Electroluminescence of double-doped diamond thin films*

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A new electroluminescence device is fabricated by microwave plasma chemical vapour deposition system and electron beam vapour deposition system. It is comprised of highly doped silicon/diamond/boron/nitrogen-doped diamond/indium tin oxide thin films. Effects of process parameters on morphologies and structures of the thin films are detected and analysed by scanning electron microscopy, Raman spectrometer and x-ray photoelectron spectrometer. A direct-current (DC) power supply is used to drive the electroluminescence device. The blue light emission with a luminance of 1.2 cd·m^{-2} is observed from this double-doped diamond thin film electroluminescence device at an applied voltage of 105 V.

Keywords: electroluminescence, double-doped diamond thin film, microwave plasma chemical vapour deposition, electron beam vapour deposition

PACC: 7860F, 6855, 8115H, 8115G

1. Introduction

In recent years, there has been aroused the considerable interest in realizing the application of diamond to electronic and optical device due to its some outstanding properties,[1,2] such as wide band-gap ($\sim$ 5.47 eV), high breakdown voltage ($\sim 10^7$ V·cm^{-1}), high thermal conductivity ($\sim$ 20 W·K^{-1}·cm^{-1}) (at room temperature) and high carrier mobility ($\sim$ 0.2 m^2·V^{-1}·s^{-1}).[3–5] Furthermore, diamond has intense luminescence occurring at wavelengths ranging from ultraviolet (UV) to green, which is called 'A' band.[6] The 'A' band light emission of diamond thin film has been investigated for a long time but the exact origin of the 'A' band is still unclear, meanwhile the blue electroluminescence (EL) intensity is also unsatisfactory. Under these circumstances, many scholars have fabricated lots of EL devices by doping various impurities into diamond thin films to increase EL intensity and research luminescence mechanism.[7–22] In the present paper, we report on a new EL device with a five-layer structure of highly-doped silicon/diamond/boron/nitrogen-doped diamond/indium tin oxide (ITO) thin films. Scanning electron microscopy (SEM), Raman spectrometer and x-ray photoelectron spectrometer (XPS) are used to detect and analyse the effects of process parameters on morphologies and structures of the thin films. The relationship between the EL intensity and the thickness of boron film is investigated. The studies of the EL intensity and the EL spectrum show that the highest luminance reaches 1.2 cd·m^{-2} when the applied voltage is 105 V, with the main emission peak at 480 nm.

2. Experimental and discussion

2.1. Fabrication of diamond thin films

First, the silicon substrates were first rubbed by diamond powder in order to obtain a rough surface morphology, and the silicon substrates rubbed were ultrasonically cleaned in 99.7% alcohol and de-ionized (DI) water for 20 min sequentially, then they were wiped with 99.7% alcohol cotton ball. After that, diamond thin films were grown on the silicon (111) substrates by microwave plasma chemical vapour deposition (MPCVD) system. The whole deposition conditions were kept as follows. The reaction gases were a mixture of H_2:CH_4 with a ratio of 42:1. The substrate

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temperature was maintained at 900 °C. A mass flow controller was used to keep the pressure of deposition chamber at 7.0×10^3 Pa. The time of deposition was 18 h, yielding a 5-μm-thick film. The thickness of the film was determined from the fringes observed in the infrared absorption spectrum. The Raman spectrum of the diamond film shown in Fig. 1, indicates that a sharp peak appears at 1332 cm^{-1} and no broad peak occurs at 1500 cm^{-1}, which means that the film has a diamond structure with very few non-diamond phases. The SEM further confirms the structural characteristics of the diamond films, which is shown in Fig. 2. It indicates that the film is composed of polycrystalline diamond grains.

