

Real-time and on-chip surface temperature sensing of GaN LED chips using PbSe quantum dots

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PbSe quantum dots (QDs) were employed as real-time and on-chip temperature sensors to monitor the surface temperature of GaN LED chips. The temperature-dependent photoluminescence spectra were achieved and confirmed to be a good method for surface temperature sensing in a micro- to nano-region. The nanosized QD sensors did not influence the LED emission spectrum due to their infrared emission and little absorption. The surface temperature of GaN LED chips was analyzed at different working times and voltages. The temperature sensitivity characterized by the photoluminescence peak position of PbSe QDs was found to be $0.15 \text{ nm } ^\circ\text{C}^{-1}$ in a range of 30–120 $^\circ\text{C}$ and the precision was determined to be $\pm 3 \text{ }^\circ\text{C}$. The QD surface temperature sensors were confirmed to have good reversibility and repeatability.

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1. Introduction

High power GaN-based light-emitting diodes (LEDs) have been widely used in many fields such as full-color displays, traffic signals, automobiles, and solid-state lighting.^{1–3} However, the elevated operation temperature induced by Joule heating at the P–N junction limits the optical performance and lifetime of LEDs.^{4,5} The surface temperature measurement can be used to monitor the working status and to analyze the performance and defects of GaN chips. Traditionally, thermocouples are embedded into micro-channels for temperature monitoring.^{6,7} However, the incorporation of thermocouples results in the increased complexity of the fabrication and is also limited to single-spot and large-area data acquisition. This method suffers the limitation when the characteristic dimension of functional structures is reduced down to the nanometer scale.

Nanoscale thermal characterization is important for devices such as GaN LEDs and integrated circuits for evaluating their performance and durability. It is challenging to achieve nanoscale spatial resolution in temperature measurement due to the limitation of currently available measurement methodologies.^{8–10} Temperature-dependent fluorescence properties of QDs, such as

CdSe, CdTe, PbS, and PbSe QDs, have been investigated as temperature sensors, which provide the far-field non-contact optical temperature monitoring for micro- to nano-structures.^{11–16} Li *et al.* reported single CdSe QDs applied in detecting micron-level resistance temperature by measuring the visible spectrum.¹⁷ However, the visible spectrum of CdSe QDs may affect the light purity of blue GaN chips and phosphor-based white GaN LEDs.

PbSe QDs have excellent size-dependent optical properties due to their strong quantum confinement. The photoluminescence can cover the near-infrared range of 1–2.5 μm which does not interfere with the visible electroluminescence of GaN chips.¹⁸ PbSe QDs also have good temperature sensitivity for relatively small and large sizes (1–10 nm) because of their narrow band gap (the bulk band gap is only 0.28 eV), large Bohr radius ($a_B = 46 \text{ nm}$, approximately eight times larger than that of CdSe), and small effective masses ($m_c = 0.07m_0$, $m_h = 0.068m_0$, where m_0 is the electron static mass).^{19–22} These electrical and optical characteristics make PbSe QDs highly promising in the field of temperature sensing, especially for a very tiny area or a single spot (micro- to nano-scale).

A method for real-time and on-chip temperature sensing was introduced in this work for a case of surface temperature measurement of GaN LED chips. The temperature-dependent photoluminescence (PL) spectra of PbSe QDs were employed to overcome the restriction of the conventional methods. According to the calibration experiments, the surface temperature of the GaN chips obtained through the PL peak shift of PbSe QDs was analyzed at different working times and voltages. The temperature sensitivity, precision, reversibility and repeatability characterized by the PL peak position of PbSe QDs are discussed. It is a promising method to be used in the field of temperature sensing in a micro- to nano-region and crack detection of the integrated circuit.

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2. Experimental section

2.1. Chemicals

Lead(II) oxide (PbO, 99.99%), selenium (Se, 100 mesh, 99.99%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%) and tri-octylphosphine (TOP, 90%) were purchased from Alfa Aesar. Methanol, acetone, tetrachloroethylene, chloroform, hexane, and toluene were obtained from Sigma-Aldrich. All chemicals were used directly without further treatment.

