White electroluminescence of n-ZnO:Al/p-diamond heterostructure devices*

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An n-ZnO:Al/p-boron-doped diamond heterostructure electroluminescent device is produced, and a rectifying behavior can be observed. The electroluminescence spectrum at room temperature exhibits two visible bands centred at 450 nm–485 nm (blue emission) and 570 nm–640 nm (yellow emission). Light emission with a luminance of 15 cd/m^2 is observed from the electroluminescent device at a forward applied voltage of 85 V, which is distinguished from white light by the naked eye.

Keywords: boron-doped diamond film, ZnO:Al, heterojunction, electroluminescence

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1. Introduction

Diamond has excellent physical and chemical properties, such as high thermal conductivity (at room temperature), a low thermal expansion coefficient, a low friction coefficient, high breakdown voltage, high chemical stability, a large band gap, and strong optical transmittance from the far infrared region to the ultraviolet. These excellent properties have wide application prospects in microelectronics, mechanical processing, optics, and other fields, especially inorganic electroluminescence (EL). Diamond is expected to be a promising, high-energy light-emitting material, so it has become a research hotspot.[1–6] At present, some researchers have successfully investigated the p-type (boron-doped) semiconductor material properties of diamond thin-film materials. Others have studied its electrical properties and achieved a minimal resistivity so the production requirements of the electronic device can be met.[4] However, a satisfactory n-type conduction diamond is difficult to achieve.

Zinc oxide (ZnO) is a hexagonal structure of the II–VI group wide band gap compound semiconductor material. It has high light transmittance, a larger optical coupling coefficient and temperature coefficient, along with low dielectric constant, easy doping, and other excellent features. So in recent decades, ZnO material and ZnO-related optoelectronic devices have been extensively studied.[7–16] If the ZnO film is doped with Al^{3+}, the conductive nonequilibrium carrier is mainly electronic, so the ZnO film will have an n-type semiconductor material property, with aluminum atom donor impurity. Because the number of valence electrons of aluminum is more than that of zinc, ZnO:Al (AZO) film possesses weakly bound electrons, which can easily break out and become electrons in the conduction band, so the concentration of current carriers will increase greatly. So, AZO has excellent conductive properties and can also be used as a transparent conductive electrode.[12–14] In a word, an n-type ZnO can be relatively easily achieved. On the contrary, a p-type ZnO is rarely achieved. Therefore, in order to obtain a wide band gap p–n heterojunction, a possible solution is to combine the n-type ZnO and p-type diamond.[8,15]

In the present work, n-type ZnO:Al (AZO) films are deposited on p-type boron-doped diamond films using the electron beam vapor deposition (EBVD) method to fabricate a heterojunction EL device. The n-AZO layer acts not only as the n-type layer, but also as the transparent conductive electrode at the same time. A rectifying behavior can be observed from the device, indicating the formation of a diode. And the EL spectrum shows that there are two visible emission bands, which are centred at 450 nm–485 nm (blue emission) and 570 nm–640 nm (yellow emission), respectively.

2. Experimental procedure

Step 1 We used a suspension liquid of diamond powder to pretreat the heavily doped silicon wafer in order to obtain more nucleation points. It was then cleaned with alcohol in an ultrasonic cleaning machine. Subsequently, we placed the silicon wafer into microwave plasma chemical vapor deposition (MPCVD), and kept the conditions constant to grow the diamond film. The deposition conditions for the present samples were maintained as follows: the CH_4/H_2 ratio was 2/100, the base pressure in the deposition chamber was 7.0×10^3 Pa, and

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the substrate temperature was kept at 900 °C. The experiment was performed for 15 h, resulting in a 5-μm thick diamond film, which was obtained from the fringes observed in the infrared absorption spectrum.

Step 2 A boron layer (0.5 μm) was deposited on the diamond film by an electron beam vapor deposition (EBVD) method using a boron (purity 99.9%) target. The typical parameters used for the EBVD process are listed in Table 1.

Table 1. The parameters employed for the EBVD process.