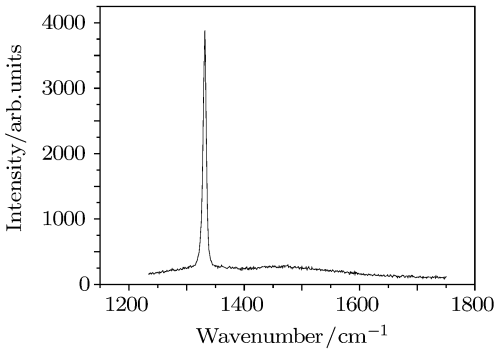


Fig. 1. Raman spectrum of diamond film.

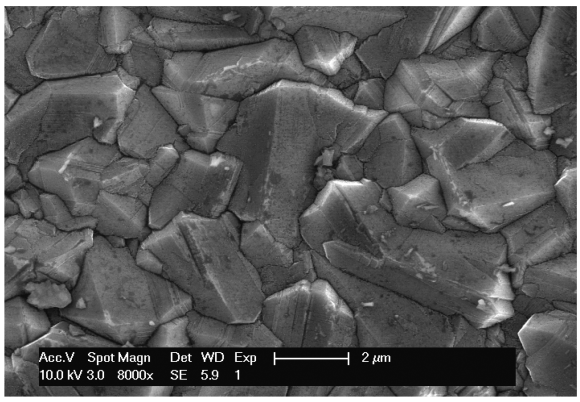


Fig. 2. SEM image of diamond film.

Secondly, the electron beam vapour deposition (EBVD) system was used for depositing boron thin films on the diamond film substrates, with high purity (99.99%) boron used as a deposition target. In the whole EBVD process, the beam current and pressure were maintained respectively at 100 mA and 9.7×10^{-2} Pa, and the substrate temperature was kept at 300 °C. The thickness of boron layer was controlled between 0.1 and 0.2 μm by a film thickness monitor. Filament current was set at 6.5 A. The whole deposition process lasted 13 min.

Thirdly, nitrogen-doped diamond films (NDFs) were deposited on the boron layer by the MPCVD system. The specific parameters used for the MPCVD process are listed in Table 1.

Table 1. Parameters employed for MPCVD process.

MPCVD process parameters	values
hydrogen/Methane/nitrogen gas flow/sccm	120:1:4
total gas pressure/kPa	8.5
substrate temperature/°C	900
deposition time/h	15
microwave power/W	1300
nitrogen impurity concentration	0.3%

1 sccm (standard cubic centimeter per minute)=1 cm^3/min= 1 ml/min=1.69×10^{-3} Pa·s^{-1}

Figure 3 shows a SEM image of the NDF. There is an obvious effect of nitrogen impurity on diamond film morphology. Raman spectrometer was used to detect the NDF as shown in Fig. 4. It obviously shows that a weak broad peak appears at 1500 cm^{-1} besides the sharp diamond peak at 1331 cm^{-1}, which indicates that there exist some non-diamond phases in the film. The nitrogen element chemical states of the NDFs were analysed by XPS, and the results are shown in Fig. 5. It clearly shows a characteristic peak of nitrogen, but no characteristic peak of boron. This can be attributed to the insensitivity of boron element, meanwhile the impurity of boron in the diamond film is too small in quantity. The thickness of boron film is less than one micron, moreover, part of boron elements were sputtered out and then pumped out during the deposition.

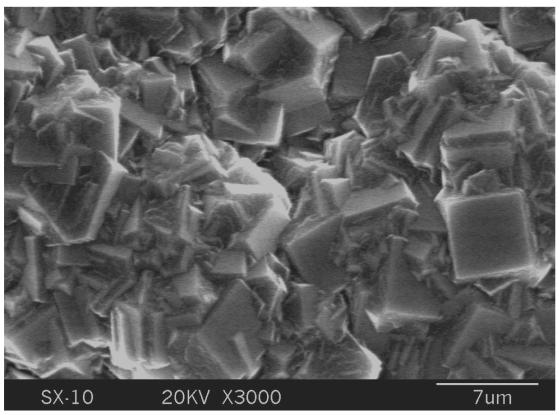


Fig. 3. SEM image of NDF.

