Visible photoluminescence from ZnO/diamond-like carbon thin films*

ZHANG Li-chun(张立春)[1]**, **LI Qing-shan**(李清山)[2], **DONG Yan-feng**(董艳锋)[1], and **MA Zi-xia**(马自侠)[2]
1. College of Physics and Engineering, Qufu Normal University, Qufu 273165, China
2. School of Physics, Ludong University, Yantai 264025, China

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ZnO/diamond-like carbon (DLC) thin films are deposited by pulsed laser deposition (PLD) on Si (111) wafer. Visible room-temperature photoluminescence (PL) is observed from ZnO/DLC thin films by fluorescence spectrophotometer. The Gaussian curve fitting of PL spectra reveals that the broadband visible emission contains three components with λ=508 nm, 554 nm and 698 nm. The origin and possible mechanism of the visible PL are discussed, and they can be attributed to the PL recombination of ZnO and DLC thin films.

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Due to the ever increasing commercial requirement for solid-state lighting devices, high-efficiency white light emitting diodes (LEDs) have attracted a great deal of attention. Two prevailing approaches have been taken by using LEDs to achieve white light emission. One is making use of a blue or ultraviolet (UV) LED to excite one or more phosphors[1,2]. However, this method would lead to an inevitable efficiency loss. The other approach is to use red, green and blue LEDs (RGB-LEDs)[3,4], the advantages of which are that they can provide a light source with a variable color point, and theoretically obtain LED-based white light with the highest efficiency.

Recently, among all kinds of wide band gap semiconductor materials, since ZnO has direct wide band gap (3.37 eV) and high exciton binding energy (60 meV, cf. 25 meV for GaN), it becomes a potential candidate for the applications in short-wavelength optoelectronic devices, especially for LEDs and laser diodes (LDs). Typically, besides UV emission, ZnO material also exhibits visible emission in green, yellow and orange regions, which makes it possible to realize efficient white light emission at room temperature[5-7]. Though the origin of the visible emission is under debate, it is generally attributed to the defects, such as oxygen vacancies, zinc interstitials[8,9]. Based on the RGB theories, ZnO material should generate white light by combining with some red light emitting material.

In the past decade, diamond-like carbon (DLC) has received much attention, for it possesses many similar properties to pure diamond, such as high hardness, low friction coefficient, good thermal conductivity, and special optical and electrical properties[10-13]. As a wide band gap semiconductor, strong visible photoluminescence (PL) at room temperature was found in hydrogenated and unhydrogenated DLC thin films[14-16]. PL in DLC is thought to occur due to the radiative recombination of electrons and holes in the band-tail states created by sp^2 rich clusters. It was reported that the luminescence center of unhydrogenated DLC films deposited by pulsed laser deposition (PLD) of graphite is between 650 nm and 700 nm, which is a typical red light emission[17]. In principle, DLC can be combined with ZnO thin films to make a white light emitting device. With good piezoelectric properties, ZnO/DLC thin films are widely used to investigate surface acoustic wave (SAW) filters[13], while ZnO/DLC thin films for optoelectronic applications haven't been touched upon.

In this paper, we investigate the PL properties of ZnO/DLC thin films deposited by PLD, and try to find a novel approach to obtain visible emission at room temperature. Also, the luminescence mechanism of ZnO/ DLC thin films is discussed.

DLC and ZnO films were deposited on Si(111) wafer by PLD using a KrF excimer laser (20 ns, 248 nm) with pulse

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** E-mail: phyzlc@163.com

repetition rate of 5 Hz. The sputtering targets are high pure graphite (99.999%) and ZnO ceramic (99.999%), respectively. The growth chamber was evacuated by a turbo molecular pump to 9×10^{-6} Pa, and then backfilled with nitrogen to the required pressure (0.5 Pa). DLC films were deposited on the Si substrate for 20000 laser shots. Having finished it, turn off the gas supply, and the reactor pressure reached 9×10^{-6} Pa again. Then ZnO films were deposited on the DLC films for 10000 laser shots. During the whole process, the temperature of substrate was maintained at 50 °C, and the distance from target to substrate was fixed at 5 cm. In order to avoid being drilled, the target was also rotated in reverse direction towards substrate, and in this way it could provide each laser pulse with a fresh surface. For comparison, the DLC and ZnO thin films deposited separately on Si(111) were also fabricated under the same conditions.

