Blue light emission properties and device applications of the nanostructured materials

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Abstract The blue light emission materials and devices have potential applications in the optoelectronics. In this paper, we mainly review the developments of the blue light emission properties, luminescent mechanism and device applications of various nanostructures in recent 3–5 years, such as *nc*–ZnO, *nc*–GaN, *nc*–CdS and *nc*–Si, *etc*. Finally, new developed directions of this studied field are predicted.

Keywords: nanostructured materials; blue light emission properties; luminescent mechanism; optoelectronic devices

1 Introduction

The blue or ultraviolet (UV) light source is very important for the integrated optoelectronics. Since first GaN–based blue light emitting diode was reported in 1993, the study of blue light emission materials and devices have made markable progress.

In recent years, the blue light emission properties of various nanostructured materials have drawn significant interest because of their potential applications in the optoelectronic devices, such as high–bright full–color light emitting diodes, high–quality flat–panel displays, high–efficient blue lasers, *etc* [1–3]. These nanostructured materials are nanodots (QDs), nanocrystallites, nanorods, nanowires and multiquantum well structures formed by ZnO, GaN, CdS and Si using different physical and chemical methods. The strongly blue light emission can be realized due to they have wide band–gap, larger exciton binding energy, or strongly quantum confinement effect (QCE).

In the paper, we review the developments of the blue light emissions properties and devices applications of the various nanostructures in recent 3–5 years, and indicated that the new developed directions of the studied field.

2 Blue light–emitting properties of various nanostructured materials

2.1 *nc*–ZnO materials

ZnO is a promising material for short–wavelength photonic devices since it has a large direct band gap of 3.37 eV, and a large exciton binding energy of 60 meV, all of which are advantages for light–emitting diode (LED) and low–threshold optical pumped laser applications at room temperature. In particular, the nanostructured ZnO materials are of great interest because of strongly quantum confined effect of carriers leads not only continuous tuning of the optoelectronic properties but also improved the device performance. Among them are ZnO quantum dots (QD), ZnO nanowires, doped ZnO nanometer films and ZnO/GaN heterojunctions, *etc*.

The light emission based on quantum confined effect is an important luminescent mechanism of the nanostructured materials[3]. Kim *et al*[4] fabricated the ZnO QDs with size of 3~7 nm embedded in the amorphous silicon oxide by plasma enhanced chemical vapor deposition (PECVD) and subsequent rapid–thermal annealing, and studied the photoluminescence (PL) properties at room temperature. The results indicate that the PL peaks at 3.31 and 3.36 eV can be attributed to the quantum confinement effect in the ZnO

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QDs. The quantum confined effect has also been observed in the ZnO nanorods formed by a colloidal synthesis method[5]. It is shown that the binding energy of excitons in these nanorods is significantly enhanced due to one-dimensional quantum confinement, and that the transition responsible for the 2.57 eV PL peak. More recently, the size dependence of PL properties from ZnO QDs has been studied by CHENG *et al* [6]. The blueshift of room temperature PL measurement from free exciton transition are observed with decreasing ZnO QD size, which is ascribed to the quantum confinement effect. For instance, the UV emission shifts to the higher energy from 3.3 to 3.43 eV as the particle size reduces from 12 to 3.5 nm.

The radiative recombination of bound excitons in the doped ZnO films can lead to blue light emission. Hirai *et al*[7] investigated the PL properties ZnO: Zn phosphor powders, It is found that the PL peak at 3.360 eV originates from an exciton bound to an intrinsic defect as a neutral donor, but PL peak at 3.365 eV can be interpreted in terms of bound excitons associated with surface defect state in ZnO:Zn phosphor. Furthermore, DUAN *et al* [8] reported the fabrication of the Ag-doped ZnO films by dc reactive sputtering, and observed the enhancement of UV emission at 348 nm was caused by excitons formed at the interface between Ag_2O nanoclusters and ZnO grains.

nc-ZnO can be used for the fabrication of UV source with higher brightness, and low threshold currents. Recently, a *n*-ZnO/*p*-GaN:Mg heterojunction LED were fabricated using pulsed laser deposition (PLD) for the ZnO and metal organic chemical vapor deposition (MOCVD) for the GaN:Mg[9]. Room temperature PL properties showed an intense main peak at 375 nm, and the LEDs showed a room temperature electroluminescence (EL) peaked at about 375 nm. A good correlation between the wavelength maxima for the EL and PL properties suggests that recombination occurs in the ZnO layer. At the same time, EL properties at 386 nm wavelength from ZnO nanowire array embedded *n*-ZnO/P-GaN heterojunction LED was observed under forward bias conditions [10]. The EL peak intensities were increased when the applied voltages were increased from 3 to 12 V. This is due to the high electron injection rate from *n*-ZnO films to ZnO nanowires increases the electron-hole recombination rate for light-emission in the heterojunction LED.