2.2. Synthesis of PbSe QDs

PbSe QDs were synthesized following the method previously reported by Yu *et al.*²³ In a typical synthesis, PbO (0.892 g), OA (2.260 g), and ODE (12.848 g) were loaded into a three-neck flask, and then heated to 170 °C under a nitrogen flow. After PbO powder completely disappeared, 6.400 g of TOP-Se solution (containing 0.640 g of Se and prepared in a glove box) was swiftly injected into the vigorously stirred solution. Subsequently, the temperature was kept at 143 °C for QD growth. The reaction was quenched by injecting excess room-temperature toluene.

Prior to the application, the QD product needs to be purified to remove excess reaction precursors and solvents.^{24–26} After the original QD sample was quenched by room-temperature toluene and taken from the reaction flask, methanol solution with an equal or larger volume to the sample solution was added for extraction. The extracted PbSe QDs were redispersed in chloroform, where excess acetone was poured to precipitate the QDs *via* centrifugation. Finally, the purified QDs were dispersed in tetrachloroethylene for further measurements. All the purification procedures described above and the following measurements should be performed under the inert gas to avoid the possible oxidation.

2.3. Characterization of PbSe QDs

Transmission electron microscope (TEM) specimens were made in a nitrogen atmosphere, where two drops of the diluted sample solution were evaporated onto the carbon-coated copper grids. TEM images were taken by a JEOL Fas-TEM-2010 TEM on several different areas of each grid. A UV-VIS-NIR (Shimadzu UV-3600) spectrophotometer and a NIR spectrometer (Spectral Products SR830) were employed to record the absorption and photoluminescence (PL) spectra of nitrogen-protected PbSe QD samples, respectively.

2.4. PbSe QD deposition and sealing

For the optical measurement at different elevated temperatures of the GaN chips, the purified PbSe QDs in solution were dropped onto the partial surface of one GaN chip by an AFM probe, then the GaN chips with QDs were coated with a silicon resin (mixture of OE6630A and OE6630B with the weight ratio of 1 : 4, Dow Corning Inc.), and heated in a vacuum oven at 100 °C for 120 min. The spectral measurements were done at an initial voltage of 2.5 V. Subsequently, the voltage was varied from 2.5 V to 3.6 V. When the LED worked at a certain voltage, it was maintained for 2 min in order to make the surface temperature stable. For the experiment of repeatability and reversibility, the

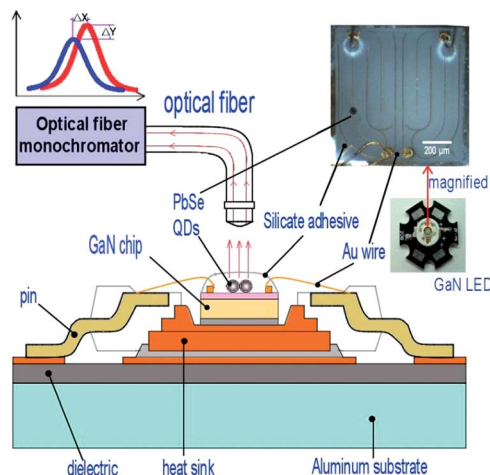


Fig. 1 Structure of non-contact temperature sensing on a GaN LED chip using quantum dots.

working bias of LEDs was increased and decreased three times to record the spectra.

Fig. 1 shows the temperature sensing schematic diagram of the GaN LED (HXGD-DZ-3w) with the PbSe QD nano-sensor. PbSe QDs were firstly dispersed in hexane. Then, this PbSe QD “ink” was deposited on the surface by an AFM (CSPM5000) tip (rinsed with ethanol, dried) using a custom-built translation stage under the optical microscope. The diameter of the sensing area was about 40 μm . When the GaN LED was working, the PL emission from PbSe QDs was collected through an optical fiber. The temperature change could be monitored according to the PL spectra.

3. Results and discussion

3.1. Optical properties of PbSe QDs

The as-synthesized PbSe semiconductor QDs had strong near-infrared emission. Fig. 2a shows the absorption and PL spectra of PbSe QDs. The first exciton absorption peak was 1204 nm while the PL peak position was 1315 nm. The PL spectrum had a perfect Gaussian shape and clearly indicated a pure band-gap emission. Fig. 2b shows a TEM image of PbSe QDs with narrow size distribution. The average particle diameter of the PbSe QD sample was 3.7 nm.

