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Quantum-dot light-emitting diodes utilizing CdSe/ZnS nanocrystals embedded in TiO₂ thin film

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Quantum-dot (QD) light-emitting diodes (LEDs) are demonstrated on Si wafers by embedding core-shell CdSe/ZnS nanocrystals in TiO₂ thin films via plasma-enhanced metallorganic chemical vapor deposition. The *n*-TiO₂/QDs/*p*-Si LED devices show typical *p*-*n* diode current-voltage and efficient electroluminescence characteristics, which are critically affected by the removal of QD surface ligands. The TiO₂/QDs/Si system we presented can offer promising Si-based optoelectronic and electronic device applications utilizing numerous nanocrystals synthesized by colloidal solution chemistry. © 2008 American Institute of Physics. [DOI: 10.1063/1.3028070]

Semiconductor nanocrystal quantum dots (QDs) synthesized via colloidal solution chemistry have been studied extensively for optoelectronic device applications such as light-emitting diodes^{1–3} (LEDs) and lasers⁴ due to their size-tunable optical properties and chemical flexibility.^{5,6} For such device applications, colloidal nanocrystal QDs have been hybridized mainly with a soft-material (e.g., polymer) matrix.^{1,2} On the other hand, the system of nanocrystal QDs embedded in solid materials such as oxides can be a promising alternative vehicle for various optoelectronic and electronic memory device applications.^{7,8} Nanocrystal QDs embedded in oxide can be more electronically and chemically stable and mechanically robust than those in a polymer matrix. Moreover, the system of nanocrystal QDs embedded in oxide is compatible with Si technology. Thus, it can be utilized for electronic and photonic integrated circuits and low-cost optoelectronic devices on Si. Recently, Eisler *et al.*⁴ reported optically pumped lasing characteristics from CdSe nanocrystals stabilized in a sol-gel derived titania matrix, indicating that colloidal nanocrystals in oxide could be used as an active optical gain medium. However, neither electroluminescence (EL) nor electrically pumped lasing characteristics have so far been demonstrated by the use of colloidal nanocrystal QDs embedded in oxide.

In this letter, we demonstrate QD LED devices utilizing core-shell CdSe/ZnS nanocrystals embedded in a TiO₂ thin film by plasma-enhanced metallorganic chemical vapor deposition (PEMOCVD). CVD has a number of advantages over other deposition techniques including a sol-gel method for compatibility of Si technology and increasing the integration levels in the Si process. As shown in Fig. 1(a), the LEDs can be formed through a simple manner when the QDs on a *p*-type Si substrate are embedded in a ~50 nm thick TiO₂ thin film, which is inherently an *n*-type semiconductor. For embedding QDs in TiO₂, the thermal stability of QDs and

the removal of organic ligands on QD surface are the key concerns.^{9,10} This is because the evaporation rate of nano-sized (~5 nm) QDs can be significantly increased due to the well-known Kelvin effect.¹¹ In addition, organic residues can create interfacial defects and act as a current blocking layer that prohibits carriers from injecting into QDs. In this work, we applied H₂ plasma treatment and replaced trioctylphosphine oxide (TOPO)/hexadecylamine (HDA) ligands, in which QDs were synthesized, with 3-mercaptopropionic acid (MPA). It can be easier to decompose MPA thermally than TOPO/HDA because of its lower boiling temperature (~110 °C). We also investigated QD stability while removing ligands by H₂ plasma and embedding QDs in TiO₂ film by PEMOCVD.

Colloidal core-shell CdSe/ZnS QDs were synthesized via pyrolysis. All chemicals used in the experiments were of the highest purity grade available and were purchased from Sigma-Aldrich. A flask containing 12.7 mg of CdO and 160 mg of dodecanoic acid was heated to 200 °C under an Ar environment before being charged separately with 2.5 g of TOPO and HDA when the temperature reached 200 °C. The resulting mixture was heated to a desired CdSe synthesis temperature (220–280 °C) before the Se solution [80 mg Se powder dissolved in 2 ml of trioctylphosphine (TOP)] was quickly injected. After injection, the temperature was main-

FIG. 1. (a) Schematic of the LED structure with nanocrystal QDs embedded in a TiO₂ thin film and (b) HRTEM lattice image of TOPO-capped CdSe/ZnS QDs synthesized at 240 °C.

