gas. Some of the key figures of merit are listed below:

- i) Sensor response: percentage change in signal, from base to peak value, on exposure to gas.
- ii) Sensitivity: sensor response per concentration of gas.
- iii) Lower limit of detection: lowest concentration of target gas detected by the sensor.
- iv) Response time: time for the signal to reach 90% of the peak signal from baseline, usually represented as t_{90} .
- v) Recovery time: time for the signal to reach 10% of the baseline signal from the peak value, represented as t_{10} .
- vi) Selectivity: ability of sensor to differentiate target gas from the interfering gases and ambient humidity, measured using corresponding sensor response.
- vii) Long-term stability: ability of sensor to maintain the same baseline signal without any drift for a long duration in extreme environments.
- viii) Reliability/Reproducibility: ability of sensor to perform consistently, with the same sensitivity and without any baseline drift in extreme environments.

1.3 Current gas sensor technology

The currently dominating gas sensor technology is the metal-oxide-semiconductor (MOS) gas sensor which work on the principle of sensor resistance change in the presence of gas. The sensor is heated such that the oxygen is adsorbed on it, which reacts with the target gas at the heated temperature. The working principle of these sensors is schematically demonstrated in Fig. 1-1. Oxides such as tin oxide and zinc oxide (n-type), are commonly used for these sensors. These sensors have the advantage of economic production cost, high sensitivity, and simple design, though possess the disadvantage of poor selectivity.

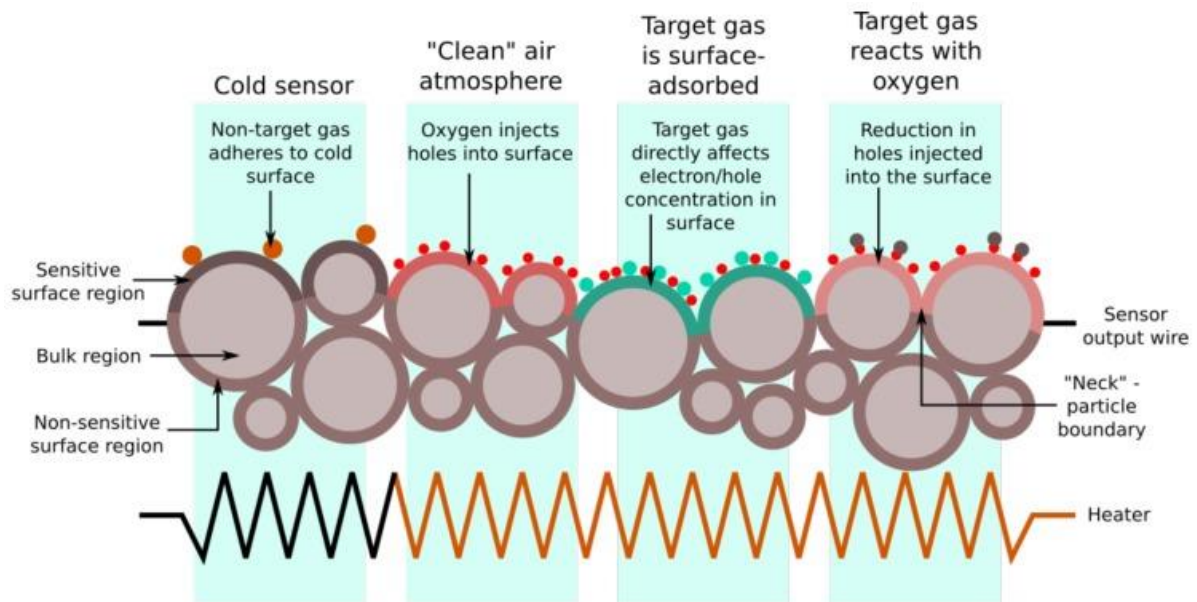


Fig. 1-1. Schematic of the interaction between atmospheric gases and an MOS sensor surface. In the leftmost region, the sensor is unpowered with heater OFF and exhibits the base resistance. The three other regions of the diagram describe different processes that occur simultaneously to varying degrees with heaters ON. The sensor's output is the resistance across the sensor material. (Source: Peterson, et al.¹)

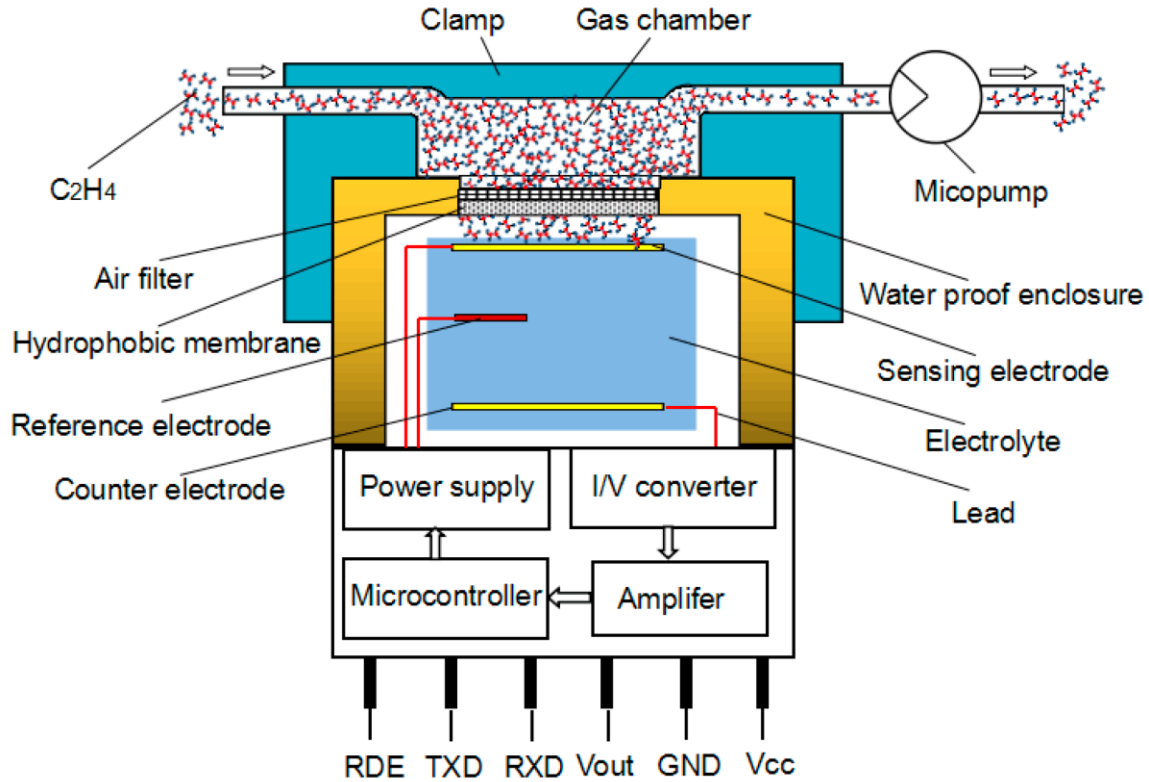


Fig. 1-2. Schematic of an ethylene electrochemical sensor (Source: Ma, et al.²)

The other common gas sensor technology is electrochemical gas sensor which utilizes oxidation-reduction reaction to detect gas concentration levels. One of the electrode is a gas-sensitive layer, at which gas molecules undergo oxidative reactions to generate ions and electrons. These ions are then transported via an electrolyte to the counter electrode, while the electrons generated are transported via the external circuit. A schematic of the sensor is shown in Fig. 1-2. These sensors have the advantage of good selectivity but have short lifespans and require regular maintenance.

1.4 Field-Effect Transistor (FET) gas sensors

FET-based gas sensor technology includes the sensors with structure and working principle same as that of MOSFET. Therefore, an FET-based sensor, like a MOSFET consists of a semiconductor substrate, drain and source regions/terminals, oxide, and a metal/semiconductor gate. Charge carriers flow from the source to drain terminal, which can be controlled by the gate voltage or/and the substrate/body voltage. The sensors consist of an active material, meaning a material which interacts highly with the target gas, and this active material can be the semiconductor substrate in some cases, or the gate in others.

For gate being the main sensing element of the FET, materials which have an established affinity towards the target gas are chosen, which is in some cases, is a combination of materials or alloy formations. When the gas comes in contact with the gate, it changes the minimum energy required to eject an electron from the surface (i.e., work function), leading to a change in the voltage necessary to keep a small constant drain current through the transistor channel (i.e., threshold voltage) and ultimately changing the channel current of the device, which is detected as the sensor signal.

For the case, when the semiconductor is the active layer, the gas interacts with the channel, acting as a dopant to change the local carrier concentration. Similar to the case of active gate, this changes the threshold voltage of the device causing a change in the current and signaling gas detection.

The main advantage of these FET-type sensors is their ability to be fabricated with a complementary metal-oxide semiconductor (CMOS) compatible process and be integrated with CMOS circuits. Therefore, they can be used for the Internet of Things (IoT) applications such as smartphones, wearable devices, and smart homes where miniaturized gas sensors need to be integrated into a large number of devices connected to each other. One of the remarkably interesting applications of the FET-based gas sensors is breath analysis for disease markers. Many studies have shown that certain exhaled concentration of gases like acetone, nitrogen dioxide, hydrogen sulfide and volatile organic compounds (VOCs) can be correlated to diseases like diabetes, asthma, renal disease, cancer etc.^{3,4} Though there are more than 900 VOCs in the exhaled breath as products of metabolism, certain gases or/and their excess concentrations can be recognized as a ‘biomarker’ for diseases.⁵ The existing technology using gas chromatography (GC) has been widely accepted but has disadvantages like large form factor, complexity, long analysis times, etc.

FET-based gas sensors have come a long way since their first inception by Lundström in 1975, who demonstrated the first gas-sensitive silicon-based field effect transistor.⁶ Lundström used the affinity of palladium to hydrogen and replaced the gate electrode of MOSFET with a thick palladium film to detect ppm-levels hydrogen. This pioneering work served as a foundation for many of the future studies focused on enhancing the performance of FET-based gas sensors.

A similar structure of FET-based gas sensor, CS-FET (chemical-sensitive field-effect transistor) has also been shown.⁷ These CS-FETs are based on bulk silicon and have a structure like the convention FETs with the exception of the gate, which was replaced by a nanoparticle sensing layer and engineered to an optimal thickness of 0.3 nm Ni 1 nm Pd layer for H₂ sensing. A body voltage application was utilized to increase the coupling between the sensing layer and the channel (Fig. 1-3). This design and measurement configuration optimization led to the CS-FET sensitivity to be >1000 % to 0.5 % H₂ gas at room temperature. The sensors also exhibited fast response (<60 s) and recovery times (<120 s), with high repeatability and negligible hysteresis and drift. This work demonstrating CS-FET as a platform built a compelling case in terms of both performance and manufacturability point of view.

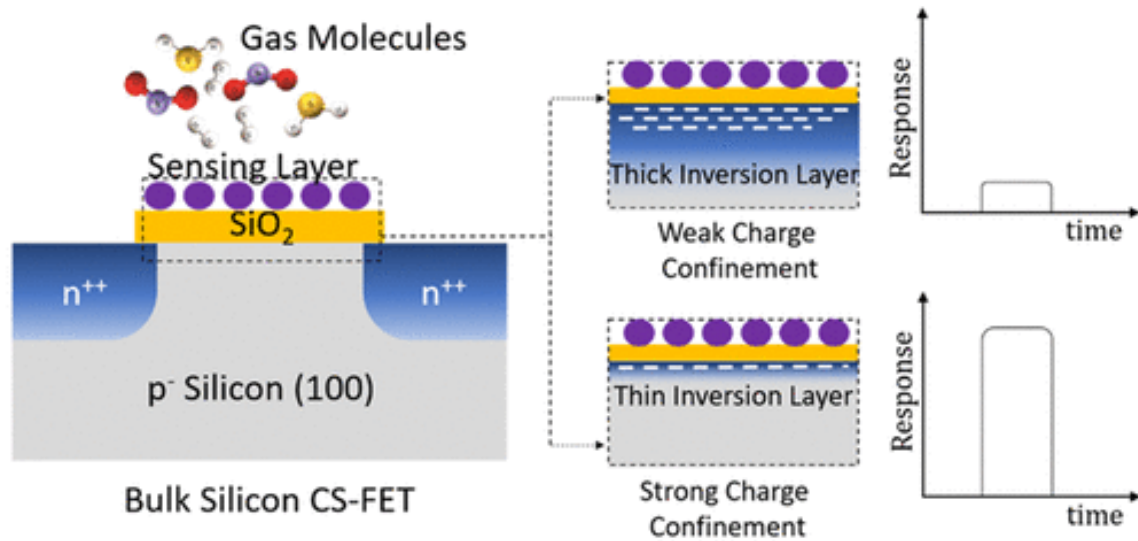


Fig. 1-3. Cross-sectional schematic of a bulk silicon CS-FET with electrostatic confinement of the charge inversion layer using body bias to achieve high gas sensitivity. (Source: Fahad, et al.⁶)

One of the problems that needed to be solved in the CS-FET technology is its response to humidity. Ambient humidity levels in the environment are always changing that can not only give a false gas sensor response, but can also render sensors unusable by damage. In CS-FETs, the problem can be tackled by using an integrated microheaters around the CS-FET, which can help raise the chip temperature just a few degrees Celsius above the room temperature, resulting in negligible response to relative humidity change of 50 to 90 % at room temperature. More details on this technique are discussed in Chapter 2.

The CS-FETs have also been shown to have a promising performance utilizing silicon-on-insular (SOI) technology (as opposed to bulk silicon), and has been used to demonstrate a

multiplexed gas sensing system for H₂S, H₂, and NO₂ at room temperature. This work by Fahad et al, engineered the sensing layer for H₂S and NO₂ as 1 nm Au 0.3 nm Pd, and 1 nm Ni respectively to enable high gas sensitivity.⁸ Studies documenting CS-FETs for application in food spoilage reported 1 nm Ru for NH₃ and 3 nm SiO_x for humidity sensing.⁹ As the library of gases that can be detected using this platform is increasing, there are certain gases that are non-polar and don't strongly interact with any materials at room temperatures. Examples of these gases are methane, CO₂, NO, etc. which have significance in applications such as greenhouse gas monitoring, petroleum industry, process control, indoor gas detection, etc. as previously discussed. And, this property of these gases, makes CS-FETs ineffective for these applications, at least at room temperature.

1.5 Non-dispersive infrared (NDIR) gas sensors

Optical gas sensors are truly relevant in these scenarios because their sensing mechanism does not depend on the interaction of the gas and the active material. Instead, they utilize the gas absorption bands specific to each gas molecule in the electromagnetic spectrum. A range of gases exhibit strong absorption in the UV/visible, near-infrared or mid-infrared regions as a result of molecular vibration at discrete energy levels, which is unique to each gas depending on the chemical bonds in the species, and therefore can be used to the 'fingerprint' the gas.¹⁰ For example, CO₂ absorbs infrared radiation at wavelengths of 2.7, 4.26 and 15 μm (wavenumbers 3703, 2349 and 667 cm^{-1}).¹²

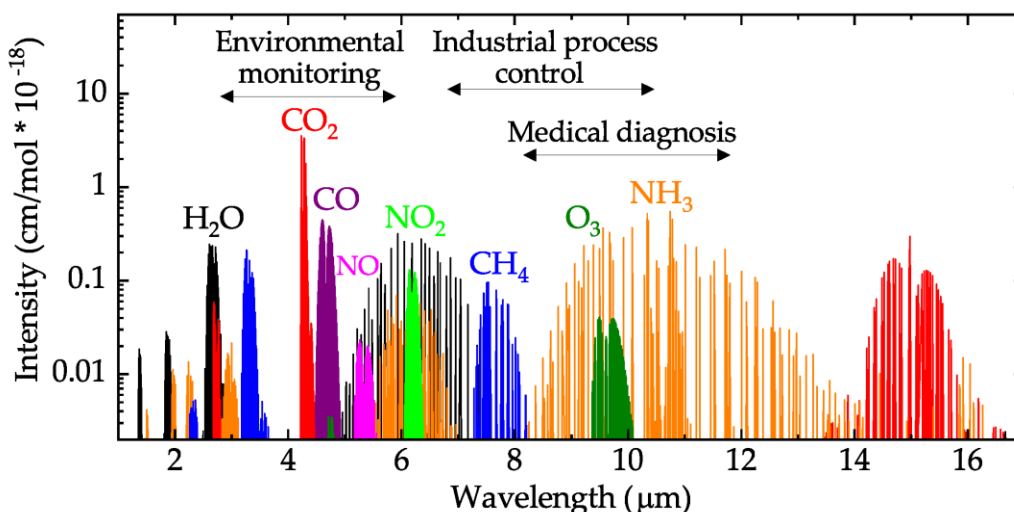


Fig. 1-4. Mid-infrared absorption spectra of selected gas molecules with their relative intensities and applications. H₂O: water; CO₂: carbon dioxide; CO: carbon monoxide; NO: nitric oxide; NO₂: nitrogen dioxide; CH₄: methane; O₃: ozone; NH₃: ammonia. (Source: HITRAN¹¹)

The diverse types of optical gas sensing technologies are non-dispersive infrared (NDIR), spectrophotometry, tunable diode laser spectroscopy (TDLS) and photoacoustic spectroscopy (PAS). NDIR gas sensors are the simplest of them, and commercially popular. They have small form factor, low cost, few components, operate at room temperature and respond to gas within seconds, and their excellent applicability for CO₂ detection has made them dominant in the industry. Typically, in the NDIR gas sensor technology, there is a gas cell, on one end of which is a broadband light emitter, and a light detector on the other. The intensity of light emitted on one end is constantly monitored by the detector, which decreases in the presence of the target gas. The source and the detector are chosen such that they emit and detect in the same wavelength range, overlapping the region of gas absorption. Filters are also incorporated in the cell, such that the sensor detector is responsive to only target gas, and the light in the absorbing wavelength range of interfering gas is not present.

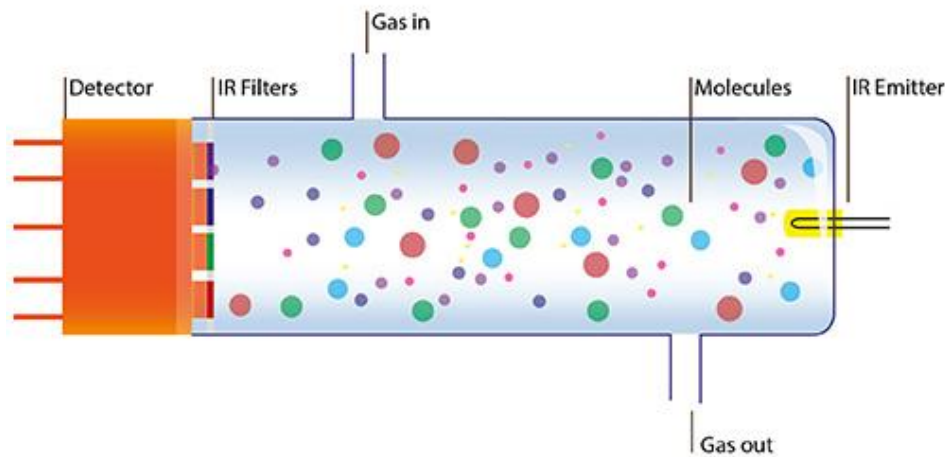


Fig. 1-5. Schematic of a typical NDIR gas sensor.

This optical gas detection is based on the Beer-Lambert Law,

$$I = I_0 \exp(-\alpha l) \quad (1-5-1)$$

where I is the light transmitted through the gas cell, I_0 is the light output of the source incident on the cell, α is the absorption coefficient of the gas, and l is the characteristic length of the gas cell.¹³ Here α is the product of the gas concentration and the specific absorptivity of the gas. For the wavelength range, mid-wave infrared (MWIR) region is specifically important for gases like CO, CO₂, NO, N₂O, and CH₄, because they strongly absorb in this region due to their fundamental rotational and vibrational transitions.

The gas sensor sensitivity is proportional to the factors such as intensity of MWIR light, absorbance characteristics of the gas molecule, length of the gas cell and concentration of gas. Given one of these contributing factors is the intensity of light, it is important that the

emitter produces bright electroluminescence with high efficiency. MWIR LEDs as emitters offer advantages of high efficiency and modulation rates compared to the thermal sources (such as a blackbody). The commercially available NDIR gas sensor technology use LEDs with active layers based on III-V and II-VI semiconductors such as InAs, InAs/InAsSb, InAlSb, GaInAsSb/GaSb/GaInAsSb/AlGaAsSb.¹⁴

Recently, black phosphorus (bP), the most stable allotrope of phosphorus has been shown to have photoluminescence (PL) in the MWIR higher than an InAs multiple quantum well.¹⁵ The rationale behind the low emitting efficiency of the compound semiconductors is their high Auger recombination coefficient, which a previous study has theoretically calculated to be much lower in bP.¹⁶ This supports the previous experimental finding that the overall quantum efficiency of bP is higher than the III-V semiconductors. To utilize this property, bP-based LED was fabricated, and it was found that with the optimal structure to enhance the photon outcoupling and reduce the parasitic resistance, external quantum efficiency and power efficiency of ~4.43 and 1.78 % can be achieved. The external quantum efficiency of this LED is significantly higher than the state-of the-art LEDs. These bP-LEDs were then incorporated in a NDIR sensor setup to detect CO₂ and CH₄. This sensor was able to detect ppm-level concentration of CH₄ and CO₂ because of the high optical power output and efficiency of the devices. One of the other valuable properties of bP is that its bandgap is tunable with strain, which can be used to block the emission for an interfering gas and enables more selective gas sensing with a single emitter. This work has been discussed in detail in Chapter 3.