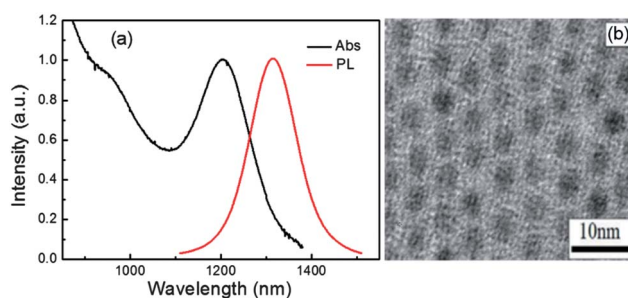


Fig. 2 (a) Room-temperature absorption and photoluminescence spectra of the as-prepared PbSe QDs; (b) TEM image of the PbSe QDs showing an average diameter of 3.7 nm.

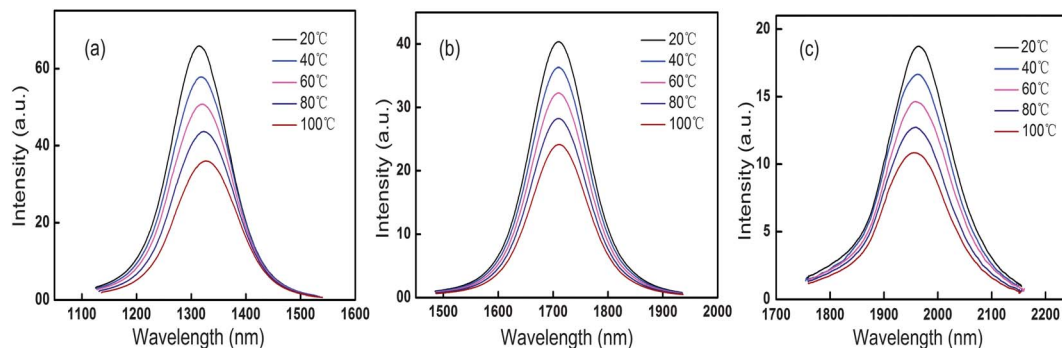


Fig. 3 Temperature- and size-dependent photoluminescence spectra of PbSe QDs with the particle sizes of 3.7 nm (a), 5.1 nm (b) and 6.0 nm (c).

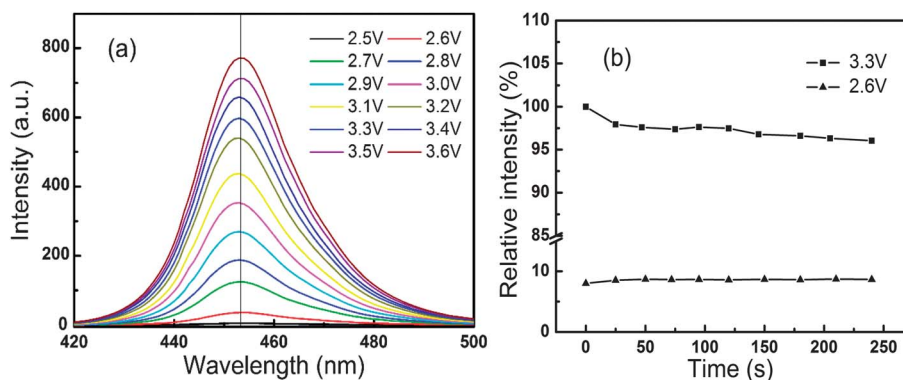


Fig. 4 (a) Electroluminescence (EL) spectrum of the GaN LED as a function of operating voltage (from 2.5 to 3.6 V); (b) EL intensity of the GaN LED as a function of working time at two operating voltages, 3.3 and 2.6 V.

