Research Paper

Colloidal Quantum Dot Photodiodes with Ligand-dependable and Photolithographic Patterning Technique

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Abstract

We patterned a quantum dot (QD) layer via photolithography and fabricated a QD photodiode using an inverted QD-light emitting diode (LED) structure. It shows behavior similar to normal photodiodes in terms of photoresponse. However, the dark current was reduced by 1/10 and the photocurrent increased 10 times in comparison with unpatterned QD photodiodes. This study is beneficial for creating multicolor QD sensors and simultaneously integrating LEDs and photosensors on the same structure. It means that the sensor works while blinking time of LED and it could be applied to advanced display technique.

Keywords: Colloidal quantum dot, Patterning, Photodiodes, Photolithography, Layer-by- Layer self-assembly

I. Introduction

Many studies have focused on the ability to detect light over a broad spectral range for use in several technological applications, including imaging, sensing, spectroscopy, and communication [1-4]. Broadband detection through simultaneous detection from multiple devices on a single chip can speed up data processing through remote control and data throughput [5]. Currently, broadband detection is performed using materials with broad absorption wavelengths, such as GaN, silicon, and graphene. However, the different colors are not distinctly visible. Meanwhile, quantum dots (QDs), which are semiconductor nanocrystals with size-dependent tunable band gaps, are considered to be a novel, promising material for use as smart photosensors in the near future. Among their advantages, in particular, excellent color discrimination, and even absorption and emission of wavelengths, can be controlled, depending on the size, from the UV (ultraviolet) to NIR (near infrared) range [6-10]. This means that broadband photodetection is possible using QD properties, which can be tuned to the desired wavelength. However, there have been few studies on broadband photodetection using QDs. Recently, a lamination method has been proposed for broadband detection [11]. However, there is a concern that signals can be mixed and QDs of different sizes will be quenched simultaneously. In this context, patterning of QD layers is an alternative method, in that it is possible to fabricate a sensor that can be easily controlled remotely without signal crosslinking. In addition, this method can be applied regardless of the QD material; thus, various materials can be used.

We have shown that assembly of QDs is compatible with photolithography, which enables the formation of high-resolution, large-scale patterns of QDs with ease [9]. We have demonstrated vertical-type QD photodiodes for high-speed image sensors using the interaction of a metal oxide with ligands [12]. In this study, we combined our previous research to fabricate patterned QD photodiodes. In particular, an inverted QD-light emitting diode (LED) structure was used and QD photodiodes were patterned. Under the illumination of light with a wavelength of 638 nm, the photocurrent increased up to several μA and the minimum current voltage, or open circuit voltage, shifted by 0.7 V. This means that the patterned QD photodiodes fabricated on the

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inverted QD-LED structure can operate as normal photodiodes and may be applicable as multiple-color photodiodes.

II. Materials and methods

QD pattern using photolithography

Figure 1(a) schematically illustrates the process of patterning QDs on a substrate using photolithography and charge-assisted layer-by-layer (LbL) assembly for the device fabrication process. An ITO/glass substrate was spin-coated with photoresist (GXR601) and exposed to a UV lamp for the photosensitized reaction. After developing and rinsing with D.I. water, UV/O$_3$ or O$_2$ plasma was induced on the patterned film for surface activation, so that the surface of the film became negatively charged. Poly (diallyldimethylammonium chloride) (PDDA) is known as a polyelectrolytes and is positively ionized when it is dissolved in water. QDs terminated with carboxylic acid and PDDA can be used together to deposit QDs self-assembled by electrostatic force [9]. This method can control the QD thickness by repeatable deposition of each QD pattern. Figure 1(b) demonstrates the clear patterns of QDs by photolithography and the charge-assisted self-assembly method through scanning electron microscope images.

More details of the patterning of the QD layers can be found in our previous study [9]. In addition, detailed information concerning the photolithography is given below for reference. GXR601 and AZ300MIF (AZ Electronic Materials, USA) were used as a positive PR and developer, respectively. Spin-coating the PR was carried out at 5000 rpm, after which the substrate was soft-baked on a hot plate. UV exposure to the sample with a mask was carried out using a MIDAS mask aligner MDA-400 M equipped with a Hg arc lamp.