BP-LEDs have shown immense potential to replace the current III-V semiconductor technology due to their properties. However, their scalability is a challenge due to the current deposition and processing techniques. BP is a two-dimensional (2D) material, and to fabricate LEDs or photodetectors, mechanical exfoliation is used resulting in a flake laterally sized much less than 1000 μm^2 . Solution-processing of bP can be useful to deposit large-scale film and keep the crystallinity of bP intact. In Chapter 4, technique to formulate bP ink has been discussed and it has been found that the films made using ink can be deposited on a millimeter-scale that show high PL quantum yield. Characterization techniques like Raman spectroscopy and secondary electron microscopy (SEM) show that the films are uniform and pin-hole free. LEDs and photodetectors based on this film were also fabricated on a large-scale format. Due to the inherent property of bP of high quantum yield, the efficiency of these devices to emit/detect light can enable high signal-to-noise ratio and a lower limit of gas detection for application in the NDIR sensors. Development of scalable bP-based LEDs and photodetectors has tremendous potential to replace the conventional materials for improving the performance these gas sensors.

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2 Elimination of humidity response in CS-FETs*

Detecting accurate concentrations of gas in environments with dynamically changing relative humidity conditions has been a challenge in gas sensing technology. We report a method to eliminate effects of humidity response in chemical sensitive field effect transistors using microheaters. Using hydrogen gas sensor with Pt/FOTS active material as a test case, we demonstrate that a sensor response of 3844% to a relative humidity change of 50% to 90% at 25 °C can be reduced to a negligible response of 11.6% by utilizing microheaters. We also show the advantage of this technique in maintaining same sensitivity in changing ambient temperatures and its application to the nitrogen dioxide gas sensors.

*This chapter has been published in a similar format in: Gupta, N., Fahad, H. M., Amani, M., Song, X., Scott, M., & Javey, A. (2019). Elimination of response to relative humidity changes in chemical-sensitive field-effect transistors. *ACS sensors*, 4(7), 1857-1863.

2.1 Problem of humidity

Selectivity is one of the most important figures of merit for gas sensors which includes insensitivity to ambient relative humidity and temperature changes. The sensitivity to these ubiquitous variations is currently the major limiting factor of important gas sensing applications such as air-quality monitoring¹⁻⁴ and medical diagnosis⁵⁻⁷. The fact that most of the active sensing materials interact with water makes achieving humidity insensitivity a challenge.⁸⁻¹⁰ Chemical or gas sensor being responsive to even slightest of environmental changes leads to deviated sensor signal following inaccurate detection of gas and/or interpretation of gas concentration. Therefore, elimination of humidity and temperature is essential to having a robust and precise sensor signal.

2.2 Current research for selectivity against humidity

Research in making gas sensors humidity and temperature insensitive can be divided into two strategies – computational and experimental methods. The computational method involves signal processing utilizing data from humidity and temperature sensors along with sensor data at different concentrations in different humidity and temperature levels to calculate exact gas concentration. Multivariate calibration methods such as principal component regression (PCR)¹¹, partial least square (PLS)¹² and artificial neural networks (ANN)¹³ have been utilized to compensate for the sensor response to humidity changes. With requirements of huge data sets needed to train the ANN and linear data sets in other methods, the computation method is also disadvantageous because of the complexity of calibration required for different combinations of relative humidity and temperature. Additionally, both of humidity and temperature sensors would need to have selective signal responses with respect to each other, which being experimentally impractical to achieve, would need further post-processing adding to the calibration complexity. Research in experimental methods include functionalization with hydrophobic materials¹⁴ and modifications to the active sensing material either by annealing¹⁵, doping^{16, 17} or specialized growth conditions^{18, 19}. These techniques decrease the sites available for water interaction, thereby reducing the response to humidity. However, the previous work studying these techniques have not been able to fully eliminate the response to humidity variations and focus on either response to gas in different humidity levels or the response to varying humidity and have not considered them as a combined problem. The dominant technology for gas sensing, metal oxide semiconductor (MOS) sensors is humidity insensitive due to high operating temperature >200 °C, boiling off any water molecule on the active sensing part but is disadvantageous due to power consumption and safety issues at these high temperatures for applications in consumer electronics.

2.3 Integration of microheaters with CS-FET

In this work, we demonstrate a simple technique to eliminate sensor response to variations to relative humidity in chemical-sensitive field effect transistors (CS-FETs) using microheaters. CS-FETs are nanoscale silicon transistors with the exception that the electrical gate is replaced by a chemical sensing layer consisting of nanoparticles. The work-function and/or morphology of the sensing layer changes upon exposure to target chemical species, resulting in strong output drain current modulation enabling high detection sensitivity. The relevant details about the device and sensing characteristics have been explained in our previous work²⁰. In the past, we utilized the microheaters by pulsing them immediately after the detection of target gas, which resulted in dramatically improved recovery times²¹. Compared to our previous work on bulk silicon CS-FETs, the distinguishing feature here is the integration of local on-chip microheaters around the sensors as shown in Fig. 2-1a (schematic of cross-section in Fig. 2-1b).

As a “litmus” test to prove this technique, active sensing layer of platinum nanoparticles on trichloro(1H,1H,2H,2H-perfluorooctyl) silane (FOTS) was chosen. The top-down image of the Pt/FOTS layer on SiO₂ grids is shown in Fig. 2-1c. This layer can be used for the detection of hydrogen gas; reason being the strong interaction between Pt and hydrogen gas²², and enhanced sensor performance characteristics with FOTS underneath Pt (Fig. 2-2).

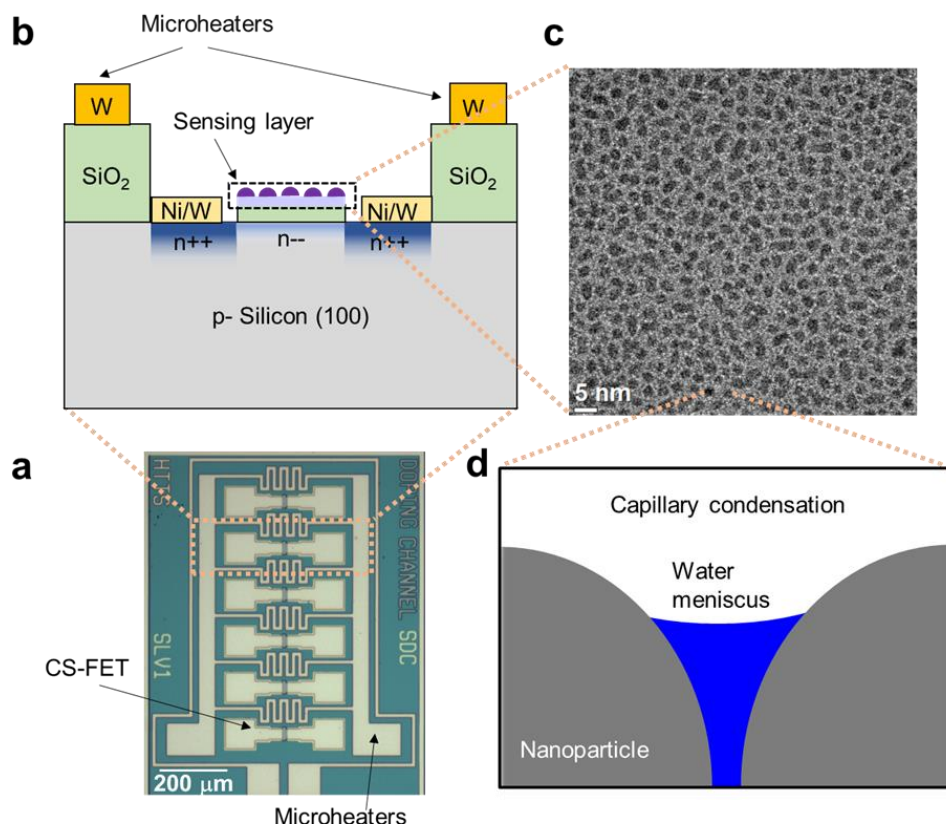


Fig. 2-1. (a) Optical micrograph of a completed chip showing the CS-FETs and microheaters, and a (b) schematic of cross-section. (c) Top-down transmission electron microscopic (TEM) image of Pt/FOTS on SiO₂ grids. (d) Schematic of capillary condensation of water occurring in the cavity between nanoparticles.

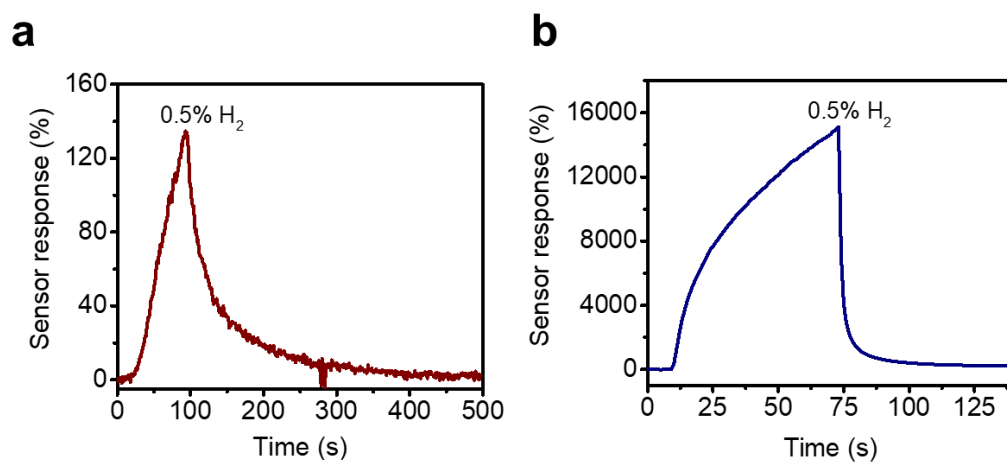


Fig. 2-2. Sensor response to 0.5% H₂ (room temperature) at $V_D = 0.1$ V with sensing layer as (a) 1 nm Pt CS-FET. (b) 1 nm Pt CS-FET with FOTS underneath.

Even though this can enable detection of hydrogen in ppm levels, it is highly sensitive to relative humidity change which made it the best candidate to prove this technique. The method to achieve negligible cross-sensitivity to relative humidity change with the CS-FET platform is to operate the microheaters in a constant voltage mode such that the chip is at a slightly elevated temperature level above room temperature. Infrared imaging of the chip under different microheater powers between zero and 560 mW suggested that the chip temperature increased linearly with power, shown in Fig. 2-3.

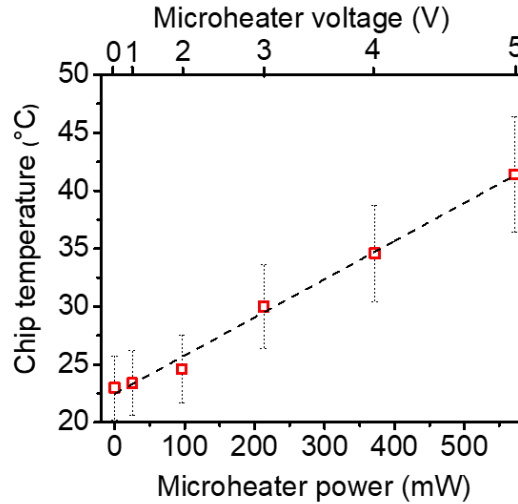


Fig. 2-3. Chip temperature vs microheater power (corresponding to the microheater voltage).

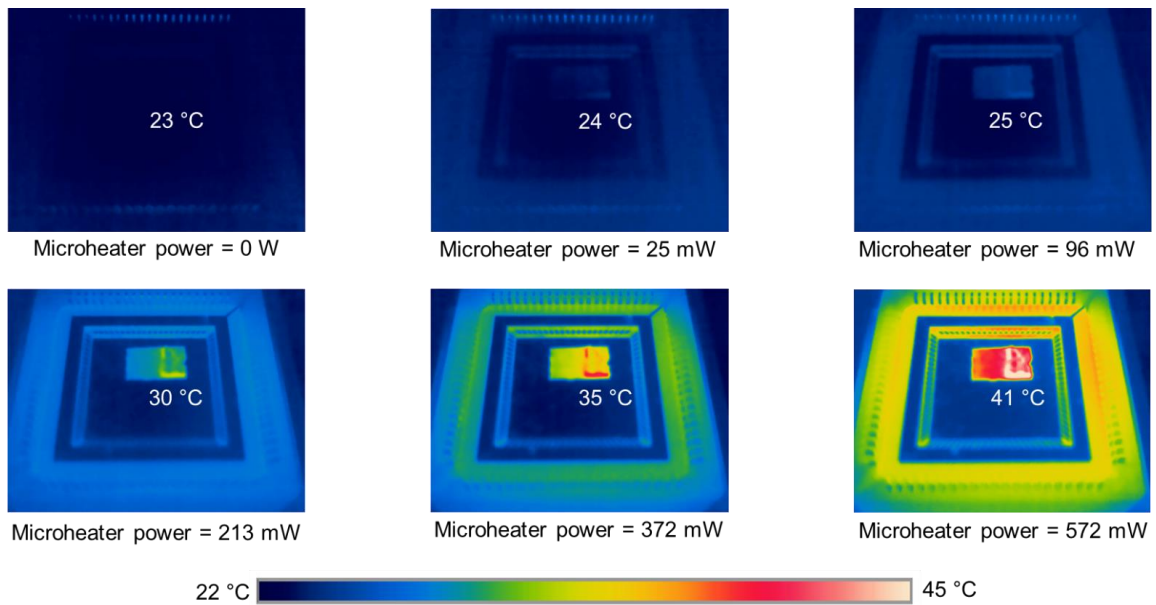


Fig. 2-4. Increasing chip temperature with microheater power level (temperature approximated has an error of $\pm 12\%$).

For a relative humidity change from 50% to 90% with a drain bias of 0.8 V, the CS-FET manifested a response of 3844%, as depicted in Fig. 2-6a. Sensor response were calculated as percentage change from the baseline current values $(I_{peak} - I_{baseline})/I_{baseline} \times 100$. The ambient temperature of the sensor was regulated at 25 °C and since relative humidity level was not increased beyond 95%, the chip was operated above the dew point for condensation to occur. However, the plot of sensor response vs humidity (Fig. 2-5) extracted from Fig. 2-6a, revealed hysteresis in the adsorption and desorption curves at room temperature, a signature of capillary condensation.²³

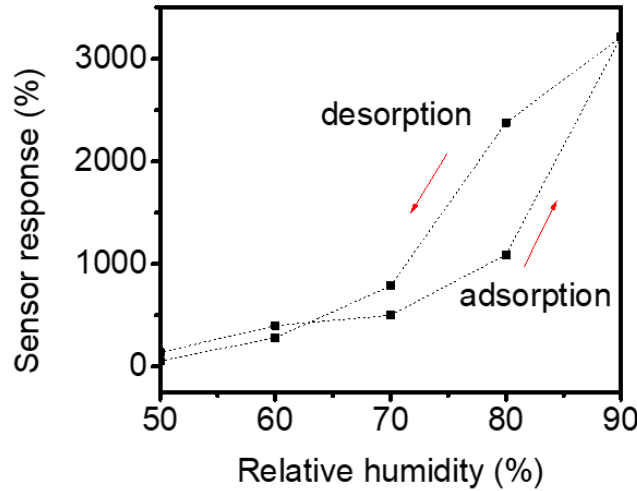


Fig. 2-5. Hysteresis in the sensor response while adsorbing and desorbing humidity indicative of capillary condensation.

A schematic of the occurrence of the phenomenon on the nanoparticles is shown in Fig. 2-1d. From our previous work²¹, the examination of cross-section using transmission electron microscopy (TEM) revealed that the thickness of the nanoparticles should be between 3-4 nm for Au_{1nm}-Pd_{0.3nm}. Since this material system was deposited using the same technique as Pt_{1nm} with the same conditions, similar range of height for Pt nanoparticles is expected. However, to find the approximate relative humidity level at which capillary condensation will occur at room temperature, it was assumed that the size of the nanoparticles is much larger than the cavity size (this might underestimate the actual level for onset according to literature where it has been shown that as the radius of curvature of the nanoparticles increases, the water meniscus height calculated using Monte Carlo simulations also increases for the same relative humidity level²⁴). The cavity size between most of the nanoparticles was found out to be 2 nm from Fig. 2-1c. Even though the validity of the Kelvin equation for sub-10 nm has been debatable, it was assumed valid for a rough approximation of the relative humidity level that creates onset of capillary condensation. The following approximate form of the Kelvin equation²⁵ was applied:

$$\frac{p_{sat}}{p_v} = \exp\left(\frac{2\gamma V_m \cos\theta}{dRT}\right) \quad (2-3-1)$$

where p_{sat} is the saturated vapor pressure, p_v is the vapor pressure, γ is the water surface tension, V_m is the molar volume of water, θ is the contact angle of water with the nanoparticle surface, d is the diameter of the capillary, R is the universal gas constant, and T is the temperature.^{26, 27} Given that pure water completely wets contaminants-free platinum²⁸, it was assumed that the platinum nanoparticles were pure in quality and exhibited zero contact angle with water. Utilizing the standard values of water surface tension as 72 dynes/cm and molar volume of 18 cm³ at room temperature, the value of relative pressure, p_v/p_{sat} which is equivalent to relative humidity, was calculated to be 59%, indicating condensation between the cavities formed in the nanoparticle assembly below the dew point pressure.

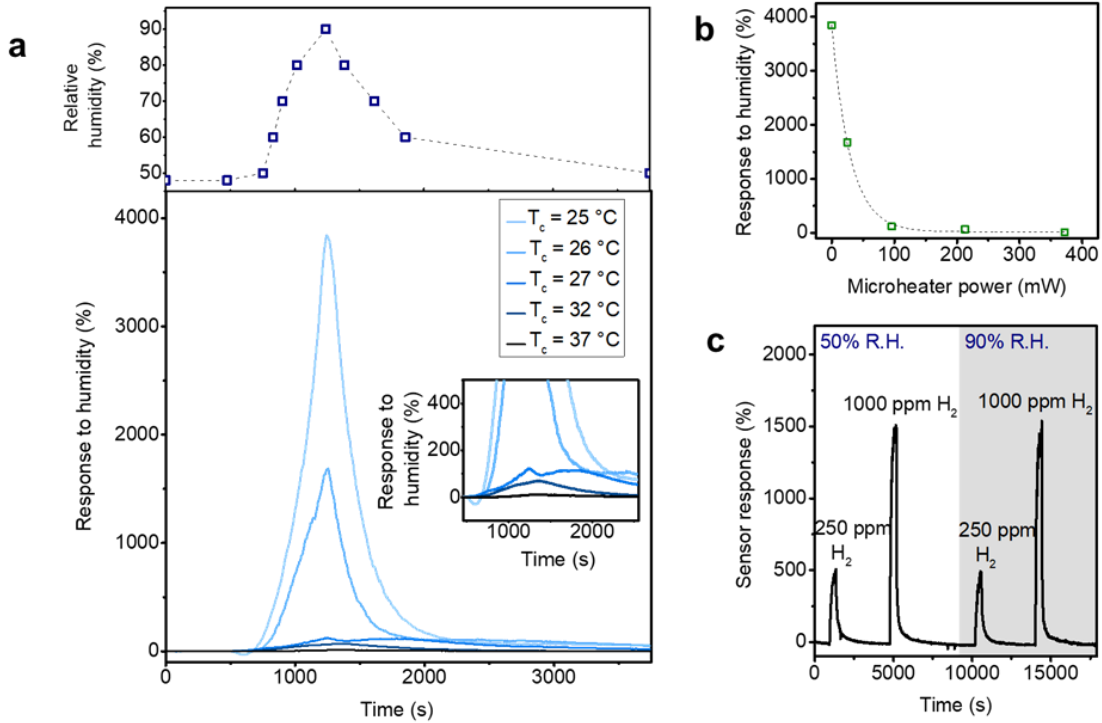


Fig. 2-6 Sensor response to relative humidity change at 25 °C for different chip temperatures (T_c) at $V_D = 0.8$ V. **(b)** Sensor response to relative humidity change from 50% to 90% vs microheater power. **(c)** Sensor response to 250 ppm and 1000 ppm H_2 in relative humidity levels of 50% and 90% with $V_D = 0.65$ V, at a chip temperature of 64 ± 8 °C.

