LIGHT EMITTING DIODES AND PHOTODETECTORS BASED ON III-NITRIDE AND COLLOIDAL QUANTUM DOT MATERIALS

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by
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ABSTRACT

In this work, we first proposed the tandem architecture for solution-processed near infrared PbSe colloidal quantum dot (CQD)-based photodetectors to address the high dark current issue. The tandem architecture not only absorbs the virtue of tandem solar cell by means of efficient photon-to-current conversion, but also functions as the effective barrier that can block the leakage current. More than three orders of magnitude reduction in dark current has been observed, along with an elevated photocurrent. The low temperature current-voltage characteristics revealed that the tandem architecture posed a high energy barrier which effectively blocks the dark current. Our results suggest that tandem architecture can be employed to developing high-performance solution-processed photodetector.

The application of tandem photodetectors was further extended to sensors on flexible substrates where little study has been reported to date. Our results on flexible tandem photodetectors validate the high efficiency and detectivity of the tandem architecture. Two different bending states have been studied which revealed the small critical bend radii of ~8mm and ~3mm for tensile and compressive bending, respectively. The photodetector performance remains stable under mechanical stress which offers great potential of CQDs-based tandem photodetectors for flexible device applications.

Furthermore, we have demonstrated the chip level integration of flip-chip light emitting diode (LED) with current rectifying GaN Schottky barrier diodes constituting the Wheatstone bridge circuitry for alternating current (AC) driving. The flip-chip LED scheme offers better p-contact, high light extraction efficiency and fast heat dissipation. The reflectance and turn-on
voltage were investigated under various p-contact annealing conditions. The flip-chip alternating current LEDs (ACLEDs) demonstrated more than \(~23\%\) improvement in terms of energy conversion efficiency over top-emissive ACLEDs and offer the potential of using such device for high brightness, high power, high efficiency and high reliability solid state lighting applications.

Finally, built on our studies of LEDs and photodetectors, and of chip level integration of LEDs and GaN Schottky barrier diodes, we, for the first time, proposed the integration of visible LEDs and UV GaN photodetectors for bi-directional optical wireless communication (OWC) applications. The LEDs function as transmitters to emit visible light signal whereas the photodetectors as receivers to collect UV signals. The crosstalk can be neglected due to the superior visible-blind property of GaN UV photodetector. The experimental results demonstrated that the LEDs and photodetectors can work together efficiently which opens up a new avenue for using such device for bi-directional OWC applications.
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Chapter 1

Introduction

Light-emitting diodes (LEDs) and photodiodes both are semiconductor diodes. Figure 1-1 shows a typical diode curves in dark and under illumination. At forward bias condition, electrons and holes are injected from electrodes into the semiconductor diode junction. The electrons and holes are recombine either radiatively by emitting photons at the active semiconductor layer, or non-radiatively. In LED devices, the former process is clearly more desirable. Accordingly, the electrical energy is converted into the photon energy through the diode device. If reverse the before-mentioned process, let a light illuminate at semiconductor diode with photon energy larger than the bandgap, the semiconductor will be able to absorb the photon energy and generate the electron-hole pair. At zero or reverse bias, electron-hole pair separates at diode junction due to build-in electric field, transports via diffusion or drift through the device and collected by the electrodes. Despite some loss of electrons and holes during the process, the photon energy is eventually converted into electrical energy. In this regard, the photon energy and the electrical energy could convert into each other through a diode device depending on different operation conditions. The definition of LEDs and photodiodes are differentiated from the functionality of whether convert the electricity into light or conversely, light into electricity. In this chapter, we will first discuss the fundamentals of LEDs and photodiodes, and then introduce III-Nitride and colloidal quantum dot materials for LED and photodetector applications. The dissertation organizations will be introduced at the end.
1.1 Fundamentals of light-emitting diodes

Within a semiconductor material, electrons and holes can recombine either radiatively, which accompanied with the photon emission; or non-radiatively, with no photon emission. The physics behind light-emitting diodes (LEDs) is the radiatively recombination process underwent the current injection. At the heart of LED is the p-n junction in which holes inject from the p-type semiconductor whereas electrons inject from the n-type semiconductor, the light emitted at the junction via radiative recombination process. However, it is impossible to eliminate the non-radiative recombination. Thus, the competition between the radiative and non-radiative recombination need to be taken into consideration for the LED device design.
Radiative recombination

Since electrons and holes are crucial to radiative recombination, the recombination rate is proportional to the population of electrons and holes. The recombination rate is given by the Bimolecular rate equation [2]:

\[ R = -\frac{dn}{dt} = -\frac{dp}{dt} = Bnp \quad (1.1) \]

where \( R \) is the recombination rate, \( n \) is the electron concentration, \( p \) is the hole concentration, \( B \) is the bimolecular recombination coefficient. The typical value of \( B \) for III-V direct bandgap materials is \( 10^{-11} - 10^{-9} \text{ cm}^3/\text{s} \).

If the semiconductor received a photoexcitation or current injection, the minority carrier concentration will be increased to a certain value. Once the excitation is terminated, the concentration of minority carriers will decay exponentially. The mean time between the generation and recombination is called minority carrier lifetime, \( \tau \). In the case of low-level excitation, the minority carrier lifetime can be derived from equ.(1.1):

\[ \tau = \frac{1}{B(n_0 + p_0)} \quad (1.2) \]

where \( n_0 \) and \( p_0 \) are the equilibrium electron and hole concentration. For doped semiconductor materials, equ.(1.2) reduces to:

for n-type \( \tau_n = \frac{1}{Bn_0} = \frac{1}{BN_A} \quad (1.3) \)

for p-type \( \tau_p = \frac{1}{Bp_0} = \frac{1}{BN_D} \quad (1.4) \)
where $\tau_p$ and $\tau_n$ are the hole and electron lifetimes, $N_A$ and $N_D$ are the acceptor and donor concentrations. The minority carrier lifetime is an important parameter characterizes radiative recombination. However, it is facing the competition of the non-radiative recombination.

**Non-radiative recombination via defects**

During non-radiative recombinations, the energy is transferred to semiconductor lattice and converted to phonons which eventually dissipated as heat. Non-radiative recombinations can taken place due to several physical mechanisms among which the most common one is the defects in the crystal. The defects with energy levels within band gap are efficient recombination centers. The electrons and holes can trapped in those defects which led to non-radiative recombination. Those deep level defects are also known as luminescence killers. Assuming the trap energy $E_T$ with concentration $N_T$, the non-radiative recombination rate due to deep level defects is given by (Shockley and Read, 1952):

$$R_{SR} = \frac{p_0\Delta n + n_0\Delta p + \Delta n\Delta p}{(N_T\nu_p\sigma_p)^{-1}((n_0+n_1+\Delta n)+(N_T\nu_n\sigma_n)^{-1}(p_0+p_1+\Delta p))} \quad (1.5)$$

where $\nu_p$ and $\nu_n$ are the hole and electron thermal velocities, $\sigma_p$ and $\sigma_n$ are the capture cross sections of the traps, $\Delta n=\Delta p$. $p_1$ and $n_1$ are the hole and electron concentrations when the Fermi energy is located at the trap level which are given by:

$$n_1 = n_i \exp\left(\frac{E_F-E_{Fi}}{kT}\right) \quad (1.6)$$

$$p_1 = n_i \exp\left(\frac{E_{Fi}-E_F}{kT}\right) \quad (1.7)$$

If $\Delta n \ll p_0$, then the minority carrier lifetime is given by:

$$\frac{1}{\tau} = N_T\nu_n\sigma_n \quad (1.8)$$
If $\Delta p << n_0$, then the minority carrier lifetime is given by:

$$\frac{1}{\tau} = N_T \nu p \sigma_p \quad (1.9)$$

**Non-radiative recombination via Auger process**

Another important non-radiative recombination process is due to the Auger recombination. In this process, the recombination energy is dissipated by exciting electrons into higher energy state in conduction band, or hole deeply into lower valence band. The two Auger processes are described by following equations:

$$R_{Auger} = c_p np^2 \quad (1.10)$$

$$R_{Auger} = c_n n^2 p \quad (1.11)$$

$c_n$ and $c_p$ are two Auger coefficients for holes and electrons, respectively. In the case of high excitation, the Auger rate equations can be reduced to:

$$R_{Auger} = (c_p + c_n)n^3 = cn^3 \quad (1.12)$$

where $c$ is the Auger coefficient. The Auger process generally became significant in the case of high concentration carriers injection, i.e. in high power LED applications.

Another non-radiative recombination mechanism like surface recombination also need to be considered in case of high surface states presented in LED device.

**Competition between radiative and non-radiative recombination**

The total minority carrier lifetime is given by:
\[ \tau^{-1} = \tau_{r}^{-1} + \tau_{nr}^{-1} \quad (1.13) \]

where \( \tau_{r} \) is the radiative lifetime and \( \tau_{nr} \) the non-radiative lifetime. The sum of all non-radiative processes is given by:

\[ \tau_{nr}^{-1} = \tau_{Defects}^{-1} + \tau_{Auger}^{-1} + \tau_{Surface}^{-1} + \ldots \quad (1.14) \]

Finally, the internal quantum efficiency of LED is expressed as:

\[ \eta_{int} = \frac{\tau_{r}^{-1}}{\tau_{r}^{-1} + \tau_{nr}^{-1}} \quad (1.15) \]

### 1.2 Fundamentals of photodetectors

The following section will introduce the operation mechanism of the photodetector. Generally, the overall performance of the photodetector can be broken into two aspects, one is the detection of light, the other one is the noise which introduced by the operating environment and device architecture. A set of figures of merit used to evaluate the photodetector performance are presented.

#### 1.2.1 Photodetector principles

Photodetectors are sensors of electromagnetic energy, or photons. The photon detection can be categorized to three types, namely photoemissive, photoconductive and photovoltaic. The photoemissive detection is based on photoelectric effect of which Albert Einstein received Nobel Prize in 1921 due to his discovery of the law of the photoelectric effect. In contrast, the photoconductive and photovoltaic detection are based on the generation of electron-hole pairs.
within the semiconductor material by the absorption of photons. The photon energy has to be equal or greater than the bandgap. The photoconductive detection is the change of conductivity in response to illumination, an external drive is needed. But the photovoltaic detection is based on photodiode that can be self-driven by build-in electric field. In this section, we focus on the current-voltage characteristic of photodiode.

The current-voltage, I-V, characteristic of photodiode is:

\[ i = i_{\text{dark}} + i_{\text{photo}}, \quad (1.16) \]

is a combination of the dark current \( i_{\text{dark}} \) and photo current \( i_{\text{photo}} \). According to I-V characteristic of diode, \( i_{\text{dark}} \),

\[ i_{\text{dark}} = i_0 \left( e^{\frac{qV}{nkT}} - 1 \right) \quad (1.17) \]

when \( i_0 \) is the reverse saturation current, \( q \) is the electron charge, \( V \) is the applied bias, \( n \) is the ideal factor, \( k \) is the Boltzmann constant, \( T \) is the temperature. The photo current, \( i_{\text{photo}} \),

\[ i_{\text{photo}} = q\eta\Phi \quad (1.18) \]

where \( \eta \) is the quantum efficiency of the photodiode, \( \Phi \) is the photon flux.

One important figure of merit that describes the performance of photodetectors is responsivity, which measures the input-output gain of a photodetector system. The responsivity of photodetectors is defined as the ratio of photocurrent flowing in a detector to incident optical power, with the unit of A/W. The general expression for responsivity is given by

\[ R_\lambda = \frac{\text{device current}}{\text{optical power}} = \frac{i_{\text{ph}}}{P_\lambda} = \frac{q}{hc} \lambda \eta_{\text{ext}} \quad (1.19) \]

where \( I_{\text{ph}} \) is the photo current, \( P_\lambda \) is the incident light power, \( h \) is the Planck’s constant, \( c \) is the velocity of light, and \( q \) is the electric charge, \( \eta_{\text{ext}} \) is external quantum efficiency. As a result, if
we measure the external quantum efficiency of the device, we can obtain the responsivity by equ. (1.19) at given photon energy, vice versa. Similarly, responsivity can be derived from the photo current and incident light power. It is also possible to estimate internal quantum efficiency (IQE), $\eta_{int}$, in following equation:

$$\eta_{ext} = \eta_{int}(1-R)(1-e^{-\alpha d}) \quad (1.20)$$

where $R$ is the optical reflectivity of photodetector, $\alpha$ is the absorption coefficient, and $d$ is the effective thickness of active region.

Another important figure of merit is specific detectivity ($D^*$) which employed to characterize the sensitivity of a photodetector. $D^*$ is the inverse of the noise equivalent power (NEP) normalized by the active area and response bandwidth of the detector and is expressed as following:

$$D^* = \frac{(\Delta f)^{1/2}}{NEP} \quad (1.21)$$

where $A$ is the area of photodetector, $\Delta f$ is the bandwidth. The $NEP$ is the radiant power that produces a signal-to-noise ratio of unity and it is dependent on the noise level of the given photodetector. $NEP$ is given by:

$$NEP = \frac{N_s}{R\lambda} \quad (1.22)$$

where $N_s$ is the noise signal density,

$$N_s = \sqrt{\langle i_n^2 \rangle} \quad (1.23)$$

where $i_n$ is the total noise current. The noise analysis of photodetector will discussed in more details in next section.

**1.2.2 Noise Analysis**
The noise response, as a random fluctuated electrical signal from a photodetector, is fundamentally limits the detectivity of photodetectors. For example, a photodetector can detect a photo signal at nanowatt \( (10^{-9} \text{ W}) \) level has higher detectivity than the one that detects at microwatt \( (10^{-6} \text{ W}) \). The noise source can be classified as external or internal. In most cases, the total noise may be dominated by one or more noise sources, depending on external environment and internal detector architecture.

**Photon Noise**

The photon noise is an external noise source independent of photodetector characteristics. It generally regarded as the lowest possible noise at the photon-noise-limited situation and as the ultimate noise limiting the detectivity of photodetector. It is impossible to lower noise at the photon-noise-limited situation. The number of photons received by the photodetector fluctuates about a average value, gives rise to photon noise. If assuming the photons are identical particles with same energy. For low-temperature blackbody radiation, short wavelength radiation \((hv \gg kT)\), visible and near-infrared radiation, the photon noise obeys Poisson statistics. The standard deviation of a Poisson distribution, \( \sigma \),

\[
\sigma = \sqrt{\hat{y}}, \quad (1.24)
\]

where \( \hat{y} \) is the mean deviation. For example, the average number of photons emits from a 300 K source is \( 10^{18} \text{ s}^{-1} \text{ cm}^{-2} \), the variation of this value is the noise. However, strictly speaking, photons have different energies and should have to obey Bose-Einstein statistics. An correction factor for bosons must be taken into consideration.
**Detector Noise**

The detector noise is the noise within the detector body itself that fundamentally limit the detector's capability of measuring small optical flux. The major contributions to the detector noise can be categorized as Johnson noise, shot noise, generation/recombination noise and $1/f$ noise.

Johnson noise, also known as thermal noise or Nyquist noise, is comes from the thermal motion of charge carriers in a resistive element. The Johnson noise is an intrinsic noise existing in all detectors. The Johnson noise current is given by [3]:

$$i_j = \sqrt{\frac{4kT\Delta f}{R}} \tag{1.25}$$

where $R$ is the circuit resistance.