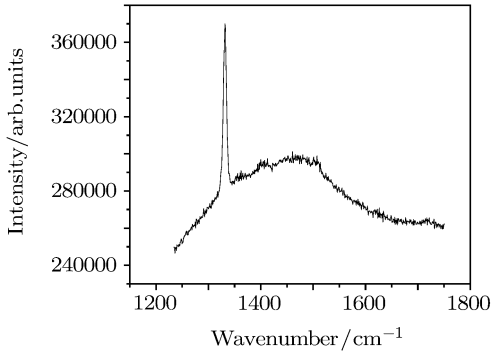


Fig. 4. Raman spectrum of the NDF.

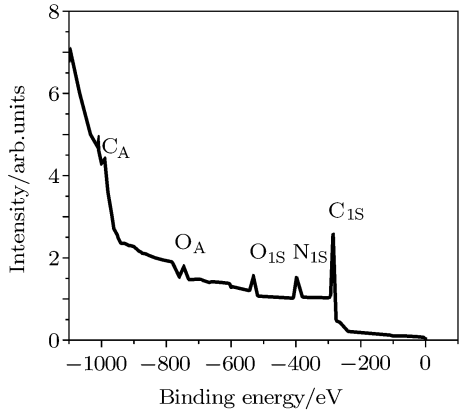


Fig. 5. XPS spectrum of the NDF.

Finally, indium-tin oxide (ITO) thin film electrodes each with 3 mm diameter were grown on the NDFs as a conductive layer by the EBVD technique. Oxygen passed into the vacuum chamber in the whole process. The typical parameters of the EBVD process are shown in Table 2.

Table 2. Parameters employed for the EBVD process.

EBVD process parameters	values
beam current/mA	23
vacuum/Pa	4.8×10^{-2}
substrate temperature/°C	369
voltage/kV	6
vapour time/min	30
filament current/A	0.6
oxygen gas flow/sccm	4

2.2. Electroluminescence results and discussion

Figure 6 shows the basic structure of the EL device which is driven by a dc power supply. The blue light emission could be observed clearly by naked eyes as shown in Fig. 7. The current–voltage (I–V) characteristic curve of the EL device is shown in Fig. 8. From Fig. 8 it follows that the current obviously increases with voltage increasing. The blue light emission appears when the voltage and the current are 30 V and 2 mA respectively. Then the EL intensity gradually turns brighter with current increasing. Finally, we obtain a highest luminance of 1.2 cd·m^{-2} from the EL device under an applied voltage of 105 V.

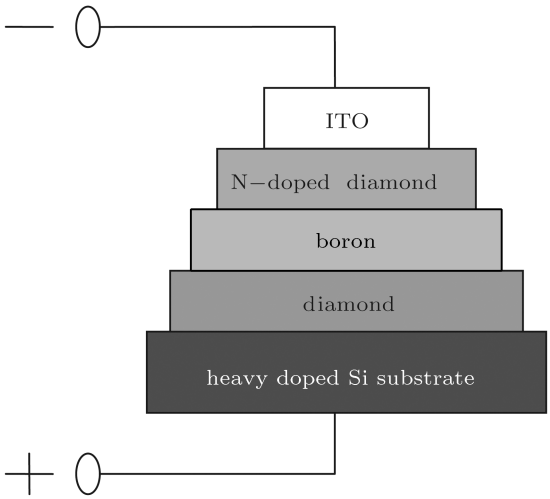


Fig. 6. Structure of EL device.

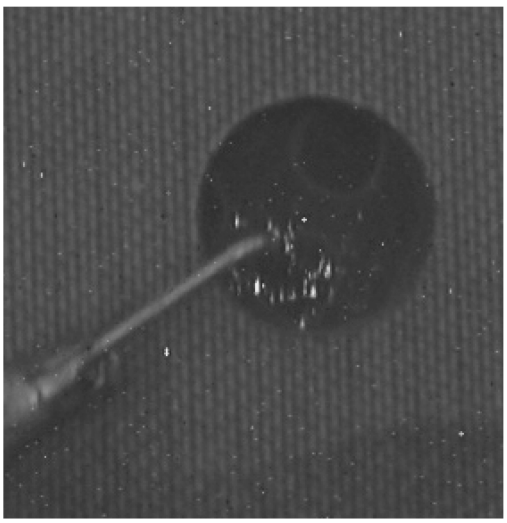


Fig. 7. Blue EL emission of EL device.