However, with increasing microheater power, the sensor response to this relative humidity change decreased exponentially (Fig. 2-6b), with negligible sensor response of 11.6% at a power of 372 mW and corresponding chip temperature of 37 ± 3 °C. The rationale behind

this is the increase in evaporation rate of any condensed water as the surface temperature is increased. Additionally, physisorption rate of water molecules on the sensing material decreases with increasing chip temperature (which can be explained by Le Chatelier's principle²⁹), given adsorption is an exothermic reaction. For the same reason, the overall hydrogen response also decreased with increasing chip temperature (Fig. 2-7), but this came at the benefit of eliminated humidity response.

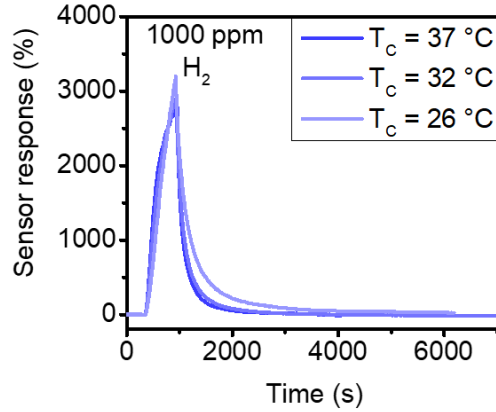


Fig. 2-7. Sensor response to 1000 ppm H_2 at ambient temperature of 25 °C for different chip temperatures (T_c) at $V_D = 0.8V$.

The reason for the relatively low chip temperatures (below <100 °C) requirement to eliminate response to humidity is the fact that water can be evaporated instead of being boiled-off, also the high surface-to-volume ratio of nanoparticles allow for high evaporation rate unlike the active ‘thick’ films in MOS sensors and other gas sensors based on field effect transistors. As a side note, the high surface-to-volume ratio of the nanoparticles is also one of the reasons for high sensitivity to humidity providing the large number of active sites for water adsorption, but if the size of nanoparticles is decreased to circumvent the problem, the sensitivity to hydrogen will also be lowered.

Additionally, we observed minor reductions in sensitivity to hydrogen in relative humidity levels of 50% and 90% with sensor response being 490% (250 ppm) and 1488% (1000 ppm), and 464% (250 ppm) and 1539% (1000 ppm), respectively, as shown in Fig 2-6c. This measurement was carried out with a different CS-FET sensor with 0.65 V of drain bias (to match the baseline current with the CS-FET with 0.8 V drain bias) for which chip temperature to eliminate humidity response was $64 \pm 8\text{ °C}$.

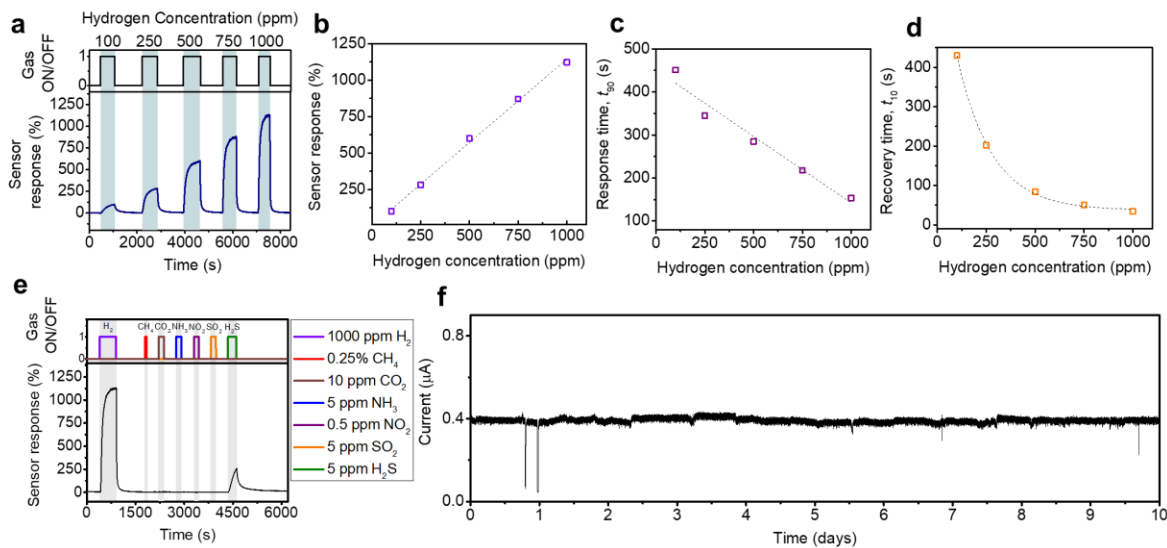


Fig. 2-8. (a) Sensor response vs time for different hydrogen concentration pulses at $V_D = 0.8$ V and chip temperature of 37 ± 3 °C. **(b)** Sensor response vs hydrogen concentration. **(c)** Response time (t_{90}) vs hydrogen concentration. **(d)** Recovery time (t_{10}) vs hydrogen concentration. **(e)** Selectivity test at $V_D = 0.8$ V and chip temperature of 37 ± 3 °C. **(f)** 10-day drift measurement with $V_D = 0.8$ V and chip temperature of 51 ± 6 °C.

The concentrations of 250 ppm and 1000 ppm of hydrogen were chosen for these tests because of the linear sensor characteristics observed between 100 ppm and 1000 ppm (Fig. 2-8a and 2-8b), enabling us to hypothesize that the sensitivity (sensor response per ppm) is constant between those concentration levels. Measurements in Fig. 2-8a were performed with chip temperature of 37 ± 3 °C to eliminate the response to humidity change. The trends of response (t_{90}) and recovery (t_{10}) times with varying hydrogen concentration are depicted in Fig. 2-8c and 2-8d, respectively. t_{90} is the time taken for the sensor to reach 90% of its peak response value from the baseline current and t_{10} is the time taken for the sensor to recover to 10% of its baseline current from the peak value. Fig. 2-8e shows that the sensor proved to be highly selective against other gases such as methane, carbon dioxide, ammonia, nitrogen dioxide and sulfur dioxide, though not against hydrogen sulfide. Even though the molecular structure of water and H₂S is the same, the CS-FET at elevated temperature is sensitive to the gas while not being to water because of the stronger interaction between the active material and the gas, also making H₂S notorious for its poisoning action to catalysts including platinum³⁰⁻³⁴. The CS-FET shown in Fig. 2-8f with microheater switched-on for ten days and chip temperature of 51 ± 6 °C exhibited negligible drift, implying that the active material and the silane layer remained intact and unaffected by continuous microheater operation. This is attributed to the operating

temperature of the microheaters, which is around 10 times lower than the degradation temperature of FOTS³⁵ and 20 times than that of Pt³⁶.

Additional advantage of using the microheaters was the insignificant variation in gas sensitivity with changing ambient temperature. Three pulses of hydrogen gas with concentration of 100 ppm, 600 ppm and 1000 ppm were injected in ambient temperatures of 15 °C, 25 °C and 35 °C with a drain bias of 0.6 V and it was seen that the sensitivity decreased by around 5 times as ambient temperature was lowered by 20 °C, from 2.2%/ppm at 35 °C to 0.4%/ppm at 15 °C as shown in Fig. 2-1a. However, when the microheaters were kept switched-on at a power of 372 mW (chip temperature of 35 ± 3 °C), the sensitivity remained roughly constant; 1.6%/ppm at 35 °C, 1.7%/ppm at 25 °C and 1.8%/ppm at 15 °C, as demonstrated in Fig. 2-9 (raw data is shown in Fig. 2-10). The benefit of maintaining the constant sensitivity regardless of the ambient temperature dramatically simplifies calibration process and ensure detection of low concentration levels as the ambient temperature lowers, for practical usage.

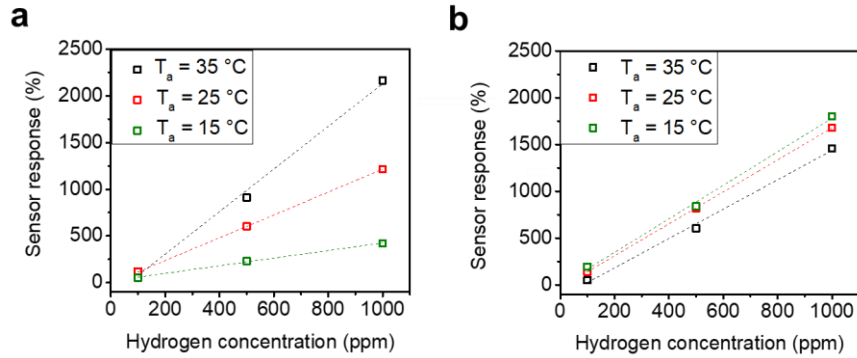


Fig. 2-9. Sensor response vs hydrogen concentration in different ambient temperatures (T_a) at $V_D = 0.6$ V (a) with microheaters off. (b) and with microheaters on at 372 mW.

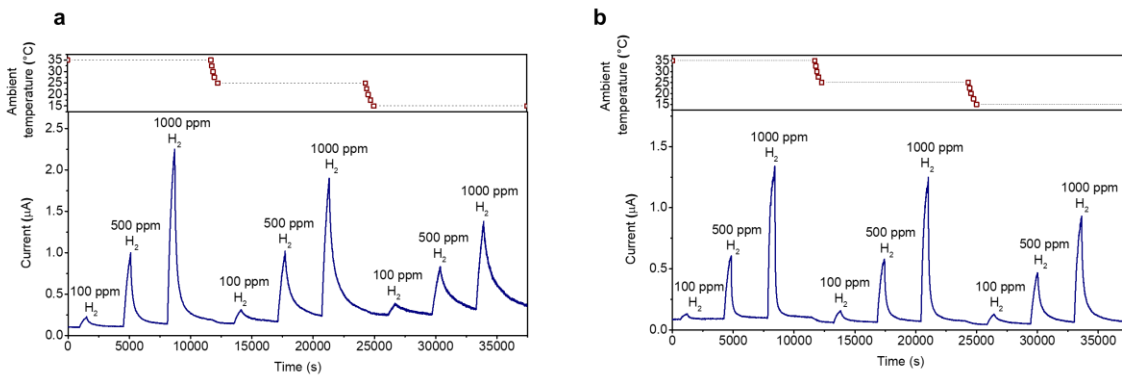


Fig. 2-10. Current vs time for 3 pulses of hydrogen concentrations (100 ppm, 500 ppm and 1000 ppm) in 35 °C, 25 °C and 15 °C, with $V_D = 0.6$ V and microheaters (a) off. (b) on at 372 mW.

In addition to demonstrating humidity selective hydrogen detection using the Pt/FOTS system, we show this technique's application to active sensing materials for other gases with the CS-FET platform. Fig. 2-11a demonstrates that the CS-FET with drain bias as 4 V and InO_x thin film (~1.5 nm) as active material responded by 895% to relative humidity change from 50% to 90%. With microheaters turned on to keep the chip temperature at 70 ± 8 °C, the sensor showed negligible sensor response to the humidity change along with constant sensor response, -56% and -52% to 100 ppb NO₂ in the humidity levels of 50% and 90% respectively (Fig. 2-11b).

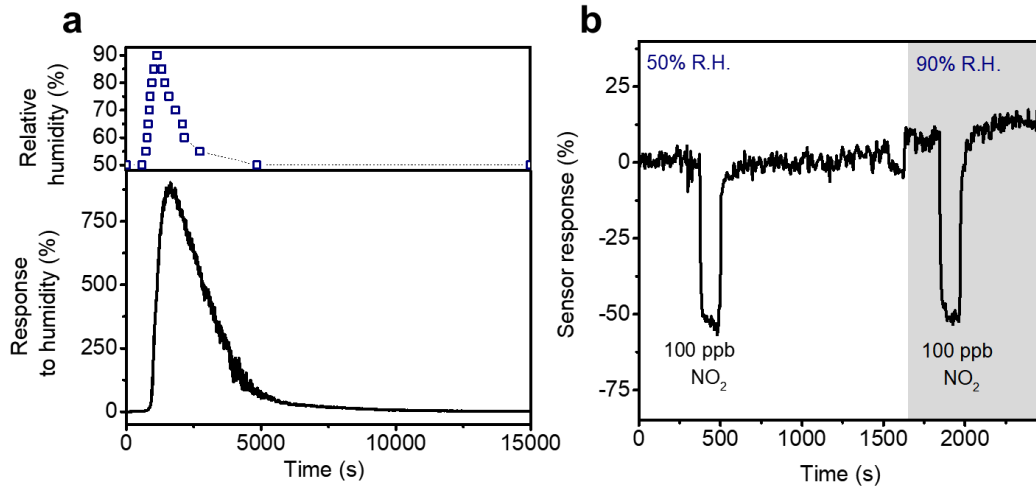


Fig. 2-11. (a) Sensor response to relative humidity change at 25 °C at $V_D = 4$ V with microheaters off. **(b)** Sensor response to 100 ppb NO₂ in relative humidity levels of 50% and 90% with microheaters on and chip temperature of 70 ± 8 °C.

In conclusion, we have demonstrated that by keeping the temperature of the CS-FET slightly higher than the ambient temperature by utilizing the microheaters, effects of relative humidity change can be eliminated. Added benefits of constant gas sensitivity using this technique in different ambient temperatures have also been proved. We showed the proof-of-concept for this technique using Pt/FOTS as active material for hydrogen sensing and its application to InO_x for nitrogen dioxide sensing.

The microheater material and design should be optimized in future and it is expected that the power needed to reach the chip temperature levels to eliminate humidity response will be much lower, extending the applicability of this technique for gas sensors in consumer electronics. Temperature sensor will be also fabricated on the same chip so that the heaters can be looped with proportional-integral-derivative (PID) controller to maintain constant chip temperature irrespective of ambient temperature for constant sensor responses to same gas concentration level.

Though the employability of this technique with other material systems, specifically their long-term sustainability to the heat emitted by microheaters remains a question now, as the library of gases detected with CS-FET platform expands, the method provides a good beginning to solve the long-standing problem of humidity response in gas sensors based on field-effect transistors.

2.4 Measurement and fabrication

CS-FET device chips were wire bonded to an 84-pin J-bend leaded chip carrier. Pure dry air was used as diluent gas and was procured from Praxair Technology Inc. for H₂ and NO₂ sensing experiments, 1% H₂ in N₂ (Gasco) and 1 ppm NO₂ (Gasco) in N₂ were used as source, respectively. Selectivity measurements were performed with 2.5% CH₄, 100 ppm CO₂, 50 ppm NH₃, 5 ppm NO₂, 50 ppm SO₂ and 50 ppm H₂S in N₂ (Mesa gas) as sources. Typical gas flow rates were from 1 to 100 sccm, and diluent (air) flow rate was approximately 1000 sccm. Gas delivery was controlled by mass flow controllers (Alicat Scientific Inc.). Measurements involving relative humidity and temperature changes were done in ESPEC Humidity and Temperature Cabinet LHU-113 with gas outlet 1-2 cm from the sensor chip, otherwise in a walk-in fumehood. CS-FET sensors were biased using a Keithley 428 current preamplifier, and the current signals were acquired using a LabVIEW-controlled data acquisition unit (National Instruments, NI USB-6211). The microheaters were powered by the Agilent E3631A DC Power Supply and all the measurements were performed with microheaters placed on the adjacent die to the one with the CS-FET. Infrared images in Supplementary figure S3 were taken using FLIR ETS320.

A schematic representing the fabrication process is depicted in Fig. 2-12.

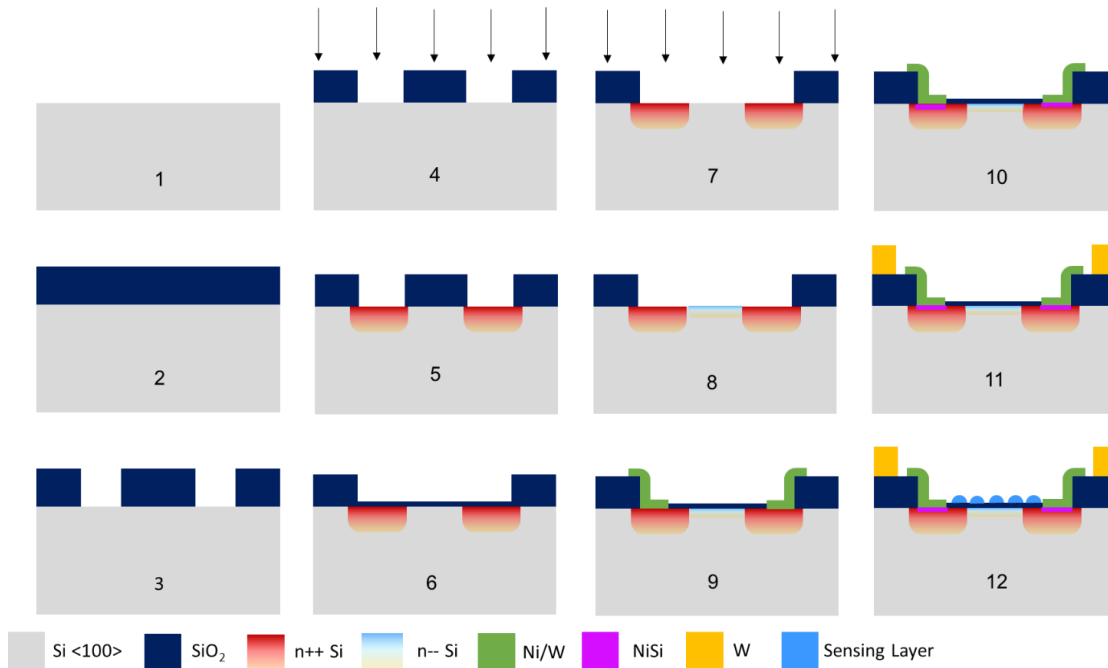


Fig. 2-12. CMOS compatible fabrication process of bulk silicon CS-FET

1. Start with prime <100> Si (sheet resistivity 10-20 ohm.cm)
2. Field oxidation 350 nm
3. Pattern/etch to open source-drain (S/D) doping regions
4. S/D doping with ion-implantation ($4.5 \times 10^{14} \text{ cm}^{-2}$, Phosphorus, 15 KeV)
5. Drive-in anneal to form n++ S/D (1050 °C for 30 s in N_2)
6. Pattern/etch to open undoped channel region
7. Channel doping with ion-implantation ($5 \times 10^{11} \text{ cm}^{-2}$, Phosphorus, 18 KeV)
8. Drive-in anneal to form n-- channel (900 °C for 1 s in N_2).
9. Pattern/etch recessed regions for 20 nm of nickel and 50 nm tungsten deposition using sputtering and lift-off for S/D metallization
10. FGA anneal at 400 °C for 5 minutes for NiSi to complete S/D metallization
11. Pattern microheaters and deposit 200 nm tungsten using sputtering
12. Deposit sensing layer (Pt/FOTS for H_2 and InO_x for NO_2 sensor)

CS-FET gas sensors were fabricated on prime grade silicon <100> wafers with sheet resistivity in the range of 10–20 $\Omega \cdot \text{cm}$. Before processing, all wafers were cleaned in a standard piranha (1:4, hydrogen peroxide/sulfuric acid) bath at 120 °C and native oxide was removed using a 10 s dip in 1:10 hydrofluoric acid. First, a 350 nm silicon dioxide was thermally grown on the silicon wafers for device isolation, using a three-step dry (5 min)–wet (55 min)–dry (5 min) oxidation process at 1000 °C, at atmospheric pressure for 55 min. Oxide thickness was verified using fixed angle ellipsometry. Next, source and drain doping regions in silicon were defined using a standard i-line photolithography process (Fujifilm, photoresist: OiR 906-12, developer: OPD-4262) and wet etching the isolation oxide (in 5:1 buffered hydrofluoric acid for 5 min). Following this, ion implantation ($4.5 \times 10^{14} \text{ cm}^{-2}$, Phosphorus, 15 KeV) was performed for source-drain doping. To complete the formation

of n+2 doped regions, phosphorus drive-in and activation was performed in the silicon source and drain by rapid thermal annealing (RTA) at 1050 °C for 30 s in N₂. The “gate” or sensing layer region was patterned next and etched in 5:1 buffered hydrofluoric acid for 4 min. The channel doping was also performed using ion implantation (5×10^{11} cm⁻², Phosphorus, 18 KeV) and subsequently rapid thermal annealing (RTA) at 900 °C for 1 s in N₂. To define source and drain contacts, a separate source-drain metallization mask was used, which underlaps the doped source and drain regions by 11 μm. After this, argon was sputtered to etch the native oxide and then, 20 nm of nickel and 50 nm tungsten were then deposited in the source and drain contact regions, also using the sputtering tool followed by lift-off in acetone. To achieve ohmic source and drain contacts, nickel silicidation (NiSi) was performed in forming gas (5% H₂ in N₂) using RTA at 400 °C for 5 min. To pattern the microheaters, photolithography was performed and consecutively, 200 nm tungsten was sputtered. The fabrication of bare CS-FET concluded with lift-off.

For the hydrogen sensor, FOTS was deposited using AMST Molecular Vapor Deposition MVD100. Following this, Pt sensing layer was deposited by electron beam evaporation of 1 nm Pt. For the nitrogen oxide sensor, InO_x sensing layer was deposited by thermal evaporation of 1.5 nm InO_x after which the chip was annealed in forming gas at 150 °C for 1 h postdeposition, which completed the sensor fabrication process.