The shot noise is originates from the charge carrier emission across a potential barrier and is a series of independent events. Only in devices with a potential barrier can allow the presence of shot noise, such as diode with built-in potential at junction. Note that the current through a photoconductor does not possess shot noise. The discrete nature of the shot noise is similar to the emission of photons, which also follows Poisson distribution. The shot noise is given by:

$$i_s = \sqrt{2q\bar{i}\Delta f} \tag{1.26}$$

where $\bar{i}$ is the mean dc current flow. Because dc current is proportional to the active area of the device, so the shot noise is proportional to the square root of the device area. In case of colloidal quantum dot photodetectors as we discussed in chapter 2, the shot noise is considered as the main source of detector noise.
The generation/recombination noise is associated with the statistical fluctuation of free carrier generation and recombination rates.

\[ i_{gr} = 2qG \sqrt{\eta E_q A \Delta f} + g_{th} A \Delta f l \quad (1.27) \]

where \( G \) is the photoconductive gain, \( \eta \) is the quantum efficiency, \( A \) is the device area, \( g_{th} \) the is thermal generation of carriers, \( E_q \) is the photon irradiance, and \( l \) is the detector thickness.

1/f noise is as a strong function of frequency which commonly seen in detectors at low frequencies (<1kHz). The 1/f noise is believes to be originated from non-ohmic contacts and variations of charge carrier traps in the time constants that disturb current flow in the detector. the 1/f noise is given by:

\[ i_f \propto \sqrt{\frac{f^{-2lf}}{f^{-1}}} \quad (1.28) \]

where \( f \) is the operating frequency.

The total noise is the sum of the power of all noise sources. Thus the noise current sources can be summed as:

\[ i_n^2 = i_f^2 + i_s^2 + i_{gr}^2 + i_f^2 \ldots \quad (1.29) \]

1.3 Fundamentals of III-Nitride materials
1.3. 1. Evolutions of III-nitride materials

Wide bandgap III-Nitride materials, which commonly refer to AlN, GaN, InGaN and their alloys, have seen enormous success in their development especially in the last two decades of the 20th century. The bandgap energy could be tuned from 6.2 eV for AlN to 3.4 eV for GaN to 0.7 eV for InN, which corresponds to a wavelength range from 200 to 1700 nm, covering a broad spectra range from deep UV to near infrared. The one of the most beneficial features of III-Nitrides for LED and photodetector application is their nature of direct bandgap. Furthermore, the wide bandgap of III-Nitrides also introduced low leakage and dark current, which are very attractive for photodetector applications. In addition, the superior physical and chemical stability of the III-Nitrides enables them to operate under harsh environments.

Since crystal III-Nitrides cannot be found in the nature environment, people regarded the growth of III-Nitrides single crystal as an impossible mission for a long time. Despite the earlier report of AlN in 1907 [4], InN in 1910 [5], GaN in 1932 [6], the As- and P-based III-V materials first reported in 1952 [7] have attracted much more interest during the early years of III-Vs research because of their easier realization of single crystal growth. In 1969, Maruska and Tietjen first reported in growing GaN single crystal on a sapphire substrate using hydride vapor phase epitaxy (HVPE) [8]. In 1971, Pankove et al. reported first bluish-green LED with a metal-insulator-semiconductor (MIS) structure [9]. However, there are two serious obstacles that diminished the popularity of III-Nitride researches on growing high-quality single crystal free from cracks and controlling the electrical properties with proper doping, particularly p-type doping. The breakthrough occurred in 1985 as Amano et al. first proposed a low-temperature-deposited (LT-) buffer layer approach employing metal-organic vapor phase epitaxy (MOVPE) [10]. The essence
of this technology is introduced a softer LT-AlN-buffer layer between the GaN epitaxy layer and highly mismatched sapphire substrate. The extremely high-quality GaN single crystal with a specular surface free from cracks was obtained. In 1989, the same group realized high efficient p-type dope using Mg as the dopant followed with the low-energy electron-beam irradiation (LEEBI) treatment [11]. This new technology has immediately led to the demonstration of first p-n junction UV and violet LED[12]. The doping of nitride alloys also achieved for p-type AlGaN and p-type InGaN in 1991 [12] and 1994 [13], respectively.

The accomplishments of two essential milestones of single crystal growth and doping spurred enormous interests and efforts in this field, consequentially led to a revolutionary development in the optical properties of III-Nitrides materials and devices. The external quantum efficiency, $\eta_{\text{ext}}$, of nitride-based blue LED was increased dramatically from 0.1% before the breakthroughs to 1.5% with the fabrication p-n junction LED in 1992 [14]. Even though the first III-nitride blue LED was commercialized in 1993, the $\eta_{\text{ext}}$ was still at a relatively low level. The other pioneer work in developing high efficient blue LED was done by Nakamura et al. [15] in 1994 who first proposed the InGaN/AlGaN double heterostructure. The essence of this work was implemented a narrow bandgap InGaN layer in between two wide bandgap AlGaN layers as an active layer. The double heterostructure can also been regarded as a single quantum well (QW) band structure where electrons and holes are confined inside QW that eventually increased the radiative recombination rate of injected carriers. In 1995, InGaN/GaN multi-quantum well (MQW) active layer, which adopted by currently used GaN-based LED, was reported[16-17]. Since then the technology transition of nitride LEDs from research labs to industry has been taken place.
1.3.2 GaN-based alternating current light emitting diodes

Solid-state lighting (SSL) based on white light emitting diodes (LEDs) has been widely recognized as among the most promising candidate to replace traditional lamp-based lighting systems because of their low energy consumption, long lifetime, high brightness and reliability. The LED based on III-nitride semiconductor such as InN, GaN AlN and their alloys are commercial available at blue/green and violet range. The LED devices typically operate at the direct-current (DC) mode because of its native rectifying characteristics. The typical operating voltages from around 2 volts for red LEDs to 3.5 volts for blue LEDs. Since alternating current (AC) sources (60Hz 110V) are generally wired in the buildings and houses in North America, it is indispensable to use DC LEDs under AC environment. One approach is to implement AC-to-DC converter separately with LED devices to change the electrical mode and amplitude to power each LED device. However, the converter-based driver introduces larger volume, high cost, low efficiency, and much less reliability comparing. According to ref.[18], the LED drive took over 20% of entire cost of LED lamps in market. Additionally, 52% of the failure of LED lamps are caused by the drive [19]. Therefore, the designs of LED chips which enables LED devices directly plug into AC power without additional driver, are highly desirable in favor of the cost reduction and reliability enhancement.

Anti-parallel ACLEDs
The first generation of anti-parallel alternating current LED (ACLED) was proposed by J. P. Ao et al. [20] and H. X. Jiang et al. [21] in 2002. The monolithic ACLED chip integrating multiple micro-LEDs with anti-parallel arrays, half of mico-LEDs can illuminate in each AC cycle while the other half reverse biased. The arrays were alternately energized and de-energized at the frequency of the AC power source. The chip size of a single device is 150 μm×120 μm with total size 1.1 mm ×1 mm for a 40 (20 + 20) LED array, the circuit diagram is shown in figure 1-2. Output power of 40 mW was obtained when the ACLED device working under 72V AC bias. Since the general operating voltage for LED devices ranging from 2V to 3.5V, the number of micro-LEDs in each arrays can be modified to target 110V for North America, or 220V for Europe and Asia, etc.
Because of the micro-LED series connection layout and sine wave AC input voltage signal, ACLED's behaviors and operation modes are quite different from the conventional DC-driven LED's, such as flickering illumination, high injection current density, and only parts of micro-LED illuminating in each AC bias cycle. The chip area utilization ratio, which defined as the proportion of the micro-LEDs illuminated in each AC bias cycle, is the most important ACLED characteristic, determining the light output efficiency and manufacture cost of the ACLED chip, is only 50% for anti-parallel ACLED. Therefore, the chip area utilization rate need to be improved for high efficiency ACLED.

**Wheatstone bridge ACLEDs**
In order to increase the chip area utilization ratio of ACLED, the 2nd generation Wheatstone bridge type (WB) ACLED was proposed by H. H. Yen et al.[222] and J. Cho et al. [23] in 2007. Figure 1-3 shows the schematic view of WB-type ACLED circuit. Two of four WB rectifying arms (C, D, E, F) would illuminate alternatively under AC bias, and output branch (G) would illuminate at all AC cycles. For example, in ref. [23], each WB arm is consists of 7 micro-LEDs, and 18 micro-LEDs at G branch, which means 32 out of 46 micro-LEDs were forward bias at all AC cycles. The merit of the WB-type ACLED is that micro-LEDs at WB arms are function as both rectifiers and illuminate elements. Thus the chip area utilization ratio of ACLED can be increased to, 60% in ref. [22] and ~70% in ref. [23]. In addition, the flickering effect can be reduced because the majority of micro-LEDs is always on. To further increase the chip area utilization ratio, the numbers of micro-LEDs at WB arms should be minimized. However, each arms of WB were suffered from reverse bias at half AC cycles. The higher reverse bias on each micro-LED, the less reliability. Therefore, the number of micro-LEDs in each WB arm should be optimized. The average reverse bias applied on single micro-LED of ref.[22] and ref. [23] were 11V and 12.3 V, respectively. H. H. Yen et al. proposed different type of WB ACLED achieved chip area utilization ratio of 65% with 9.06 reverse bias on each micro-LED at WB arm [24]. W. Y. Yeh et al. reported red ACLED with chip area utilization ratio 60% and 82% [25]. G. A. Onushkin reported a ladder type circuit ACLED with chip area utilization ratio of 66% and 8.8V reverse bias on each rectifying micro-LED[26]. All the summary of previous reported anti-parallel ACLED and WB ACLED is shown in table 1-1.
The WB ACLED has demonstrated higher chip area utilization ratio and better electrical and optical performance than anti-parallel ACLED. However, the high reverse voltage applied on rectifying micro-LEDs resulted in a short lifetime and fast failure phenomena. H. H. Yen et al. [27] reported that positive charges accumulated in the n-type GaN layer under reverse bias and accelerated the generation of GaO$_x$ oxidation grains. The expansion of GaO$_x$ degraded the opto-electrical properties and eventually led to the failure of WB ACLED. The lifetime of WB ACLED under which each rectifying micro-LED reverse biased -13.1 V and -6.7 V exhibited lifetime from being less than 650 hours to greater than 1500 hours. These values are far lower than the lifetime of DCLEDs (~10,000 hours). Therefore, Wheatstone bridge Schottky barrier diodes (SBD) ACLEDs have been proposed to address this problem and will be discussed in next section.

Table 1-1. Summary of anti-parallel and WB ACLEDs.

<table>
<thead>
<tr>
<th>References</th>
<th>ACLED Type</th>
<th># of micro-LED Devices</th>
<th>Operate Voltage (V)</th>
<th>Chip Area Utilization ratio</th>
<th>Reversed bias on rectifying LED (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 20</td>
<td>Anti-parallel</td>
<td>40</td>
<td>72</td>
<td>50%</td>
<td>3.6</td>
</tr>
<tr>
<td>Ref. 22</td>
<td>WB</td>
<td>55</td>
<td>110</td>
<td>60%</td>
<td>11</td>
</tr>
<tr>
<td>Ref. 23</td>
<td>WB</td>
<td>44</td>
<td>72</td>
<td>70%</td>
<td>12.3</td>
</tr>
<tr>
<td>Ref. 24</td>
<td>WB</td>
<td>45</td>
<td>110</td>
<td>66%</td>
<td>8.15</td>
</tr>
<tr>
<td>Ref. 26</td>
<td>WB</td>
<td>114</td>
<td>220</td>
<td>66%</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Wheatstone bridge Schottky barrier diode (WB SBD) AC LEDs

As discussed in the previous section, the number of micro-LEDs in the rectifying arms of WB ACLEDs was hard to reduce because micro-LEDs cannot endure a high breakdown voltage and cannot maintain a long lifetime under the high reverse bias stress. In order to solve this problem, the third generation ACLED, namely Wheatstone bridge Schottky barrier (WB SBD) ACLED, was proposed. The idea was to replace micro-LED rectifiers with small area and less amount of SBDs featuring a very high breakdown voltage. The previous studies reported breakdown voltage over 450V for undoped GaN SBDs [28,29], which make GaN SBD an ideal candidate for rectifier application. The circuit diagram and schematic of the prototype SBD ACLED structure are shown in figure 3. At least four GaN SBD rectifying elements forming a WB circuit which are highly tolerant of reverse bias and feature low forward turn-on bias. The idea of SBD ACLED was won 2008 R&D 100 Award [30]. However, the realization of this idea remaining a challenge today.

Figure 1-4 shows that the SBD was fabricated on an undoped GaN layer by etching away the top structure via standard semiconductor process. Green SBD LEDs operating under 12 V AC bias was demonstrated [25]. However, because of the plasma damage introduced by etch process, breakdown voltages of SBDs fabricated on an un-doped GaN layer was too low for high AC voltage, such as 110V or 220V.
W.Y. Yeh et al. [25] have proposed two approaches to address this problem. One is re-growing the SBD epitaxial structure on the LED surface (SBD/LED); The other one is re-growing LED structure on the SBD epitaxial layer (LED/SBD). The schematic illustrations are shown in figure 1-5. However, for the first approach, the leakage current was too high to be suitable for SBD ACLED. For the latter approach, the cracks of LED/SBD wafer was out of control. It was very challenge to combine the SBD and LED together without any degradation. Despite the experimental difficulties, they have filed a patent for the first approach [31].
Figure 1-5. Epitaxial structures of (a) SBD/LED, and (b) LED/SBD wafers

J. I. Chyi et al. [32, 33] have proposed a selective re-growing method for the integration of LEDs and SBDs. The method was first to form a junction layer on a substrate, and then defining the first growth area and the second growth area on the junction layer. Sequentially growing the SBD and LED structure on the first growth area and the second growth area. The selective growth SBD demonstrated reverse current 75 µA at -200V and forward current 20 mA at 2.75V. However, this method also exhibited poor uniformity, multiply leakage paths between SBDs and LEDs, complexity, and high cost. Unfortunately, the overall efficiency of the SBD ACLEDs was lower than the control WB ACLEDs.

1.3.3 GaN high breakdown voltage rectifiers

Wide band gap material, like SiC and GaN, have numerous advantages over more conventional Si rectifiers, achieving much higher electric field breakdown voltage and much lower on-state resistance ($R_{ON}$) at a given voltage [34-38]. Even though the SiC high power rectifier is more mature than GaN, GaN offers several unique advantages. First, the possibility of chip level integrating GaN rectifier with GaN/AlGaN heterojunctions and GaN-based LED devices which are not available in SiC system. Second, it is possible to adopt AlN and AlGaN to achieve higher electric field breakdown voltage. Some key material properties of Si, GaAs, SiC and GaN is shown in table 1-2 [38-40].
Table 1-2. Material properties of Si, GaAs, SiC and GaN at room temperature.

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>GaAs</th>
<th>4H-SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap, $E_g$ (eV)</td>
<td>1.12</td>
<td>1.42</td>
<td>3.25</td>
<td>3.41</td>
</tr>
<tr>
<td>Dielectric constant, $\varepsilon$</td>
<td>11.8</td>
<td>12.8</td>
<td>9.7</td>
<td>9</td>
</tr>
<tr>
<td>Break down field, $E_c$ (MV/cm)</td>
<td>0.3</td>
<td>0.4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Electron mobility, $\mu$ (cm$^2$/V s)</td>
<td>1500</td>
<td>8500</td>
<td>1000</td>
<td>1250</td>
</tr>
<tr>
<td>Maximum velocity, $V_s$ ($10^7$ cm/s)</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Thermal conductivity, $k$ (W/m K)</td>
<td>150</td>
<td>50</td>
<td>490</td>
<td>230</td>
</tr>
<tr>
<td>JFOM=$E_c^2V_s^2/4\pi^2$ (normalized to Si)</td>
<td>1</td>
<td>1.8</td>
<td>400</td>
<td>1600</td>
</tr>
<tr>
<td>BFOM=$\varepsilon\mu E_c^3$ (normalized to Si)</td>
<td>1</td>
<td>14.6</td>
<td>548</td>
<td>1507</td>
</tr>
<tr>
<td>CFOM=$k\varepsilon\mu V_s E_c^2$ (normalized to Si)</td>
<td>1</td>
<td>3.6</td>
<td>358</td>
<td>520</td>
</tr>
</tbody>
</table>

Johnson's figure of merit (JFOM) is based on the maximum electron drift velocity and critical electric field, which determining the high frequency capability of the material. The JFOM of GaN appears to be 1600 times than that of Si and 4 times than that of SiC, suggesting that GaN is a better candidate for high frequency applications. Baliga's figure of merit (BFOM) is associated with the dielectric constant, electron mobility and critical electric field, which measuring the minimizing conduction losses in power field effect transistors (FETs) [41]. The BFOM of GaN is more than 1500 times higher than that of Si and nearly 3 times higher than that of SiC. The combined figure of merit (CFOM) evaluate the overall high power, high temperature and high frequency capability of the material. In this regard, GaN exhibits a far better performance than conventional semiconductors like Si and GaAs, and expects to outperform the SiC. These
characteristics of GaN material make it attractive for hybrid electric vehicles and advanced radar subsystems applications[35,37,38,42-45].