The temperature- and size-dependent optical spectra of PbSe QDs have been investigated in the previous work.¹⁶ As illustrated in Fig. 3a, when the temperature increased, the corresponding PL spectra of 3.7 nm PbSe QDs shifted to red, accompanied by a gradual decrease of intensity. For the 5.1 nm PbSe QDs, no obvious shifts could be observed (Fig. 3b). When PbSe QDs became further larger (e.g., 6.4 nm in Fig. 3c), the PL spectra switched to blue shifts with the increase of temperature. It can be seen that with the increase of particle sizes, the initially positive temperature coefficient becomes zero, and then negative. Therefore, PbSe QDs with medium particle size were not suitable for temperature sensing and the 3.7 nm PbSe QDs were employed for example in the following temperature detection of LED chips.

3.2. Optical properties of GaN chips

Fig. 4 shows the electroluminescence (EL) spectrum as a function of operating voltage from 2.5 to 3.6 V and the EL intensity as a function of working time for the GaN LED with a PbSe QD temperature sensor (the black spot on the bottom left of the LED). The luminous intensity of the LED increases with the increase of working bias, while the peak wavelength merely changes as shown in Fig. 4a. These results were the same for the “clean” GaN LED without the QD sensor (data not shown). This means that the existence of the PbSe QDs did not affect the EL optical properties of the GaN LED chips.

The thermal stress and degradation of LEDs have been studied and it is well known that the luminance and lifetime decrease when LEDs are operated at elevated temperatures.²⁷ It has been also reported that localized Joule heating can degrade the brightness homogeneity and this effect becomes worse as the device temperature is higher (at higher working voltage) as shown in Fig. 4b. The thermal distribution and surface temperature of the light-emitting area were measured from the front side of each LED chip as shown in Fig. 5 by using an infrared (IR) thermal image camera (FLIR T250). The IR thermal images were captured every 10 seconds after the LED was operated at a bias of 3.4 V (Fig. 5, top panel). The thermal distribution at different voltages is also shown in Fig. 5, middle panel. It can be seen that the thermal distribution is highly localized around the light-emitting areas (chips). The relationship between the surface temperature and the working time or operating voltage is given in Fig. 5, bottom panel. The temperature increases with the increase of working time, and becomes stable after two minutes. The temperature also increases with the working bias. These results were the same for the “clean” GaN LED without the QD sensor (data not shown).

3.3. Temperature sensing and calibration of PbSe QDs

Fig. 6a shows the full emission spectrum (from 400 to 1500 nm) of the GaN chip coated with PbSe QDs at a bias of 3.2 V.