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3 NDIR sensors with highly efficient bP-LED

3.1 Introduction*

The mid-wave infrared (MWIR) wavelength range plays a central role in a variety of applications including optical gas sensing, industrial process control, spectroscopy, and IR countermeasures. Among the MWIR light sources, light-emitting diodes (LEDs) have the advantages of simple design, room-temperature operation, and low cost. Owing to the low Auger recombination at high carrier densities and direct bandgap of black phosphorus (bP), it can serve as a high quantum efficiency emitting layer in LEDs. In this work, we demonstrate bP-LEDs exhibiting high external quantum efficiencies and wall-plug efficiencies of up to 4.43% and 1.78%, respectively. This is achieved by integrating the device with an $\text{Al}_2\text{O}_3/\text{Au}$ optical cavity, which enhances the emission efficiency, and a thin transparent conducting oxide (indium tin oxide, ITO) layer, which reduces the parasitic resistance, both resulting in order of magnitude improvements to performance. We also show that non-dispersive infrared (NDIR) gas sensors integrated with these bP-LEDs can detect ppm-level of CO_2 and methane for greenhouse gas monitoring applications.

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3.2 Significance of bP*

The mid-wave infrared spectral range (MWIR, $\lambda=3-8 \mu\text{m}$), is classified as eye safe, which makes it attractive for applications including target imaging, illumination, and free-space optical communication. In addition, MWIR covers fundamental vibrational resonance bands of a wide range of materials including water, polymers, toxic and explosive agents, and molecular gases such as CO_2 and methane.¹ An application related to the latter, i.e., gas sensing, has lately been of much interest, e.g., for smart homes, oil and gas production, and wearable health monitoring. This growing market has motivated the development of III-V and II-VI semiconductor-based laser technologies such as quantum-cascade lasers (QCLs), interband cascade lasers (ICLs), and quantum-well lasers. These provide high optical power and narrow spectral width but with the tradeoff of system complexity, and high-power requirement and fabrication cost.² Inexpensive alternatives such as thermal light emitters come at the cost of broad spectral width and limited modulation frequencies.^{2,3} By contrast, light-emitting diodes (LEDs) present the opportunity for low cost, but also have favorable characteristics such as brightness adjustment via pulse-width modulation and narrow spectral width.

Conventional MWIR LEDs based on III-V and II-VI semiconductors exhibit low efficiencies (even theoretically) due to high Auger recombination coefficient which is inherent to semiconductors with small bandgap and large asymmetry in carrier effective masses.⁴ Therefore, there is a tremendous technological need for the development of a new emitter material in the MWIR with higher quantum yield and efficiency. Black phosphorus (bP), a two-dimensional (2D) material, has a much lower Auger recombination coefficient compared to III-V and II-VI semiconductors with similar bandgaps due to smaller asymmetry in effective masses, presenting opportunity as the emitting layer for more efficient MWIR LEDs.⁵⁻⁷ A lower Auger recombination coefficient leads to a higher quantum yield (QY), which is the fraction of recombination events that emit photons and is given by the ABC model as:

$$QY = \frac{B(np - n_i^2)}{A(np - n_i^2)/p + B(np - n_i^2) + 2Cn(np - n_i^2)} \quad (3-1-1)$$

where A , B and C are the Shockley-Read-Hall (SRH), radiative bimolecular, and Auger recombination coefficients, respectively, and n_i and n/p are the intrinsic and total electron/hole concentrations, respectively. BP has a much higher MWIR photoluminescence (PL) intensity than indium arsenide (InAs) multiple quantum well (MQW), confirming its prospects for photonic applications.⁸ Another advantage of bP is that its PL emission is linearly polarized.⁹ Owing to its puckered honeycomb lattice, bP shows novel anisotropic optical, electronic, mechanical, thermal, and optical properties along the two orthogonal directions of armchair and zigzag.^{10,11} Furthermore, the material shows high hole mobility and has a direct and widely tunable thickness-dependent bandgap

that ranges from 0.3 to 2 eV, a spectral region containing absorption lines of numerous gases.^{12,13} This confirms the prospects of bP-based LEDs for applications involving selective sensing of gases.

3.3 Optimization of bP-LED*

BP-LEDs investigated so far are in the form of bP/MoS₂ heterojunctions, which have intrinsic p-type and n-type characteristics, respectively, and produce MWIR electroluminescence.^{14,15} It has also been shown that high output power can be achieved when the device is modified to include graphene electrodes to allow the injection of high current into the bP layer.¹⁶ Even though these works have documented bP-LEDs with remarkable properties, there have not been extensive efforts to improve their external and wall-plug efficiencies. In this work, we demonstrate techniques to improve these metrics by addressing two key problems.

The first problem is that of limitations to the wall-plug efficiencies of the previously demonstrated bP-LEDs, due to the high parasitic resistances of the materials. Even though MoS₂ forms a low Schottky barrier height with metal contacts (such as Au or Ni) for electron injection into bP, there is still considerable scope for reducing the overall resistance of device. To shunt the lateral parasitic resistance of the MoS₂ layer, we employ a thin film of indium tin oxide (ITO). ITO has low resistivity because it is an n-type degenerate semiconductor.¹⁷ We chose ITO rather than a metal due to its high optical transparency. Furthermore, mitigation of the parasitic resistance is critical not only for improving wall-plug efficiency, but also for extending operating lifetime. This is because high parasitic resistances can lead to excessive device temperatures due to joule heating. This can contribute to melting/vaporizing/diffusing processes occurring in the device and accelerate void formation, which can ultimately lead to permanent device degradation and/or failure.^{18,19}

Another issue with the bP-LED devices demonstrated thus far, is that a large fraction of the generated photons is lost either via emission through the bottom side or total internal reflection, while only the extracted optical power determines the overall device performance. To improve the light extraction efficiency in conventional LEDs, various methods including die shaping^{20,21}, textured semiconductor surfaces^{22,23}, contact geometries^{24,25}, anti-reflection optical coatings²⁶, transparent contacts²⁷, flip-chip packaging²⁸⁻³⁰, and resonant cavities³¹⁻³³ have been employed. In particular, resonant cavities result in not only an enhanced light outcoupling, but also a more directed far-field emission pattern, which makes resonant-cavity light emitting diodes (RC-LEDs) desirable for optical communication systems.³⁴ Optical cavities have also been employed for enhancing the light absorption and thus photodetection performance of 2D materials.^{35,36}

In this study, optical cavity consisting of gold and Al₂O₃ films was formed under the light-emitting bP/MoS₂ heterojunction such that the emission couples to the resonant mode of the cavity, and therefore, enhances the emission efficiency of the bP-based LEDs.

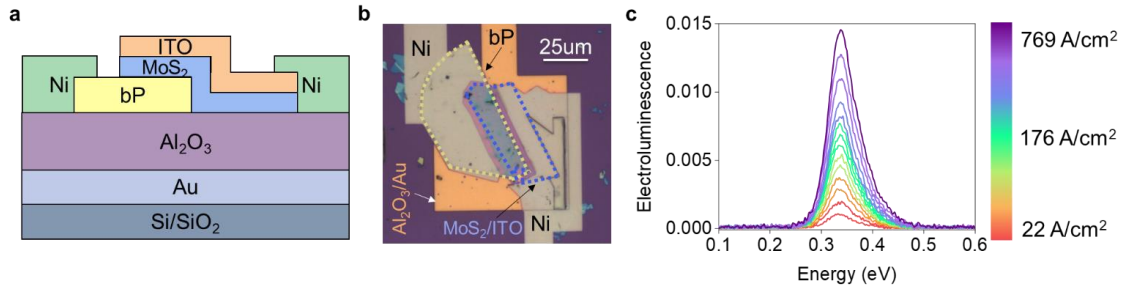


Fig. 3-1. (a) Schematic showing the device cross-section. **(b)** Optical micrograph of a typical device with 80 nm bP, 8 nm MoS₂, 10 nm ITO, and 360 nm Al₂O₃ layer. **(c)** Electroluminescence measured from the device shown in (b) as a function of injection current density with a peak emission at 0.34 eV.

A schematic of the cross-section and an optical microscope image of the device are shown in Fig. 3-1a and Fig. 3-1b, respectively. The fabrication process is as follows:

Firstly, the optical cavity was fabricated by firstly depositing Ti/Au/Ti (5 nm/120 nm/5 nm) using ebeam evaporation followed by sputtering 360 nm Al₂O₃. MoS₂ was mechanically exfoliation on 50 nm SiO₂/Si substrate onto which 10 nm ITO was sputtered. bP (Smart Elements) due to its air sensitivity was exfoliated in a glove box. The thicknesses of the flakes were measured using AFM (Atomic Force Microscopy, Bruker Dimension Icon with ScanAsyst) and the stack was prepared using dry-transfer technique. Utilizing poly (methyl methacrylate) or PMMA as carrier, the MoS₂/ITO stack was lifted and transferred to the bP, after which the whole stack was placed onto the cavity to create the final structure. Next, the contacts were patterned using the high-resolution write-head in the uPG-101 Laser Lithography System, followed by thermal evaporation of 40 nm Ni contacts and overnight liftoff in anhydrous acetone (in glovebox) to conclude the fabrication process.

BP flakes with thicknesses 40 ± 5 nm and MoS₂ flakes with thicknesses 8 ± 2 nm were used in all experiments. This results in an emission peak at ~ 0.34 eV ($\lambda = 3.65$ μ m) in our bP-LEDs with a full-width at half maximum (FWHM) of ~ 0.7 μ m. Using bP flakes with appropriate thickness is important here, as its bandgap is strongly modulated by thickness. The bandgap of MoS₂ remains constant at 1.29 eV for bulk thicknesses.³⁷ Typical emission spectra measured at different injection current densities are shown in Fig. 3-1c. The electroluminescence intensity increases with higher current injection density without any change in the peak energy. This confirms that the emission originates from the bP band edge recombination.

These spectra were collected using a double-modulated lock-in detection technique, as described as follows:

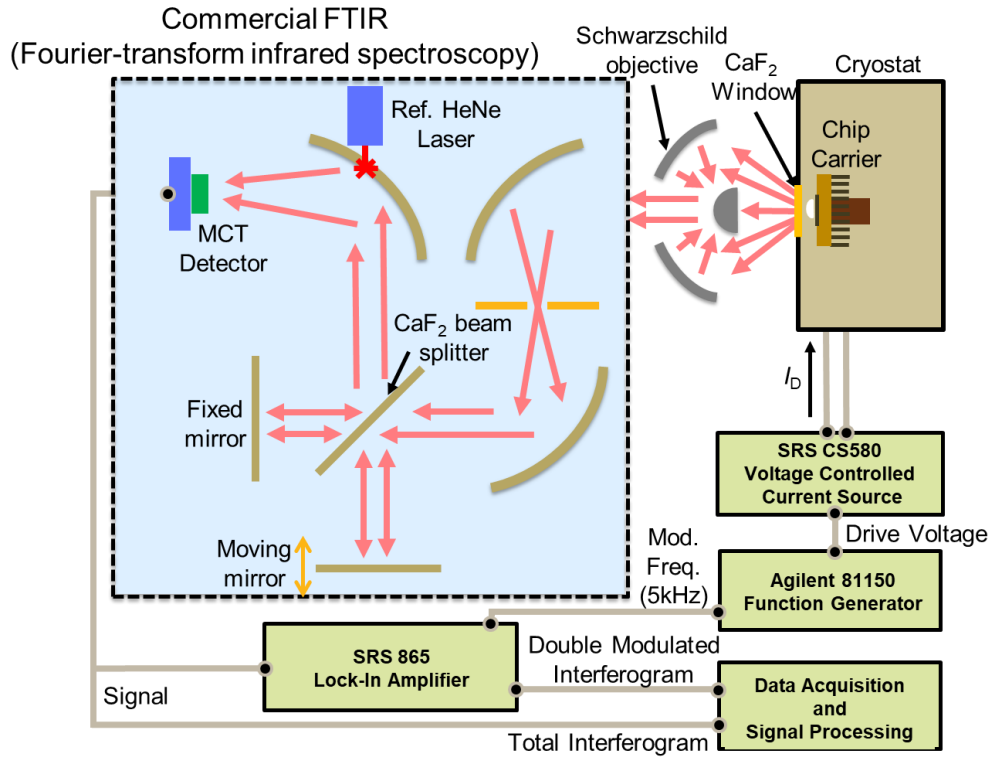


Fig. 3-2. Schematic of the measurement setup.

Electrical measurements (I - V characteristics) were performed using Agilent 4155C Semiconductor Parameter Analyzer and the junction area was analyzed using ImageJ software. Sheet resistance of ITO was measured using Guardian SRM-232. For the estimation of input carrier and power density, and output power density, it was assumed that distribution is uniform across the junction area. For the optical measurements, devices were wire-bonded in a 24-pin chip carrier and placed in a Janis cryostat evacuated to a base pressure $< 10^{-4}$ Torr. One of the major challenges in infrared emitter measurements is the separation of the electroluminescence of the diode from the thermal background, therefore, a double modulation scheme was used to solve this problem. The first modulation was executed using function generator (Agilent 81150) inputting voltage at a frequency of 5 kHz and 50% duty cycle to a voltage controlled current source (CS589 Stanford Research Systems) injecting current into the device inside the cryostat. The modulated light output from the device passed through a CaF₂ window in the cryostat and then a 15 $\times$ Schwarzschild objective to the external source port of FTIR (iS50, Thermo Fisher) where the emitted light was modulated for a second time. The beam splitter and detector used for these measurements were CaF₂ and liquid-N₂ cooled HgCdTe (MCT) detector respectively and the FTIR optical velocity was set at 0.0657 cm s^{-1} . The signal from the FTIR was de-

modulated using a lock-in amplifier (SR865) which locked-in the signal at 5 kHz (the frequency of the injected current) and outputted the separated signal from the background to the oscilloscope. Thereafter, the data was acquired and processed in a custom-built LabView program in which Fast Fourier Transform (FFT) was performed to convert the signal from interferogram in the time-domain to the frequency-domain to collect the bP-LED emission spectrum. The cryostat was mounted on translation stages and x-, y- and z-controllers were adjusted to maximize the signal from the device. The setup schematic has been shown in Fig. 3-2. For the drift measurement, the device was modulated at a frequency of 1 kHz, and the de-modulated signal from the lock-in amplifier was sampled at frequency of 1s and recorded in a different LabView program.

The characterization of the polarized emission from the LED is shown in Fig. 3-3.

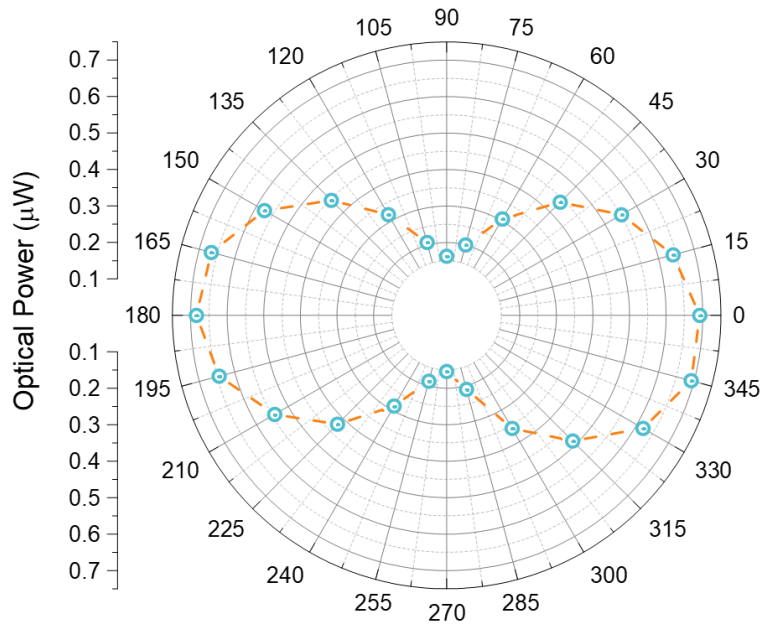


Fig. 3-3. Polarized Optical Power from bP-LED as a function of polarization angle.

The Al₂O₃/Au optical cavity was designed using optical simulations. For an emitter with a low intrinsic quantum efficiency, the emission enhancement factor provided by an optical structure can be expressed as $f_p \times \eta_{oc}$, where f_p is the Purcell factor (i.e., spontaneous emission rate enhancement provided by the optical medium) and η_{oc} is the outcoupling efficiency (i.e., fraction of radiated photons that escape the optical structure and reach the upper half-space where they get collected).³⁸ The Al₂O₃/Au cavity can contribute to the emission enhancement through both of these factors. In the presence of the optical cavity, the portion of the emitted light travelling downwards gets reflected from the mirror and interferes with the emitted light from bP. In order for the interference to be constructive, the spacer thickness should be $\sim \lambda/(4n_s)$, where n_s is the refractive index of the Al₂O₃ spacer layer and λ is the wavelength of the emitted photons. Hence, the optical cavity with proper spacer thickness enhances the outcoupling efficiency by redirecting the emitted light to the upper half-space where it can be collected. This is schematically illustrated in Fig. 3-4a. Fig. 3-4b shows the optical power variation along the depth of the device for Al₂O₃ thicknesses of 50 nm, 360 nm, and 500 nm at $\lambda = 3.65 \mu\text{m}$. The simulation details are as follows:

The simulations to extract the outcoupling efficiency and Purcell Factor were modelled in Lumerical FDTD Solutions. The refractive index data of Au and Al₂O₃ was used from the material data base in the software, and refractive index of MoS₂ chosen as 4.227. The structure was setup to mimic the device structure with the thicknesses used for the experiments. The light source was chosen as a dipole placed in bP, whose peak wavelength changed with the bP thickness (thickness changes the optical bandgap for bP). To eliminate the errors caused by the dipole source in the infrared absorbing media, the imaginary refractive index of bP was set to 0 and the real part of the refractive index used was 3.997 (xx), 2.891 (yy) and 3.575 (zz), owing to the anisotropic properties of the material. Mesh size was chosen such that each layer had at least 10 elements and the boundary conditions were used as perfectly matched layers (PMLs). Purcell factor was computed using the transmission through the source monitor box tightly enclosing the dipole source and the outcoupling efficiency was determined by the ratio of the transmission of far-field monitor to that through the source monitor.

It can be seen that a spacer thickness of 360 nm leads to the highest light outcoupling, and thus far-field optical power. Fig. 3-4c plots the outcoupling efficiency as functions of Al₂O₃ and bP thicknesses at fixed thicknesses of 10 nm ITO and 8 nm MoS₂. For bP thicknesses smaller than 50 nm (on 325 nm Al₂O₃/Au cavity), the outcoupling efficiency is enhanced by more than ~ 50 times compared with the case without Al₂O₃ spacer. While the outcoupling efficiency of this structure reaches its maximum value of $\sim 21\%$ for bP thickness of 20 nm, the Purcell factor is not the highest in this range of bP and Al₂O₃ thickness.

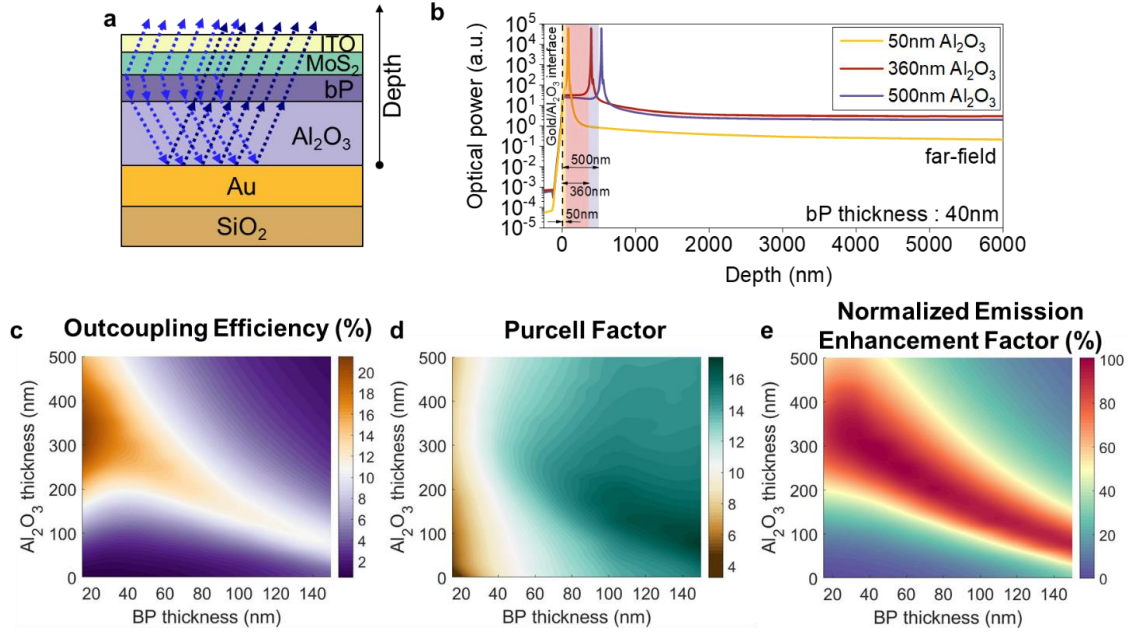


Fig. 3-4. (a) Schematic of device cross-section showing the constructive interference of emitted light due to optical cavity. (b) Simulated vertical profile of the optical power for Al₂O₃ thicknesses of 50nm, 360nm and 500nm for fixed bP thickness of 40nm. Optical simulations showing the (c) outcoupling efficiency, (d) Purcell Factor and (e) normalized emission enhancement factor variation for the device structure as a function of bP and Al₂O₃ thickness for MoS₂ thickness of 8 nm and ITO thickness of 10 nm.