EBVD process parameters	Values
Beam current/mA	80
Substrate temperature/°C	350
Voltage/kV	6
Thickness/Å	500
Filament current/A	0.65
Coating vacuum/Pa	8.2×10^{-2}
Non-coating vacuum/Pa	2.5×10^{-3}

Step 3 A diamond layer (2.0 μm) was deposited on the boron layer using an MPCVD system. The typical parameters used for the CVD process are listed in Table 2.

Table 2. The parameters employed for the MPCVD process.

MPCVD process parameters	Values
Methane/hydrogen gas flows/sccm	2/100
Substrate temperature/°C	900
Total gas pressure/kPa	7.0
Plasma processing time/h	10
Microwave power/W	1700

Step 4 An AZO layer (1.0 μm) was deposited on the boron film with an EBVD system from a ZnO:2.5 wt% Al_2O_3 target (purity: 99.99%). The typical parameters used for the process are listed in Table 3.

Table 3. The parameters employed for the EBVD process.

EBVD process parameters	Values
Beam current/mA	30
Substrate temperature/°C	400
Voltage/kV	6
Filament current/A	0.6
Oxygen gas flow/sccm	6
Coating vacuum/Pa	2.0×10^{-2}
Non-coating vacuum/Pa	1.5×10^{-3}

The surface morphologies and microstructures of the films were characterized by a Raman spectrum, field emission scanning electron microscopy (FE-SEM), an X-ray diffraction (XRD) spectrum, and an energy diffraction spectrum (EDS). Based on these measurements, an n-AZO/p-diamond heterojunction structure EL device was made, as shown in Fig. 1. Here, the n-AZO layer acted not only as an n-type layer, but also as the transparent conductive electrode at the same time. It was driven by a direct-current (DC) power supply, and the current–voltage (I–V) and EL characteristics were measured by an I–V characteristics detector, UV-visible grating spectrometer (model ZLX-PL-02), and brightness meter, respectively.

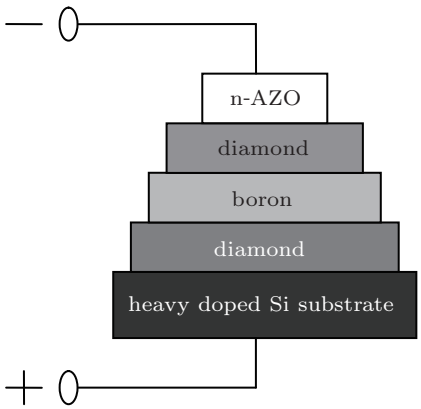


Fig. 1. The structure of the EL device.

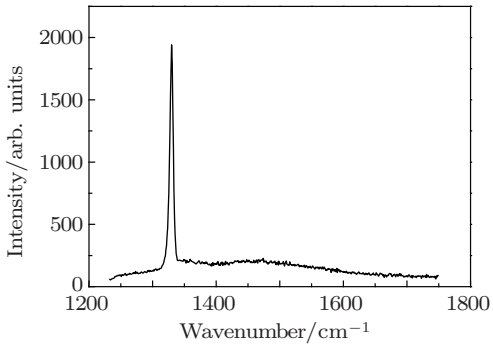


Fig. 2. The Raman spectrum of the diamond sample.

3. Results and discussion

The Raman spectrum of the sample (Fig. 2) shows that there is a sharp peak at 1331 cm^{-1} but no broad peak at 1580 cm^{-1}, meaning that the film has a diamond structure with very few non-diamond phases. The XRD pattern of the film also reveals two prominent diffraction peaks, which correspond to the (111) and (220) faces of the diamond, respectively. The FE-SEM, which is shown in Fig. 3(a), further confirms that the film deposited on the substrate is a polycrystalline diamond film.

The FE-SEM is used to take images of the AZO layer, as shown in Figs. 3(b) and 3(c). Because the thickness of the AZO film is too thin (only 1 μm), the XRD spectrum of the AZO film layer contains not only the peaks of the ZnO layers but also the peaks of the (111) and (220) faces of the previous diamond layer. Similarly, the energy diffraction spectrum (EDS) of the AZO film (as shown in Fig. 4) shows that the characteristic C, O, Al, and Zn peaks occur.