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FIG. 2. PL spectra of reference TOPO-QDs and QDs embedded in TiO_2 thin films at various deposition temperatures of 100, 200, 300, and 400 °C for 10 min. The reference TOPO-QDs were synthesized at 260 °C.

tained for 3 s and then was dropped back to 200 °C. For the formation of ZnS shell, a mixture of 1 ml diethylzinc, 250 μl hexamethyldisilathiane, and 2 ml TOP was injected dropwise to the reaction mixture at 200 °C, which was vigorously stirred for 1 min. Upon injection, the resulting mixture was allowed to reach a low temperature of 180 °C, while stirring was maintained for 1 h. The flask was then cooled to room temperature and the TOPO-capped CdSe/ZnS QDs (referred to here as TOPO-QDs) were collected. To replace the TOPO ligands of QDs with MPA, 500 μl TOPO-QDs in chloroform was mixed with 30 ml methanol and 1 ml MPA under an Ar environment. The stirred mixture was heated and refluxed at $\sim 60\text{--}65$ °C for 6 h. The solution was then centrifuged to obtain the MPA-capped CdSe/ZnS QDs (referred to here as MPA-QDs).

For LED fabrication, the QDs were spread on *p*-type Si wafers via spin coating. H_2 plasma cleaning was performed at a rf plasma power of 40 W under a chamber pressure of 1.2 Torr. The mixed gas of $\text{Ar}(90\%)/\text{H}_2(10\%)$ was supplied at a rate of 200 SCCM (SCCM denotes cubic centimeter per minute at STP). TiO_2 thin film was deposited over QDs/Si by using titanium tetra isopropoxide ($\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$) as a titanium precursor, bubbled with an Ar flow of 50 SCCM at 30 °C. The rf plasma power, chamber pressure, O_2 flow rate, and total gas flow rate were fixed at 40 W, 1.2 Torr, 30 SCCM, and 200 SCCM, respectively. Standard photolithography and wet chemical etching procedures were used for mesa LED devices with diameters of 200 and 300 μm . A 0.1 μm thick indium tin oxide transparent film was deposited at 150 °C by pulsed-laser deposition to serve as top contact and current spreading layer.

Figure 1(b) shows a typical transmission electron microscopy (TEM) lattice image of TOPO-QDs synthesized at 240 °C. A TEM study revealed that QDs had a high microstructural quality and an average size of ~ 5 nm. Figure 2 shows the photoluminescence (PL) (a 325 nm helium-cadmium laser excitation) spectra of TOPO-QDs on Si (referred to here as reference TOPO-QDs), as well as QDs embedded in TiO_2 thin films at various deposition temperatures of 100, 200, 300, and 400 °C for 10 min. The PL intensity of QDs was decreased when they were embedded in ~ 200 nm

FIG. 3. PL spectra of reference TOPO-QDs and QDs exposed under an H_2 plasma environment at various temperatures of 100, 200, and 300 °C for 10 min.

thick TiO_2 . This can mainly be due to the absorption of incident laser beam (325 nm) by TiO_2 film. However, the possibility of interfacial defects between QDs and TiO_2 cannot be ruled out. The QDs embedded in TiO_2 at 200 °C showed better PL efficiency than those at 100 °C. The substrate temperature of 100 °C may not be high enough to decompose surface ligands (TOPO) completely because the boiling temperature of TOPO is ~ 201 °C. The residues of TOPO can create interfacial defects between QDs and TiO_2 , which can trap photoexcited carriers. Although a high substrate temperature will be advantageous for the removal of TOPO, this can cause the thermodynamic instability of QDs. Indeed, the PL peak (563 nm) of QDs embedded at 200 °C was slightly blueshifted with respect to that (570 nm) of the reference QDs while the PL peak of those QDs embedded at 100 °C did not change. The QDs embedded at 300 °C not only showed further blueshifted PL peak (543 nm) but also a significantly decreased PL intensity. Finally, a discernable PL peak could not be observed at all at 400 °C, indicating that the well-known Kelvin effect was very pronounced for such small CdSe/ZnS QDs. When the surface ligands (TOPO) were removed above ~ 200 °C, QD surface would be easily oxidized upon exposed O_2 during TiO_2 deposition.^{12,13} Moreover, oxide forms could be desorbed from the QD surface.¹² Thus, the PL peak position was blueshifted and the PL efficiency was significantly deteriorated due to the reduced effective QD size and the increased surface defects. By contrast, when the QD surface was stabilized by TOPO, the surface oxidation process could be significantly restrained. We also note that the tendency of PL results was not affected by luminescence intermittent characteristics of CdSe/ZnS QDs because the samples were prepared from the same batch of QDs and had a similar shell structure each other.