As illustrated in Fig. 3-4d, the Purcell factor is greater at an Al₂O₃ thickness of ~100 nm and bP thickness of 100-150 nm. Fig. 3-4e. plots the normalized emission enhancement factor ($f_p \times \eta_{oc}$) as functions of Al₂O₃ and bP thicknesses. The bP films used in the experiments were 40 nm thick. Accordingly, an Al₂O₃ thickness of 360 nm should be chosen to maximize the emission enhancement factor. It should be noted that the optical behavior of ITO depends on the material defect density and thus sputtering conditions.^{39,40} Thus, the refractive index values of ITO to be used in the simulations were determined for our specific deposition parameters.

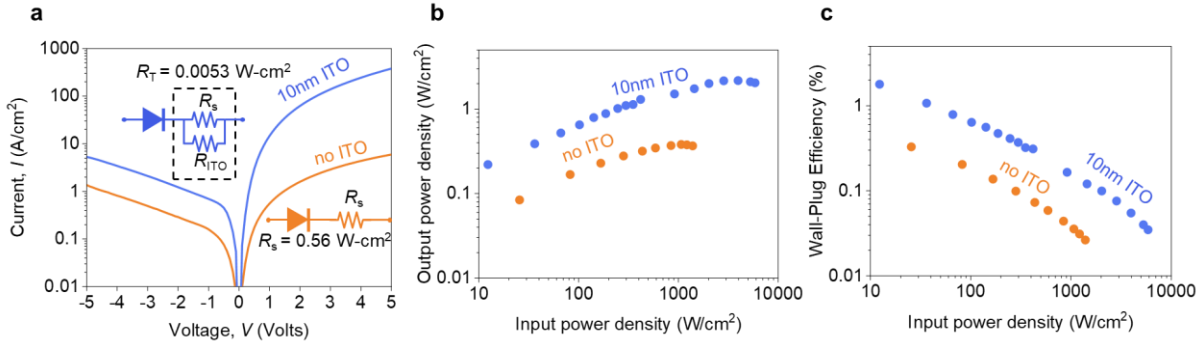


Fig. 3-5. (a) I - V characteristic and extracted series resistance for devices with and without 10-nm-thick ITO film. **(b)** Output power density and **(c)** wall-plug efficiency as functions of input power density for LEDs with and without 10-nm-thick ITO film.

To reduce the parasitic resistance, we employed a 10-nm-thick ITO layer, which has a relatively low sheet resistance of $300 \text{ } \Omega/\text{sq}$. The effect can be quantified by comparing current-voltage (I - V) characteristics of devices with and without ITO, as shown in Fig. 3-5a. These devices have similar junction areas of $353 \text{ } \mu\text{m}^2$ (with ITO) and $424 \text{ } \mu\text{m}^2$ (without ITO). For large forward-bias voltages where series resistance becomes important, the current per unit junction area for the device with ITO is higher by more than an order of magnitude compared to the device without ITO. The forward-bias series resistance is evaluated using the following method.³⁴ The diode is assumed to have a very high parallel resistance ($R_P \rightarrow \infty$), yielding the following forward-bias I - V relation,

$$I = I_s \exp \left(\frac{q(V - IR_s)}{n_{\text{ideal}} kT} \right) \quad (3-2-1)$$

Here, I_s is the reverse-bias saturation current, R_s is the series resistance, n_{ideal} is the ideality factor, k is the Boltzmann constant, q is the electric charge on an electron, and T is the absolute temperature of the diode. Equation (3-2-1) leads us to:

$$\frac{dV}{dI} = R_s + \frac{n_{\text{ideal}} kT}{q} \frac{1}{I} \quad (3-2-2)$$

The slope of the plot of IdV/dI vs I (Fig. 3-6) is then used to determine R_s , which is $0.0053 \Omega\text{-cm}^2$ and $0.56 \Omega\text{-cm}^2$ and for devices with and without ITO, respectively. Hence, an about two orders of magnitude reduction in series resistance is achieved. The reduction in parasitic resistance via the ITO layer improves the maximum output power density and the power efficiency of the device. Fig. 3-5b shows that the device with 10-nm-thick ITO layer produces a maximum optical power of 2.2 W/cm^2 , which is more than five times higher than that for the device without ITO, i.e., 0.4 W/cm^2 . Despite having a slightly lower photon extraction efficiency, the device with ITO shows higher brightness per unit area. This can be attributed to the reduction in series resistance achieved via ITO layer, which improves the voltage drop across the device.

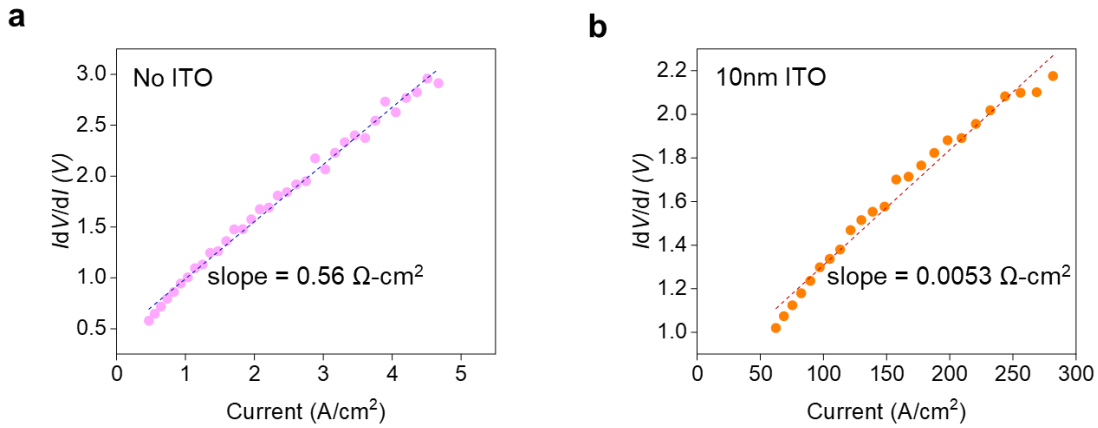


Fig. 3-6. IdV/dI as a function of I (current normalized by junction area) to find series resistance, slope of the graph for (a) no ITO and, (b) 10 nm ITO.

The LED with low parasitic resistance outperforms the device without ITO in terms of power efficiency as well, as shown in Fig. 3-5c. This is also called wall-plug efficiency (η_{power}) and is the ratio of the total detected optical power (P) to the total input electrical power injected into the device,

$$\eta_{\text{power}} = \frac{\text{detected optical power}}{\text{input electrical power}} = \frac{P}{IV} \quad (3-2-3)$$

The device with ITO achieves a wall-plug efficiency of 0.3% at an input power density of 418 W/cm^2 , while for the device without ITO, the wall-plug efficiency is 0.07% at a (similar) input power density of 435 W/cm^2 .

The output power density increases sub-linearly with input power density according to the “efficiency-droop” effect, i.e., external quantum efficiency (η_{EQE}) is reduced due to Auger recombination at higher carrier densities.^{41,42} η_{EQE} is defined as the ratio between the number of detected photons and the number of electrons injected into the device,

$$\eta_{\text{EQE}} = \frac{\text{number of detected photons}}{\text{number of injected electrons}} = \frac{P/(hc/\lambda)}{I/q} \quad (3-2-4)$$

Here, h is Planck’s constant, c is the speed of light, and λ is the wavelength of the emitted photons. For devices with and without 10 nm ITO layer, the output power density saturates at input power densities of $\sim 3000 \text{ W/cm}^2$ and 1000 W/cm^2 , respectively, and it starts drooping with increasing input power. It is anticipated that junction temperature plays a significant role here, as Auger recombination coefficients increase exponentially with increasing temperature⁴³ and no temperature control mechanism (e.g., heat sinking or thermoelectric cooling) is implemented here. This results in further deterioration of external quantum efficiency (and consequently, the output power) at higher input powers. Therefore, a possible rationale for the delayed onset of droop in devices with ITO is the lower junction temperature compared with devices without ITO. The dramatic decrease in the wall-plug efficiency with increasing input power also originates from the reduced external quantum efficiency. While the ITO layer reduces the parasitic resistance of MoS₂, it does not affect the parasitic resistance of bP and the contact resistance.

The power output from the device was determined by calibration of the setup. The calibration method essentially needed a “counts-to-power” conversion factor which can be used to multiply to the arbitrary counts obtained from the emission spectrum ($C_{\text{bP-LED}}$, area under the spectrum) in the software. For this, we chose a $4.05 \text{ }\mu\text{m}$ quantum cascade laser (Thorlabs QF4050T1) as the reference light source, reason being the narrow bandwidth and closer emission wavelength to the bP emission wavelength. Since the light from the laser is a directed beam unlike broad distribution beams that most LEDs show, instead of directly putting the laser in front of the objective, the light from the laser was first collimated using a CaF₂ lens, then a second CaF₂ lens which converged the collimated light, and lastly through a mirror which reflected that converging light and finally reflecting off from a Labsphere reflection standard (setup represented in Fig. 3-7). The reflection standard reflected the laser light in a Lambertian distribution which afterwards followed the same optical path and electrical instrumentation as bP-LED to collect counts from the laser spectrum (C_{ref}). The laser power falling onto the reflector was measured by replacing it with the highly sensitive Ophir Nova 7Z01500 power meter (setup shown in Fig. 3-8), and this power was divided by the reflectivity of the reflection standard at $4.05 \text{ }\mu\text{m}$ to find out the power reflecting from it (P_{ref}). The counts from the spectrum measurement and the power from the power meter were then used to calculate counts-to-watt conversion factor. To use this factor for finding the bP-LED power, the correction for difference in detector sensitivity for the bP emission wavelength ($3.65 \text{ }\mu\text{m}$) vs the laser emission wavelength

(4.05 μm) was also needed. This called for the evaluation of the instrument function (IRF) of the MCT detector in the FTIR which was evaluated by dividing the measured spectrum to the theoretical spectrum of blackbody at 400°C. The theoretical spectrum of the black body was calculated using the equation:

$$M_e(\lambda, T) = \frac{2\pi hc^2}{\lambda^5 (e^{hc(k\lambda T)^{-1}} - 1)} \quad (3-2-5)$$

where M_e is Planks law for spectral exitance and T is the temperature. The correction factor was represented as the ratio of the instrument function value at laser wavelength (IRF_{ref}) to that at the bP-LED emission wavelength ($IRF_{\text{bP-LED}}$). The second correction factor that was required in the calibration process, was for the slight dissimilarity between the angular distribution of the Lambertian reflection standard and bP-LED. The bP-LED angular distribution shown in Fig. S9 was extracted from the far-field monitor in the optical simulations performed using Lumerical FDTD Solutions. This dissimilarity is important because the reflective objective only accepts light at angles ranging from 11.6° to 35.4° from the normal incidence. The correction factor was obtained by integrating the light intensity accepted by the objective for laser (A_{ref}) and bP-LED ($A_{\text{bP-LED}}$), and calculating their ratio. Finally, the device power output, P was found from the following equation:

$$P = C_{\text{bP-LED}} \times \frac{P_{\text{ref}}}{C_{\text{ref}}} \times \frac{IRF_{\text{ref}}}{IRF_{\text{bP-LED}}} \times \frac{A_{\text{ref}}}{A_{\text{bP-LED}}} \quad (3-2-6)$$

The differences in the FTIR gain and the lock-in-amplifier were also accounted for the power output and efficiency calculations along with the fact that the device was operated at 50% duty cycle.

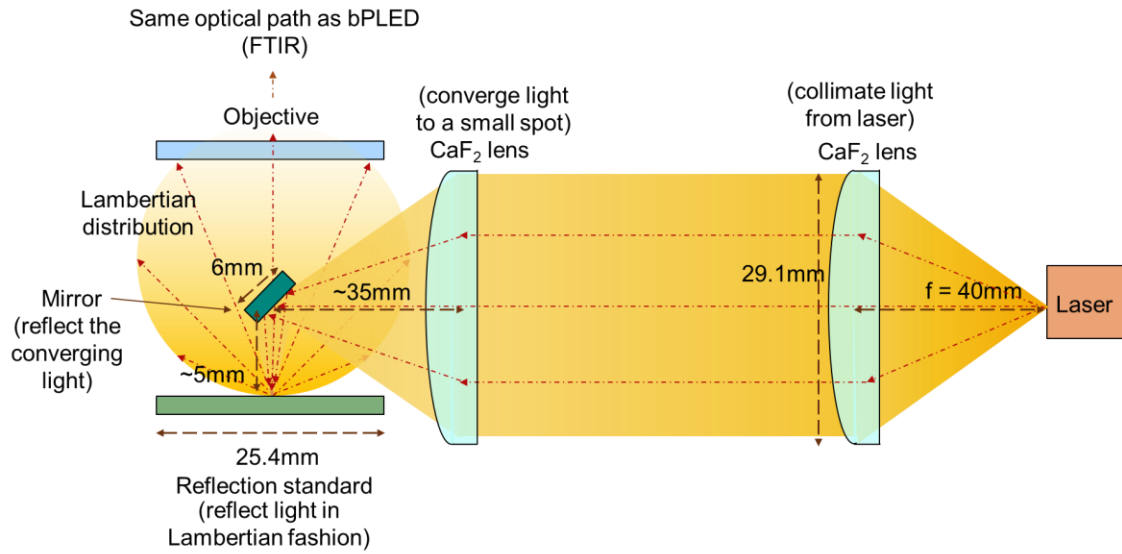


Fig. 3-7. Schematic of calibration setup to measure the counts of reference laser.

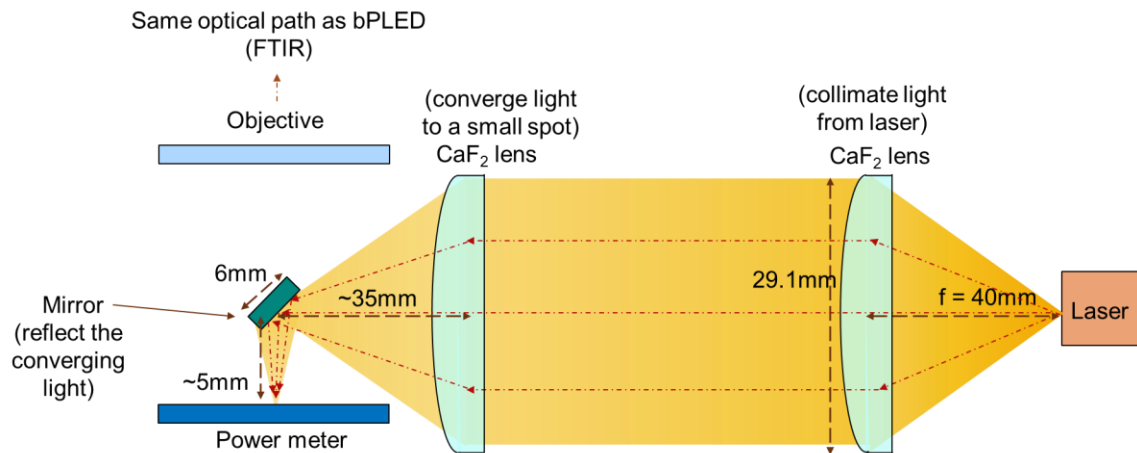


Fig. 3-8. Schematic of calibration setup to measure power of reference laser.

Next, we performed a statistical study on 45 devices to determine the device-to-device variations. The results are presented in Fig. 3-9. The “efficiency-droop” effect can be clearly observed in Fig. 3-9a, with the peak external quantum efficiency of the champion device being 4.43% at the input current density of 14 Acm^{-2} and reducing to 0.90% at the current density of 638 Acm^{-2} . The corresponding output power densities at these current densities are 0.22 W/cm^2 and 2.04 W/cm^2 , respectively. The maximum output power density recorded from this device with area of 353 μm^2 is 2.17 W/cm^2 (i.e., output power = 7.68 μW) at an injected carrier density of $6.2 \times 10^{21} \text{ cm}^{-2}$. The device with the lowest peak external quantum efficiency of 0.49% at the current density of 15 Acm^{-2} exhibits a wall-plug efficiency of 0.15%, as shown in Fig. 3-9b. Its maximum output power is 2.21 μW , achieved at an input current density of 304 Acm^{-2} . The highest wall-plug efficiency amongst the 45 devices (i.e., for the champion device) is 1.78%, achieved at a current density of 14 Acm^{-2} . This device exhibits a power efficiency of 0.035% at the highest injected current density of 638 Acm^{-2} .

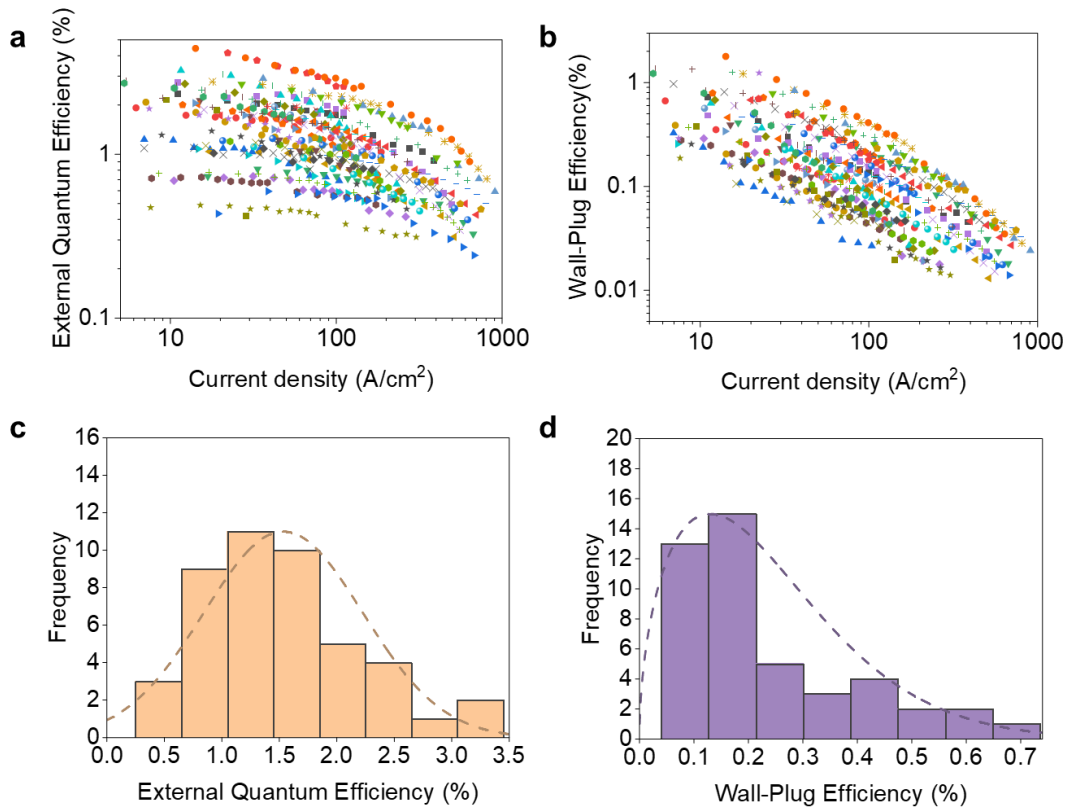


Fig. 3-9. (a) External quantum efficiency and (b) wall-plug efficiency as functions of input current density plotted for 45 devices fabricated with constant MoS₂, bP, ITO, and Al₂O₃ thicknesses (8 nm, 40 nm, 10 nm, and 360 nm, respectively). Histograms of (c) external quantum efficiency and (d) wall-plug efficiency with Gaussian and Weibull fits, respectively, at the current density of 50 Acm^{-2} .

Histograms of the external quantum efficiency and wall-plug efficiency of the 45 devices are presented in Fig. 3-9c and Fig. 3-9d, respectively. For fair comparison, the performance of the devices is evaluated at the same injection current density (of 50 Acm^{-2}), which is done through interpolation. The histogram of the external quantum efficiency follows a normal distribution with a mean of $\sim 1.5\%$, as shown in Fig. 3-9c. The minimum and maximum quantum efficiencies are 0.45% and 3.33% , respectively. The histogram of the wall-plug efficiency, as shown in Fig. 3-9d, follows a Weibull distribution with a shape value less than 3 (right-skewed) and a peak at $\sim 0.17\%$. The minimum and maximum power efficiencies are 0.05% and 0.70% , respectively. This variability is attributed to the minor differences in the thicknesses of the layers (which modifies the extraction efficiency) and air exposure of bP during fabrication.

