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Optical properties of ZnO thin films grown on diamond-like carbon by pulsed laser deposition*

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ZnO/diamond-like carbon (DLC) thin films are deposited by pulsed laser deposition (PLD), and the room-temperature photoluminescence (PL) is investigated. Using a fluorescence spectrophotometer, we obtain the PL spectra of DLC/Si and ZnO/Si thin films deposited at different substrate temperatures. The ZnO/DLC thin films show a broadband emission almost containing the entire visible spectrum. The Gaussian fitting curves of PL spectra reveal that the visible emission of ZnO/DLC thin films consists of three peaks centered at 381 nm, 526 nm and 682 nm, which are attributed to the radiative recombination of ZnO and DLC, respectively. The Commission International de l'Eclairage (CIE) 1931 (x, y) chromaticity space of ZnO/DLC thin films indicates that the visible PL spectrum is very close to the standard white-light region.

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Nowadays, the solid state lighting (SSL) source with essential features such as energy-saving, pollution-free, and apt to develop has already become the important trend to solve the energy crisis of the world. Among the solid state materials, ZnO is one of the most promising materials because of its wide bandgap (~3.37 eV) and large exciton-binding energy (60 meV)[1-4]. Furthermore, deep level defects (intrinsic and extrinsic) in ZnO can lead to an emission band covering the whole visible spectrum, which makes it possible to realize efficient white light emission at room temperature[5-7]. To obtain the ZnO homojunction light-emitting diodes and laser diodes, both n-type and p-type ZnO are required. It can be easily doped to n-type because of the existence of oxygen vacancy and zinc interstitial for pure ZnO. However, it is difficult to grow the stable and reproducible p-type ZnO with high conductivity and high mobility, due to its self-compensating effect, deep acceptor level and low solubility of acceptor dopants[8,9]. As a feasible alternate, ZnO-based heterojunction devices can be realized by depositing n-ZnO on different p-type semiconductors[7,10].

Diamond is a wide-bandgap semiconductor with an energy gap of 5.47 eV and binding energy of 80 meV at room temperature. It has a unique set of properties, such as ultra hardness, low thermal expansion coefficient, high mobility, special optical and electrical properties, and can be used as a biocompatible substrate[11,12]. Up to now, it has been possible to prepare p-type diamond semiconductor, but n-type diamond semiconductor has been found very difficult to obtain[13-15]. However, as diamond can't be easily acquired, attention has been shifted to the diamond-like carbon (DLC). It not only has similar properties to those of diamond, but also is easier to obtain without the high-temperature substrate requirement or the restriction on size[16,17]. As a wide-bandgap semiconductor, visible photoluminescence (PL) was found in hydrogenated and unhydrogenated DLC thin films at room temperature[18,19]. It has been reported that the luminescence center of unhydrogenated DLC films deposited by PLD is between 650 nm and 700 nm, which is a typical red light emission[20]. Based on the complementary color theories, white light can be obtained by the red light emitted from DLC films and the yellow-green light emitted from ZnO, which can be a novel approach to obtain ZnO-based heterojunction devices

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with visible emission at room temperature.

In this paper, ZnO/ DLC thin films are deposited by pulsed laser deposition (PLD) on Si (111) wafer. The PL and colourometry properties of ZnO/DLC thin films are investigated, and the luminescence mechanism of ZnO/ DLC thin films is discussed.

The DLC and ZnO films were prepared by PLD with high pure graphite (99.999%) and ZnO ceramic (99.999%) targets, respectively. The COMPexPro 201 KrF excimer laser (Coherent Inc.) was employed, operating with wavelength of 248 nm. Thin films were deposited on Si (111) substrates which had been ultrasonically cleaned in acetone and alcohol separately and then rinsed in de-ionized water repeatedly. Substrates were loaded into the vacuum chamber immediately after being dried with nitrogen. Before the deposition, the growth chamber was evacuated using a turbo molecular pump to 8×10^{-7} Pa, then backfilled with high-pure nitrogen to the required pressure (0.5 Pa). Firstly, DLC films were deposited on the Si substrate for 20000 laser shots. Subsequently, the gas supply was cut off. When the vacuum degree recovered to 8×10^{-7} Pa, ZnO film (~ 100 nm) was deposited onto DLC films.

During deposition, the laser energy (250 mJ) and the distance between target and substrate (5 cm) were fixed. The substrate temperature and the repeating frequency of laser pulses can be adjusted under the requirement. In order to avoid being drilled, the targets were also rotated in reverse direction towards the substrate.

The Raman spectroscopy (DXR-microscope) was used to measure the microstructure properties of DLC films. The X-ray diffraction (XRD) measurements were performed by D/MAX2500V diffractometer. The room-temperature PL measurements were performed by a fluorescence spectrophotometer (RF-5301 PC) which uses a xenon lamp as the excitation source. The PL spectra of ZnO/ DLC thin films were fitted by the typical Gaussian function and the chromaticity coordinates of the PL spectra were calculated.