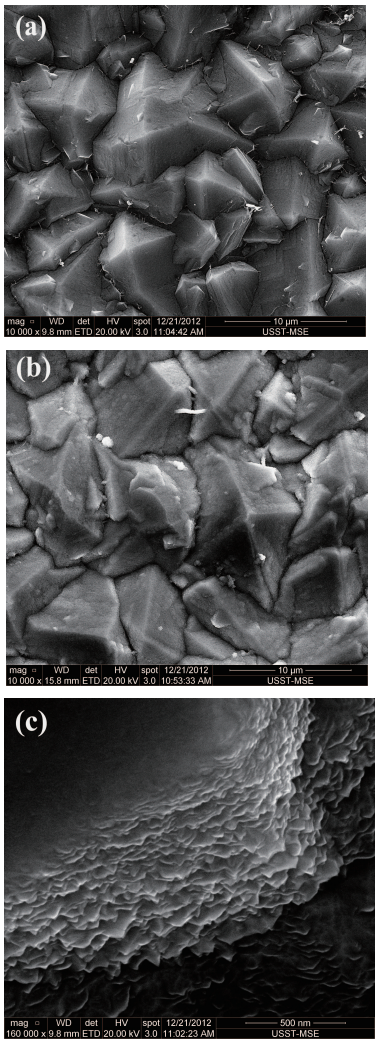


Fig. 3. SEM images of the samples after depositing (a) the diamond layer, (b) the AZO layer, and (c) the magnified AZO layer of panel (b).

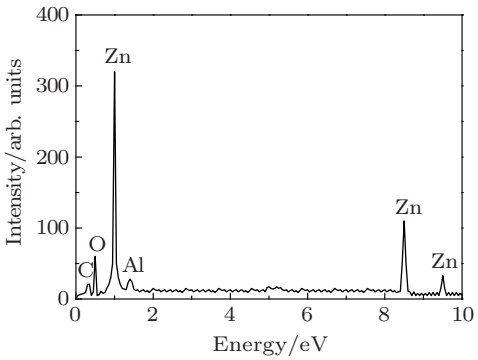


Fig. 4. The EDS of the AZO film layer.

The current–voltage (I–V) characteristic of the n-AZO/p-diamond heterojunction in the dark is measured by an I–V characteristic detector (see Fig. 5), which shows a rectifying behavior at 80 V, indicating the formation of a heterojunction diode. The leakage current for the heterojunction is especially weak when the applied reversed bias voltage changes from 0 V to 85 V. The turn-on voltage of the heterojunction is found to be around 50 V.

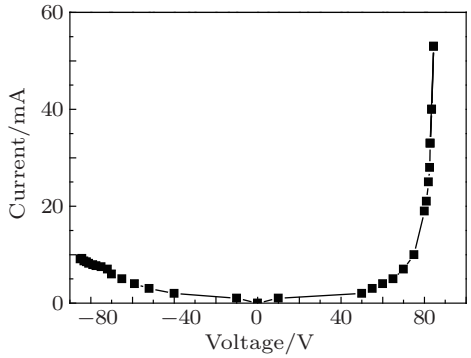


Fig. 5. The I–V characteristic of the AZO/boron-doped diamond heterojunction.

The EL spectrum is measured by a UV-visible grating spectrometer (model ZLX-PL-02) (see Fig. 6). Generally, the EL device exhibits two visible bands centred at 450 nm–485 nm (blue emission) and 570 nm–640 nm (yellow emission), respectively. The EL brightness of the device reaches a maximum of 15 cd/m^2 at a forward applied voltage of 85 V. The white light emission could be observed at room temperature by the naked eye. Figure 7 shows a light emission image of the EL device.