The surface morphology of the films is characterized by a Veeco DISPM atomic force microscope (AFM), and the measurements are performed in tapping mode. The room-temperature PL measurements are performed by Shimadzu RF-5301 PC fluorescence spectrophotometer, which uses a xenon lamp as the excitation source. The PL spectra of ZnO/DLC thin films are fitted by the typical Gaussian functions.

Figs.1 and 2 show the three dimensional (3D) AFM images of the DLC films deposited on Si(111) and the ZnO thin films deposited on DLC/Si(111), respectively. As shown in Fig.1, the surface of DLC thin films reveals granular and nanocrystal morphology with uniform grain size. Fig.2 shows AFM micrograph of the ZnO films deposited onto the DLC surface. It is clear that there are some bigger grains on the surface of ZnO films. Due to the larger lattice mismatch between ZnO and DLC, the grain size of ZnO films is bigger than that of DLC thin films.

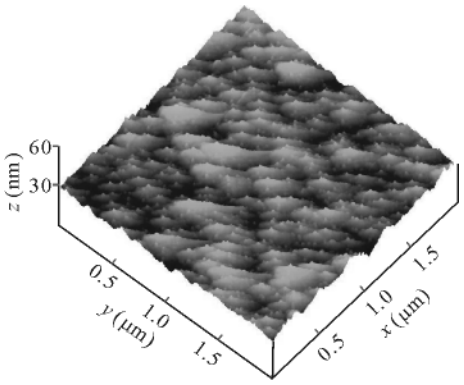

Fig.1 3D AFM image of DLC thin films on Si

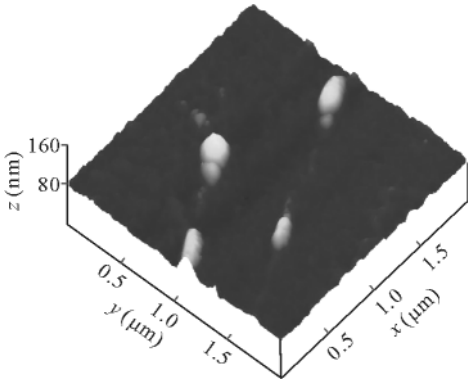

Fig.2 3D AFM image of ZnO thin films on DLC/Si

Fig.3 illustrates the room-temperature PL spectrum of DLC thin films deposited on Si(111) substrate. The excitation wavelength for DLC is 488 nm. From the PL spectrum, we can find that there is a red PL band from 670 nm to 730 nm. DLC is a metastable form of amorphous carbon with sp^3 bonding. The optical properties of carbon films are largely governed by the sp^2 phase, with the tribological properties determined by the sp^3 phase. PL in DLC occurs due to the radiative recombination of electrons and holes in the band-tail states created by sp^2 rich clusters[17].

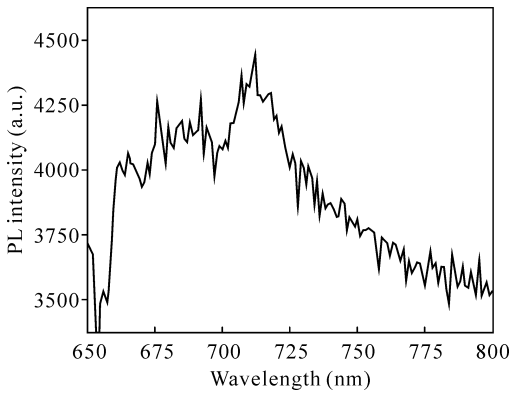

Fig.3 PL spectrum of DLC thin films on Si(111)

Fig.4 shows the room-temperature PL spectrum obtained from the ZnO thin films deposited on Si(111) substrate. The excitation wavelength of ZnO is 325 nm. It can be seen that all samples show a typical luminescence behavior with two emissions of a narrow UV peak centered around 382 nm and a broad deep level peak centered around 510−540 nm. The

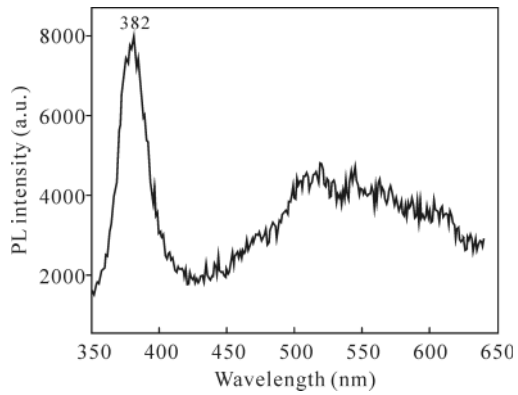

Fig.4 PL spectrum of ZnO thin films on Si(111)

UV emission is usually considered as the characteristic emission of ZnO, and attributed to the band edge transition or the exciton combination. However, various mechanisms have been proposed for the visible emission (from blue to green)[8,9,18]. The origin of the deep level emission, which is still under debate, is generally attributed to the defects, such as oxygen vacancies and zinc interstitials.