GaN Schottky barrier rectifier is the key element of SBD AC-LEDs, low turn-on voltage and high reverse breakdown voltage are highly desirable. The forward turn-on voltage for Schottky rectifier is given by [46]:

\[ V_F = \frac{n k T}{q} \ln \left( \frac{J_F}{A^{*}T^2} \right) + n \Phi_B + R_{ON} * J_F \quad (1.30) \]

where \( n \) is the ideality factor, \( k \) is the Boltzmann’s constant, \( T \) is the absolute temperature, \( q \) is the electron charge, \( A^{*} \) is the Richardson’s constant, \( \Phi_B \) is the Schottky barrier height, \( R_{ON} \) is the on-state resistance, \( J_F \) is the forward current density at \( V_F \). The ideality factor at \( \sim 2 \) suggesting recombination current as the main carrier transport mechanism. While the ideality factor at \( \sim 1 \) suggesting the dominance of diffusion current. Low \( R_{ON} \) is desirable for low turn-on voltage. \( R_{ON} \) is a sum of drift region resistance, contact resistance and substrate resistance.

\[ R_{ON} = R_{drift} + R_{sub} + R_{contact} \quad (1.31) \]

\( R_{sub} \) and \( R_{contact} \) are depend on substrate and contact, \( R_{drift} \) is given by:

\[ R_{drift} = \int \frac{dx}{q \mu N_D} = \frac{W_D}{q \mu N_D} \quad (1.32) \]

where \( \mu \) is the electron mobility (1250 cm\(^2\)/Vs for GaN), \( N_D \) is the doping concentration of drift region and \( W_D \) is the thickness of drift region. The on-state drift resistance can be expressed by reverse breakdown voltage as [47]:

\[ R_{drift} = 2.4 \times 10^{12} V_B^{2.5} (\Omega \text{cm}) \quad (1.33) \]

where \( V_B \) is the reverse breakdown voltage. The higher breakdown voltage, the higher on-state drift resistance. As a result, a trade-off between on-state resistance and breakdown voltage is need to be considered.
High reverse breakdown voltage of GaN Schottky rectifiers is critical for SBD ACLED realizations. The breakdown of GaN Schottky rectifiers is generally due to avalanche multiplication, which introduced by the collision of high-energy carriers to host atoms. When the high-energy carrier driven by high electric field collides with host atom, it will generate a new electron-hole pair (EHP). The EHP accelerates the multiplication very rapidly and eventually causes the avalanche breakdown. A simple model for avalanche breakdown of GaN is [37]:

$$V_B \approx 1.95 \times 10^{15} N_D^{-0.7} \quad (1.34)$$

However, the potentially high breakdown voltage of GaN rectifiers generally limited by the presence of defects, and by breakdown initiated at the region near shape electrode corners. As for SBD ACLED applications, minimizing surface defects is critical.

1.4 colloidal quantum dots

Quantum dots (QDs) are semiconductor particles in nanometer scale, for which three dimensions of the particle are strongly confined by quantum confinement effects that fundamentally different from the corresponding bulk material properties which determined by the quasi-infinite periodic lattice structure. If the size of semiconductor particle is smaller than the bulk exciton Bohr radius $\frac{\hbar^2}{\mu e^2}$, where $\hbar$ is the dielectric constant of the material, $h$ is the reduced Plank constant, $\mu$ is the bulk exciton reduced mass, $e$ is the electric charge [48], the quantum confinement effect will be dominate in terms of the electrical and optical properties of the particle.
There are two approaches of making QDs, one is via epitaxial growth [49-51] and the other one is via colloidal synthesis [52]. The epitaxial growth method is to grow a very thin layer of semiconductors down to atomic precision via molecular beam epitaxy (MBE) or MOCVD, because of the build-in strain between the growing semiconductor and substrate, the semiconductor thin layer can self-assembled into small islands (QDs) on substrate. The mechanism is analogous to the water forming countless small droplets on top of hydrophobic substrates. However, neither the size of QDs can be precisely controlled by self-assembly formation, nor did the narrow size distribution can be achieved. The other approach is colloidal synthesis technology introduced by Murray et al. [53], so-called colloidal quantum dots (CQDs), which performed a very good control of size and size distribution, and the fabrication process will be further discussed in next section. CQDs have recently drew considerable attention as a promising material for optoelectronic applications including solar cells [54], light-emitting diodes [55-58], lasers [59], and photodetectors [60]. One major merit of colloidal QDs is the tunable optical absorption and emission spectra through the quantum size effect [48]. Moreover, Solution-synthesized colloid QDs can readily be deposited on almost limitless variety of substrates, which offers dramatically lowered cost, large-area, lightweight and flexible platform.

1.4.1 CQDs synthesis

According to LaMer's theory [61], there are generally four stages of mono-disperse colloidal synthesis: rapid precursor injection, burst nucleation, growth, and occasionally self size focusing. In LaMer's theory, it is critical to avoid aggregation, or a non-disperse colloid, during the transition of nucleation phase to growth phase. In 1993, the colloidal quantum dots (CQDs) were
first directly synthesized by an organometallic chemical method, or also known as three-neck flask synthesis developed by Murray et. al. [53], as shown in figure 1-6. The process started from injecting an organometallic precursors, dimethyl cadmium and trioctylphosphine selenium in this case, into a hot mixture (~300 °C) of organic solvent (trioctylphosphine oxide or oleic acid). The metallic and non-metallic reaction occurred at high temperature to burst a spontaneous nucleation. The nuclei were surrounded by a ligand layer from coordinating solvent that impeded the nuclei from aggregating during or after growth. As a result, the CQDs can grown uniformly in solution. The CdSe CQDs growth can be stopped by cooling the solution down to room temperature rapidly. A very good control of CQDs size and narrow size distribution can be obtained by this method. The size of CQDs and corresponding emission/absorption spectra were determined by growth temperature, nucleation and growth time, precursor concentration, stabilizing ligands, and coordinating solvents.
1.4.2 Fundamentals of colloidal quantum dot

A quantum dot (QD) is a semiconductor particle whose excitons are confined in all three spatial dimensions. In order to understand the physics of quantum effects in QDs, we first examine the simplest model of one dimensional particle (infinite potential well) from the basis of quantum mechanics. The simplicity of this model will not only offers an analytic solution, but also allows insight into the physics of quantum effects without complicated mathematics.
In infinite potential well model, the Schrödinger equation within the one dimensional well is:

\[-\frac{\hbar^2}{2m^*} \frac{d^2 \varphi(z)}{dz^2} = E \varphi(z) \quad (1.35)\]

By applying the infinite potential well boundary condition, the solution within the well is:

\[\varphi_n(z) = A \sin(k_n z + n\pi/2) \quad (1.36)\]

where \(n\) is an integer that gives the quantum number of the states, and

\[k_n = \frac{n\pi}{d} \quad (1.37)\]

where \(d\) is the length of the quantum well, the energy corresponds to the \(n\)th level is given by:

\[E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*} \left(\frac{n\pi}{d}\right)^2 \quad (1.38)\]

The physical meaning of the result suggests that the QD’s energy states are discrete and can never have zero ground energy. More importantly, the energy gaps between different energy levels are as a function of \(d\), which means the energy gap of QDs is depend on the size of particles. The size independence property of QD offers an unique opportunity to tune the electrical and optical properties of semiconductor material by size. Figure 1-7 (left) shows initial wavefunctions of the first four states in an infinite potential well and (right) shows the energy states of a particle in an infinite potential well (black circles) and a free particle (grey line). However, the free particle have continuous energy states while the particle in a box may only have certain, discrete energy levels. Even though this concept derived from one dimension particles, is can also be applied to QDs which are quantum confined in three dimensions.
More complicated model of needed for describe the mechanism of three dimensional QDs. By using Burs model [62], the band gap of QDs is given by:

\[ E_g = E_{bulk} + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_h + m_e} \right) - \frac{1.8e^2}{4\pi \varepsilon_0 \varepsilon_r r} \]  \hspace{1cm} (1.39)

where \( E_{bulk} \) is the band gap of bulk semiconductor, \( \varepsilon_r \) is the dielectric constant of the material, \( r \) is the radius of QDs. The second term on the right hand is inversely proportional to \( r^2 \) which is similar to particle in box model. The third term on the right hand is associates with the Coulombic attraction force between electron and hole pair which turn to be inversely proportional to \( r \). As a consequence, the smaller the size of QDs, the larger the band gap.
CQDs are synthesized via three-neck-flask method. Organic precursors are injected into a flask and, through control of precursor concentrations, ligand selection, temperature and reaction time, QDs of a desirable size and shape can be delivered. The size of the QDs synthesized by this approach is near uniform and can be controlled precisely. Generally, QDs optical absorption and emission spectra are widely tunable through the quantum size effect. Figure 1-8 shows an absorption spectrum of PbSe CQDs from previous works in our group [63], the absorption peak varies with the QDs size. Additionally, the bandwidth of emission and absorption spectra of the
QDs can be as narrow as \(~50\text{nm}\). Moreover, Solution-synthesized colloid QDs can readily be deposited on almost limitless variety of substrate, which offers dramatically lowered cost, large-area, lightweight and flexible platform. Therefore, the CQD is a promising material for optoelectronic device applications.

### 1.5 Dissertation organizations

The following Chapter 2 of this dissertation focuses on the development of solution-processed infrared PbSe CQD-based photodetectors. The high dark current, considered as the major noise source that limiting the performance of CQD photodetectors, is typically significant due to the CQDs' nature of small band gap and large surface state densities. To address this problem, we first proposed the tandem architecture for CQD-based infrared photodetector device fabrications. Firstly, the tandem photodetector shares the same photocurrent transport mechanism with the tandem solar cell. This design strategy has ensured the high level of photocurrent collection in which virtually no photocurrent will be lost. Secondly, the tandem architecture fundamentally changed the dark current transport mechanism comparing to single architecture. In tandem photodetectors, the dark current is regulated by the carrier recombination at intermediate layer, which function as a valve that brings more possibilities to manipulate the current flow. More than three orders of magnitude reduction of dark current has been demonstrated by employing tandem architecture, accompanied with an elevated photocurrent. The low temperature current-voltage characteristics revealed that the intermediate layer poses a high energy barrier at the interface which effectively blocks the dark current. The specific detectivity of the tandem
photodetector at 1100nm achieved \(8.1 \times 10^{13}\) Jones, the highest detectivity value reported so far for CQD-based NIR photodetectors. The pronounced improvement of the device performance suggests that our study opens up new avenues for developing high-performance solution-processed photodetectors with the tandem architecture.

In chapter 3, we extended the application of newly developed tandem photodetectors on flexible substrates. Flexible optoelectronics have attracted a great deal of research attentions for their potentials in future paper display, portable, wearable and energy-storage devices. However, little study has been reported in high performance and flexible near-infrared CQD photodetectors. Here, we report a solution-processed high-performance colloidal quantum dot (CQD)-based near-infrared tandem photodetector fabricated on flexible substrates. The tandem photodetectors on poly(ethylene terephthalate) substrates exhibited very low dark current and high detectivity, demonstrating detectivities \(\sim 10^{13}\) jones over visible and NIR spectrum near 0 bias. Two different bending states, tensile and compressive bend, has been studied which demonstrated small critical bend radii of \(\sim 8\)mm and \(\sim 3\)mm, respectively. The photodetector performance remains stable under mechanical stress which makes it a promising candidate for flexible optoelectronic device applications.

Chapter 4 is focuses on the demonstration of flip-chip alternating current (AC) LED. We first proposed a chip level integration of flip-chip LEDs with Schottky barrier diodes as the rectifying arms in Wheatstone bridge circuit. The anneal study of Ni/Ag p-contact indicated that the operating voltage of single LED can droop to 3.1V under 350°C for 600sec in air, whereas the reflectance of the p-contact was obtained around 63%~66% at the wavelength range from 450nm
to 750nm. The operating voltage of the flip-chip ACLEDs is ~101V which suggested more than ~23% improvement in terms of energy conversion efficiency comparing to top emissive ACLED. Our study of flip-chip ACLEDs has the potential of featuring high brightness, high power, high efficiency and high reliability LED devices.

LEDs and photodetectors, with reverse physical mechanism to each other, are like twins or the two faces of a coin. However, they are usually have applications in their own territory which has little intersection to each other, like a face of the coin never meet the other sister face. Fortunately, built on the studies of photodetectors and LEDs in previous chapter, we have opened up a new revenue that enables the applications with the chip level integration of LEDs and photodetectors. In chapter 5, we, for the first time, proposed the integration of visible LEDs and UV photodetectors on chip for bi-directional optical wireless communication (OWC) applications. The GaN Schottky barrier diodes serve not only as the rectifiers who can tolerate high reverse breakdown voltage for ACLED application, but also as UV photodetectors with high sensitive in UV range and superior visible-blind property which form the building block for bi-directional OWC applications. Owing to the newly developed plasma damage passivation technology for ACLEDs, the GaN Schottky barrier photodetector in our study achieved responsivity up to 0.2 AW$^{-1}$ at 365nm and nearly two orders of cut-off ratio of UV to visible sensitivity. The integrated LEDs and photodetectors can function as transmitters to emit visible light signals and as receivers to collect UV signal, respectively, without interference each other due to the superior visible-blind property of GaN UV detectors, which offers the potential of using such device for bi-directional optical wireless communication (OWC) applications.
In chapter 6, the future works in this area will be discussed. First, the idea of developing novel infrared CQD LEDs has been proposed featuring high-efficiency high performance infrared LEDs. Then the idea of integrating silicon avalanche photodiode and infrared CQDs LED has also been suggested for bi-directional OWC applications.

Reference


Chapter 2

Tandem colloidal quantum-dot infrared photodetectors

Solution-processed colloidal quantum dots (CQD) near infrared (NIR) photodetectors are promising due to their mechanical flexibility, light weight, low temperature operation and low cost. However, the dark current, which serves as the main noise source that limits the performance of photodetectors, is typically significant due to small bandgap energies and high surface-state densities of infrared CQD materials. To address this issue, we propose, for the first time, the tandem architecture for solution-processed CQD photodetectors. The electrical transport mechanism of tandem photodetector has been fundamentally changed in which the recombination of electrons and holes at intermediate layer becomes dominant rather than carriers hopping between nearest neighbors in CQD materials. This hypothesis has been supported by the band structure engineering and low temperature current-voltage characteristics. Compared to photodetectors with single active CQD layer, the tandem photodetectors exhibit vast decrease of dark current by over three orders of magnitude and their calculated detectivities show nearly two orders improvement. The specific detectivity of the tandem photodetector at 1100nm achieved $8.1 \times 10^{13}$ Jones, the highest detectivity value reported so far for CQD-based NIR photodetectors.