Device fabrication

Depleted heterojunction photodiodes with double-charged blocking layers were fabricated with a solution-processed ZnO electron transport layer (ETL)/hole blocking layer and a MoO$_x$ hole transport layer (HTL)/ electron blocking layer, respectively. More details regarding the solution-processed ZnO layer can be found in our previous study [12]. CdSe/ZnS QDs were used and patterned on the ZnO surface by photolithography. The photoluminescence (PL) and absorption peaks of these QDs are 638 and 633 nm, respectively. The transfer time for these QDs was only 0.41 ns. In the sensor, a fast carrier transfer time is advantageous for the speed and efficiency of carrier extraction. Therefore, it was applied to this device to take advantage of these characteristics of the QDs. The QDs were coated using the method mentioned above. The process was repeated until a thickness of approximately 50 nm was reached. Poly-TPD was dissolved in 1,2-dichlorobenzene with a density of 1 wt%. The poly-TPD solution was spin-coated on to the device at 2000 rpm for 15 s. The MoO$_x$ HTL and Au anode were continuously deposited
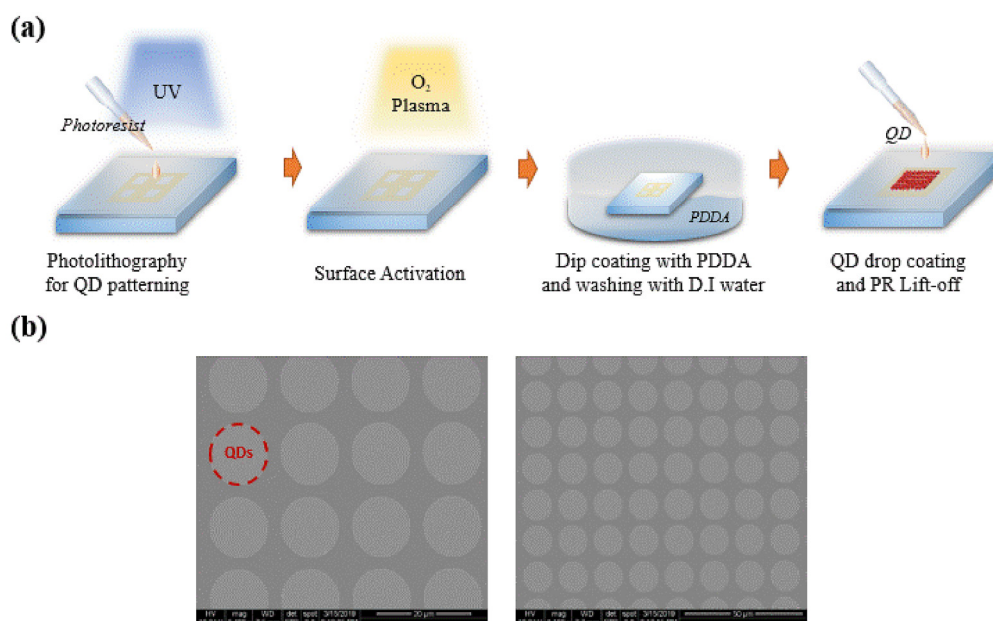

Figure 1. (Color online) (a) Photolithographic QD patterning process and (b) SEM images.

through a thermal evaporator, with thicknesses of 6 and 100 nm, respectively. The device was stored in a nitrogen glove box to prevent oxidation.

Device characteristics measurements

We measured the current-voltage (I-V) characteristics, shown in Fig. 3, where a 638-nm laser diode (L638 P040, Thorlabs) was used as the device illumination source. The output of the photogenerated current was measured using a Keithley 6487. The active area of the device was 2×2 mm^2, and the focused beam spot size was 3.46 mm^2, as measured by a Beam Profiler (LBP-1-USB, Newport). The light was incident perpendicular to the device, and the incident power of the laser on the device surface was 100 μW.

To measure the photoresponsivity, we used a spectral incident photon to current efficiency measurement system (K3100, McScience). A xenon lamp was used as a light source (K240 XE300, McScience). Similar to the I-V measurements, the incident direction of light was perpendicular and was incident on the device surface through a slit.