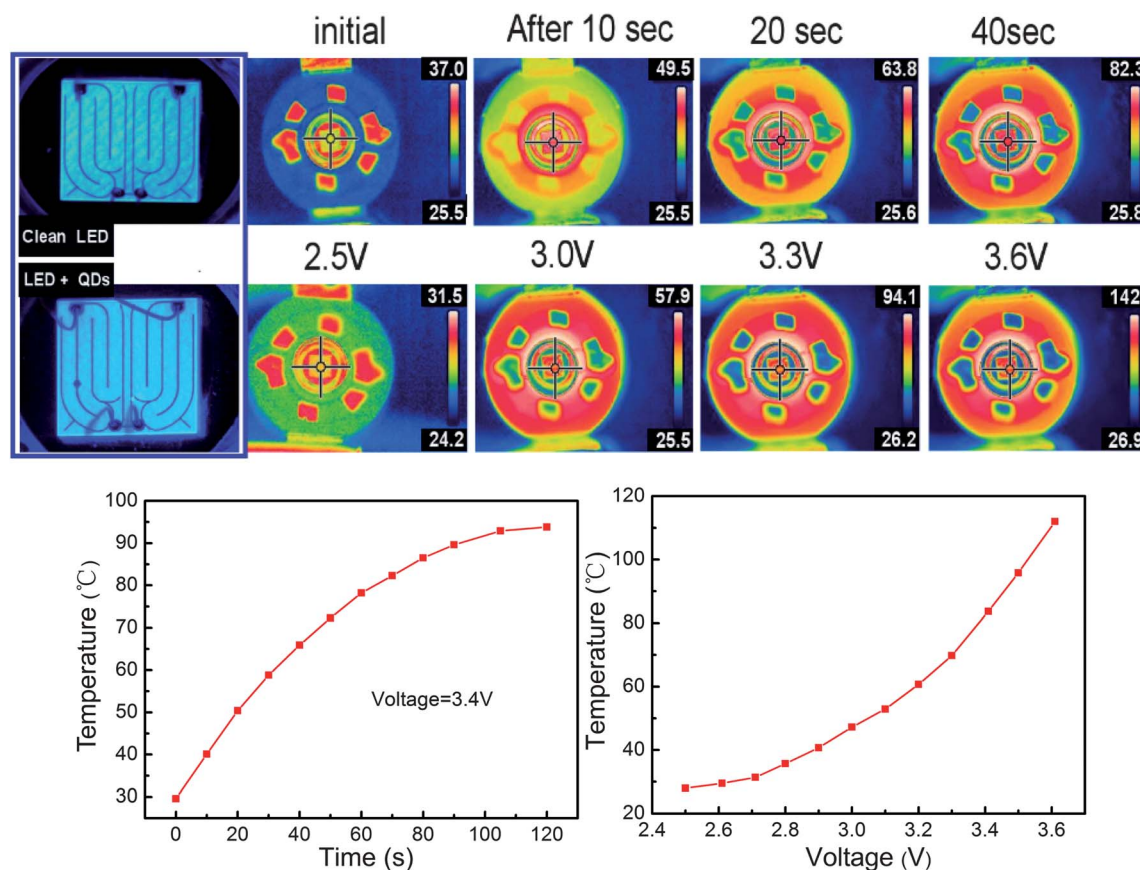


Fig. 5 Thermal images of the thermal distribution of the GaN LED at different working times (3.4 V, top panel) and operating voltages (2.5 to 3.6 V, middle panel). The bottom panel shows that the chip surface temperature stabilizes after 2 min (left), and the equilibrium surface temperature at different operating voltages (right).

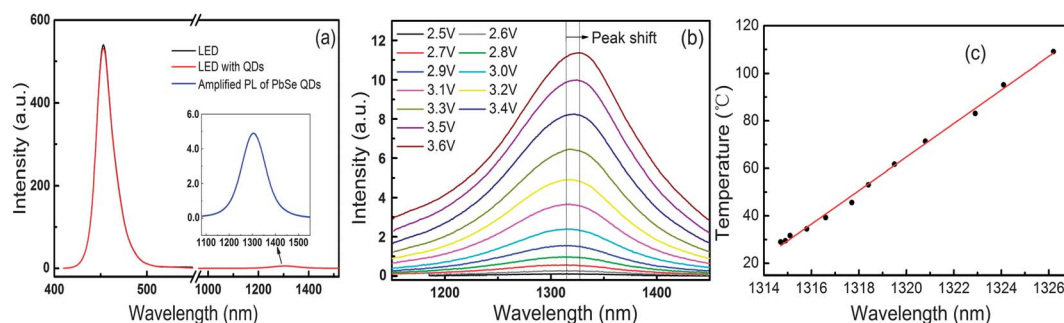


Fig. 6 (a) EL spectra of GaN LED with the 3.7 nm PbSe QD sensor at the bias of 3.2 V (the inset shows magnified PL signal from QDs); (b) PL spectra of PbSe QDs on the GaN chip at different operating voltages, a red shift is observed; (c) the temperature–PL peak position relationship of the QD temperature sensor.

Although the GaN chips emitted strong visible spectral light at 453 nm, the near-infrared light (1315 nm) from PbSe QDs could be still observed due to the spectral interval (Fig. 6a, inset).

A little amount of the blue emission from the GaN chip was absorbed by the coated PbSe QDs, and excited their near-infrared emission (Fig. 6a, inset). This near-infrared PL emission was found to be temperature-dependent. When the increased bias induced the increase of the LED surface temperature, the corresponding near-infrared PL spectrum of this 3.7 nm PbSe QDs would shift to red.¹⁶ Experiments showed that when the voltage increased from 2.5 to 3.6 V, the PL peak

changed from 1314.7 to 1326.9 nm (Fig. 6b). The PL spectra of PbSe QDs on the GaN chip varied with the voltage (in fact with the surface temperature of the chip) in the same trend (red shift) as the temperature-dependent absorption spectra of colloidal PbSe QDs in solution.^{16,28} Though both the PL peak intensity and position of PbSe QDs are temperature-dependent, PL intensity relies on many other factors such as the measurement time and the spectrometer calibration. It is difficult to use the PL intensity to detect the temperature. Therefore, the temperature-dependent band shift (PL peak position change) was employed in the following calibration and temperature sensing.