2.1 Introduction

High-performance, solution-processed colloidal quantum dots (CQDs) photodetectors are of great interest due to low cost, low temperature processing, large device area, mechanical
flexibility, which can hardly be achieved by photodetectors made of epitaxially grown crystalline semiconductors. In addition, the bandgap of CQDs is tunable over a broad range from visible to NIR, making them attractive for visible and NIR sensing applications. G. Konstantos et al. [1] reported a photoconductor device based on PbS CQDs with normalized detectivities of $\sim 10^{13}$ jones at 1300nm at room temperature under 40V bias. However, the lateral conduction path design requires large driving voltage which is too high to be compatible with conventional electronic driver circuits. CQD photodiode devices are preferable due to their capability operating at small or zero voltage. J.P. Clifford et al.[2] reported a PbS CQD photodiode device with a normalized detectivity around $\sim 10^{12}$ jones at near infrared range at 250K near 0 bias.

PbSe CQDs in a visible and NIR photodetector are attractive because they allow synthetically accessible range of 2.5nm to 7nm (corresponding to absorption peak 0.9μm to 2.0μm) [3]. However the dark current, which consider as the main limiting factor for the detectivity, is inevitably high due to the narrow bandgap and high density of surface states of PbSe CQDs. One approach to reduce the dark current is to passivate the surface states of PbSe CQDs by replacing the long insulating oleate ligands with shorter and more conductive surfactant molecules, such as ethanedithiol (EDT) and benzenedithiol (BDT) [4,5]. However, surface passivation alone is often insufficient to resist the dark current [6].

Previous studies have also proposed an epitaxial unipolar barrier to suppress the leakage current for infrared photodetector via epitaxial growth technique [7-9]. The unipolar barrier describes a barrier within a photodetector band structure that blocks one type of carriers (electron or hole) but allows the flow of the other if proper engineered. In doing so, several current components,
including Shockley-Reed-Hall (SRH) current, surface current, trap assisted tunneling (TAT) current and direct band-to-band tunneling (BTB) current, can be effectively filtered out [10]. Nevertheless, the dark current component, such as diffusion current, which shared the same transport pathway with photogenerated current, cannot be eliminated by the unipolar barrier. The band structure engineering through the use of carrier blocking layers to suppress the charge injection is also proposed for organic and CQD-based infrared photodetectors [6, 11]. But it is difficult to obtain dark current suppression and photo current harvest at the same time, because the difference of thermal excited carriers and light excited carriers for diffusion current transport is typically unrecognizable to photodetectors.

In this work, we address the high-dark current drawback by proposing a novel tandem architecture for the solution-processed NIR CQD PDs. The tandem architecture implements ZnO and Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)- benzidine] (poly-TPD) intermediate layer in between two cascaded PbSe CQD active (absorber) layers. The unique merit for the tandem PD is that the intermediate layer functions as effective energy barrier that blocks the dark current leakage, whereas the photocurrent is harvested via high-efficiency carrier recombination at the intermediate layer. In doing this, the role of the CQD material itself played in electrical transport mechanism has no longer been the major limiting factor for the detector performance. The measured dark current of the tandem PD exhibits a drastic reduction of more than three orders of magnitude compared to that of the PD with a single active layer (In the following context, it will refers to single-layer PD unless otherwise noted), which is also accompanied with an elevated photocurrent. NIR specific detectivity achieved 8.1×10^{13} Jones at -0.1V which is among the highest detectivity values for the CQD-based NIR PD reported to date. The low-temperature
current-voltage (I-V) characteristics reveal that the carrier recombination at the intermediate layer plays the key role in the electrical transport mechanism of the CQD tandem PDs under study. Our results validate the effectiveness of dark current blocking in tandem CQD PDs and opens up a new avenue to further suggest that the tandem architecture can be employed to develop high-performance solution-processed light detection devices.

2.2 Tandem photodetector fabrications and characterizations

**Solution preparation:** PbSe CQDs, ZnO, poly-TPD were dissolved in chlorobenzene, ethanol and chlorobenzene with concentration of 20mg/ml, 15mg/ml and 15mg/ml respectively. The solutions were prepared and stored inside a nitrogen glovebox. Colloidal PbSe QDs were synthesized following the noncoordinating solvent technique developed by Yu [12]. The ZnO nanocrystals (NCs) were synthesized through the sol-gel method [13]. For a typical process, 0.44g zinc acetate was dissolved in 30 ml ethanol, then the solution was heated to reflux for 30min before cooled down to room temperature. 10ml 0.5M NaOH in ethanol was injected into the zinc acetate solution then reacted under N₂ environment for 12 hours. The final product was washed several times by ethanol and hexanes and kept in ethanol for further fabrication process.

**Device preparation:** The patterned ITO glass substrates (sheet resistance ~15Ω□) were cleaned sequentially by ultrasonicating in de-ionized water, acetone and IPA for 15 minutes each, and then exposed to UV-zone for 15 minutes. The poly (ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) (30 nm thick) was spin-coated on top of ITO glass followed by thermal annealing at 150°C for 15 minutes. Then the substrates were immediately transferred to
glove box for rest process. PbSe QDs films were spin-coated and treated with 1,2-Ethanedithol (EDT) according to the same procedure described in our previous work [14]. ZnO NCs, poly-TPD, PbSe CQDs, ZnO NCs were spin-coated in sequence and annealed for 30 minutes at 80°C for each layer. The thickness of PbSe CQDs layer, ZnO NCs layer, poly-TPD layer were 75nm, 40nm, 45nm, respectively. Finally, the devices were completed by thermally evaporating 150nm-thick aluminum layer as the cathode and encapsulated for further characterization. The area of the devices is 2×2 mm².

**Device Characterization**: All measurements were done in the ambient. The current-voltage (I-V) characteristics of the photodetectors were measured with a Keithley 2612 analyzer, a 650nm laser diode was used to obtain the photocurrent. To obtain the spectral response of the photodetectors, the devices were irradiated under monochromatic light through Newport monochromator using a xenon lamp as the light source. The illumination intensities were measured using calibrated Newport 818 and Newport 818IR for visible and infrared range respectively. The intensity of incident light was tuned by using a set of attenuators.

### 2.3 Tandem photodetector characterizations and discussions

Figure 2-1 shows the architecture and simplified band diagram of the tandem PD: Glass/ITO/PEDOT:PSS/PbSe CQDs/ZnO/poly-TPD/PbSe CQDs/ZnO/Al. The ZnO hole blocking layer (HBL) and the poly-TPD electron blocking layer (EBL) are used as intermediate layer to connect and separate the bottom (in front of the light illumination) and the top (back) detectors. The intermediate layer is used as a recombination center allowing the recombination of
the electrons from one sub-detector with the holes from the other detector. The tandem PD employs the PbSe CQDs of the same bandgap for bottom and top active layers, ensuring the sensitivity to a monochromatic light wavelength. The simplified band diagram in figure 2-1 illustrates the electrical transport mechanism of the tandem PD. The thermal or optical generated electron-hole (e-h) pairs are separate at the junctions of both sub-detectors. The holes from bottom detector are captured by the anode and electrons from top detector are collected by the cathode; meanwhile the electrons from the bottom detector recombine with holes from the top detector at ZnO/poly-TPD interface. Therefore, the carrier transportation is determined by the recombination at the interface of ZnO and poly-TPD. As a result, the recombination of electrons and holes at ZnO/poly-TPD interface of the tandem architecture functioning as a valve brings more possibilities to manipulate the current flow.

As a control, figure 2-1 also shows the architecture and simplified band diagram of the single-layer PD: Glass/ITO/PEDOT:PSS/poly-TPD/PbSe CQDs/ZnO/Al. The e-h pairs generated at PbSe layer via thermal or optical excitation will be separated at the PbSe/ZnO junction by the built in potential or the reverse bias. Holes go through the poly-TPD can be captured by anode and electrons go through the ZnO can be captured by cathode. Virtually no energy barrier present at the transport pathways, thus the single-layer architecture is unlikely to suppress the dark current leakage. As a result, single-layer CQD PDs have been suffered from high leakage dark current originating from CQD materials.
One important figure of merit that describes the performance of photodetectors is responsivity, which measures the input-output gain of a photodetector system. The responsivity of a photodetector is defined as the ratio of photocurrent flowing in a detector to incident optical power, with the unit of $A/W$. The general expression for responsivity is given by:

$$R_{\lambda} = \frac{I_{\text{ph}}}{P_{\lambda}} = \frac{q}{hc} \lambda \eta_{\text{ext}}$$  \hspace{4mm} (2.1)

where $I_{\text{ph}}$ is the photo current, $P_{\lambda}$ is the incident light power, $h$ is the Planck’s constant, $c$ is the velocity of light, and $q$ is the electric charge, $\eta_{\text{ext}}$ is external quantum efficiency.
Another important figure of merit is specific detectivity ($D^*$) which utilized to characterize the sensitivity of a PD. At high frequency where $1/f$ noise is negligible, the shot noise limited $D^*$ is given by [6,15,16]:

$$D^* = \frac{R_\lambda}{\sqrt{2qJ_d+(4kT/AR_d)}} \quad (2.2)$$

where $R_\lambda$ is the responsivity at wavelength $\lambda$, $q$ is the electric charge, $J_d$ is the dark current density in Acm$^{-2}$, $A$ is the device area, $R_d$ is the dynamic resistance.

Figure 2-2 shows the dark and photo I-V characteristics of the single-layer and tandem PDs. The photocurrents were measured under 37.5mW/cm$^2$ illumination at 650nm. The dark current of the tandem PD drops more than three orders of magnitude than that of the single-layer PD, whereas
the photocurrent is slightly greater than that of the single-layer PD. The rectification ratios of the single-layer and tandem PDs at +/-1V are 5 and $1.19 \times 10^4$, respectively. The small rectification ratio of the single-layer PD is due to a large density of trapped states present at the surface of CQDs which serve as transport pathways and recombination centers [17,18].

![Figure 2-3](image.png)

**Figure 2-3.** Responsivity and calculated detectivity as a function of voltage for single and tandem photodetectors.

Figure 2-3 shows the responsivities and calculated shot noise limited detectivities of the single-layer and tandem PD as a function of reverse bias under 37.5mW/cm$^2$ illumination at 650nm. The $R_\lambda$ of the tandem PD is greater than that of the single-layer PD, and $D^*$ shows nearly two orders of magnitude improvement. For tandem PD at -0.5V bias, $R_\lambda = 0.36$ A/W, $D^* = 1.4 \times 10^{12}$
Jones, the detectivities are over $\sim 10^{13}$ Jones when approaching to 0V. The external quantum efficiency (EQE) at -0.5V is $\eta_{\text{ext}} = 69\%$ which indicates high recombination efficiency at the poly-TPD/ZnO interface.

Figure 2-4 (a) shows the absorption spectrum of PbSe QDs in solution and film after EDT treatment. A red-shift was observed after EDT treatment, it may due to the densification of PbSe QDs film which caused the change in oscillator strength and dipole–induced dipole coupling [5]. Figure 2-4 (b) shows the detectivity of single and tandem photodetectors as a function of wavelength at -0.5V bias. The detectivity spectrum corresponds closely to the absorption spectrum. The detectivity of tandem photodetector exhibits nearly two orders improvement than single photodetector, and is greater than $6.7 \times 10^{11}$ Jones at wavelengths from 450nm to 1200nm with an excitonic peak value $1.08 \times 10^{12}$ at 1120nm. The result shows that the detectivity of tandem photodetector outperformed previously reported PbSe-based photodetector [11] ($D^* > 10^{11}$ Jones at wavelengths from 600nm to 1200nm). Operating at room temperature, these detectivity values over infrared spectrum make the CQD tandem photodetector an attractive alternative to InGaAs infrared photodetector with detectivity typically greater than $10^{12}$ Jones [5, 19, 20].
Figure 2-4. (a) Absorption spectra for PbSe QDs solution and PbSe QDs film after EDT treatment, and (b) Detectivity across the visible and IR wavelengths for single and tandem photodetectors.

Although detector performance has been greatly improved by employing tandem architecture, the mechanism underlying these observations is still unclear. To understand the roles the CBL played, PDs devices with following structures were characterized in detail:

(i) PD1: Glass/ITO/PEDOT:PSS/PbSe CQDs/ZnO/poly-TPD/PbSe CQDs/ZnO/Al

(ii) PD2: Glass/ITO/PEDOT:PSS/PbSe CQDs/ZnO/PbSe CQDs/ZnO/Al

(iii) PD3: Glass/ITO/PEDOT:PSS/poly-TPD/PbSe CQDs/ZnO/Al

(iv) PD4: Glass/ITO/PEDOT:PSS/ZnO/poly-TPD/PbSe CQDs/ZnO/Al

(v) PD5: Glass/ITO/PEDOT:PSS/PbSe CQDs/ZnO/poly-TPD/ZnO/poly-TPD/PbSe CQDs/ZnO/Al
Figure 2-5 shows the simplified band diagrams of these 5 devices. The ZnO hole blocking layer (HBL) and the poly-TPD electron blocking layer (EBL) are serve as the energy barrier to block two types of carriers. PD1, PD2 and PD5 consists of two active PbSe CQD layer, whereas PD3 and PD4 only one active PbSe CQD layer. All devices under study have at least two CBLs to block the leakage current injected from electrodes. Figure 2-5 also shows the diffusion current transport pathways of these 5 devices. In PD3, the electron-hole (e-h) pairs generated at PbSe layer via thermal excitation get separated at the PbSe/ZnO junction by electrical field, holes go through the poly-TPD can be captured by anode and electrons go through the ZnO can be
captured by cathode. Virtually no energy barrier present at the transport pathway, thus the diffusion current leakage, arising from the large density of surface states at PbSe/ZnO junction which serves as transport pathways and recombination center, cannot be blocked [17,18]. Such hypothesis has been supported by the experimental result where PD3 shows the highest dark current among those devices as shown in figure 2-6. To better suppress leakage current, one more ZnO HBL has been introduced in PD4 which blocks the hole diffusion pathway as shown in figure 2-5, resulting in relatively lower dark current. Nevertheless, figure 2-7 shows that the photocurrent of PD4 is also lower than that of PD1 which means the ZnO HBL pitches off the leakage current and photocurrent simultaneously.

![Graph](image-url)

Figure 2-6. Dark current-voltage characteristics of PD1, PD2, PD3, PD4 and PD5.
Figure 2-7. Photo current-voltage characteristics of PD1, PD2, PD3, PD4 and PD5, measured with 37.5mW/cm² illumination at 650nm.

Like tandem solar cells, PD1, PD2 and PD5 consists of two active PbSe CQD layers. The band diagram of the PD1 shows that both electron and hole diffusion currents are blocked by the intermediate ZnO HBL and poly-TPD EBL layers, while in PD2 only the hole diffusion current is blocked. The reverse dark currents of these two devices are almost the same which indicates that ZnO HBL layers are effectively blocked the diffusion current leakage. However, the photocurrent of the PD1 is clearly higher than that of the PD2 as shown in figure 2-7. The photocurrent transport mechanism of PD1 and PD2 is the same to that of the tandem solar cell. In PD1, the light-induced e-h pairs are separate at the PbSe/ZnO junctions, the holes from left
active PbSe layer are captured by the anode and electrons from right are collected by the cathode; meanwhile the electrons from left recombine with holes from right at ZnO/poly-TPD interface. As a result, the carrier transport relies on the recombination efficiency at the intermediate layer, which lead to the harvest of the photocurrent. The higher photocurrent in PD1 is due to the present of the poly-TPD EBL which traps electrons at ZnO/poly-TPD interface for an enhanced recombination efficiency. In other words, the overflow of the electrons with the absence of poly-TPD EBL caused a reduced carrier recombination efficiency of PD2 at intermediate layer (as shown in figure 2-7). Therefore, the structure of PD1 offers a way to block diffusion current leakage without pitching off photocurrent.