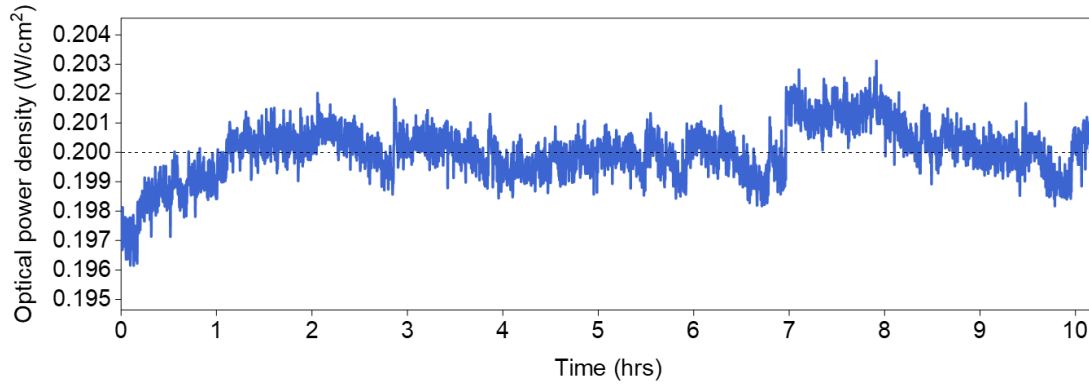


Fig. 3-10. Drift of optical power density measured for a duration of 10 hours at a modulation frequency of 1 kHz, injection current density of 20.4 A/cm^2 , and output power of $\sim 0.2 \text{ W/cm}^2$. The dotted line shows the mean of the signal.

Fig. 3-10 presents the drift characteristics of a test device. It shows a maximum variation of less than 2% from the mean signal in the measurement period of more than 10 hours, indicating high stability. Finally, the performance of our bP-LEDs is benchmarked against the state-of-the-art MWIR light sources such as LEDs, interband, and quantum cascade lasers having emission wavelengths in the range 2 to $4.3 \mu\text{m}$. As shown in Table 3-1, our bP-LED outperforms the LEDs based on conventional material systems in terms of maximum optical power density (W/cm^2) and peak η_{EQE} (%) at room temperature. Though lagging behind the highly efficient quantum cascade laser technology, our device exhibits higher external quantum efficiency than commercially available LEDs and shows an overall comparable performance to interband cascade lasers.

Material system	Technology	Wavelength	Max. Optical Power Density	Peak η_{EQE}	Reference
bPLED	LED	3.65 μm	2.17 W/cm ²	4.43%	*this work
InAs	LED	3.3 μm	3.14 W/cm ²	0.44%	[44]
CdHgTe	LED	3.2 μm	0.97 mW/cm ²	0.02%	[45]
InAsSb	LED	4.3 μm	0.32 W/cm ²	0.35%	[46]
GaInAsSb	LED	2.34 μm	0.4 W/cm ²	2.5%	[47]
InAs/GaInSb/InAs	Interband Cascade	3.8 μm	2.4 mW/cm ²	0.65%	[48]
InAs/GaInSb/InAs	Interband Cascade	3.8 μm	2 W/cm ²	3.1%	[49]
InGaAs/AlInAs	Quantum Cascade	3.56 μm	857 W/cm ²	95.7%	[50]
InGaAs/AlInAs	Quantum Cascade	3.5 μm	139 W/cm ²	10%	[51]
Hamamatsu L13454		3.9 μm	0.6 mW	0.9%	[52]
Boston Electronics LED38TO8TEC		3.8 μm	0.2 mW	0.1%	[53]
Thorlabs LED3800W		3.8 μm	1.5 mW	0.2%	[54]

Table 3-1. Benchmark comparison of the bP-LED demonstrated in this work with the state-of-the-art MWIR light emitters.

3.4 Gas sensing with bP

Non-Dispersive infrared (NDIR) gas sensors are demonstrated by utilizing these bP-LEDs for infrared emission. Fig. 3-11a shows measured EL spectra of LEDs with bP thicknesses of 6, 12, and 238 nm. These thickness of bP were chosen because the emission peak at these corresponding thickness has the maximum spectral overlap with absorption peaks of water vapor (H₂O, 2.7 μm), methane (CH₄, 3.3 μm), and carbon dioxide (CO₂, 4.3 μm), respectively. A NDIR gas sensor was setup (Fig. 3-11b), using LEDs with 238 and 12 nm bP, commercial detector on the other end, and bandpass filters to detect CO₂ and CH₄ as shown in Fig. 3-11d-e. The measurements proved detection of trace gas concentration with a lower limit of detection (LOD) as low as 20 ppm for CO₂, and 100 ppm for CH₄. The power output from the emitter measured by the detectors as a function of target gas concentrations was fit using the modified Beer-Lambert law model, given by:

$$FA = \frac{(I_{N_2} - I_x)}{I_{N_2}} = 1 - \exp(-kLx) \quad (3-3-1)$$

where FA is fractional absorbance of the target gas, I_{N_2} and I_x are the EL intensity measured by the detector for the gas cell filled with nitrogen and, at a target gas concentration of x , respectively, k is a fitting constant, and L is the chamber length, shown in Fig. 3-11c.

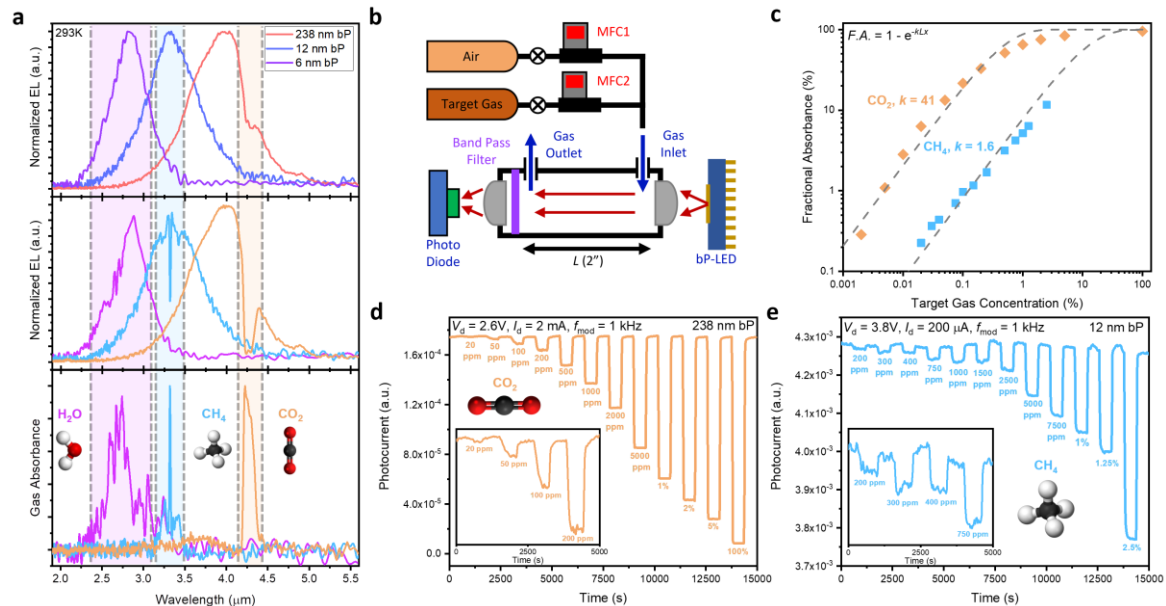


Fig. 3-11 (a), Normalized EL spectra of a LEDs with bP thickness of 238 nm, 12 nm, and 6 nm thick bP, in the presence and absence of CO₂, CH₄, and H₂O gases, respectively. The absorption spectra of the gases are calculated as the difference of the measured spectra. **(b)** Schematic of the NDIR sensor with bP LED and commercial photodetector on the ends of a gas cell. **(c)** Fractional absorbance (%) of CO₂ and CH₄ as a function of gas concentration. **(d)** Measured signal from the gas sensor with 238 nm bP LED with varying concentrations of CO₂ present in the optical path. **(e)** Measured signal from the gas sensor with 12 nm bP LED with varying concentrations of CH₄ present in the optical path. (Reprinted by permission from Amani.⁶¹)

Application of strain to bP can be also utilized to closely match the dominant absorption peaks of H₂O, CH₄, and CO₂. Since the emission spectrum of our bP-LED under compressive strain had the maximum overlap with the absorption spectrum of CO₂ (Fig. 3-12b) and was able to detection CO₂ concentrations varying from 0.005 to 100% (Fig. 3-12d). In contrast, bP-LED under 0.3% tensile strain was used to detect CH₄ gas (Fig. 3-12c) with a concentration range of 0.05 to 2.5% (Fig. 3-12e). Since the emission wavelength can be tuned by the application of strain, a single bP-LED is sufficient to facilitate multiplexed gas sensing with high selectivity. Response by the sensor for gas pulses consisting of 0.2% CO₂, 2% CH₄, and H₂O at 5% relative humidity (R.H.) is shown in Fig. 3-12f.

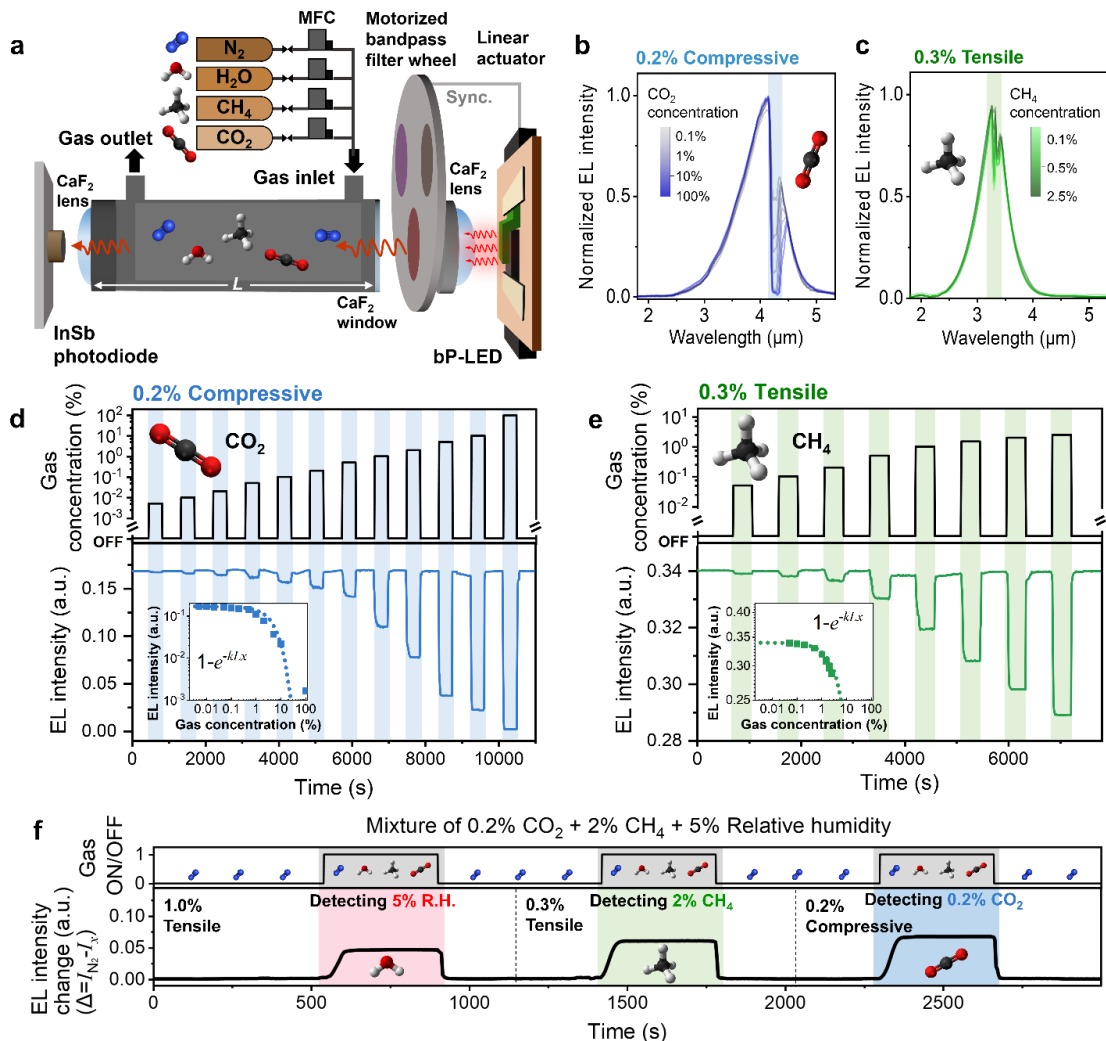


Fig. 3-12. (a) Schematic diagram of the NDIR gas sensor. Normalized EL spectra of (b) bP-LED under compressive strain in presence of CO₂ gas and (c), bP-LED under tensile strain in presence of CH₄ gas at different concentrations. Gas sensor characteristics using (d), bP-LED under compressive strain for varying concentrations of CO₂ pulses and (e), bP-LED under tensile strain for varying concentrations of CH₄ pulses. Inset contain data fit using Beer-Lambert law model. (f) Real-time monitoring of H₂O (5 % R.H.), CH₄ (2 %), and CO₂ (0.2 %), using bP-LED under 1.0 % tensile, 0.3 % tensile, and 0.2 % compressive strain, respectively. (Reprinted by permission from Kim, et al.⁷)

In conclusion, we have demonstrated a bright and efficient electroluminescent MWIR light emitter based on bP. This is accomplished by leveraging the low Auger recombination rate in bP, an $\text{Al}_2\text{O}_3/\text{Au}$ optical cavity to enhance the photon extraction, and a thin transparent and conductive ITO layer to reduce the high n-side parasitic resistances. Furthermore, utilizing the thickness and strain-dependent emission from bP, we have demonstrated that these devices can be employed in NDIR gas sensors targeting CO_2 , CH_4 , and H_2O . We suggest several topics for future work. Investigation of diode failure mechanisms would help to improve the injectable power and thus the maximum optical power. Strategies to encapsulate air-sensitive bP with oxides, 2D materials and organics should be investigated and may further enhance the long-term stability of the device.^{55,56} Studies on tuning the bP bandgap via strain engineering^{7,57}, designing optical coupling structures, such as nano-antennas, for light emission enhancement³⁸, and designing waveguides for integration with silicon photonic platforms¹⁶ would help advance bP-LEDs for real-world applications. The device performance may also be improved via better alternative electron contacts to MoS_2 , electrical/chemical doping⁵⁸, double-heterostructure⁵⁹, and other high extraction efficiency designs⁶⁰. The future works on these topics can be rewarding, due to the potential of bP-LEDs to serve as the next-generation MWIR sources.

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4 Large-scale films with bP ink*

Abstract:

Due to the exceptional properties of black phosphorus (bP), bP-based optoelectronics like light emitters and detectors have shown to outperform the state-of-the-art commercial devices. However, the scalability of these devices remains questionable because of the limitations of current bP deposition and growth techniques. Here, we report a bP ink formula to deposit millimeter-scale uniform and pin-hole free films, which have internal photoluminescence quantum yield of $\sim 0.9\%$, higher than the III-V and II-VI semiconductors with similar bandgaps. Using this ink as a ‘phosphor,’ we demonstrate that a high electroluminescence (EL) external quantum efficiency of $\sim 0.25\%$ can be achieved. We also show that these films can be integrated in a heterostructure devices for both emission and detection, achieving EL with external quantum efficiency of $\sim 0.05\%$ and a high photoresponsivity of 47 mA/W.

*This chapter will be submitted in a similar format for publication.

4.1 Scalability issue with bP-based optoelectronics

Black Phosphorus (BP), the most stable allotrope of phosphorus, finds its application in numerous electronics and photonics due its unique properties. For example, the high carrier mobility and high hole saturation velocity in bP has enabled realization of bP-based high-speed field-effect transistors.¹ In addition, bP has a direct bandgap, which can be tuned between 0.3 to 2 eV depending on its thickness.² The bandgap of bP in the bulk form, 0.3 eV, allows for room temperature operation of bP photodetectors compared to the traditional HgCdTe infrared detector in the mid-wave infrared range (MWIR), which requires cryogenic cooling. Furthermore, bP-based photoconductors have been shown to have a specific detectivity higher than the commercially available MWIR detectors.^{3,4} The bP photodetectors while showing high responsivity, also bring polarization sensitivity without external optics because of the anisotropic properties of bP leading to its polarization-dependent absorption.⁵ The bandgap of bP is further tunable with application of strain which can be utilized for efficient short-wave infrared (SWIR) optoelectronics.⁶ BP light-emitting diodes (bP LEDs) have also been shown to have outstanding efficiencies compared to the state-of-the-art LEDs based on III-V and II-VI semiconductors.⁷ This superior performance is primarily driven by its the lower Auger recombination coefficient in bP, which results in higher photoluminescence (PL) quantum yield than the compound semiconductors.^{2,8}

However, most of the prior work on bP-LEDs and photodetectors are based on a small-sized bP flakes, with a lateral area less than 1000 μm^2 , which is produced using the non-scalable mechanical exfoliation method. This is because bP belongs to the two-dimensional (2D) semiconductor group, and as a layered material, large-scale deposition of highly crystalline bP for device fabrication is challenging. The mechanical exfoliation technique involves delamination of sheets of the material from its crystal using a scotch tape, which are then transferred onto a substrate. One of the first bP crystal synthesis was done using the Bridgman method, which uses a high temperature of 200-300 °C and a high pressure of 1-4 GPa to convert white/red phosphorus to bP.⁹ The comparatively lower pressure techniques, mercury catalysis (35-45 MPa) and liquid bismuth recrystallization (50 kPa) possess disadvantages of slow processes (20 hours to couple days), along with the unwanted presence of toxic mercury/bismuth in the final bP crystal.^{10,11} The current main method of synthesizing bP is a conversion technique from red phosphorus via mineralizer-assisted chemical vapor transport (CVT) with Sn/SnI₄.¹² This process does not require complicated high-pressure equipment, nonetheless, is a very gradual and time-consuming one, requiring raw material heating for 5-10 days at a high temperature of 800 °C.

As an alternative to the most-utilized method of mechanical exfoliation, previous studies have also explored liquid phase exfoliation (LPE) techniques to produce bP flakes and fabricate photo electronics¹³, but because of poor dispersibility of bP in most solvents

or/and high boiling point of the solvents, the solution containing bP, as it is, cannot be used for drop-casting or spin-casting to make large-scale uniform films, resulting in the device area again limited by the size of the bP flake, as in the case of mechanical exfoliation. Other works have shown large-scale bP based solar cells but require addition of another key component of the active layer to the solution, reducing the applicability of the solution.^{14,15} The development of 2D ‘inks’ in the past years has enabled a scalable approach to deposit the 2D materials.¹⁶ Their formulation consists of a solvent, binder, surfactants, and other additives, etc. apart from the material itself. Considering the relevance of these materials for electronics and photonics, some of these 2D inks are now commercially available products such as the graphene inks for screen printing, MoS₂ ink for spin and spray coating.

The recipes to formulate bP ink for inkjet-printing have also been explored.^{17,18} Studies demonstrating these formulation processes play a significant role in moving a step forward towards more scalable bP-based electronics. Despite these works having documented bP films with suppressed coffee ring effect, and good spatial uniformity, the focus has been on a micrometer-level scale uniformity and realization of large-scale efficient MWIR optoelectronics has not yet been attempted to the best of our knowledge.

4.2 Ink formulation procedure

In this work, we show a unique formulation of bP ink, which can be spin-coated to make uniform pinhole-free films in a large-scale format from a single droplet or dip-pen printed for patterning, as represented in Fig. 4-1a. The films made using this technique produce bright PL with high quantum yield. Given the high quantum yield of bP, we show that this ink can be used as a ‘phosphor’ on commercial LEDs as a proof-of-concept, to produce MWIR electroluminescence (EL). Phosphor-converted LEDs are currently used in a variety of applications such as display and lighting. The light from the LED optically excites the phosphor, which is then down-converted to emit light at a longer wavelength. Here, the role of the phosphor is absorption of the LED light, conversion, and re-emission with high efficiency. In addition to this, large-scale heterojunctions emitting EL based on these bP films were also fabricated with a layer structure like that of the quantum dot LEDs (QD-LEDs). We find that these devices have comparable efficiencies to the state-of-the-art QD-LEDs with peak emission wavelength near to that of bP. Finally, we also show that films made using the ink have high absorbance in the infrared regime, and consequently, devices based on these films can be configured in a reverse-bias condition to be used as photodetectors to respond to MWIR light.