The room-temperature PL spectrum of ZnO/DLC thin films is shown in Fig.5. The ZnO/DLC thin films show a broadband emission containing the entire visible spectrum. Its main emission bands are observed at 519 nm and 712 nm. The shape of the PL spectra is similar to that of the solar spectra in winter[19].

To better understand the underlying mechanisms, the PL spectrum of ZnO/DLC thin films is resolved into several Gaussian components. As shown in Fig.5, three components with λ=508 nm, 554 nm and 698 nm in the PL spectrum of ZnO/DLC thin films are noticed. From the PL spectra of DLC and ZnO thin films in Figs.3 and 4, it can be easily identified that the peaks at 508 nm and 554 nm are attributed to the ZnO, while the 698 nm emission peak comes from DLC films. In addition, the intensity of PL spectra in long wavelength (greater than 600 nm) is weaker than that in short wavelength (less than 600 nm), which possibly results from the weaker intensity of DLC thin films and the absorption of ZnO thin films on the surface.

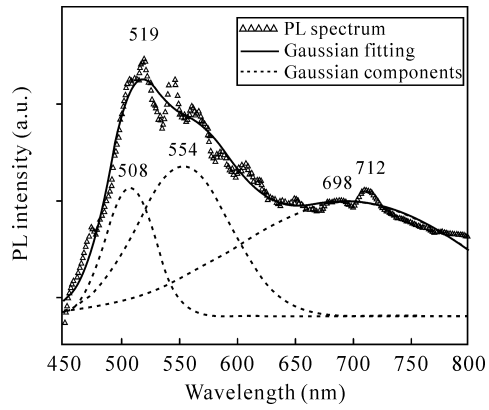

Fig.5 Room-temperature PL spectra of ZnO/DLC thin films on Si(111)

In nature, the visible PL from ZnO/ DLC thin films is attributed to the combination of different lights emitted by two separated film layers. Fig.6 shows a schematic diagram of the white light emission by ZnO/ DLC thin films. When the samples are irradiated by the excitation source (325 nm), ZnO thin films lying on the surface can form a shallow luminescence center, and can show UV and visible PL peaks (from blue to green region). A part of the light generated by ZnO emits outside, and the other can get through the sublayer of the ZnO thin film and arrive at the DLC layer, which can be used as the excitation source for DLC and another luminescence center in DLC films can form. The red light emitted by DLC thin films can partly get through the transparent thin films and combine with the light emitted by ZnO, and then the visible PL is obtained. From the PL spectrum of ZnO/ DLC, we can find that the light intensity of long wavelength part is weaker, largely due to the absorption of DLC and ZnO thin films. To obtain better visible spectra, we should adjust the portion of light by controlling the thickness of DLC and ZnO films.

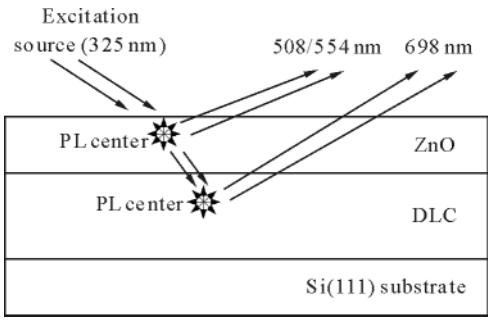

Fig.6 Schematic diagram of the PL from ZnO/DLC thin films on Si(111)

In summary, we prepare ZnO/DLC thin films on Si(111) by PLD. Using a fluorescence spectrophotometer, we obtain the PL spectra of DLC thin films, ZnO thin films and the ZnO/DLC thin films, respectively. Excitated by the xenon lamp, we can find there is a red PL band in DLC and the typical luminescence behavior with two emissions from ZnO thin films. Moreover, the ZnO/DLC thin films show a broadband emission from 450 nm to 800 nm, which contains the entire visible spectrum. With the help of PL schematic diagram, the luminescence mechanism of ZnO/DLC thin films is discussed.

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