It is noteworthy that no photovoltaic effect can be observed for PD4 (no photocurrent at 0 bias). Because PD4 can be seen as PD1 with only right PbSe CQD active layer, hence zero carrier from left lead to virtually zero recombination at intermediate layer without bias. Nevertheless, the dark current of PD4 is much higher than that of PD1, suggesting that simply insert one more ZnO HBLs do not necessarily lead to efficient suppression of leakage current. Furthermore, the dark current of the PD5 is higher than that of the PD1, which means two more CBLs inserted in the middle of the PD1 also not be able to further reduce the dark current. It can only be attributed to the CBLs that prevent the carriers from recombining with each other at the intermediate layer (shown in figure 2-5), which implies that the recombination at intermediate layer plays a key role in leakage current suppression without which the PD5 can only be regarded as two single-layer PD3 connected in series with a high resistive poly-TPD/ZnO layer. The coupling of two active PbSe CQD layers through carrier recombination is the key to obtain efficient suppression of diffusion leakage current. Therefore, the recombination of electrons and holes at intermediate
layer created a new pathway that simultaneously blocks diffusion leakage current and harvests photogenerated current. As a result, the two-active-layer PD1 exhibits more than three orders of magnitude reduction of leakage current comparing to single-active-layer PD3, along with an elevated photocurrent.

Figure 2-8. Responsivity spectrum across visible and IR wavelengths for different top PbSe QDs film thickness (A, B, C).

The photocurrent of tandem photodetectors, like of tandem solar cells, is dominated by the recombination efficiency of electrons and holes at the intermediate layer. The carrier balance between bottom and top detector is the key to obtain high photocurrent. To further investigate this hypothesis, we set the thickness of bottom PbSe CQDs layer as constant (75nm), and the thickness of top PbSe CQDs layer 50nm, 75nm and 100nm, for device A, B and C, respectively.
Figure 2-8 shows the responsivity of these three devices over visible and infrared wavelength range. The device A exhibits the lowest responsivity over the entire spectrum which suggests that the 50nm top PbSe CQDs layer absorbed less light than bottom layer (75nm) that led to less carriers generated in top detector, the imbalance of carriers rendering insufficient recombination at the ZnO/poly-TPD interface which ultimately cause low responsivity at given illumination power. When the thickness of the top PbSe CQDs layer increased to 75nm, the responsivity increased accordingly because more carriers generated in top detector thus more electrons and holes recombined at the intermediate layer. Moreover, when the thickness of top PbSe CQDs layer further increased to 100nm, the responsivity is saturated and even slightly decreased at infrared range. This saturation phenomenon suggest that the photocurrent of tandem photodetectors is subject to the sub-detector with less number of carriers been generated. The above experimental results verified our hypothesis that photocurrent transport mechanism of tandem photodetectors is same to tandem solar cells.

To further understand the electrical transport mechanism underpinning single-layer and tandem architecture, low temperature I-V characteristics have been investigated. Figure 2-9 (a) and (b) show the reverse dark current of single and tandem photodetectors at different temperature, respectively. When temperature decreased, the dark current of tandem photodetectors drops much faster than that of single photodetectors at near room temperature. It reflects different electrical transport mechanism between tandem and single photodetectors. For a disordered system, conductance $G(T)$ may be expressed as[21]:

$$G(T) = G_0 \exp \left[ -\left( \frac{T_0}{T} \right)^p \right] \quad (2.3)$$
where the preexponential factor $G_0$ may be independent of $T$ or a slowly varying function of $T$, $T_0$ is a constant of the material. The value of $p$, ranging from $1/4$ to $1$, depends on the $T$ range of measurement and the nature of the transport process of the devices. The dependence of $\ln(G(T))$ at -0.5V bias with the inverse of absolute $T$ for single and tandem photodetectors are shown in Figure 2-10(a) and (b), respectively. Several distinct regions are clearly observed which similar to disordered semiconductors.

![Graph](image-url)
Figure 2-9. (a) Dark current of single photodetectors at different temperature, and (b) dark current of tandem photodetectors at different temperature.
The graphs shown illustrate the relationship between $\ln(G)$ and $1000/T$ for single and tandem photodetectors.

For the single photodetector, the graph shows a decrease in $\ln(G)$ as $1000/T$ increases, indicating a decrease in the system's response with increasing temperature.

Similarly, the graph for the tandem photodetector also shows a decrease in $\ln(G)$ with increasing $1000/T$, suggesting a similar thermal response behavior.

The data points for both photodetectors are represented by squares, with the single photodetector's data distributed at higher $\ln(G)$ values compared to the tandem photodetector, indicating a higher response at lower temperatures.
Figure 2-10. (a) ln(G) as a function of inverse T for single photodetectors, and (b) ln(G) as a function of inverse T for tandem photodetectors.

The observed Arrhenius-like dependence ($p=1$) for both single-layer and tandem PDs near room temperature (275K~300K, 3.33~3.64 on 1000/T scale) is related to a thermally activated transport process. Equation 2 can be reduced to $G=G_0\exp(-E_a/k_BT)$, where $E_a$ is the activation energy for charge transport. From the slope of the Arrhenius plots we found $E_a\approx48.5$ meV for the single-layer PD. This value is in agreement with other single-layer PbSe CQD devices where $E_a\approx25$ meV [22], ~52.2 meV [23] and ~95 meV [24], respectively. The bandgap of PbSe CQDs is $E_g\approx1.3$eV, which means the carrier density of thermally excited CQDs is negligible and the electrical transport mainly originates from carriers hopping between nearest neighbors (NNH) [24]. In contrast, $E_a$ found to be 0.89 eV for tandem PDs near room temperature. In intrinsic semiconductor materials where the transport mechanism dominated by generation-recombination process, $E_a=E_g/2+\Delta E$, where $\Delta E$ is the Coulomb barrier [24]. The activation energy of the tandem photodetector is in reasonable agreement with $E_g\approx1.3$eV, which means it possesses an intrinsic generation-recombination transport arising from the thermal activated carriers across bandgap at two active PbSe CQD layers which annihilated by recombining with each other at intermediate layer. Thus the NNH transport in PbSe CQD material becomes negligible in the tandem photodetectors. On the other hand, the tremendous increase in the activation energy of tandem PDs also indicates an effective energy barrier present at tandem PDs, which eventually blocks the leakage current. The $T$ dependence of the photocurrent at 650nm light illumination has also been investigated, the activation energy found to be $E_a\approx72$ meV at
near room temperature. The much smaller activation energy of the photocurrent is probably due to the charge accumulation at the poly-TPD/ZnO interface that enables field-assisted recombination. As a result, the dark current blocking and photocurrent harvesting can occur simultaneously in tandem PD device. At lower temperature region (<200K), a much slower decreasing of dark current has been observed for both single-layer and tandem PDs which indicate the dominance of Efros-Shklovskii variable-range hopping (ES-VRH) (p=1/2) and Mott-variable-range-hopping (M-VRH) (p=1/4) [21, 24].

Figure 2-11. Shot noise limited detectivities of the tandem photodetector at -0.1V at 1100nm wavelength as a function of temperature.
Figure 2-11 shows the specific detectivities of the tandem photodetector at -0.1V at wavelength 1100nm and various temperature. The $D^*$ value is increased with the decreasing of operating temperature. The $D^*$ achieved $4.7 \times 10^{13}$ Jones at 275K and $8.1 \times 10^{13}$ Jones at 100K, which are among the highest detectivity values of the CQD-based NIR photodetector reported up to date [1,2,11].

![Graph showing the specific detectivities of the tandem photodetector at different temperatures.](image)

Figure 2-12. Photo current density of tandem photodetectors at different illuminate intensities.

Another figure of merit for photodetectors is the linear dynamic range (LDR), or photosensitivity linearity (typically quoted in dB), LDR is given by:

$$LDR = 20 \log(J^*_{ph}/J_d) \quad (2.3)$$

where $J^*_{ph}$ is the photocurrent measured at light intensity of 1mW/cm$^2$. Figure 2-12 shows the linearity of tandem photodetector at 0.5V reverse bias under 650nm illumination. Good linearity...
has been observed from 2.85 μW/cm$^2$ to 37.5 mW/cm$^2$. Under -0.5V bias, the LDR at 650nm and 1100nm are 66dB and 64dB, respectively. These results are equal or close to that of InGaAs photodetectors (66dB) [6]. When comes to smaller reverse bias, the LDR of tandem photodetector will gives higher LDR value.

### 2.4 Conclusions

In summary, we implemented the tandem architecture in order to block dark current of PbSe CQD infrared photodetectors. The tandem architecture fundamentally changed the electrical transport mechanism in which carrier recombination at the poly-TPD/ZnO plays a much important role than the NNH in CQD materials. As a result, the performance of the tandem PDs has been greatly enhanced in regardless of the intrinsic unfavorable properties of the CQD materials. Up to date, the highest specific detectivity value of $8.1 \times 10^{13}$ Jones is reported for CQD-based NIR photodetectors, rendering the tandem architecture as a promising design for developing ultra-sensitive solution-processed photodetectors.

### References


Chapter 3

Solution-processed High-performance Colloidal Quantum Dot Tandem Photodetectors on flexible substrates

In this chapter, we report a high-performance colloidal quantum dot (CQD)-based near-infrared (NIR) tandem photodetector fabricated on flexible substrates via solution-processed method. The tandem photodetector on poly(ethylene terephthalate) substrates exhibited low dark current and high detectivities over $\sim 8.8 \times 10^{11}$ Jones at near infrared range at -0.5V bias and over $\sim 10^{13}$ Jones near 0 bias. The critical bend radii of $\sim 8$mm and $\sim 3$ mm have been demonstrated for tensile and compressive bending respectively. The performance of photodetectors remains stable under mechanical stress, making PbSe CQD material a promise candidate for flexible infrared sensing applications.

3.1 Introduction

Flexible electronic and optoelectronic devices have spurred widespread interests for their potential applications in future paper display, portable, wearable, and energy-storage device [1-8]. There are two approaches to fabricate flexible device: one is to create a free-standing nanomembrane (NM) from rigid substrate and then mount it onto a flexible substrate. By implementing this approach, NMs-based flexible devices consisting of silicon[9-13], GaAs [14-16], GaN [17,18] and InP [19] have previously been demonstrated. However, this approach introduced complexity, high cost and low throughput which impeded its further industry
penetration. The other approach is directly fabricate the device on flexible substrate on the basis of relative soft materials, such as organic [20], nanowires [21] and colloidal quantum dot (CQD) materials [22]. The latter approach is usually more preferred because of lower complexity, cost-efficient, enabling large area and high throughput. In particular, CQD materials allow their bandgap to be tunable over a wide range from visible to near-infrared (NIR), making them attractive for visible and NIR sensing applications. Additionally, the photodetector based on CQD materials enabling solution process at low cost and bringing the possibilities to directly integrate with more functional substrates such as silicon, plastic and etc. Several groups have reported photoconductor [23] and photovoltaic [24, 25] NIR photodetectors based on CQDs. However, there has been little research reported on the performance and flexibility of NIR CQDs photodetector on flexible substrate.

In this work, we investigated solution-processed flexible NIR tandem photodetectors based on PbSe CQDs. Very low dark current of photodetectors has been obtained due to the employment of the tandem architecture. The detectivity of PbSe CQD photodetectors found to be more than $8.8 \times 10^{11}$ Jones over visible and infrared range at -0.5V bias, and exceed $10^{13}$ Jones over entire spectrum at bias near 0. The impact of two different bend states, tensile bending and compressive bending, has been analyzed. The critical bend radii for tensile and compressive bending were 8 mm and 3 mm, respectively. Linearity response and modulation capacity have also been studied.

3.2 Flexible photodetector device fabrications
Colloidal PbSe QDs were synthesized following the noncoordinating solvent technique developed by Yu [26]. The ZnO nanocrystals (NCs) were synthesized through the sol-gel method [27]. The schematic illustration of flexible tandem photodetector device structure is shown in figure 3-1. The patterned ITO-coated poly(ethylene terephthalate) (PET) (sheet resistance ~35Ω/□) substrates were cleaned sequentially by ultrasonication in de-ionized water, acetone and IPA for 15 minutes each, and then exposed to UV-zone for 15 minutes. The PET was mounted onto a hard glass substrate and will be released after the device fabrication. The poly (ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) (30 nm thick) was spin-coated on top of ITO-coated PET followed by thermal annealing at 150°C for 15 minutes. Then the substrates were immediately transferred to glove box for rest process. PbSe QDs films were spin-coated and treated with 1,2-Ethanedithiol (EDT) according to the same procedure described in
our previous work [28]. ZnO NCs, poly-TPD, PbSe CQDs, ZnO NCs were spin-coated in sequence and annealed for 30 minutes at 80°C for each layer. The thickness of PbSe CQDs layer, ZnO NCs layer, poly-TPD layer were 75nm, 40nm, 45nm, respectively. Finally, the devices were completed by thermally evaporating 150nm-thick aluminum layer as the cathode. The area of the devices is 2x2 mm². The current-voltage (I-V) characteristics of the photodetectors were measured with a Keithley 2612 analyzer. To obtain the spectral response of the photodetectors, the devices were irradiated under monochromatic light through Newport monochromator using a xenon lamp as the light source. The illumination intensities were measured using calibrated Newport 818 and Newport 818IR for visible and infrared range respectively. The intensity of incident light was tuned by using a set of attenuators. All the measurements were performed under room temperature.

3.3 Flexible photodetector characterizations and discussions

Figure 3-2 shows the dark and photo current-voltage characteristics of the flexible tandem photodetectors. The photo illumination were at 850 nm and 1100 nm, respectively, with respect to power intensity of 24.3 µW/cm², 7.2 µW/cm², respectively. The dark current was found at ~10⁻⁸ A range from -1V to 0V, the very low dark current is due to the unique carrier block mechanism of tandem photodetectors where dark current can be significantly impeded by intermediate energy barrier, the detailed discussion can be found in our previous report [29].
Figure 3-2. Current-Voltage characteristics of flexible tandem photodetector under 850nm, 1100nm and no illumination.

One important figure of merit characterizes the performance of photodetector is responsivity, which given by:

$$R_{\lambda} = \frac{\text{device current}}{\text{optical power}} = \frac{I_{ph}}{P_{\lambda}} \quad (3.1)$$

where $R_{\lambda}$ is the responsivity, $I_{ph}$ is the photo current, $P_{\lambda}$ is the incident light power.
(a) Absorbance (a.u.) vs. Wavelength (nm)

- Black line: PbSe Solution
- Red line: PbSe film

(b) Responsivity and Detectivity vs. Wavelength (nm)

- Black line: Responsivity (AW⁻¹)
- Blue dashed line: Detectivity (Jones)

Wavelength ranges:
- Absorbance graph: 600-1400 nm
- Responsivity and Detectivity graph: 600-1400 nm
Another important figure of merit is specific detectivity (D*) which employed to describe the sensitivity of the photodetector. Because of the small bandgap of PbSe, the shot noise from dark current is dominate. In this case, the D* can be derived from following equation [30]:

\[ D^* = \frac{R_\lambda}{\sqrt{2qJ_d}} \] (3.2)

where q is electric charge, J_d is dark current density. As such, D* is determined by dark current and responsivity.