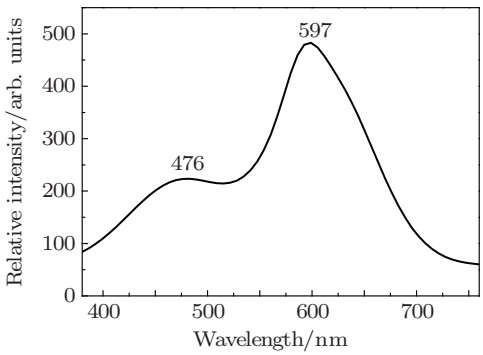


Fig. 6. The EL spectrum of the EL device.

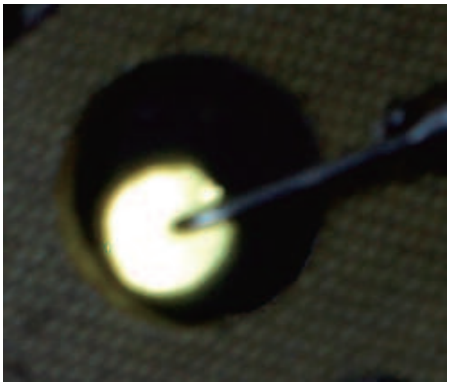


Fig. 7. A light emission image of the EL device.

In order to explain the origin of each EL spectrum peak, it is necessary to understand the energy band diagram of the n-AZO/p-diamond heterojunction. Figure 8 shows the energy

band diagram of the n-AZO/p-diamond heterojunction in the thermal equilibrium. When the n-type AZO and p-type diamond are joined, a large barrier exists between the conduction bands, and the electrons are injected with difficulty into the p-type diamond side. However, between the valence bands a small barrier exists, and the holes can easily be injected into the n-type AZO side. Therefore, the injection current of the n-AZO/p-diamond heterojunction is dominated mainly by the injected holes in the valence bands from the side of the diamond. The blue emission is attributed to the recombination of the electron–hole pairs. The electron comes from the n-AZO layer and the hole originates from the p-diamond layer. The yellow emission should be caused by the recombination of the electron with the deeply trapped hole. According to the reported results in Refs. [11] and [14], the electron comes from the bottom of the conduction band of the AZO, and the hole level is formed by the oxygen interstitial (O_i^-) defect in the AZO film.

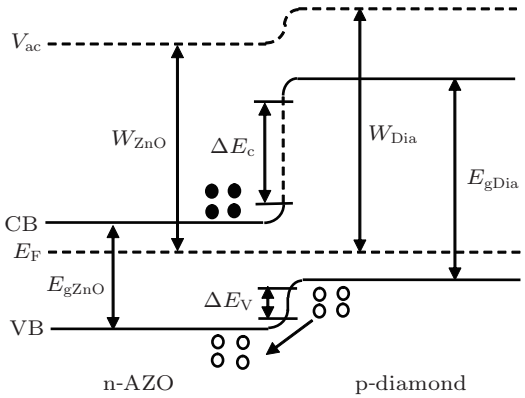


Fig. 8. The energy band diagram of the heterojunction at thermal equilibrium. W_{ZnO} (W_{Dia}) is the work function of ZnO (diamond), ΔE_c (3.85 eV) the conduction band offset, ΔE_V (1.75 eV) the valence band offset, $\Delta E_V = E_{gZnO} + \Delta E_c - E_{gDia}$, where E_{gZnO} (E_{gDia}) is 3.37 eV (5.47 eV) for the band gap of ZnO (diamond), V_{ac} the vacuum level, E_F the Fermi energy, CB the conduction band, and VB the valence band.

4. Conclusions

We fabricated an n-AZO/p-boron-doped diamond heterojunction EL device that shows a rectifying behavior. Its highest luminance is 15 cd·m^{-2} when the forward applied voltage is 85 V. The EL spectrum exhibits blue (450 nm–485 nm) and yellow band emission (570 nm–640 nm). We believe that the blue band light emission comes from the recombination of the electron–hole pairs: the electron comes from the n-AZO layer, and the hole originates from the p-diamond layer. The yellow band light emission is caused by the oxygen interstitial (O_i^-) in the AZO film.

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