III. Results and discussion

Figure 2 shows the schematics of the device, indicating a vertically structured photodiode. The structure differs from that in our previous study with QD photodiodes in that it introduces an electron blocking layer, i.e., poly-TPD, and a patterned active layer [12]. ZnO was used as an electron transport layer (ETL); in our previous study, we demonstrated that ZnO can help extract carriers from QDs to the contact layer [12]. QDs were only coated in the active area using the photolithographic patterning method; the size of the active area was 2×2 mm^2. To ensure formation

of an active layer with QDs, the LbL assembly process was repeated four times each to make the active layer sufficiently thick. Poly-TPD is known as a hole transport and electron blocking material, and it was chosen to block electrons, which can cause leakage current in the devices. The MoO$_x$/Au contact, which is also used as a HTL, helps to extract holes from the QDs. The insertion of a MoO$_x$ thin film between the QD active layer and anode improves device performance [13]. In terms of energy flow in the device, which has a vertical structure, electrons generated in the QDs were extracted to ITO through ZnO, and holes were extracted to Au through Poly-TPD and MoO$_x$ [12]. The high-work function MoO$_x$ film pins the Fermi level of the anode contact, which can impede the extraction of holes from QDs [13]. The energy transfer mechanism is described in detail with an energy diagram in previous reports [9,12].

In terms of applications, the structure as well as most of the materials used to fabricate the device are the same used for an inverted QD-LED that we report previously [9]. The type of QD is the only difference in the QD-LED and QD photodiodes. QDs with different structures should be used because a QD's quantum well structure is strongly affected by the carrier movement. In the LED, QDs are used with a relatively long photon lifetime because recombination should be efficiently generated in the active layer. However, in terms of a sensor, the carrier extraction should be performed in the active layer, so the structure of the QD used in the sensor must be different from that used in the LED. The time-resolved PL data related to the applications according to the type of QD are described in detail in our previous reports [9,12]. Therefore, this sensor structure not only can be used as an LED by changing the type of QD, but it also
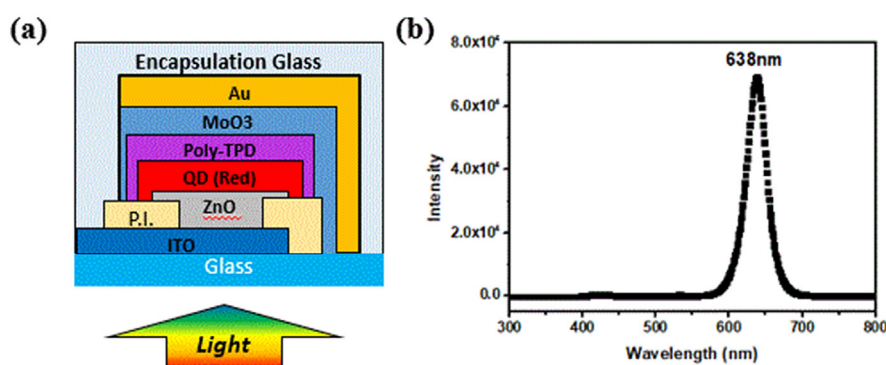

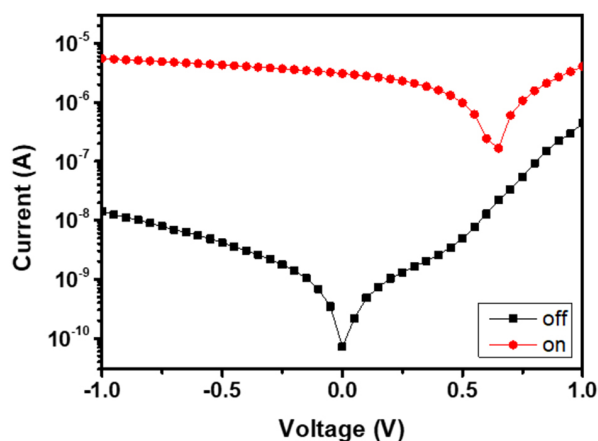**Figure 2. (Color online) (a) A schematics of the device and (b) photoluminescence of CdSe/ZnS (excited by 266 nm).**

Figure 3. (Color online) Leakage current and photo-current of QD photodiodes as light existence.