The absorption spectra of PbSe QDs in solution and deposited as a film with EDT treatment are shown in figure 3-3 (a). A clear red-shift was observed for PbSe film with EDT treatment which probably due to the densification of PbSe QDs film which caused the change in oscillator strength and dipole–induced dipole coupling [31]. The spectra of responsivity and detectivity under 0.5V reverse bias in room temperature are shown in figure 3-3 (b). It was found that the responsivity and detectivity decreased with the increasing of wavelengths, and an excitonic peak at 1100nm was observed which closely agreed with the absorption spectrum of PbSe film. The responsivity at 850nm and 1100nm are 0.34 and 0.27 A/W, which associated with external quantum efficiency (EQE) of 49.6% and 30.4%. The detectivity is above 10^{12} Jones at wavelengths smaller than 990 nm, and is 8.8\times10^{11} Jones at 1100 nm. Furthermore, the detectivities near 0V at 850 nm and 1100 nm are 1.11\times10^{13} Jones and 1.03\times10^{13} Jones, indicating that the detectivity spectrum of the photodetector is over ~10^{13} Jones over entire infrared range. These results were comparable to tandem photodetectors on rigid substrate [29]
and make it a promising alternative to InGaAs infrared photodetector which detectivity typically above \(~10^{12}\) Jones [30, 34 35].
Figure 3-4. Current characteristics of photodetectors as a function of radius of curvature under (a) stretch bending, and (b) compressive bending.

The flexibility of PET-based tandem photodetectors was investigated with the bend state under mechanical stress at various radii. The inset of figure 4-4 (a) and (b) show the different bend state: a) tensile bending where the device was on the convex side, and b) compressive bending where the device was on the concave side. The dark and photo current of tandem photodetectors at -0.5V as a function of bending radii are shown in figure 4a and 4b for tensile and compressive bending, respectively. In case of tensile bending, it was found that the dark and photo current remains largely the same at bending radii no greater than 8 mm which suggests the performance of tandem photodetectors was not submitted to any degradation under such mechanical stress. However, for further bending, both the dark and photocurrent at 850nm and 1100nm decreased.
dramatically. Since the organic molecular and QDs components are highly stretchable [22], this leaves the delamination of the solution-deposited films from electrodes the most likely failure mechanism. Such postulation is supported by the observation of delamination of the polymer film from the metal surface after bending, whereas the polymer surface under peeled electrode was completely undamaged in the previous studied polymer LEDs [32]. In case of compressive bending, the critical bend radius was found to be ~3mm where both dark and photo current remain almost unchanged at the radius greater than that. But considerably increase of both dark and photo current occurred at smaller radius. The increase of stress-induced current through the device is probably due to the field-assisted tunneling current through the QDs arising from the decrease of interparticle space of QDs under compressive deformation [33]. The performance of photodetectors found to be reversible at critical radii for both tensile and compressive bending.
Figure 3-5. The photocurrent of tandem photodetectors as a function of light intensity at 800 nm illumination at compressive bending with curvature radius of 4 mm.

The linearity of flexible photodetector under bending state has been studied. Figure 3-5 shows the photo current as a function of incident light power density at 850 nm when the photodetector was under compressive bending with radius at 4 mm. The photocurrent at bending was almost as the same as that without bending which suggests that the deformation was caused a negligible loss of the photodetector property. A good linearity can be observed from very low light intensity ~ $1 \mu$W/cm$^2$ to ~1 mW/cm$^2$.

The modulation capacity of photodetectors has also been studied. Figure 3-6 shows the frequency response of photodetector with compressive and without bending. The 3dB frequency are 124 Hz and 103 Hz for photodetector with and without bending. The relative higher 3 dB frequency at compressive bending is probably due to the condensation of device active thickness during the bending. These results indicates that the flexible photodetector can meet the requirement of 30 frames-per-second for imaging.
3.4 Conclusions

In conclusion, we designed and fabricated a CQD-based NIR photodetector on ITO-precoated PET substrates, featuring low dark current and high detectivities. The detectivities found to be more than $8.8 \times 10^{11}$ Jones over visible and infrared range at -0.5V bias, and exceed $10^{13}$ Jones over entire spectrum at bias near 0. Mechanical stress under two different bending states suggested two different failure mechanisms, and gave critical bending radii of ~8mm and ~3mm for tensile and compressive bending, respectively. Our studies demonstrated the potential of
using CQDs materials for their applications in large area, roll-up, solution processed flexible optoelectronics.

Reference


Chapter 4

Flip-chip Alternating Current Light Emitting Diodes

4.1 Introduction

Since the pioneer work of first GaN-based double heterostructure light emitting diodes (LEDs) by Nakamura et. al. [1] in 1994, GaN-based semiconductor has spurred widespread interest over the last two decades for their applications in developing high efficient and high bright LEDs [2-8]. The alloys of GaN and InN allow the bandgap of emissive layer be tunable from 3.4 eV to 0.7 eV depending on the composition of the alloy, covering the wavelength range from visible to ultraviolet (UV) [9,10]. Consequently, these properties make the GaN-based LED a promising candidate for next-generation white light sources. Two types of white LEDs are currently available: (i) separate red-green-blue (RGB) emitters or (ii) blue emitter in combine with phosphors. The former approach enables high color rendering but involves more complexity and high cost. The latter approach is usually preferred because of cost-efficient and lower complexity.

4.1.1 Introduction to flip-chip LEDs

The typical schematic structure of GaN-based LEDs is shown in figure 4-1. The LED wafer was grown on sapphire substrate, an undoped intrinsic low-temperature-deposited GaN buffer layer
was first grown on sapphire substrate, a multiply InGaN/GaN quantum well emissive layers were sandwiched in between the n-type and p-type GaN layer. The LED mesa structure was defined by the standard lithography and inductively-coupled-plasma (ICP) etching processes. Then the n-type metal contact and p-type metal contact were patterned, deposited and annealed.

Figure 4-1. Schematic view of typical GaN-based LEDs

For conventional LED, the light always emits from the top side and heat sinks from the bottom side as indicted in figure 4-1. Specifically, conventional GaN-based LEDs implemented top-emitting scheme using Ni/Au semi-transparent p-type contact as the anode [11-14]. The high work function of Ni ensuring small specific contact resistance of Ni/Au electrode. However, it is
very difficult to avoid the significant amount of light absorption when the light propagating through semi-transparent Ni/Au, n contact, bond pads and wire bonds. In addition, the thinner Ni/Au film, the smaller loss due to metal absorption. It must be thin p contact layer to minimize the light absorption. But the thin Ni/Au film also caused high resistance and poor current spreading which eventually impeding the improvement of the overall efficiency of LED.

Figure 4-2. Schematic cross section view of FCLEDs

The light absorption issue of the p contact can be solved by employing indium tin oxide (ITO) as the transparent p contact[15]. However, the contact resistance between ITO and GaN is much larger than that of Ni and GaN. Consequently, the turn on voltage is typically higher with
relatively poor reliability [16]. Furthermore, the light extraction efficiency is relatively low for top emissive LED because the downward propagating light cannot be efficiently redirect up by bottom reflective mirror through the sapphire substrate. Additionally, the thermal conductivity of sapphires is about 27 W/m K, the heat generated in LED flows through several hundred micrometer thick sapphire substrate cannot be sufficiently release to the heat sink. Accordingly, the reliability of LED is compromised and thus more complicated and expensive heat sinks is needed for high power applications.

In order to address above issues, the flip chip LED (FCLED) design has been proposed in early 2000s [17-18]. The schematic cross section view of typical FCLED is shown in figure 4-2. Two solders have been deposited on top of the n and p contacts. The FCLED is finally fabricated by flip-chip bonding the LED to a submount via interconnecting solders on both p and contacts as shown in the cross section in figure 2-2. There are many advantages of the FCLED proposal. Firstly, light is emits through a transparent substrate rather than through p contact, and downward light emission is reflected up by the sidewalls and reflective p metal contact [19, 20] (see the blue arrows which indicate the light propagating of LED ), of which mechanism eventually led to the improvement of the extraction efficiency. Secondly, the spreading resistance of p contact is reduced because the contact resistance between Ni and GaN is much smaller than that of ITO and GaN which account for much lower operating voltage of FCLEDs. Thirdly, the heat generated in the LED flows out directly through the solders to submount rather than through thermal resistive sapphire substrates. For instance, silicon has thermal conductivity as high as 148 W/m K and AlN has high thermal conductivity up to 285 W/m K. The employment of silicon or AlN submounts has demonstrated much effective heat dissipation and
incremented luminous efficiency of FCLEDs in previous study [21]. Therefore, the FCLED is featuring high power and high extraction efficiency with high thermal stability.

4.1.2 High-voltage and AC LEDs

LEDs can only drive under DC current due to the rectifying nature of diode. The operating voltage for the GaN-based LED is usually around 3~5V[22]. However, AC sources with voltages up to 110~220V are wired in almost all the household. The conventional approach widely used today to address this issue is implementing a driving circuit into the LED light source which can convert 110~220V AC source into a suitable DC voltage [23]. However, the power loss will be introduced by AC-to-DC driver, the cost accompanied with the electrical component can hardly be reduced, and the electrical components are significantly comprised the lifetime and reliability of LED light sources. Therefore, ACLED devices that enable LED directly plug into AC power without additional electrical components are highly desirable.
Since the operating voltage of single LED device 3~5V was much lower than the household AC source (110~220V), the first step to enable LED directly plug into the AC power is to connect multiply LED devices in series to adopt higher operating voltage. The LED device electrically connect multiply single LEDs on the same substrate is known as high-voltage (HV) LEDs. Figure 4-3 shows the side view of HV LED arrays. The wafer was divided into multiply single LED devices and then electrically connected with metals after proper passivation and isolation. It can been seen that the HV LED structure is very similar to the traditional single LED. Each connected single LED device in HV LED differs from traditional LED only in size. Therefore, most features of traditional LED employed to enhance the efficiency of LED, such as surface roughness, transparent conductive layer, patterned sapphire substrate, are transferable to HV LEDs. The key in the fabrication of HV LED is the insulation trench etch and interconnection metal deposition across the sidewalls.
The ALED devices, on the basis of on-chip connected HV LEDs, are drawing great deal of attentions in research area over the last decades. Three generations of ACLED have been proposed, namely anti-parallel ACLED, wheatstone bridge (WB) ACLED, and wheatstone bridge Schottky barrier diode (SBD) ACLED. The first generation anti-parallel ACLED consists of two series of LEDs that connected in an anti-parallel manner, the schematic circuit illustration can be seen in figure 4-4(a) [24, 25]. Only half of the LEDs devices were emitted light alternatively during each AC current cycle. This method introduced low chip area utilization ratio and flickering problems.

The next generation of ACLED is WB ACLED [26, 27]. The schematic circuit illustration is shown in figure 4-4(b). A bunch of LEDs served as rectifiers at WB branches, while the rest of LEDs were connected in series and always forward biased during the operation. The number of LEDs at each WB branch can be tuned to optimize the chip area utilization ratio, which eventually can be increased to 60% to 80%. However, the higher utilization ratio, the smaller number of LEDs at WB branch. Furthermore, the LEDs at WB branch will underwent a high reverse bias which eventually shorten the lifetime of LED device [28].
Figure 4-4. Schematic illustrations of the circuit of (a) anti-parallel ACLED, and (b) Wheatstone bridge AC LED, and (c) Wheatstone bridge Schottky barrier diode ACLED.

The third generation Wheatstone bridge Schottky barrier diode (WB SBD) ACLED has recently been proposed featuring high chip area utilization ratio and high reliability [29]. Figure 4-4 (c) shows the circuit diagram of WB SBD ACLED, the four arms of the bridge are consist of four Schottky barrier diodes, and all LED devices are connected in series on chip. However, the previous study shown that SBD ACLED suffered from very low operating voltage because of
plasma damage at Schottky contact introduced by etch process [30]. The operating voltage of SBD ACLED (~12V) was too low to subject to household AC sources, such as 110V or 220V.

### 4.2 Chip level flip-chip Wheatstone bridge Schottky barrier diode ACLEDs

In this study, we demonstrated the design, fabrication and characterization of chip level flip-chip Wheatstone bridge Schottky barrier diode ACLEDs. The device we fabricated can directly plugged into a 110V household AC power. Furthermore, the marriage of SBD ACLEDs and FCLEDs is in combine all merits of ACLEDs with FCLEDs, which featuring high efficiency, high power, high reliability of ACLED applications.

#### 4.2.1 Device structure of Wheatstone bridge Schottky barrier diode ACLED

![Diagram](image)

Figure 4-5. (a) the circuit diagram and (b) the schematic cross section of SBD ACLED structure
As we discussed in previous section, the plasma damage introduced by etch process impeded high breakdown voltage of Schottky barrier diode (SBD). Our study has demonstrated a unique way to cure the damage on u-GaN surface [31]. As a consequence, the breakdown voltage of SBD was measured to be greater than 120V. This achievement makes it possible to integrate SBD with LEDs arrays at chip level and enables SBD ACLED directly plugged into AC sources in household. The circuit diagram of SBD ACLED is shown in figure 4-5 (a). At least four SBD are needed to comprise four branches of WB. Whatever AC cycles applied, the current would constantly flow through LED arrays at forward direction, while two branches of SBD were underwent alternative forward and reverse bias. It is crucial to obtain forward bias on SBD as low as possible for minimum power loss and breakdown voltage of SBD as high as possible for less number of SBD needed at WB branches.

Figure 4-5 (b) shows the cross section of SBD ACLEDs. The device can be fabricated on commercial available LED wafers without extra requirements. The mesa structure can be obtained via the standard semiconductor lithography and etch process. The key is to fabricate the SBD on exposed u-GaN surface with minimum defects. Finally, we flip chip bond the ACLEDs on to a submount. More detailed process and discussion can be seen in next section.

**4.2.2 Flip-chip ACLED device fabrication processes**

Figure 4-6 from (a) to (j) illustrates the whole process flows of flip-chip ACLED device fabrication. Figure 4-6 (a) shows the schematic cross section view of LED wafer. The LED
wafers in this study were purchased from Xingguanlian Technology Co., Ltd. The wafer consisting of a patterned sapphire substrate, an undoped GaN buffer layer (~2.5 µm), an n-type GaN layer (~2 µm, $N_d \sim 1 \times 10^{18}$ cm$^{-3}$), eight pairs of 2.5 nm-thick In$_{0.1}$Ga$_{0.9}$N sandwiched in between 12 nm-thick GaN barriers (~110 nm), a p-type GaN capping layer (~100 nm, $N_a > 1 \times 10^{18}$ cm$^{-3}$). n-dopant and p-dopant in the LED heterojunction are silicon and magnesium, respectively.

The fabrication procedures are very much similar to the single LED fabrication. The first fabrication process is shown in figure 4-6 (b), the sample was patterned by standard semiconductor lithography process and etched to n-GaN by inductively-coupled-plasma (ICP) etching method. Followed by other two lithography and etch steps, etch isolation trench to sapphire substrate for the isolation of LED devices (as shown in figure 4-6 (c)) and then etch to u-GaN to define Schottky contact (as shown in figure 4-6 (d)). The mesa structure (shown in figure 4-6 (d)) was finally obtained after the three-step etching process.

Figure 4-6 (e) shows the p-contact and n-contact metal deposition. The metal areas were defined by standard lithography and lift-off process. The p-contact of Ni/Ag (3nm/200nm) and n-contact of Ti/Al/Ti/Au (10nm/40nm/40nm/100nm) were deposited via electron beam (E-beam) evaporator and followed by proper annealing. Then the LED and SBD devices were passivated and isolated with 400 nm SiO$_2$ by plasma enhanced chemical vapor deposition (PEVCD), as shown in figure 4-6 (f). After passivation, the Ni/Al/Ti/Au (40nm/1000nm/150nm/100nm), serves as both Schottky contact and interconnection metal, was patterned and deposited by E-Beam evaporator as shown in figure 4-6 (g). Figure 4-6 (g) also can be regarded as the structure
illustration of SBD ACLED, because SBD ACLED devices were accomplished after the Schottky contact metal deposition.