The Raman spectra of DLC thin films and the typical fitting curve of the Raman signal using two Gaussian curves centered at approximately 1367 cm^{-1} (D band) and 1554 cm^{-1} (G band) are shown in Fig.1. Generally speaking, the D and G peaks are attributed to the breathing mode of aromatic rings and the stretching-vibration mode of any pair of sp^2 bonded C atoms, respectively[18,20]. Fig.2 shows the XRD patterns of ZnO/ DLC thin films. From Fig.2, we can see that only the diffraction peaks of ZnO (002) are observed. The XRD suggests that ZnO films grow along the *c* axis on the surface of DLC thin film. The broad band between 20° and 30° in the XRD patterns indicates that there is an amorphous carbon phase in the DLC thin films.

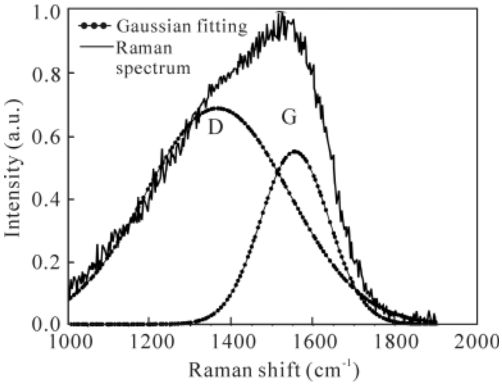


Fig.1 Raman spectra of DLC thin films

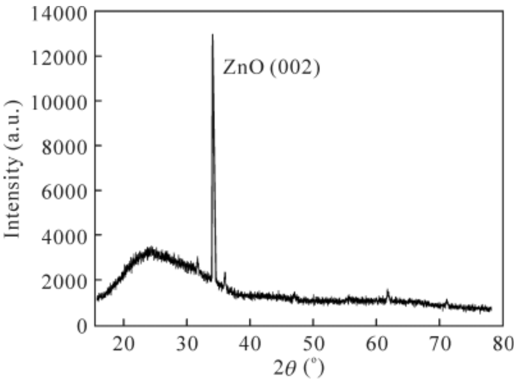


Fig.2 XRD patterns of ZnO/ DLC thin films

Fig.3 shows the PL spectra of DLC thin films deposited on Si (111) substrate with different temperatures. With visible excitation (488 nm), these spectra show a variety of features. Firstly, the PL centered at 700 nm is a typical red luminescence. Secondly, it is found that the intensities of PL emission peaks decrease with the increase of substrate temperature from room temperature to 200 °C. The optical properties of DLC films are largely governed by the sp^2 phase, and the tribological properties are determined by the sp^3 phase. PL in DLC is thought to occur due to the radiative

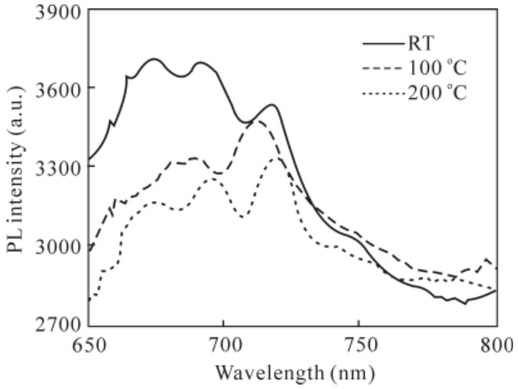
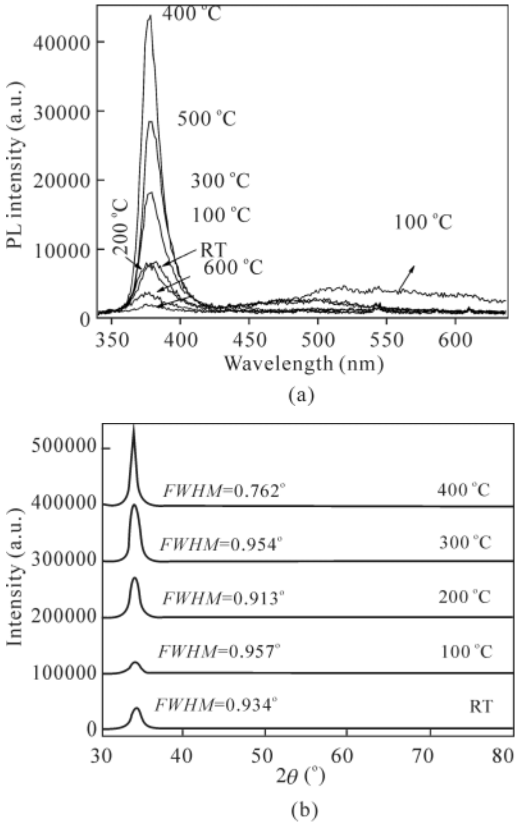


Fig.3 PL spectra of DLC/ Si (111) thin films deposited at different substrate temperatures

recombination of electrons and holes in the band-tail states created by sp^2 rich clusters[20]. The higher substrate temperature provides larger bonding energy for sp^3-bonded C, and more sp^3-bonded structures are favorably formed. Meanwhile, with the increase of substrate temperature, the fraction of sp^2-bonded C present in the films decreases, which causes the number of illuminant centers to decline. For the strongest emission, we choose room temperature as the optimum growth temperature for PL emission.