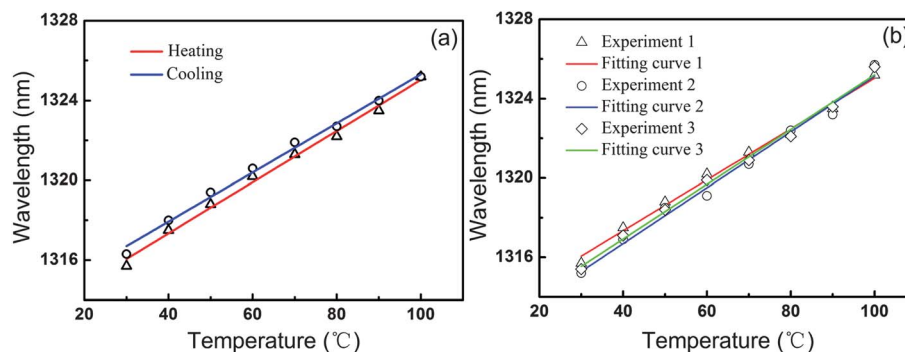


Fig. 7 Tests for reversibility (a) and repeatability (b) of the 3.7 nm PbSe QD temperature sensor on GaN chips.

In order to correlate the actual chip temperature and the PL spectrum shift, we used a thermal image camera to measure the local temperature where PbSe QDs were deposited; at the same time, a fiber-optic spectrometer was used to detect the near-infrared PL peak wavelength of PbSe QDs. The relationship between the temperature and peak wavelength is shown in Fig. 6c.

It can be seen from Fig. 6c that the PL peak position of the examined PbSe QDs corresponds almost linearly to temperature in a range of 30–120 °C. The peak shifted from 1315 to 1326.9 nm. The corresponding sensitivity of the PL peak shift thus can be found to be $0.15 \text{ nm } ^\circ\text{C}^{-1}$, which is higher than that of CdSe QDs.¹⁷ This PL peak position temperature sensitivity is also the same as the absorption peak position for PbSe QDs with a similar size reported before.¹⁶ The local temperature of the LED chip *versus* the PL peak position (wavelength) was obtained in the following equation as shown in the fitting curve in Fig. 6c,

$$T (^\circ\text{C}) = 6.908\lambda (\text{nm}) - 9054.5 \quad (1)$$

where T and λ are the local temperature (Celsius) and the PL peak wavelength (nm) of the 3.7 nm PbSe QDs, respectively.

3.4. Precision, reversibility, and repeatability of PbSe QD temperature sensing

The multiple heating and cooling cycles were performed to investigate the reversibility and repeatability by increasing and decreasing the bias as shown in Fig. 7a. It was found that the temperature-induced shifts were well reversible in the cycles. A further examination was made to examine the repeatability of the PbSe QD-sensor as shown in Fig. 7b. The repeatability enables PbSe QDs for on-chip and real-time temperature sensing of GaN chips.

Through the repeated temperature monitoring experiments with PbSe QDs, we collected the experimental points and compared them with eqn (1). It was found that the precision was within $\pm 3^\circ\text{C}$, and the relative deviation was less than 5%.

4. Conclusions

A real-time and on-chip temperature sensor for the GaN chip was investigated based on the temperature-dependent emission spectral shift of PbSe QDs. Near-infrared QDs were deposited on

the surface of the GaN chip and exhibited a linear response in a range of 30–120 °C, in which the temperature sensitivity was found to be $0.15 \text{ nm } ^\circ\text{C}^{-1}$ and the precision was measured to be $\pm 3^\circ\text{C}$. The reversibility and repeatability experiments of the on-chip sensor confirmed that PbSe QDs were promising candidates as real-time and *in situ* micro- to nano-scale temperature sensors of the GaN chip. Furthermore, the nanometer-size QD sensors may be employed to detect the temperature and its changes for an individual element in a chip with thousand or million units. This could be significant in performance or defect analysis of extremely small elements in a nanodevice.

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