ZHANG *et al* [11-12] reported the measurements of ZnO nanawire nanolaser quantum efficiency. The external differential quantum efficiency of lasing ZnO nanowires was determined to be about 60% for a 7.5 μm long nanowire, and the absolute emission power of ZnO nanowire nanolaser was measured at approximately 0.1 mW per nanowire under 266 nm light excitation at the lasing threshold. Very recently, UV lasing in three-dimensional ZnO photonic crystals is demonstrated at room temperature [13]. Changing the lattice constant of the photonic crystals leads to a shift in lasing wavelength from 383 nm to 415 nm, closely matching the shift in the high order band structure. The gain spectrum of ZnO is centered at ~390 nm.

2.2 *nc*-GaN materials

GaN of band gap ~3.5 eV has been established to be an excellent and stable UV light emitter. Nanometer scale GaN, such as luminescent crystallites, quantum dots and nanorods can be utilized as tunable band-gap engineered components and optoelectronic devices.

Inoue *et al* [14] demonstrated the growth of pillar-like GaN nanostructures on Si substrate by a hot-wall epitaxy technique. The PL and cathodoluminescence (CL) measurements show the strong near-band-edge emissions at room temperature. The PL peak was located at 367 nm, while the CL peak was located at 370 nm. These strongly PL and CL are related to high crystal quality of the dislocation-free GaN nanopillars. One-dimensional dislocation-free vertical GaN nanorods have been grown by PECVD method [15], the investigations of PL properties showed two distinct features. First, the PL peak at energy of 3.477 eV corresponding to the free exciton transition. Second, the PL peak energy blueshifts with decreasing diameter of the GaN nanorods.

For the realization of the highly efficient ultraviolet light emission, quantum dot structures are promising because the zero-dimensional electronic states in the QDs play an essential role for improving luminescent properties. In particular, in order to realize the lasing operation, the vertical stacking of the QDs in important to increase the total QD density. Hoshino *et al* [16] reported the PL properties of multiple-layer staked GaN QDs, and indicated that the PL peak occurs at around 3.6 eV, which originates from the QD structure. Furthermore, the PL intensity was increased with an increasing number of stacked layers. Gogneau *et al* [17] also studied the effects of stacking on the PL properties of self-organized GaN/AIN QDs, and observed a homogenization of the island distribution and a redshift the luminescent peak. This redshift is attributed to an increase of the quantum Stark effect due to the increase of the piezoelectric contribution to the internal electric field.

Potential applications of *nc*-GaN materials is used for the blue light-emitting laser diodes. GaN nanowire lasers with low lasing thresholds have been achieved [18]. Optical excitation studies demonstrate that the lasing peak was centered 373 nm, with sharp 12 nm full width at half maxmum (FWHM), quality factor Q was about 500-700, and the threshold current density was only 22 kW/cm^2. A GaN-based photonic-crystal (PC) membrane nanocavities with Q values up to 800 have been realized of the wavelength of ~480 nm [19]. Theoretically, high-Q photonic crystal membrane nanocavities with GaN QDs will lead to the realization of low threshold PC lasers and single photon sources at the blue wavelengths. A high power GaN-based blue violet laser diodes with AlGaN/GaN multiquantum barriers have also been fabricated by using MOCVD [20]. The threshold current and slope efficiency of the laser diode are 32 mA and 1.12 W/A, respectively.

2.3 *nc*-CdS materials

CdS is one of the most important Ⅱ-Ⅵ semiconductor compounds. Up to date, nano-sized CdS has been intensively studied due to advantages such as a band-gap energy in the visible region (E_g ~2.5 eV) and relatively simple fabricated process. Various CdS nanostructures, such as nanoparticles, nanorods, nanobelts, nanowires often present novel properties and have been widely used in light emission diode, solar cell, laser, and microelectronic devices.