Figure 3 shows the PL spectra of the TOPO-QDs exposed under an H_2 plasma environment at various temperatures of 100, 200, and 300 °C for 10 min. The QDs treated at 100 °C not only had the same PL peak position but also showed a PL efficiency as high as that of the reference TOPO-QDs. As the temperature increased to 200 °C, the PL efficiency dropped dramatically because of the thermal and

FIG. 4. Typical I - V curves of plasma-treated TOPO-QD and MPA-QD LEDs (300 μm mesa). Inset shows the I - V curve of TOPO-QD LED. The CdSe/ZnS QDs were synthesized at 240 $^{\circ}\text{C}$.

plasma damages of QDs. At 300 $^{\circ}\text{C}$, the PL efficiency was further decreased and the PL peak was blueshifted to 545 nm. Therefore, the H_2 plasma treatment temperature has been determined at 100 $^{\circ}\text{C}$ for LED fabrication.

Figure 4 shows the current-voltage (I - V) curve of the TiO_2 /QDs/Si device structure previously presented in Fig. 1(a) with the TOPO-QDs treated by H_2 plasma for 10 min (referred to here as plasma-treated TOPO-QD LED). The QDs synthesized at 240 $^{\circ}\text{C}$ were embedded in a ~ 50 nm thick TiO_2 film at 200 $^{\circ}\text{C}$, and the mesa diameter of devices was 300 μm . We note that the typical I - V characteristics of p - n diodes could be observed. Moreover, the QDs yielded efficient EL. Figures 5(a) and 5(b) show the visible-light EL images of the plasma-treated TOPO-QD LEDs of 200 and 300 μm diameter mesas, respectively, which were taken by a charge-coupled device (CCD) camera. The images confirmed that EL occurred uniformly from QDs spread over Si. Meanwhile, very poor and unstable EL characteristics (not shown here) were observed from the LEDs with TOPO-QDs, which were not cleaned by H_2 plasma (referred to here as TOPO-QD LEDs). For the TOPO-QD LEDs, the TOPO ligands of QDs were just thermally decomposed while the

FIG. 5. (Color online) CCD images of the EL characteristics of (a) 200 μm mesa at 15 V and (b) 300 μm mesa at 30 V of plasma-treated TOPO-QD LEDs, and (c) 200 μm mesa at 18 V and (d) 300 μm mesa at 25 V of MPA-QD LEDs.

substrate temperature increased to 200 $^{\circ}\text{C}$ for TiO_2 deposition. As seen in the inset of Fig. 4, the current of the TOPO-QD LEDs was approximately three orders of magnitude smaller than that of the plasma-treated TOPO-QD LEDs at forward bias. This might be due to the residues of TOPO ligands acting as a current blocking layer. As a result, carriers were prohibited from injecting into QDs and the EL efficiency dropped significantly. In contrast, the LEDs with MPA-QDs (referred to here as MPA-QD LEDs) showed good EL characteristics without H_2 plasma treatment, as seen in Figs. 5(c) and 5(d). The MPA-QD LEDs showed an even larger forward current than the plasma-treated TOPO-QD LEDs (Fig. 4). This implies that MPA ligands were decomposed effectively at 200 $^{\circ}\text{C}$ because of their low boiling temperature (~ 110 $^{\circ}\text{C}$). It should be emphasized that the EL efficiency of the MPA-QD LEDs was also better than that of the plasma-treated TOPO-QD LEDs although the PL efficiency of the MPA-QDs was slightly lower (not shown here).

In summary, we demonstrated QD LED devices on Si wafers by embedding CdSe/ZnS nanocrystals in a TiO_2 thin film. It was very important to remove the surface ligands of QDs effectively for the high performance of LEDs. The H_2 plasma cleaning procedure at 100 $^{\circ}\text{C}$ was effective in realizing efficient EL characteristics from TOPO-QDs. By exchanging TOPO ligands with MPA, QD LEDs yielded a better EL efficiency even without H_2 plasma treatment because of the more effective thermal decomposition of MPA. The results indicate the feasibility of promising large-area Si-based optoelectronic device applications based on the TiO_2 /QDs/Si system.

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