The first step of the formulation process of the ink is to crush the bP crystal into powder form in a mortar and pestle. The powder was then added to NMP in a vial which was ultrasonicated to further reduce the size of the bP particles. NMP was chosen as the solvent

during this process, because of its suitable Hansen solubility parameters and surface tension to disperse and stabilize 2D materials, the reason that it is the most-used solvent for liquid-exfoliation of these materials.¹⁹ The solution of bP in NMP cannot be spin-coated at room temperature because of high boiling point of NMP of 202 °C. Therefore, after the sonication, NMP was separated from the solution by centrifugation, and the pellet containing the bP particles was re-dispersed in toluene and a small amount of binder, oleyl amine was added. Oleyl amine is a commonly used capping agent in studies related to nanomaterials and quantum dot research.²⁰ Toluene was used because it dissolves oleyl amine and its property of high vapor pressure facilitates faster drying during spin coating. The excess of the binder in the solution was washed with another centrifugation step and re-dispersed in toluene, and finally spin-coated on a quartz chip sized ~ 5 mm x 5 mm. Image of the ink in a vial and an example film on quartz substrate is shown in Fig. 4-1b and Fig. 4-1c, respectively. The thickness of these films can be varied depending on the loading of the bP in the ink (Fig. 4-3) The ink can be also printed with a dip-pen directly on any substrate such as paper along with flexible ones like polyethylene terephthalate (PET), polydimethylsiloxane (PDMS), etc. as shown in Fig. 1d-f. The images of top-view and cross-sectional-view of scanning electron microscope (SEM) are presented in Fig. 4-1g and Fig. 4-1h, respectively, which provide a magnified view of the film microstructure at the micrometer level. The large-scale dark-field microscopic and SEM images of the bP film are included in the Fig. 4-4 which suggest full coverage of bP particles on a millimeter-scale showing no coffee-ring effects or pin-holes. Comparison of the Raman spectra in Fig. 4-1i demonstrates that the crystal structure of the bP in the ink is intact and matches that of a mechanically-exfoliated ~ 50 nm bP flake, showing typical bP characteristics peaks at 363, 441, and 468 cm⁻¹, attributed to the A_g^1 , B_{2g} , and A_g^2 phonon modes in bulk bP. The comparison of the film was done with a thicker bP flake because the film consists of bulk bP sized particles, and the Raman peak positions and relative intensities depend on the number of layers in the bP flake.²¹ Raster-scanning was performed on the bP film to generate a Raman intensity map at the 468 cm⁻¹ peak $I(A_g^2)$ for a 1 mm x 1 mm area with a step size of 5 μm, illustrated in Fig. 4-1j.

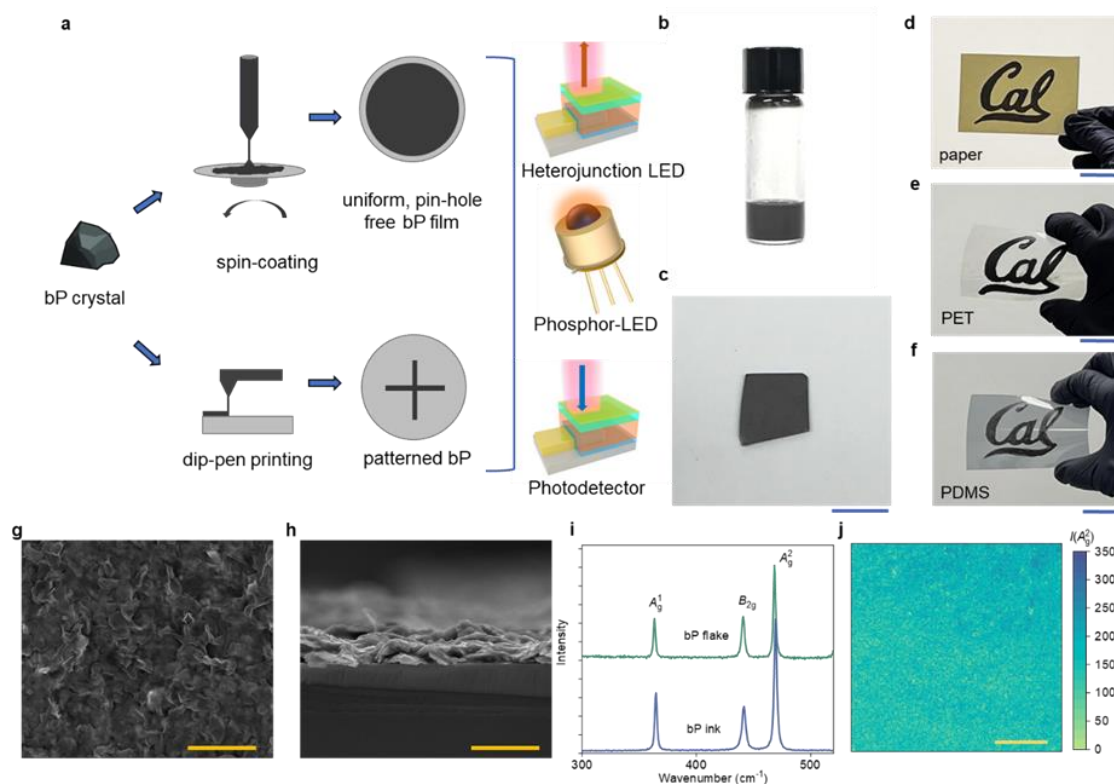


Fig. 4-1. (a) Schematic showing deposition techniques and applications of bP ink. (b) Photograph of bP ink. (c) Image of bP film made using spin-coating of the bP ink on a ~ 5 mm x 5 mm quartz substrate, *scale bar*, 5 mm. Image of ‘Cal’ calligraphed with dip pen on (d) paper, (e) PET, and (f) PDMS, *scale bar*, 25 mm. (g) Top-view of SEM image of bP film on 50nm SiO_2/Si , *scale bar*, 10 μm . (h) Cross-sectional-view of SEM image of bP film on 50nm SiO_2/Si , *scale bar*, 10 μm . (i) Raman spectrum for exfoliated bP, and bP ink. (j) Raman map of intensities at 468 cm^{-1} , $I(A_2^2)$ with 5 μm spatial step on a $\sim 1 \text{ mm} \times 1 \text{ mm}$ area of bP film, *scale bar*, 250 μm .

The detailed bP ink formulation process is as follows. A schematic of ink formulation process is shown in Fig. 4-2. Firstly, the bP (Smart Elements) crystal was crushed in a mortar and pestle into a powder form, of which around 5-20 mg was added to a glass vial along with anhydrous 1.5 mL of n-methyl-2-pyrrolidone (NMP). The solution was ultrasonicated with 150-Watt Cole Parmer Ultrasonic Processor for a total duration of 30 minutes at a 60 % amplitude and 50 % duty cycle. The solution was then subjected to centrifugation at a speed of 8000 rpm for 30 minutes in 5 mL sized plastic vials. The supernatant was removed, and 2.5 mL of toluene was added to the vial. An important note here is that not all of the supernatant is removed, few microliters of bP in NMP is still left intentionally to improve the dispersibility of bP in the final solution. In fact, it was seen that if most of supernatant was removed, the bP particles start crashing in toluene.

Following addition of 0.25 mL toluene, 150 μ L of oleyl amine (Sigma Aldrich) was added to the same vial, and then bath sonicated for 30 seconds. This solution was again centrifuged at a speed of 8000 rpm for 3 minutes, and then the supernatant was removed to add 0.25mL of toluene. This was followed by final bath sonication of the ink for 30 seconds and then the ink was ready to be spin-coated. Quartz substrates sized ~ 5 mm x 5 mm were manually cut using a scribe and pre-cleaned using DI water, acetone and IPA prior to the spin-coating. Ink was then spin-coated on the chip at a constant speed of 300 rpm, which was allowed to dry for 1-5 minutes at room temperature. The slow speed during the spin-coating enabled for the solution to stay on the chip.

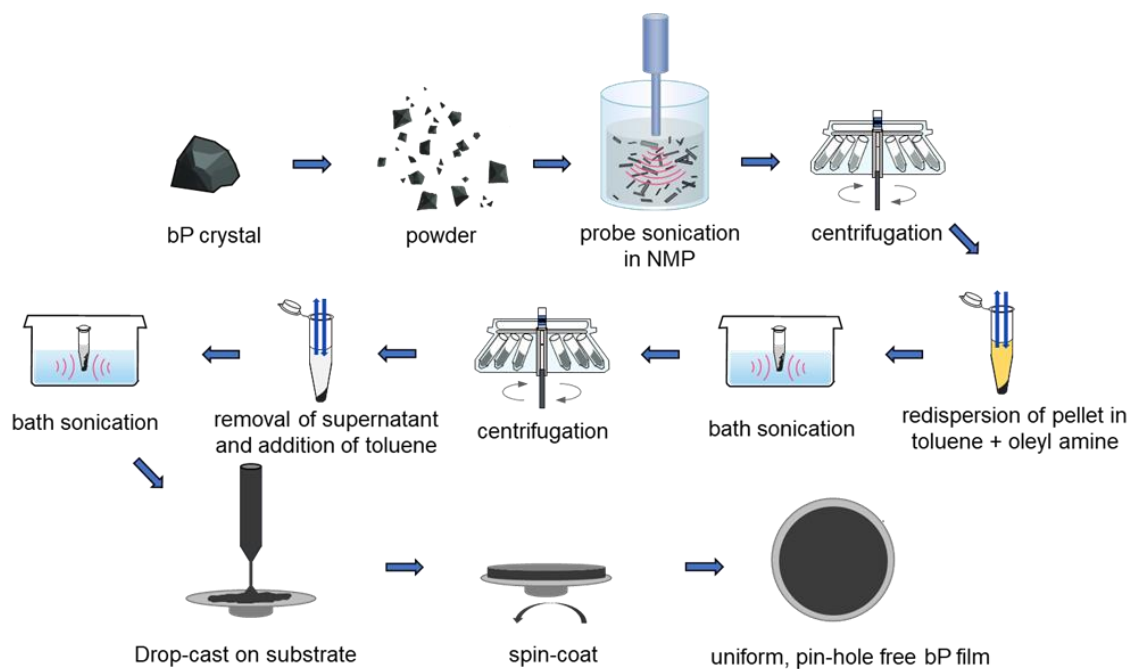


Fig. 4-2. Schematic showing the steps of bP ink formulation and film deposition process.

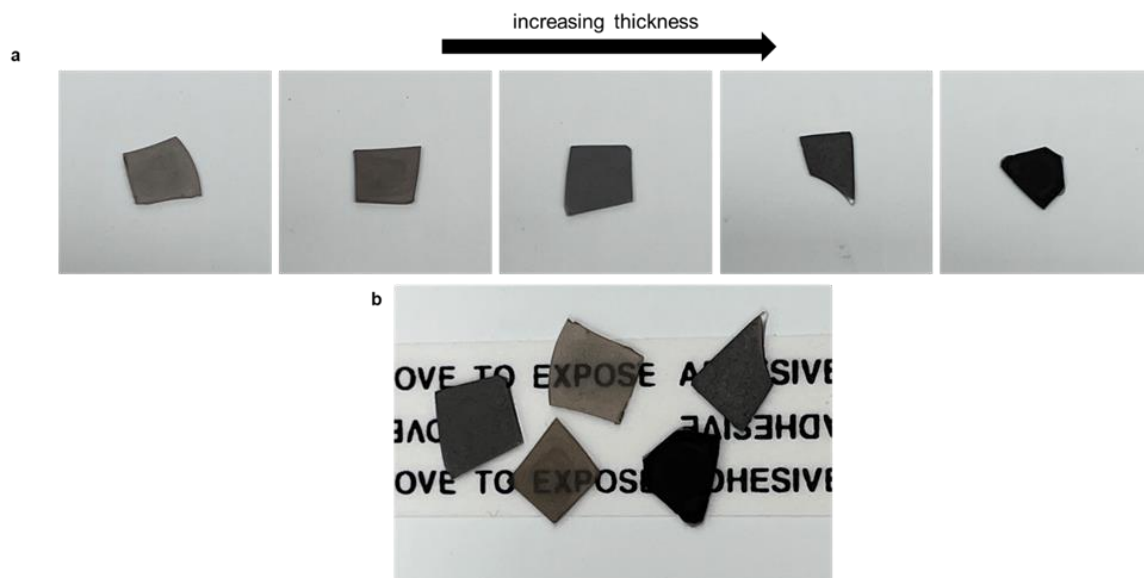


Fig. 4-3. (a) Photographs of bP film samples placed in order of increasing thickness. (b) Photograph of bP ink samples shown in (a) placed on a non-blank paper for checking visual transparency.

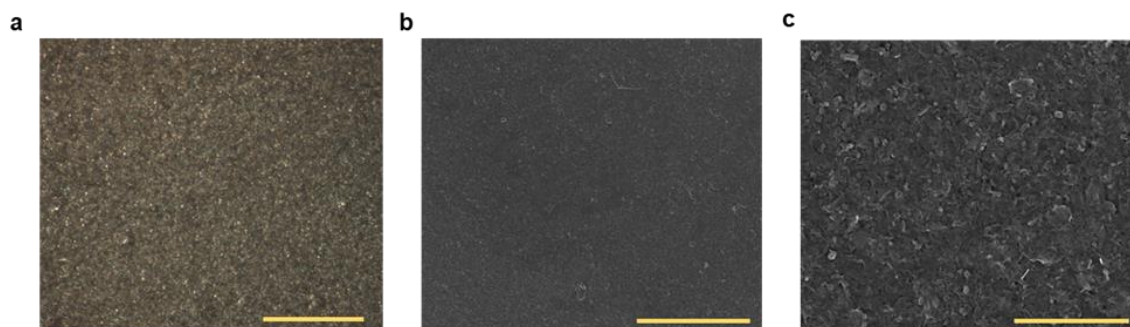


Fig. 4-4. (a) Dark-field micrograph of bP film on quartz, *scale bar*, 500 μm . (b) Top-view of SEM image of bP film on 50nm SiO_2/Si , *scale bar*, 500 μm . (c) Top-view of SEM image of bP film on 50nm SiO_2/Si , *scale bar*, 50 μm .

Normalized spectrally-resolved PL of the bP film also matches that of the exfoliated ~ 50 nm bP flake, of which the bandgap is ~ 0.3 eV and the full width half maximum (FWHM) is ~ 520 nm, as depicted in Fig. 4-5a. This corroborates the data in Fig. 4-1i, that the bP flakes in the ink are in bulk thicknesses (more than 10 layers), and not thinner, which would instead result in a spectrum at a higher energy range. The spectra were obtained at different pump powers, and the internal PL quantum yield of the bP film was calculated at the

varying carrier concentration in Fig. 4-5b. The internal PL quantum yield (η_{QY}) of the film is defined as the ratio of the number of photons emitted to the number of carriers generated in the film.

$$\eta_{QY} = \frac{\text{number of photons emitted}}{\text{number of carriers generated}} \quad (4-2-1)$$

Theoretically, it can be represented by the ABC model shown in the equation below:

$$\eta_{QY} = \frac{B(np - n_i^2)}{A(np - n_i^2)/p + B(np - n_i^2) + 2Cn(np - n_i^2)} \quad (4-2-2)$$

where A , B and C are the Shockley-Read-Hall (SRH), radiative bimolecular, and Auger recombination coefficients, respectively, and n_i and n/p are the intrinsic and total electron/hole concentrations, respectively. In Fig. 4-5b, measured η_{QY} of the bP film is shown in contrast to the theoretical η_{QY} of III-V and II-VI semiconductors such as InAs, PbSe, and GaSb with bandgap similar to bulk bP, calculated using equation (2) and parameters documented in the previous studies^{6,22-26}. The efficiency of bP film is found to be much higher than these compound semiconductors because of its property of lower Auger recombination coefficient at higher carrier densities.⁸ The η_{QY} of the film increases from ~0.68 to 0.91% in the SRH regime in the generation rates between $1 - 5 \times 10^{25} \text{ cm}^{-3}$ following a droop in the profile due to Auger recombination, leading to a decrease in the η_{QY} at high carrier generation rate.²⁷ The reflection and the transmission profiles in the MWIR region at ten different spots on the bP film are included in Fig. 4-6. The values of reflection and transmission are similar proving bP uniformity and negligible spot-to-spot variation. The absorbance of the bP film, calculated from the averaged reflection and transmission is shown in Fig. 4-5c. It can be deduced from this figure that bP ink film absorbs wavelengths lower than ~4.2 μm (0.29 eV), which is the band edge of bulk bP, and a property of thick bP flake.⁵ As an evidence of the presence of a minor quantity of oleyl amine in the film, its characteristic absorption peaks at ~3 μm (3231 cm^{-1}), ~3.4 μm (2927 cm^{-1}) and ~3.5 μm (2850 cm^{-1}) are observable in this data.²⁸ The absorption profile of bP solution without oleyl amine is also presented in comparison, which doesn't possess the signature oleyl amine peaks. To investigate the PL uniformity, the sample was raster-scanned over an area of ~ 3.7 mm x 3.7 mm with a step size of 50 μm . The integrated PL (area under the spectrum) at each of those spots was normalized such that 0 and 1 indicate zero (no PL) and maximum signal (of all the data points), respectively. This data is illustrated in Fig. 4-5d, substantiating film uniformity over a large scale. Since, bP is air-sensitive, the PL of bP ink film was checked for several hours to examine the drift in air (Fig. 4-5e).

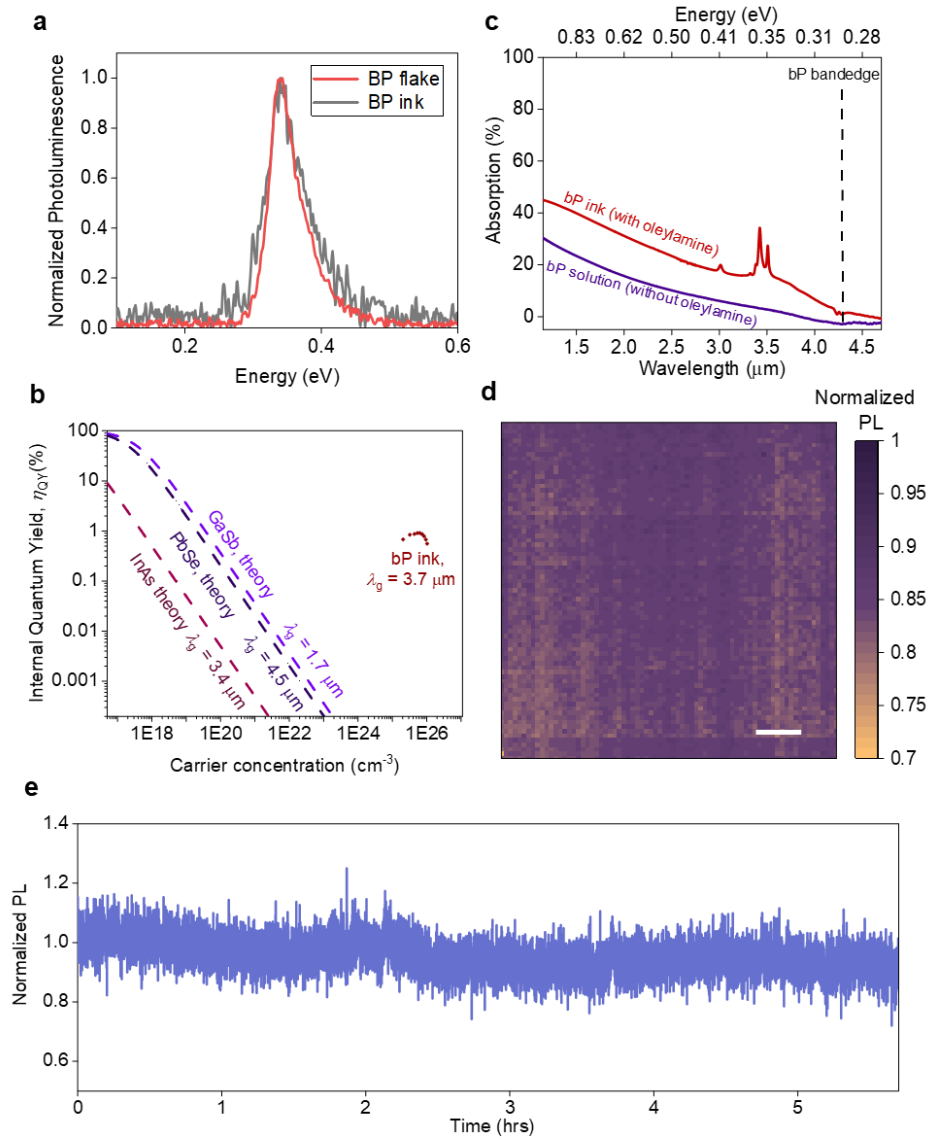


Fig. 4-5. (a) Normalized spectrally-resolved photoluminescence of bP flake and bP ink. (b) Internal PL quantum yield of bP ink film as a function of carrier concentration, compared with the theoretical quantum yield of compound semiconductors, InAs, PbSe and GaSb. (c) Mid-wave infrared absorption of bP ink with and without oleyl amine. (d) PL intensity map measured on an area of $\sim 3.7 \text{ mm} \times 3.7 \text{ mm}$ with a step size of $50 \mu\text{m}$, scale bar, $500 \mu\text{m}$. (e) Drift measurement of PL for ~ 5.5 hours at a pump power of 9 mW in air.