In order to flip chip bond the SBD ACLED on to a submount. A 400 nm isolate protection layer (SiO₂) was deposited on top of entire wafer, only a small area at electrode pad was opened by removing SiO₂ with lithographic patterning and wet etch as shown in figure 4-6 (h). Then solder layer with 2.2 µm Tin and silver alloys was patterned and deposited via thermal evaporator. Then the bottom sapphire was ground and polished for light emitting. Finally, the ACLED devices were flip chip bond on to a silicon submount.
Figure 4-6. (a) schematic cross section of LED wafer, (b) etch to n-GaN, (c) etch to sapphire for device isolation, (d) etch to u-GaN for Schottky contact, (e) p and n contact metallization, (f) SiO$_2$ isolation before interconnection metal deposition, (g) Schottky contact and interconnect metal deposition, (h) SiO$_2$ isolation entire device with opening etched at electrode pad area, (i) solder metallization, and (j) flip chip bond to submount.

4.3 Flip-chip ACLED Device characterizations and discussions

4.3.1 p-contact metal study
For flip-chip light-emitting diodes (FCLEDs) featuring high extraction efficiency and low operating voltage, it is crucial to form p-type Ohmic contact to p-GaN material that obtain both high reflectivity and low contact resistance. The conventional p-contact is Ni/Au bilayer annealed at around ~500℃ under nitrogen environment [32-33]. This scheme exhibited a good electrical properties, but it also introduced a poor performance in terms of reflectivity which obtained only ~31% reflectance from 470nm to 520 nm range. Al and Ag are well known as the best reflector at blue and UV wavelength range [34]. It was found that Al and Ag have average reflectance of 84% and 96% at 470 nm to 520 nm for 120-nm thick layers [35]. Therefore we chose Ag as the reflector in favor of its higher reflectivity for our flip chip LED device fabrication.

Figure 4-7. Schematic illustration of p-contact test single LED devices
Figure 4-7 shows the schematic view of single LED device for p-contact study. The n-contact Ti/Al/Ti/Au (10nm/40nm/150nm/100nm) was first deposited by E-beam evaporator and followed by 500°C for 120 sec in nitrogen environment. Then p-contact Ni/Ag (3nm/200nm) was deposited by E-beam evaporator. The anneal condition of p-contact was studied to optimize the LED performance.

![Image](100μm)

As grown  300°C  350°C  400°C  450°C

Figure 4-8. The top view of p-contact of LED: as grown, anneal in the air at 300°C for 180 sec, at 350°C for 600 sec, at 400°C for 180 sec, and at 450°C for 180 sec, respectively.

Figure 4-8 shows the top view of LED under different anneal condition in air: as grown, at 300°C for 180 sec, 350°C for 600 sec, 400°C for 180 sec and 450°C for 180 sec, respectively. It is clearly seen from the images that the surface roughness was increased with the increasing of
annealing temperature. The surface roughness may effects the reflectance of p-contact reflector. Thus the reflectance of Ni/Ag p-contact was measured at different anneal conditions as shown in figure 4-9. The reflectance of as-grown Ni/Ag is 78%~86% at wavelength range from 450nm to 750nm. This value after anneal decrease to 64%~68% at 300℃ for 180sec, to 63%~66% at 350℃ for 600sec, to 53%~56% at 400℃ for 180sec and to 46%~49% at 450℃ for 180sec. The degradation of contact morphology is probably due to the formation of new interfacial phases [36,37] and Ag agglomeration [38]. Low temperature is clearly preferable for achieving high extraction efficiency.

Figure 4-9. The reflectance of Ni/Ag on GaN: as grown, anneal at 300℃ for 180 sec, 350℃ for 600 sec, 400℃ for 180 sec and 450℃ for 180 sec, respectively.
The electrical properties of LED after p-contact anneal have also been investigated. If we define

Table 4-1. Operating voltage of LED and reflectance of Ni/Ag p-contact under different anneal conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_o$ (I=20mA)</th>
<th>Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>As grown</td>
<td>4.2V</td>
<td>78%~86%</td>
</tr>
<tr>
<td>300°C-180sec</td>
<td>3.3V</td>
<td>64~68%</td>
</tr>
<tr>
<td>350°C-600sec</td>
<td>3.1V</td>
<td>63%~66%</td>
</tr>
<tr>
<td>400°C-180sec</td>
<td>3.2V</td>
<td>53%~56%</td>
</tr>
<tr>
<td>450°C-180sec</td>
<td>3.2V</td>
<td>46%~49%</td>
</tr>
</tbody>
</table>

the forward voltage of LED at 20mA is the LED's operating voltage, $V_o$. The $V_o$ of LED and
the reflectance of Ni/Ag p-contact under different anneal condition is shown in table 4-1. It was
shown that as-grown Ni/Ag introduced high $V_o$ which indicating low energy conversion
efficiency. The $V_o$ decreased to 3.3V after 300°C anneal for 180sec and further decreased to 3.1
after 350°C anneal for 600sec. The lower operating voltage and better ohmic contact is due to the
formation of NiO phase at the p-contact [39]. Taking into account both operating voltage and p-
contact reflectance, the optimized anneal condition is found to be anneal at temperature 350°C
for 600sec.

4.3.2 Flip-chip ACLED characterizations
First, the SBD ACLED following the design rules as illustrated in figure 4-6 (g) was fabricated. Figure 4-10 (a) shows the top view of the chip level SBD ACLED in microscopic picture. The micro size LEDs and SBDs were integrated on the same LED wafer. In a SBD ACLED device, 26 micro-LEDs were electronically connected in series, and each rectifier branch of WB have three SBDs. Figure 4-10 (b) shows the top view of working SBD ACLED device, the device was emitting light under all cycles of AC voltage. The electrodes were wired by two probes. Flickering can hardly be observed by human eyes.
Figure 4-11. The microscope top view of ACLED device with patterned solder metal.

The SBD ACLED then followed the fabrication process from figure 4-6 (g) to figure 4-6 (j) to fabricate a flip-chip ACLED device. Figure 4-11 shows the top view of ACLED device with patterned solder metal (cross section view can be seen in figure 4-6 (i)). The two electrode pads were isolated by the PECVD-deposited SiO$_2$ layer. The big solder pad ensures the easy processing of flip chip bonding. Finally, The FCLED device was obtained after the flip-chip bonding process.

![Current-voltage characteristics of the FCLED device.](image)

Figure 4-12. Current-voltage characteristics of the FCLED device.
The current-voltage (I-V) characteristics of FCLED has been measured with Keithley 2612 semiconductor analyzer as shown in figure 4-12. The I-V curve shows that the FCLED with 26 micro-LEDs arrays is capable of operating at all AC current cycles. The operating voltage (when the current equals to 20mA) is 101V. Comparing to the top emissive ACLED operating voltage at 105V with 22 micro-LEDs [31], even assuming the same extraction efficiency, the estimated efficiency of FCLED is about ~23% higher than top emissive AC LED. Figure 4-13(a) shows the electroluminescence spectrum (EL) of FCLED, the emission peak is located at 458.2 nm. The full width at half maximum (FWHM) bandwidth is 20.7 nm which indicate a good purity of the light. Figure 4-13 (b) also shows the CIE1931 chromaticity diagram. The black "+" (as indicated by the black arrow) is the chromaticity coordinate (x=0.1491, y=0.0310) of the FCLED which located at the very edge of the chromaticity diagram. This value justified the superior purity of the LED light source and is very promising for white LED applications.
Figure 4-13. (a) Electroluminescence spectrum of the FCLED and (b) CIE1931 Chromaticity Diagram.

4.4 Conclusions

In summary, this chapter proposed a chip level flip-chip ACLED with Schottky barrier diodes as the rectifiers at Wheatstone bridge circuit. The integration of high-reverse-voltage bearable Schottky barrier diode and high-voltage micro-LEDs series is the key scheme for ACLED applications. The anneal study of Ni/Ag p-contact shows that the operating voltage of single LED can droop to 3.1V under 350°C for 600sec in air, while the reflectance of the obtained around 63%~66% at the wavelength range from 450nm to 750nm. Flip-chip ACLED devices have been fabricated with our unique designed masks and through the standard semiconductor processing. The operating voltage of the flip-chip ACLED is 101V which suggested more than ~23% improvement in terms of energy conversion efficiency comparing to top emissive ACLED. The electroluminescence spectrum indicate a pure blue emission from the FCLED device with peak wavelength at 458.2nm and the FWHM bandwidth is as low as 20.7nm. The study of flip-chip ACLED provide a new roadmap of ACLED applications featuring high brightness, high power, high efficiency and high reliability LED devices.

Reference


[20] L. B. Chang, C. C. Shiue, M. J. Jeng, "Formation process of high reflective Ni/Ag/Au


Chapter 5

Integration of Visible LEDs and UV photodetectors on chip for optical wireless communication applications

In this chapter, GaN-based visible light-emitting-diodes (LEDs) and GaN Schottky barrier UV photodetectors (PDs) monolithically integrated on chip for bi-directional optical wireless communication (OWC) applications is presented. Responsivity up to 0.2 AW$^{-1}$ at 365nm for GaN PDs has been achieved in despite of dry etch process. Spectral responsivity indicated a good visible-blind property of PDs. The mechanism of PDs response to visible light has been studied, current-voltage characteristics are derived in the reverse regime. It was found that the internal photoemission absorption (IPA) and Schottky barrier lowering play major role in response to visible illumination. The experimental results demonstrated that the GaN-based LEDs and GaN Schottky barrier PDs can work together with negligible crosstalk at UV illumination low to 7.16×10$^{-4}$ W/cm$^2$ at 365 nm. Our studies brings a new concept to minimize the crosstalk for bi-directional OWC application.

5.1 Introduction

Solid-state lighting (SSL) based on white light emitting diodes (LEDs) has been recognized as among the most promising candidate to replace traditional lamp-based lighting systems because of their low power consumption, long lifetime, high brightness and reliability. In particular, white LEDs as signal transmitter using for optical wireless communication (OWC) application
offers several advantages over traditional radio frequency (RF) wireless communication including low cost, license free, electromagnetic interference free, high data rate and better security [1-4]. Use of white LEDs not only for lighting indoor but also as means for wireless indoor communication could significantly reduce the implementing cost of OWC, which can be hardly achieved with infrared (IR) free space communication. Two types of white LEDs are currently available for OWC applications: (i) separate red-green-blue (RGB) emitters or (ii) blue emitter in combine with yellow phosphors. The former approach enables high color rendering and wide bandwidth. The latter approach is usually preferred because of cost-efficient and lower complexity, but the bandwidth limited to several MHz due to the slow response of the phosphor.

Silicon avalanche photodiodes (APDs) has been widely used as data receiver for OWC applications [6-8]. In addition, organic photodetectors (OPDs) also has been proposed to be the receiver in favor of its high flexibility [9]. However, the crosstalk between white LEDs and Si APDs brings challenges for bi-directional communication. Recently, bi-directional communication has been realized by subcarrier multiplexing (SCM)- wavelength division multiplexing (WDM) OWC based on RGB LEDs and phosphor-based LEDs, demonstrating data rate of 575-Mb/s downstream and 225-Mb/s upstream, respectively [5]. The essence of this method is to separate wavelength of bi-directional talk. The downstream signals were carried by the red and green emitters of RGB LEDs, whereas upstream signals were carried by blue emitter of phosphor-LEDs. In this way, the crosstalk between downlink and uplink can be significantly minimized by using different optical filters. Since the engineering of LED wavelengths and the using of Si APDs as receiver increase cost, size and weight, it is desirable to integrate LED and photodetector (PD) on chip. The integration of LEDs and PDs offers low cost, simplicity,
compact and makes such device very promise for bi-directional OWC applications. However, to our best knowledge there is no evidence that LEDs and PDs have been integrated on chip for bi-directional OWC application. Two major challenges are: (i) the inherent heterogeneity between GaN-based LEDs and silicon APDs and (ii) The significant crosstalk between white LED and visible PD. To address above two issues integration of GaN-based LEDs and GaN PDs on chip has been proposed in this letter.

GaN, with wide bandgap energy 3.41 eV at room temperature, is one of the most promising materials for the fabrication of ultraviolet (UV)-sensitive and visible-blind PDs [10, 11]. Previous studies proposed GaN-based Schottky barrier PDs for visible-blind applications [10, 12-18]. Thus on chip integration for bi-directional OWC application can be realized by integrating GaN-based LEDs and GaN Schottky barrier PDs. The easy fabrication of GaN Schottky barrier PDs offers the opportunity to integrate with GaN-based LED. On the other hand, the excellent visible-blind property of GaN PD makes it possible to minimize the crosstalk between UV PD and visible LED.

In this work, we demonstrated the integration of GaN-based LEDs and GaN Schottky barrier PDs on chip (In the following chapter, PDs refers to GaN Schottky barriers PDs unless otherwise noted). In order to have LEDs and PDs integrated and worked together with negligible interference, it is essential to fabricate a high performance visible-blind PDs in the neighbor of LEDs in despite of the dry etch process under which inevitably introduces a great amount of surface defects at the Schottky interface that generally lead to a severe degradation of PD's performance. PDs in this letter overcame this issue and achieved responsivity as high as 0.2 A/W
at -10V bias. This result is comparable to epitaxial grown counterparts of which device fabrication involved no etch process. The responsivity of PDs at UV range is nearly two orders of magnitude higher than that at visible range which makes the PD a good candidate for visible-blind applications. The mechanism in which the PD respond slightly to visible light have been studied, the numerical fittings indicate that the major contributors are internal photoemission absorption (IPA) and dark current increase due to lowering Schottky barrier effect. The work range where LED and PD working with negligible crosstalk has been discussed. The measured data demonstrated that LEDs and PDs can work together very efficiently even at very low UV illumination. Our study brings more opportunities to integrate LEDs and PDs for OWC applications.

5.2 LED and photodetector device fabrications and characterizations

Samples used in this study were all grown on c-face (0001) sapphire substrates by metalorganic chemical vapor deposition (MOCVD). Figure 5-1 illustrates the wafer structure which consists of 2.6 μm unintentional doped GaN (u-GaN), 2 μm n-GaN, 100nm InGaN/GaN multiple quantum wells and 600nm p-GaN. The LED and PD mesa structures were formed by standard photolithography and dry etch processes. The n-type Ohmic contact was deposited by evaporated Ti/Al/Ti/Au and the p-type Ohmic contact for LED was deposited by sputtered Ni/Ag. The Schottky contact of GaN PD on u-GaN was formed by evaporated Ni/Al/Ti/Au. The effective area of LED and PD were 295μm×255μm and 127μm×20μm, respectively. The distance between LED and PD was 250 μm. The current-voltage (I-V) characteristics of the LED and PD were measured with a Keithley 2612 analyzer. To obtain the spectral response of the detector, the
devices were irradiated under monochromatic light through Newport monochromator using a xenon lamp as the light source. The illumination intensities were measured using calibrated Newport 818UV and Newport 818 for UV and visible range respectively.

![LED schematic](image)

Figure 5-1. The schematic illustration of LEDs and photodetectors on chip.

