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Nonlinear Current-Voltage Characteristics and Electroluminescence of cBN Crystal *

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Abstract: The current-voltage (I-V) characteristics of cBN crystal sandwiched between two metallic electrodes are measured and found to be nonlinear. Over 20 samples are measured at room temperature with various electrodes, and the resulting curves are all similar in shape. When a voltage of about 560V is applied to the cBN crystal, the emitted light is visible to the naked eye in a dark room. We explain these phenomena by the space charge limited current and the electronic transition between the X and Γ valleys of the conduction band.

Key words: n-cBN crystal; nonlinear I-V characteristics; space charge limited current; electronic transition in two valleys

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1 Introduction

Ever since Wonterf[1] first synthesized semiconducting cubic boron nitride (cBN) at high pressures (HP) and high temperatures (HT), its properties and applications have been studied extensively. Compared to diamond, cBN crystal has better heat resistance, oxidizable resistance, chemical stability, and semiconducting characteristics. It can be made into both p-type and n-type semiconductors when doped with suitable impurities[2], and it has the widest energy gap (about 6.3eV) of all Ⅳ and Ⅲ-Ⅴ materials. The indirect transition in cBN crystal is from the Γ point of the valence band to the X point of the conduction band[3,4]. Therefore, cBN crystal has wide applications in high-frequency, high-temperature, and high-power electronic devices.

Because of the limitations on synthesis conditions, each synthetic cBN crystal is slightly different from all others. The biggest one is no more than 3mm[5]. Only a few experiments have been done to clarify the fundamental electrical characteristics of cBN polycrystalline[6].

In 2002, Takashi *et al.*[5] measured the impurity level of nonintentionally doped cBN crystal by Hall measurements with $E_d = 0.47$eV. Wentorf reported that oxygen is the responsible impurity[7]. Takashi *et al.* obtained colorless crystals from nonintentionally doped n-type amber crystals. The oxygen concentration in the colorless crystals is less than that in the nonintentionally doped n-type amber crystals.

In this paper, we report the current-voltage (I-V) relationship in nonintentionally doped cBN crystal and the observation for the first time of the electroluminescence of cBN crystal. We explain these phenomena by the space charge limited current (SCLC) and the electronic transition between the X and Γ valleys of the conduction band.

2 Experiment

2.1 Synthesis of cBN wafer

Nonintentionally doped cBN crystal, which is

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an n-type amber crystal, is transformed from hexagonal boron nitride (h-BN) under HP and HT using nitride as a catalyst[8]. This may be a result of the responsible oxygen impurity, since it is extremely difficult to exclude oxygen from the reaction mixtures. The cBN crystal has a high resistivity in the range from 10^5 to $10^9\,\Omega\cdot$cm at room temperature[7]. Most synthetic cBN crystals have an irregular octahedron structure; however, this structure is inconvenient for the measurement of electrical characteristics, so we obtained cBN wafers with several hundreds of microns in size using a cubic anvil high-pressure apparatus. The sample shown in the top left of Fig. 1, whose opposite planes are parallel and approximately equal, was used in our experiment.

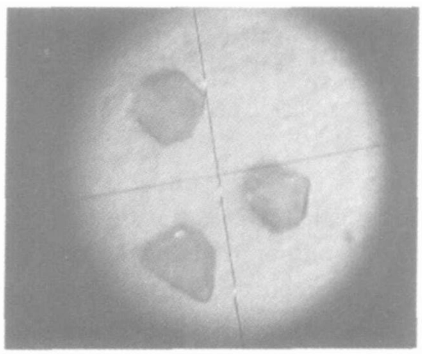

Fig. 1 Microscope photograph of cBN sample The cBN in top left corner was used in our experiment. S = 0.1427mm^2, L = 0.06mm

2.2 Measurement of I-V relationships and light emission of the cBN wafer

At room temperature, over 20 cBN crystals were measured using various electrodes, such as platinum wire, copper board, aluminum board, wolfram, and ITO. The shapes of the *I-V* curves for various cBN crystals are similar, as shown in Fig. 2 (triangles). Each synthesized cBN crystal is different, so their measured values are slightly different. For the same cBN crystal, the measured values are approximately equal and independent of the electrodes.

The light emitted from the cBN crystal is visible to the naked eye in a dark room when the voltage applied to the cBN crystal is about 560V. At the voltage at which the emission begins, the light is so weak that we cannot characterize it. The light intensity increases as the voltage increases. A photograph of the light emission of cBN crystal is

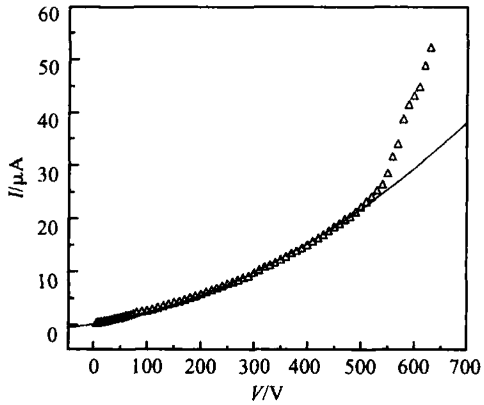

Fig. 2 Current versus applied voltage of cBN crystal

shown in Fig. 3.