Fig.4 shows the PL spectra and XRD patterns of ZnO thin films deposited on Si (111) substrate at various temperatures. The excitation wavelength for ZnO is 325 nm. It is seen that all the samples show a typical luminescence behavior with two emissions of a narrow UV peak centered at 382 nm and a broad visible emission which ranges from 450 nm to 600 nm. As substrate temperature increases from room temperature to 400 °C, the intensity of UV emission increases. When the substrate temperature is above 500 °C, the intensity of UV emission descends. It should be noted that the visible emission changes slightly and the strongest emission appears at 100 °C. Typically, the UV emission comes from the near-band-edge emission which depends on the crystal quality of the film, while the visible emissions are relevant to various intrinsic defects in ZnO crystal. The origin of the deep level emission, though under debate, is generally attributed to defects, such as oxygen vacancies and zinc interstitials[21,22]. It is well understood that PL spectra depend on the substrate temperature because of the different crystal qualities of ZnO thin films[23]. From Fig.4(b), we can see that the full width half maximum (FWHM) of ZnO (002) is the biggest when the substrate temperature is 100 °C, which means that the ZnO thin film is grown with the poorest crystal quality. In our experiment, 100 °C is chosen as the optimum growth temperature for the visible emission.



(a)

(b)

Fig.4 (a) PL spectra and (b) XRD patterns of ZnO/ Si (111) thin films at different temperatures

The room temperature PL spectra of ZnO/DLC thin films are shown in Fig.5. It can also be seen that the ZnO/DLC thin films show a stronger UV emission centered at 381 nm and a broadband visible emission from 500 nm to 800 nm. To understand the underlying mechanisms better, the visible PL spectra of ZnO/DLC thin films are resolved into several Gaussian components. As shown in Fig.5, three emission bands centered at 381 nm, 526 nm and 682 nm in the PL spectra of ZnO/DLC thin films are noticed. As shown in Figs.3 and 4, the two PL emission peaks from the ZnO/DLC thin films are roughly consistent with the PL peaks of individual thin films, indicating that the radiative recombination occurs in both DLC side and ZnO side of the ZnO/DLC thin films[24]. Furthermore, the intensity of the spectra in long wavelength region (greater than 650 nm) is weaker than that in short wavelength region (less than 600 nm), which probably results from the weaker intensity of DLC thin films and the partial absorption by ZnO thin films on the surface.

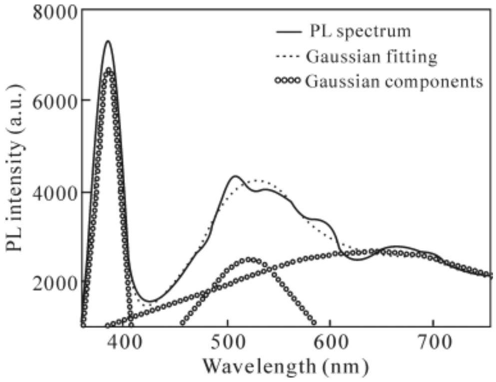


Fig.5 Room temperature PL spectra of ZnO/DLC/ Si (111)

Fig.6 shows the CIE 1931 color space chromaticity diagram of the PL spectra in the (x, y) coordinate system. The chromaticity coordinates are (0.73, 0.27), (0.27, 0.43), (0.34, 0.41) with correlated color temperatures (CCTs) of 7370.9 K, 7371.8 K and 5074.9 K for the DLC (RT), ZnO (100 °C) and ZnO/DLC thin films, respectively. It can be seen that the chromaticity coordinates of ZnO films and DLC films lie in yellow-green and red regions, respectively. However, the PL spectrum of ZnO/DLC thin films is close to the standard white-light region (0.333, 0.333).

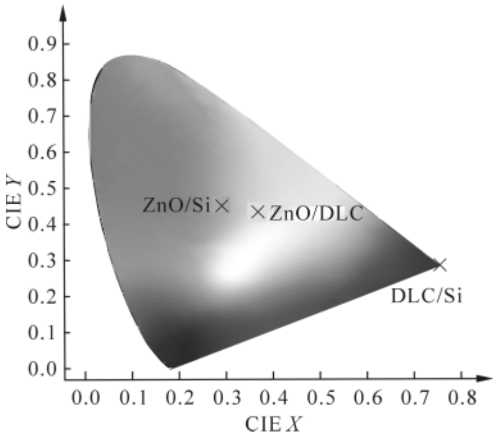


Fig.6 CIE 1931 (x, y) chromaticity space of DLC (RT), ZnO (100 °C) and ZnO/DLC thin films

In summary, ZnO/DLC thin films are prepared by PLD, and the visible room-temperature PL spectra are observed using fluorescence spectrophotometer. It can be seen that there are a red PL band in DLC and a typical luminescence behavior with two emissions from ZnO thin films. In nature, the visible PL from ZnO/ DLC thin films is attributed to the combination of different lights emitted by two separated film layers. It is found that the visible PL spectrum is much closer to the white light region in the CIE 1931 color space chromaticity diagram.

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