5.3 Results and discussions: Integration of LEDs and photodetectors for bi-directional optical wireless communication applications
The performance of PDs is essential to the integration of LEDs and PDs on chip. Firstly, high responsivity of PDs at UV active range is required to maximize the conversion efficiency. Secondly, the PD response at visible range where the LED emitting light should be minimized in order to obtain negligible crosstalk. Figure 5-2 shows the responsivity spectra of PDs at -10V, -5V and 0V respectively. The peak at 365 nm with responsivity values of 0.2, 0.11, 0.06 AW$^{-1}$ for -10, -5, 0 V, which indicate the external quantum efficiency (EQE) of 73.5%, 37.4%, 20.4%, respectively. This result is comparable to previously reported GaN Schottky barrier PDs involving no dry etch process (0.18 AW$^{-1}$ at -5V [10]). A clear cut-off wavelength around

Figure 5-2. Responsivity spectra of UV PDs under -10V, -5V and 0V bias, respectively. The blue solid line represents the EL spectrum of LEDs. Figure 2 inset: The output power of LEDs as a function of operating current.
375nm has been observed. The responsivity at 365 nm is nearly two orders of magnitude higher than that at 450 nm, which makes the PD a good candidate for UV sensitive and visible-blind applications. However, a slight absorption of photons with energy smaller than the bandgap has been observed. This response probably due to the internal photoemission absorption (IPA) [19, 20] and the presence of deep level defects in the materials [21-24].

Figure 5-3. The responsivity at wavelengths 365nm and 450nm as a function of reverse bias voltage. The black solid lines represent the experimental results, while the red dash lines represent the theoretical calculation.

In order to understand the mechanism of PD's response to visible light which photon energy lower than the bandgap of the GaN material, theoretical calculations were made. Usually, several effects contribute to the responsivity. These effects can be categorized into two types: (i)
photo}
current generation due to the bulk photogeneration, and IPA [25,26], (ii) Schottky barrier lowering due to electrons trapped by the surface states at the metal/u-GaN interface, and the image forces arising from the applied electric field [27]. Taking all above effects into consideration, the responsivity $R$, which will be negative in magnitude due to the applied reverse bias, can be expressed as:

$$ R = \frac{I_{\text{illumination}}}{P}, \quad (5.1) $$

where $P$ is the incident optical power, and $I_{\text{illumination}}$ is the current under illumination given by:

$$ I_{\text{illumination}} = \exp\left(\frac{\Delta \varphi_{sb}}{kT}\right)I_{\text{dark}} - I_{ph} - I_{IPA}, \quad (5.2) $$

where $I_{ph}$ is the photogenerated current [28], $I_{IPA}$ is the internal photoemission current calculated from Vickers’ model [29], $\Delta \varphi_{sb}$ is the lowering in the Schottky barrier height due to the image forces and charge trapped at the interface. When charge trapped at the interface due to interface defects and created net charge $Q_s$, the decrease in Schottky barrier height $\Delta \varphi_{sb1}$ can be expressed as [25]:

$$ \Delta \varphi_{sb1} = \frac{Q_sd}{\varepsilon_s \varepsilon_0} \quad (5.3) $$

where $d$ is the depletion width of Schottky diode, $\varepsilon_s$ is relative dielectric permittivity of semiconductor and $\varepsilon_0$ is the permittivity of free space.

The dark current $I_{\text{dark}}$ is taken to be:

$$ I_{\text{dark}} = A A^* T^2 \exp\left(-\frac{\varphi_{sb}}{kT}\right)\left(\exp\left(\frac{qV}{nkT}\right) - 1\right), \quad (5.4) $$
where \( A \) is the area of the photodetector, \( A^* \) is the effective Richardson constant, \( \varphi_{sb} \) is the Schottky barrier height, and \( q, K, T, n \) are the electron charge, Boltzmann’s constant, the temperature, and the ideality factor, respectively.

\[
I_{IPA} \propto (h\gamma - qV_B)^2 \tag{5.5}
\]

The theoretically calculated responsivity is plotted versus the reverse applied voltage in Figure 5-3 and compared to the experimental data for wavelengths at 365 nm and 450 nm. The comparison shows a very good agreement between the theoretical and experimental data. At wavelength 365 nm, the photogeneration current is dominating the responsivity when voltage applied is low. As the voltage increases the dark current contribution to the responsivity becomes significant. This increase of the dark current is due to the lowering Schottky barrier effect [28]. Figure (2) depicts that the photogeneration current peaks at wavelength 365 nm. It is expected that all the electron traps at the interface are occupied at this wavelength [30]. However, at wavelength 450 nm no bulk photogeneration current is contributing to the responsivity and interface electron traps are not fully occupied. At this wavelength the IPA current and the dark current are dominating the responsivity [31]. In the region 365 nm < \( \lambda < 450 \) nm, the responsivity decays exponentially as the wavelength increases due to the existence of Urbach band tail [32].

Figure 2 also shows the electroluminescence (EL) spectrum of LED, the EL peak at 450nm where the PD has little absorption. The inset of figure 2 plots the LED output as a function of operating current, the output power almost linearly increased with increasing current. The light output power at 1.32 mA/mm\(^2\), 13.2 mA/mm\(^2\), 26.5 mA/mm\(^2\), 66.7 mA/mm\(^2\), 132.5 mA/mm\(^2\) and 265 mA/mm\(^2\) are 0.05mW, 0.9mW, 1.8mW, 4.5mW, 9mW, 18mW, respectively. The
measured EQE of the unpacked LED is 30%, considering the internal quantum efficiency of LED is generally exceed 90%, the estimated light trapped inside LED that contributing to the response of the PD at 1.32 mA/mm$^2$, 13.2 mA/mm$^2$, 26.5 mA/mm$^2$, 66.7 mA/mm$^2$, 132.5 mA/mm$^2$ and 265 mA/mm$^2$ are about 0.1 mW, 1.8 mW, 3.6 mW, 9 mW, 18 mW and 36 mW, respectively. Because of the great amount of light trapped inside the device, the performance of the PD under which the LED operating in the neighbor need to be investigated.

![Figure 5-4](image_url)

Figure 5-4. The electrical characteristics of PD when the current through neighbor LED were 265 mA/mm$^2$, 132.5 mA/mm$^2$, 66.7 mA/mm$^2$, 13.2 mA/mm$^2$, 6.67 mA/mm$^2$, 2.65 mA/mm$^2$ and OFF, respectively. The blue line represents photocurrent of PD at 365nm illumination with power intensity of 7.16×10$^{-4}$ W/cm$^2$. 
Figure 5-4 shows the I-V characteristics of the PD when the current applied to neighbor LED were 265 mA/mm², 132.5 mA/mm², 66.7 mA/mm², 13.2 mA/mm², 6.67 mA/mm², 2.65 mA/mm² and OFF, respectively. The current of PDs increased monotonically with increasing LED's current, which indicates the noise of PDs increased accordingly due to the response to visible LED illuminations. The blue solid line represents photocurrent of PDs at 365nm illumination with power intensity of 7.16×10⁻⁴ W/cm². The photocurrent signal can be clearly distinguished from the background noise. It should be noted that at high reverse bias (-10V ~ -20V), the photocurrent of PD at 365 nm varies more rapidly than that under LED illumination. This phenomenon is probably due to more considerable lowering Schottky barrier effect at 365 nm illumination. As seen in equation (3), at 365 nm, maximum $Q_s$ can be obtained because interface traps are fully occupied, thus lowering Schottky barrier effect became significant. However, at visible LED illumination, a much weaker photocurrent generation mechanism, IPA, is dominating. As a result, the interface traps only partially occupied, lowering of Schottky barrier plays less important role. Furthermore, the photo generated current at 365nm within depletion region are also contributing to the rapid increase of photocurrent at high voltage whereas no such photogeneration occuring at LED illumination. Therefore, less crosstalk is expected at higher reverse bias.
Figure 5-5. The responsivity spectra of photodetector under LED operating currents are OFF, 1.32 mA/mm\(^2\), 13.2 mA/mm\(^2\), 132.5 mA/mm\(^2\), and 265 mA/mm\(^2\), respectively. The reverse biases applied on photodetector are (a) 0V, (b) -10V, (c) -20V.

To further identify the operating range, the responsivity spectra of PDs as a function of various neighbor LED illuminations were shown in Figure 5-5. The current density through LED are OFF, 1.32 mA/mm\(^2\), 13.2 mA/mm\(^2\), 132.5 mA/mm\(^2\), and 265 mA/mm\(^2\), respectively. The applied biases on the PD are at: (a) 0V, (b) -10V, (c) -20V. Figure 5-5(a) shows that at 0 bias, the peak value of responsivity remained constant when current density through LED lower than 13.2 mA/mm\(^2\). However, the responsivity increased significantly when current density higher than
132.5 mA/mm² because the current generated by LED illumination lifted up the entire responsivity spectra. It should be noted that the responsivity has been lifted more at 365nm than at visible range. This phenomenon probably due to the IPA and lowering Schottky barrier effect. At 0 bias, the IPA process is dominating and I_{IPA} is a function of Schottky barrier height. At 365nm, the lowering Schottky barrier effect became significant due to the electron trapped at the interface, thus lead to higher I_{IPA} compared to visible range. When the reverse bias increased to -10V as shown in figure 5(b), the peak value of responsivity at 365 nm became close. When the bias further increased to -20V, the responsivity spectra at UV range were almost independent on LED illumination.
Figure 5-6. The photocurrent of PDs as a function of voltage at 365nm illumination with power intensity of $7.16 \times 10^{-4}$ W/cm$^2$. The photocurrent was measured under which the current applied to the neighbor LED were OFF, 1.32 mA/mm$^2$, 13.2 mA/mm$^2$, 26.5 mA/mm$^2$, 66.7 mA/mm$^2$, 132.5 mA/mm$^2$ and 265 mA/mm$^2$ respectively.

Figure 5-6 shows the photocurrent of PDs when the current through the neighbor LED were OFF, 1.32 mA/mm$^2$, 13.2 mA/mm$^2$, 26.5 mA/mm$^2$, 66.7 mA/mm$^2$, 132.5 mA/mm$^2$ and 265 mA/mm$^2$, respectively. Under 365nm illumination with power intensity of $7.16 \times 10^{-4}$ W/cm$^2$, the crosstalk is negligible either when the reverse bias exceeding 15V or the current through neighbor LED is lower than 26.5 mA/mm$^2$. The inset of figure 5-6 shows the photocurrent from reverse bias 15V to 20V for different LED operating currents, the variation of photocurrent are only 7%-5%. Under such circumstances, the LEDs and PDs can work together very efficiently for bi-directional OWC applications.

Human exposure to the UV light could be beneficial or harmful depending on the UV photon energy and dose. The single pulse maximum permissive exposure (MPE) for near UV light is 384.6 mW/cm$^2$ [34], which is ~536 times higher than the dose used in our experiment ($7.16 \times 10^{-4}$ W/cm$^2$). In this regard, there is enough room to increase UV light power to get less negligible crosstalk for bi-directional communication. Additionally, the spatial pulse position modulation (SPPM) can be applied for OWC thus the UVA illumination power could be substantially reduced [35].
Figure 5-7. The modulation ratio of PD for current through neighbor LED is OFF and 265 mA/mm$^2$, respectively.

Figure 5-7 shows the modulation capacity of PD under no bias when current through neighbor LED is OFF and 265 mA/mm$^2$. The plots indicate that modulation frequency is almost independent of neighbor LED. The 3 dB bandwidth of UV detector is 5.4 MHz, which is comparable to the bandwidth of white phosphor-based LEDs ~3 MHz [36]. The previous studies have observed that modulation capacity of GaN Schottky PD with same vertical structure was RC limited [10, 37], which suggests modulation capacity has the potential to increase to tens or hundreds MHz by reducing the device area and applying reverse bias.
5.4 Conclusions

In summary, we proposed the integration of LEDs and PDs on chip. PDs with responsivity as high as 0.2 AW$^{-1}$ at 365nm has been achieved. Excellent visible-blind property of PDs assured that it can work with LED together with illumination low to $7.16 \times 10^{-4}$ W/cm$^2$. The modulation capacity of the PD has also been studied. Our study opens a new avenue to develop LED and PD on chip for OWC bi-directional applications.

References


Chapter 6

Future works

This dissertation covering wide range studies of Photodetectors and LEDs devices based on colloidal quantum dots (CQDs) and gallium nitride (GaN) materials. For the future work, there are some ideas can be noted in the following aspects.

6.1 Novel infrared colloidal quantum dot light emitting diodes

In chapter 2 of this dissertation, we first proposed a tandem architecture of PbSe CQDs-based near-infrared photodetector which effectively suppressed dark current noise. PbSe QD is also considered as a promising material for LED device applications. The development of high efficiency, high power and low cost infrared CQDs LEDs spurred a myriad of applications in night version, sensing and optical communications. In 2012, our group proposed a PbSe CQDs LED with a multi-layer architecture, achieving external quantum efficiency (EQE) of LED of 0.73% at 1412nm [1]. L. Sun et al. have proposed PbS CQDs infrared LED through inter-dot spacing control, demonstrating a world record EQE of 2.0% for infrared CQDs LED at 1054nm [2]. Because of the long insulate ligands of CQDs and low carrier mobility of organic transport layer, infrared CQDs LED has been suffered from low current injection efficiency, electrons-holes injection imbalance and exciton ionization which eventually led to relative low LED efficiency [3]. Inspired by the pioneer work of GaN-based double heterostructure LED [4], we first propose a novel CQDs LED with a similar quantum well (QW) structure for solution-
processed CQDs LED. In the design of double heterostructure LED, the injected electrons and holes are confined to the active region between double heterojunctions which led to an pronounced increase of radiative recombination within active region. Nevertheless,
Figure 6-1 (a) The schematic illustration of single QW solution-processed LED device structure and (b) The band diagram of single QW solution-processed LED device.

Our newly proposed QDs LED architecture and its band gap diagram are shown in figure 6-1. Owing to the high band gap tunability of CQDs materials, we are be able to implement a narrow band gap CQDs sandwiched in between two wide band gap CQDs to form a quantum well (QW) structure instead of double heterojunctions proposed by Nakamura et al. [4]. There are several advantages of QW CQDs LED. First, the carriers confined in QW active region will enhance the radiative recombination efficiency of LED. Second, the hole transport layer (HTL) and electron transport layer (ETL) are also function as electron-blocking layer (EBL) and hole-blocking layer (HBL) which prevent the carrier from escaping out of the active region. Third, the purity of emission spectra is maintained by energy transfer from wide band gap CQDs to narrow band gap CQDs via Förster resonance energy transfer (FRET).
Figure 6-2: Photoluminescence spectra of narrow bandgap PbSe film, wide bandgap PbSe film and narrow bandgap PbSe sandwiched in between two wide bandgap PbSe films.

Figure 6-2 shows the preliminary results of photoluminescence (PL) spectra of PbSe CQDs for different different bandgap and sandwiched as a QW structure. Virtually no PL emission of wide bandgap PbSe CQDs can be observed from sandwiched film which demonstrated a very high energy transfer efficiency from wide bandgap CQDs to narrow bandgap CQDs. It is reasonable to assume that the electroluminescence (EL) spectra of the proposed CQDs LED will obtain the same level of emission purity as illustrated in the PL spectra of PbSe CQDs films.

If we deposit the CQDs film with monolayer accuracy, it is also possible to adopt multiple QWs structure in future work. More investigations need to be done in the future work for high efficiency infrared CQDs LED applications.

6.2 Integrate infrared LED with Si avalanche photodiodes

As discussed in chapter 5, we first integrated GaN-based LEDs and photodetectors on chip for bi-directional optical wireless communication (OWC) applications. The concept of monolithic integration of LED and photodetector can be further extended to other functional materials and to more broad wavelength range of the spectrum. In this regard, we can design a new scheme of integrated visible photodetector and infrared LED as the downlink source, whereas visible LED and infrared detector can be used as the uplink source. Since silicon avalanche photodiode (APD) has been widely used as the data receiver for OWC applications [5-7], silicon APD wafer can be
seen as the visible photodetector for bi-directional OWC application that need to be integrated with infrared LED. The solution-processed CQD PbSe infrared LED can be considered as ideal candidate to integrate with silicon APD due to their fabrication process can be implemented on almost limitless variety of substrate. Therefore, it is possible to develop the integrated silicon APD with CQD infrared LED.

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SELECTED PUBLICATIONS


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