Highly ordered CdS nanoparticle arrays were fabricated on silicon substrates [21]. PL measurements on the CdS nanoparticle arrays show a strong emission spectrum at 473 nm, which are attributed to quantum confinement effects. WANG *et al* [22] investigated the PL properties of CdS nanobelts, the results indicate that the emission peak at 2.540 eV is attributed to excitons bound to neutral donors, and the emission peak at 2.550 eV is assigned to excitons bound to ionized donors. The results of a study of optical properties of single CdS nanorods show that the two peaks located at 2.515 and 2.520 eV were observed due to the recombination of free excitons and excitons bound to netural donors and neutral acceptors [23].

An important application of CdS nanostructures in the optoelectronic devices is blue light laser. A CdS single-nanowire electrically driven laser fabricated on Si wafer has been reported by DUAN *et al* [24]. The nanowire laser has a strong and sharp blue emission at 495 nm with a linewidth of 0.8 nm. This nanoscale lasers can be integrated as single or multi-colour laser source arrays in Si microelectronics and lab-on-a-chip devices. In addition, CHAN *et al* [25] also found the tunable room temperature amplified spontaneous emission and lasing from blue emitting core shelf CdS/ZnS nanocrystals stabilized in a sol-gel derived silica matrix. The fabricated laser has strongly room temperature lasing properties at 480 nm with a line width less than 1nm. The quality factor and modal gain are 600 and 100 cm^{-1}, respectively. The observation of optical gain of CdS quantum dots dispersed in toluene at room temperature was carried out by Darugar *et al* [26]. The optical gain lifetime was found to be as long as 20 ps under pump fluence as low as 0.77 mJ/cm^2. The low threshold is the result of long lifetime of electrons and holes and narrow emission bandwidth. These result suggest that CdS quantum dots in solution are excellent gain media for optically pumped high power blue laser.

2.4 *nc*-Si materials

It is well known that Si is an indirect band-gap semiconductor, so that the efficience of spontaneous emission is very low. In order to overcome the indirect band-gap limitations, the fabrications and luminescent properties of various Si-based nanostructured material, such as Si nano-crystals, Si-QD, SiO$_2$/Si superlattices, Ge/Si QD heterojunctions, have been deeply studied by many researchers.

The blue emission of *nc*-Si materials has important applications for the fabrication of Si-based blue LED and laser. Nayieh *et al* [27] prepared the ultrabright blue luminescent Si nanoparticles with size of ~1 nm by electrochemical etched methods. The emission spectrum of the samples shows the blue band at 390 nm under excitation with 355 nm UV radiation. Moreover, the stimulated blue emission were observed when average incident intensity was ~106 W/cm^2. Strong blue PL properties from α-Si:H/SiO$_2$ multilayers confirmed that the PL peak blueshifts from 466 to 437 nm with controlling the thickness of the α-Si:H sublayer from 4 to 1.5 nm [28]. The mechanism of blue PL properties may be ascribed to the recombination of electrons and holes in the band-tail of α-Si:H sublayer embedded in α-Si:H/SiO$_2$ multilayers. Kim *et al*[29-30] investigated the blue PL properties of Si nanocrystallites embedded in silicon oxide, and indicated the blue emission is related to the quantum size effect of Si nanocrystallites.

The other blue emission mechanism of Si nanocrystals is oxgen-related defects model. For example, the 370 nm luminescence in Si oxide nanostructures originates in the -SiO$_3$ group, which bound to Si structural surface[31]. Unique structured SiO$_x$N$_y$-capped Si nanowie arrays were fabricated via electrolsis metal deposition. An enhanced blue PL band was observed at 440 nm. The PL spectral analyzes strongly suggested that the generation of photoexcited carriers takes place in the quantum confined Si nanowires, while their radiative recombination occurs at Si-N bonds of SiO$_x$N$_y$ nanocaps[32].

3 Outlook

The fabri cation of high-quality nanostrutures with strong quantum confined effect, such as ordered nanocrystallites and quantum dots, is very important for the realization of stable and efficient blue light emission. In addition, the correlations between the structural characteristics and blue light emission properties should be experimentally and theorietcally studied, so that we can deepen understanding for the blue light emission mechanism of various nanostructures. In order to realize high-efficient blue light LED and laser, the device structures need to be optimistically designed, and the active region materials should be reasonably choiced. In particular, an electrically pumped blue light devicesdevice is requirement for practical applications.

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