Figure 4. (Color online) Comparison the spectral responsivity of devices with QD's absorption.

can drive an LED and sensor with one device using QDs patterned by photolithography. The structure and characteristics of the LED have been discussed in detail in a previous report, and we have examined the optoelectronic characteristics of photodiodes.

When our photodiodes were exposed to light, as shown in Fig. 3, the I–V characteristics of the QD photodiodes are clearly those of a Schottky diode and exhibit an increase in photocurrent of approximately three orders of magnitude at -1 V. As a result, not only was the leakage current reduced by approximately 1/10 but also the photocurrent increased by an order of magnitude when similar light intensity was applied; the light intensity was 110 μW in a previous study. This shows that the responsivity is increased; the measured spectral responsivity increased by ten-fold as compared with that in the previous study. By patterning the active area, the leakage current can be reduced as the area is narrowed. In addition, poly-TPD causes the leakage current to decrease by blocking electrons diffusing in opposite directions, and the photo-current also increases because the number of carriers to be extracted shows a relative increase because the blocked electrons have exited in the forward direction.

There are two different thresholds, depending on whether the devices are exposed to light or not. With exposure to light, the voltage of the minimum current, or the open circuit voltage, shifts toward a positive bias because of the photovoltaic effect. In the dark, the threshold is 0 V because there are no other external factors. When the light is incident on the surface of the devices, however, it could change the internal energy barrier as a result of excess carriers. After applying light, the threshold voltage is 0.65 V, which
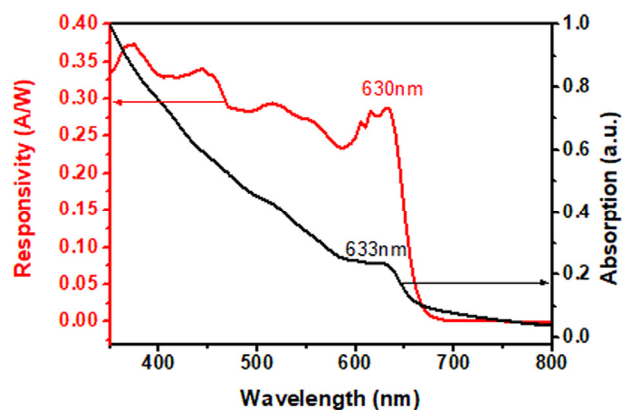
is shifted because of the photovoltaic effect, and the amount of the shift can be affected by the light intensity [12]. Here, we used a 638-nm wavelength laser diode as the incident light source, and the intensity of the light was fixed at 100 μW. The light source was chosen so that its wavelength would be close to that of the absorption peak of the QDs (Fig. 4). The wavelength-dependent photoresponsivity of our device was measured under zero applied bias, from which we observe the photocurrent converging to zero when the incident photon energy is lower than that of the 630-nm wavelength. There appears to be correspondence between the spectral responsivity and the absorption spectrum of QDs, which suggests that the photoresponsivity of our device originates from excitation of QDs and subsequent exciton dissociation. The power of the lamp was not as uniform as the wavelength because a xenon lamp was used with a monochromator, which may be related to the fluctuation of the curve in the 350–600 nm range. The reason that the responsivity in the 300-400 nm region is low is because of absorption by the ITO/glass substrate. However, there is clearly a peak similar to the absorption peak of QDs and in the cut-off range. Oertel et al. presented a study of a colloidal quantum dot photodiode that has a structure similar to that of our device; its dark current was approximately 10^{-4} A at 1 V [10]. Their leakage current was approximately 10^{-4} A larger than our value of leakage current, 10^{-8} A. The responsivity of our device was also approximately 30% higher than that reported by Oertel et al. because the leakage current decreased and the photocurrent increased as a result of the active layer pattern and the blocking of e-diffusion with application of poly-TPD.

IV. Conclusions

We proposed a method of broadband photodetection capable of mass and large-scale processing using a photolithographical QD patterning method and proved the possibility by showing that the patterned QD photodiode operates well as a normal photodiode. One thing to note is that the patterned QD photodiode was fabricated on the same structure as the well-known inverted QD-LED. This means that QD photodiodes and QD-LEDs can be fabricated on the same structure by adapting the QD patterning method. We expect that such a result can be useful for future smart devices.

Acknowledgements

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