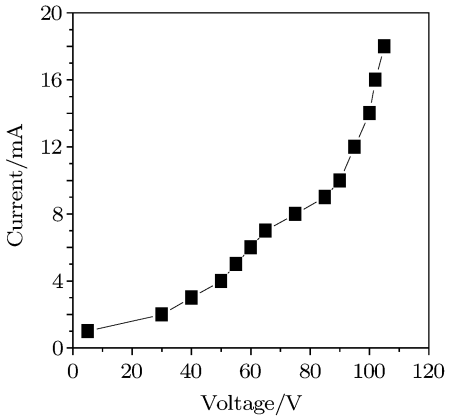


Fig. 8. I–V characteristic curve of the EL device.

The curves for EL intensity versus excitation voltage for two boron films with different thicknesses are shown in Fig.9. It clearly shows that the emission intensity of EL device with 0.2-μm-thick boron film is higher than that of the 0.1-μm-thick one at the same excitation voltages. It is illustrated that the thickness of boron film has a positive influence on the emission intensity of the EL device. An optical multi-channel analyzer (OMA) was used to measure the EL spectrum which is shown in Fig.10. The highest emission peak appears at 480 nm which has been referred to as 'A' band already. The highest peak locating in the blue region (480 nm) is explained to be due to the recombination of the donor (nitrogen)–acceptor (boron) (D–A) pairs.[23] Under our experimental condition, the donor (nitrogen atom) come from the NDFs by doping N_2. The acceptor (boron atom) originates from the boron-layer which was deposited on the diamond film from a boron evaporation source. When the nitrogen impurity was fixed at a certain level in quantity, only the thickness of boron film was increased from 0.1 μm to 0.2 μm, so the quantity of boron impurity would increase in diamond films, meanwhile the number of D–A pairs which acted as the emission centres would increase, eventually led to the increase of the EL intensity. Therefore, we believe that the main emission peak in the blue region is due to the recombination of the D–A pairs.

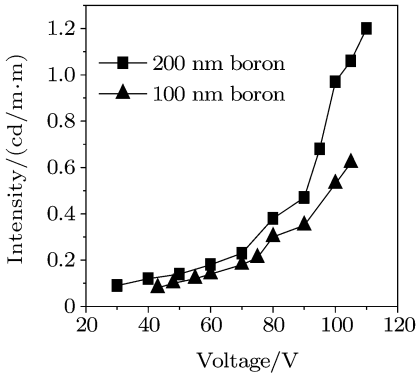


Fig. 9. EL intensities of EL device versus applied voltage for 0.1- and 0.2-μm-thick boron films.

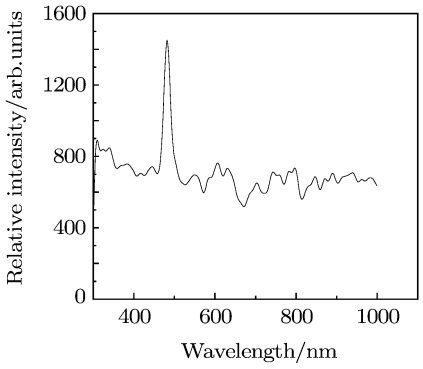


Fig. 10. EL spectrum of EL device.

3. Conclusion

The main emission peak of the EL spectrum appears at 480 nm and the highest luminance of EL device is 1.2 cd·m^{-2} when the applied voltage is 105 V. According to the experiment results, we believe that the blue light emission come from the recombination of D–A pairs.

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