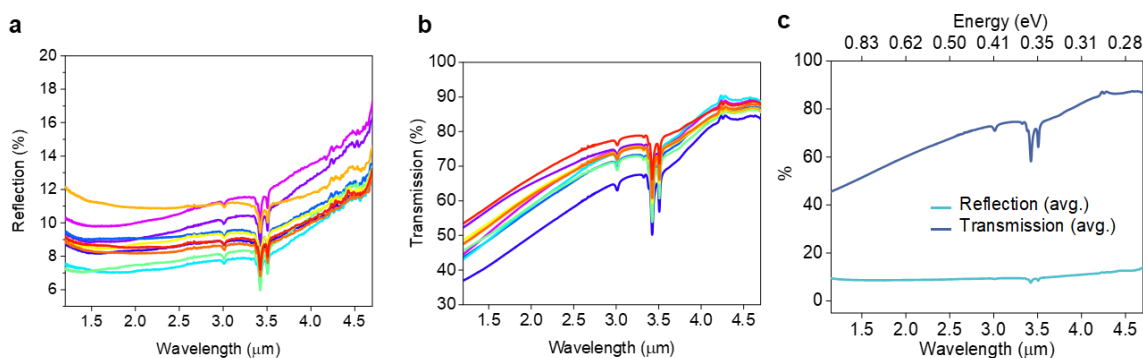


Fig. 4-6. (a) Reflection, (b) transmission of bP film in the MWIR at 10 different spots. (c) Average reflection and transmission of the film

4.3 LEDs and Photodetectors based on Ink

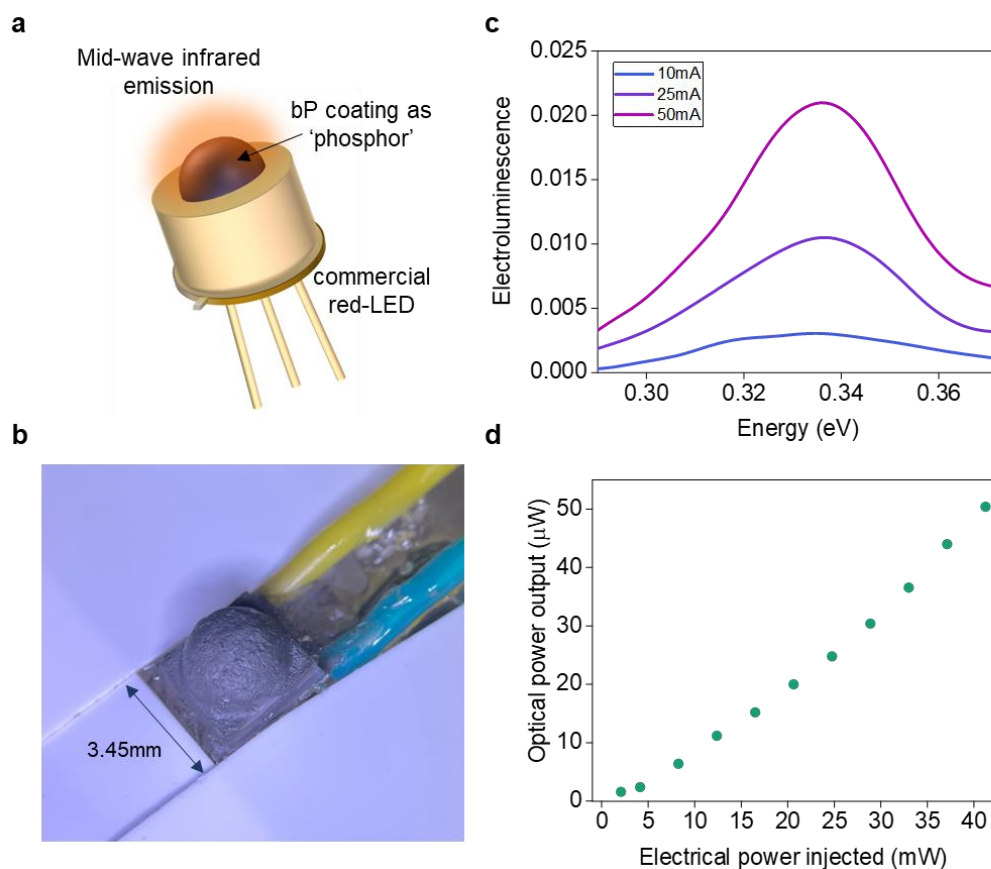


Fig. 4-7. (a) Schematic of bP as 'phosphor' on red LED. (b) Image of bP ink film as a 'phosphor' on a commercial-red LED. (c) Electroluminescence from the bP-LED shown in (c) at injected currents 10, 25 and 50 mA at the bP emission peak of ~ 0.33 eV. (d) Optical power output from the bP-LED as a function of total electrical power injected.

Since the bP ink has high emitting efficiency, it was utilized as a ‘phosphor’ on a red LED which has electroluminescence peak energy higher than bP bandgap and can serve as a pump to the bP film, schematically shown in Fig. 4-7a. To illustrate this concept, bP was drop-casted on millimeter-sized LEDs emitting at a peak wavelength of 660 nm, as presented in Fig. 4-7b. The spectrally-resolved EL is shown in Fig. 4-7c, same as PL spectrum shown in Fig. 4-5a. The spectrum intensity increases as more current is injected into the device, with an external quantum efficiency (η_{EQE}) of $\sim 0.27\%$. η_{EQE} is defined as the ratio between the number of detected photons and the number of electrons injected into the device,

$$\eta_{\text{EQE}} = \frac{\text{number of detected photons}}{\text{number of injected electrons}} = \frac{P/(hc/\lambda)}{I/q} \quad (4-3-1)$$

Here, h is Planck’s constant, c is the speed of light, P is total detected optical power, I is the injected current, and λ is the wavelength of the emitted photons. The total power output from this integrated bP ink/LED device was also analyzed as a function of the input power, and is plotted in Fig. 4-7d.

In order to make large-scale efficient heterostructure LEDs based on charge-injection, we utilized electron transport layer (ETL) and hole transport layer (HTL) along with the anode and cathode, a concept common in organic light-emitting diodes (OLEDs) and QD-LEDs.²⁹ We opted for PEDOT: PSS and zinc oxide (ZnO) as the HTL and ETL respectively for the device, that can be spin-coated on a large area to facilitate MWIR large-scale bP-LED as a proof-of-concept. This is in stark contrast to the design structure conventionally used for bP-LEDs, where the electron injection layer is either MoS₂ or WS₂, which are mechanically exfoliated to get a micrometer-scale flake and, also one of the reasons limiting the device emitting area. For the hole (bottom) and electron (top) contact, Au, and indium tin oxide (ITO) were chosen, respectively. A thin film of ITO was used as the top electrode due to its optical transparency in the bP emission region. The schematic representation of the LED structure is shown in Fig. 4-8a and the energy band diagram in Fig. 4-8b is represented using energy levels documented in previous studies.²⁹⁻³¹

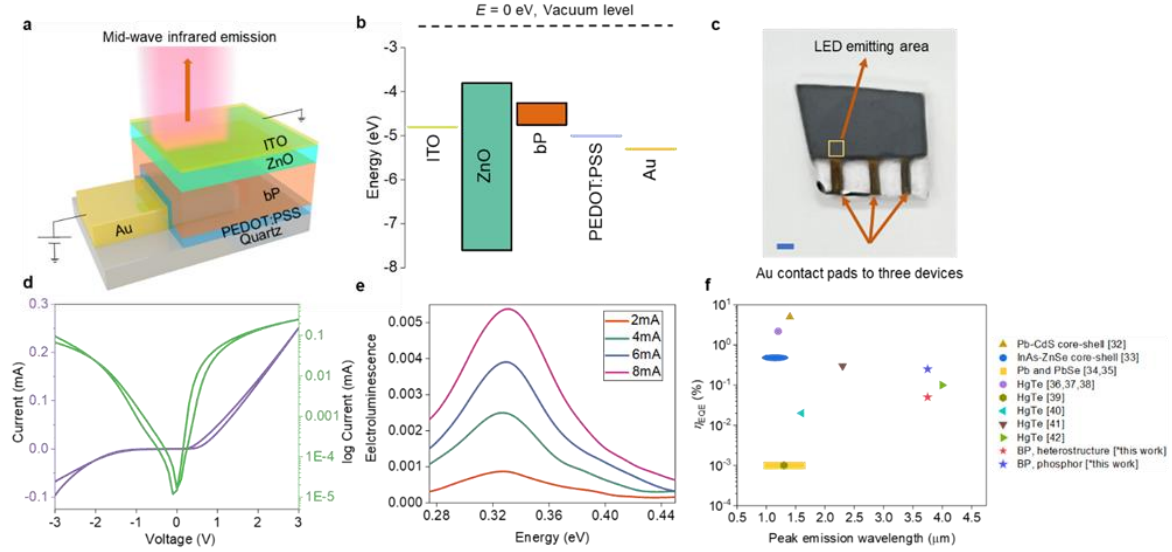


Fig. 4-8. (a) Schematic showing the top-emitting LED cross-section. (b) Energy band diagram showing electron and hole transport. (c) Photograph of the chip containing three devices, *scale bar*, 1 mm. The device emitting area ($\sim 1 \text{ mm} \times 1 \text{ mm}$) can be marked with a yellow boundary line and is located in the area where the bottom gold electrode overlaps with the bP film. (d) I - V characteristics of the device (e) Electroluminescence from the device at a peak emission of 0.33 eV at injection currents of 2, 4, 6, and 8 mA. (f) External Quantum Efficiency (η_{EQE}) of the MWIR emitting bP heterostructure and bP-phosphor LED benchmarked against state-of-the-art QD-LEDs.

Detailed fabrication procedure is as follows. The devices were made on quartz substrates sized $\sim 5 \text{ mm} \times 5 \text{ mm}$ which firstly was cleaned with water, acetone, and IPA. 10 nm Ti and 100nm Au was evaporated on the chip for electrodes and patterned on the chip using shadow masking. The spin-coating process of PEDOT:PSS (Clevios P VP AI 4083) was a two-step one, with 2500 rpm for the first 30 seconds, and 4000 rpm for the next 1 min. It was seen that this process resulted in a thickness of 20 nm. The chip was then annealed at a temperature of 170 °C for 15 minutes. Then, the bP ink was spin-coated at 300 rpm and the chip was then annealed in a N₂-filled glovebox at 100 °C for 1 hour. Then Kapton tape was used to mask the bottom Au electrodes. Subsequently, $\sim 1 \text{ mL}$ of ZnO (Sigma Aldrich) was dynamically spin-coated on the chip at a speed of 2000 rpm, which resulted in a thickness of $\sim 1.8 \text{ }\mu\text{m}$. Finally, 20 nm of indium tin oxide (ITO) was sputtered followed by removal of the tape. The device SEM cross-sectional images are included in the Fig. 4-9. An image of a typical chip with devices is shown in Fig. 4-8c, where the three gold lines are the bottom hole contacts for three different devices. The emitting device area is $\sim 1 \text{ mm} \times 1 \text{ mm}$, where the Au lines overlap with bP film and visible to the naked eye, unlike a

typical bP-LED which has an emitting area less than $1000 \mu\text{m}^2$. Fig. 4-8d shows typical current-voltage (I - V) characteristics exhibited by one of these devices. The LED produces electroluminescence when forward-biased, with increasing output intensity as the injected current density is increased, as shown in Fig. 4-8e. The variation of η_{EQE} between device-to-device was found to be low and ranged between 0.02%-0.05%. These efficiencies of the champion device and the bP ink-phosphor LED are benchmarked against the state-of-the-art QD-LEDs emitting in the bP energy range, based on materials such as Pb-CdS, InAs-ZnSe, Pd, PbSe and HgTe.³²⁻⁴² As shown in Fig. 4-8f, these LEDs have efficiencies comparable to the QD-LEDs with similar design and peak emission region. Admittedly, the efficiency is lower compared to the state-of-the-art bP-LED, but given the high roughness of the bP film, the light outcoupling efficiency is one of the constraining factors, apart from the optimization of the device structural design. The internal quantum efficiency (η_{IQE}) of this charge-injection device, which is the number of internally generated photons, is calculated to be $\sim 0.9\%$ by accounting for losses in light outcoupling using optical simulations,

$$\eta_{\text{IQE}} = \frac{\text{number of total photons}}{\text{number of injected electrons}} \quad (4-3-2)$$

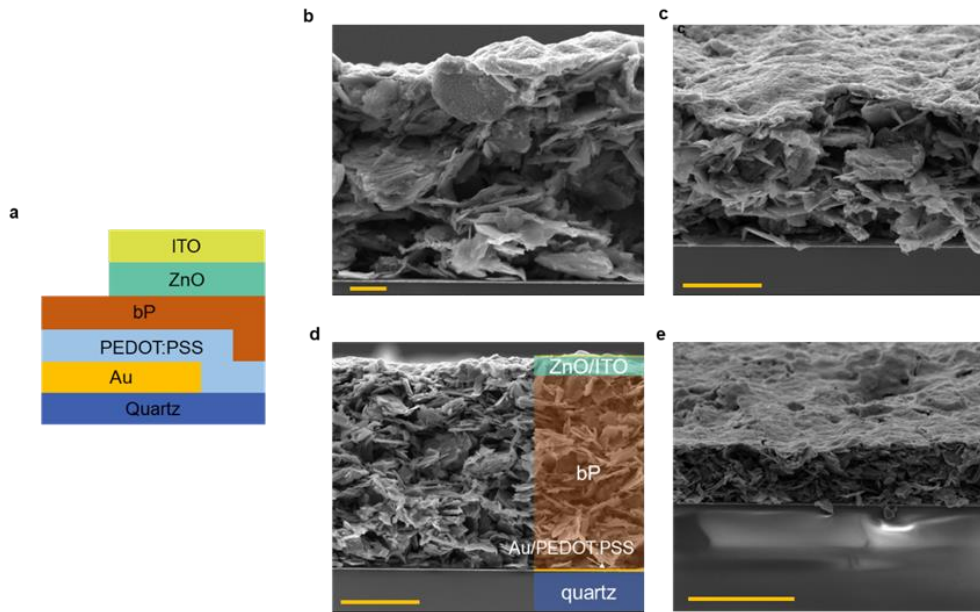


Fig. 4-9. (a) Device schematic. Cross-sectional SEM image of device at (b) scale bar, 1 μm , (c) scale bar, 3 μm , (d) scale bar, 5 μm , and (e) scale bar, 10 μm .

Due to the light absorbing properties of bP film, the device shown in Fig. 4-10a for LED application can also be utilized as a photodetector, but in reverse-bias configuration. This is validated from the spectrally-resolved photo response of the device at different reverse bias conditions, shown in Fig. 4-10b. The peak MWIR photoresponsivity of the device is calculated to be 22 mA/W and 47 mA/W at a reverse bias of 2.5 V and 5 V, respectively, and showed a linear trend of higher photoresponsivity as higher reverse bias were applied (Fig. 4-10c). The photoresponsivity as a function of incident light intensity ($\lambda = 638\text{nm}$) was examined at reverse biases of 1, 3, and 5 V in Fig. 4-10d, which corroborated the fact that the higher light power results in higher photoresponsivity.

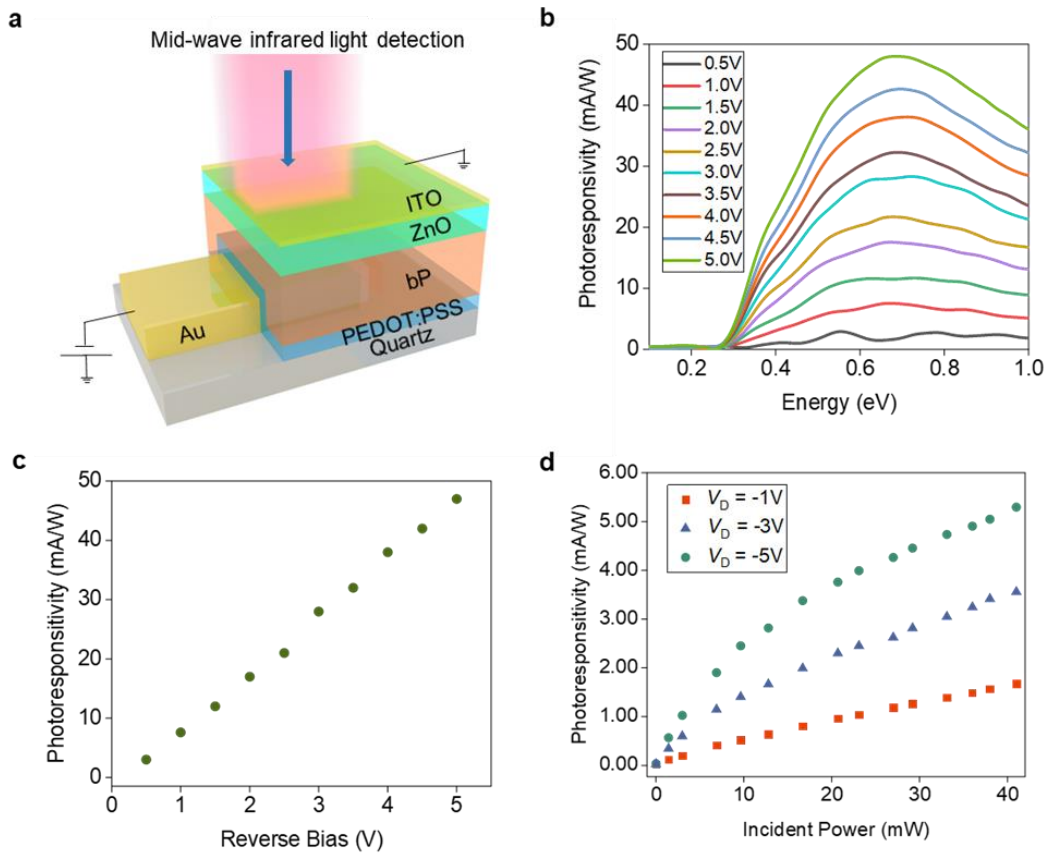


Fig. 4-10. (a) Schematic showing the photodetector device cross-section. (b) Spectrally-resolved photo response of the devices to infrared light at different reverse-biases. (c) Peak photoresponsivity as a function of reverse-bias. (d) Photoresponsivity as a function of incident light power ($\lambda = 638\text{ nm}$) measured at different reverse-biases.

In conclusion, we have demonstrated formulation of bP ink that can dip-pen printed or spin-coated. We show that these films match the high-performance attributes of a bP flake, while also offering a significant advantage of scalability. We demonstrate multiple device structures to demonstrate the optoelectronic properties of this bP ink including the demonstration of bP ‘phosphor’ LED as well as integrating bP ink with carrier transport layers to accomplish bP based MWIR light emitters. Moreover, we also present that the photodetectors based on these bP inks show high responsivity to infrared light, given the high absorption of these films. For future work, other ETLs or HTLs that will further improve the LED efficiency, and strategies to improve light absorption in the photodetectors should be explored. Encapsulation techniques to prevent degradation of air-sensitive bP ink with oxides, 2D materials and organics can prove to be useful as well.^{43,44} The future topics should be valuable given the tremendous potential of bP to serve as the leading candidate for next-generation MWIR electronics.

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5 Conclusion

Thousands of flammable and toxic gas sensors are being used globally in today's world and requires extensive utilization of gas detection instruments to enable the safety of our community by reducing the risk of exposure.

The most important aspect of these sensors is their performance and manufacturability. CS-FET is a promising low-power consuming platform which can sensitively detect low concentration of gases at room temperature, but are not selective against humidity. Here, the problem of humidity response in the CS-FETs was solved by using a simple solution of raising the chip temperature just a few degrees Celsius above the room temperature to evaporate water. This was done by integrating microheaters on the chip, which are CMOS-compatible. The advantage of this technique is that the response to gas remains unchanged during varying humidity.

However, one of the limitation of CS-FET is that it cannot be used to detect non-polar gases like methane and CO₂. Optical gas sensors like NDIR gas sensors can detect these gas sensitively because they depend on the infrared light absorption of the gas. The current sensors use LEDs based on III-V and II-VI semiconductors which show lower efficiencies at high injection carrier density due to their high Auger recombination coefficient. BP emits MWIR light with high quantum yield due to its property of low Auger recombination, giving bP an inherent advantage which was used to fabricate highly efficient bP-LEDs. To further improve their performance, an optical resonant cavity to increase the light outcoupling and indium tin oxide (ITO) layer to remove the parasitic resistances was integrated. These bP-LEDs demonstrated efficiencies which are much higher than the state-of-the-art published and commercial LEDs. It was also shown that these LEDs can be incorporated in the NDIR sensor setup to detect ppm concentration of CO₂ and methane.

BP-based optoelectronics have shown high performance due to the unique properties of bP. However, bP is a two-dimensional (2D) current processing technique to make these electronics require the non-scalable mechanical exfoliation process because of which only micrometer-scale devices can be fabricated. Deposition of large-scale films has been shown to be possible by formulating an ink solution which can be deposited via spin-coating. These scalable films can then be utilized to make millimeter-scale bP-based LEDs and photodetectors.

The future steps to improve these devices should be in the direction of improving the stability of bP using packaging techniques to prevent degradation in air. Techniques to improve the outcoupling of trapped photons from the films can enable much higher brightness of the LEDs. These solutions have the potential to improve the scalability of bP-LEDs from a manufacturing point of view and importantly, enable more sensitive detection via NDIR sensors.