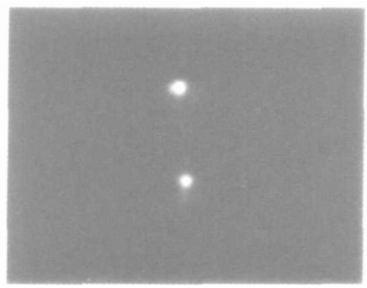

Fig. 3 Photograph of the electroluminescence of cBN crystal

3 Results and discussion

The *I-V* curve at room temperature is shown in Fig. 2 (triangles). The nonintentionally doped n-cBN crystal has a nonlinear *I-V* curve. This is in agreement with the space charge limited current (SCLC) theory of Lampert and Mark[9]. SCLC was proposed for an ideal dielectric. For a semiconductor with a certain conducting ability, its dielectric relaxation time is longer than its transit time so long as it has a high enough resistance. In this case the SCLC theory is valid[10,11]. The current density J in the material can then be divided into the ohmic and space charge limited regimes, which are expressed by[9]

$$J_\Omega = n_0 q\mu V/L \tag{1}$$

$$J_s = 9\theta\varepsilon\varepsilon_0\mu V^2/L^3 \tag{2}$$

where $\theta = \frac{n}{n + n_t}$, n is the injected carrier concentration, and n_t is the concentration of the electrons occupying the traps. For cBN crystal, θ is not determined because the trap concentration is not known. S and L are the area and thickness of the cBN crystal, respectively, n_0 is the thermal equilibrium carrier concentration, ε is the dielectric permittivity, ε_0 is the permittivity of free space, and μ_n is the electron mobility. The solid curve along the triangles in Fig. 2 represents the best fit of the data to Eq. (3) between 0 and 530V, and its equation is

$$I = \frac{S}{L}\sigma V + \frac{9\theta\varepsilon\varepsilon_0\mu_n S}{8L^3}V^2$$
$$= 1.589 \times 10^{-8} V + 5.5 \times 10^{-12} V^2 \quad (3)$$

The two contributions to the measured current on the right-hand side of Eq. (3) are ohmic and SCLC.

According to the ohmic term in Eq. (3), the conductivity of cBN is

$$\sigma = 6.8 \times 10^{-8}\Omega^{-1} \cdot cm^{-1} \quad (4)$$

The dielectric relaxation time is then

$$\tau_d = \frac{\varepsilon\varepsilon_0}{\sigma} = 9.2 \times 10^{-6} s \quad (5)$$

In our experiment, when the voltage applied to the cBN crystal is 5V, the current is measured and the field inside the crystal is assumed to be uniform, so the transit time of an electron is

$$T = \frac{L}{\mu_n V/L} = 3.6 \times 10^{-7} s \quad (6)$$

where $\mu_n = 20 cm^2/(V \cdot s)$ [5]. As soon as the current through the cBN is detected, the SCLC effect plays a role in the cBN crystal.

The carrier concentration at room temperature estimated from the ohmic term in Eq. (3) is $10^{10} cm^{-3}$. For other measured samples, the carrier concentration is on the same order, which is less than that ($10^{12} cm^{-3}$) in Ref. [5]. In Ref. [5], the cBN crystal was synthesized with the temperature gradient method with a solvent of lithium boron nitride (Li_3BN_2) at HP and HT. According to the experimental results, there are fewer impurities in the cBN crystal synthesized by us than in Ref. [5] due to the different synthesis conditions.

At thermal equilibrium, the carrier concentration for the intrinsic transitions in the cBN crystal is

$$n_0 = (N_c N_v)^{1/2} \exp(-E_g/2kT) \quad (7)$$

N_c, N_v, and E_g are known[12]. At room temperature, n_0 was estimated to be

$$n_0 = 5.65 \times 10^{-34} cm^{-3} \quad (8)$$

Even at $T = 1000K$, n_0 equals $1.64 \times 10^6 cm^{-3}$. This indicates that the electrons are not produced by the intrinsic transition, but by ionized impurities in the cBN crystal.

As shown in Fig. 2, the I-V curve becomes steep and does not fit Eq. (3) above 530V. At about 560V, weak emission from the cBN is visible in a dark room.

In 1999, Zhao et al. discussed the intervalley distribution in ZnS-type thin film electroluminescent devices[13]. We think the electronic transition between the two valleys of the conduction band leads to these phenomena we have observed in the cBN crystal.

When the voltage applied to the cBN crystal is about 560V, some electrons produced by ionized impurities and injected electrons are transmitted between the X and Γ valleys of the conduction band. According to the energy-band structure[3,4,12] (Fig. 4), when the electrons in the *X* valley obtain adequate energy from the electric field, the electrons transfer from the heavy-mass, low-mobility *X* valley to the light-mass, high-mobility Γ valley. The energy in the *X* valley is about 3eV less than that in the Γ valley, but the electrons in the Γ valley have a tendency to return to the *X* valley. In the radiative transition produced by these electrons, the energy is liberated by means of photons, so the cBN crystal luminesces. The light intensity increases as the voltage increases.

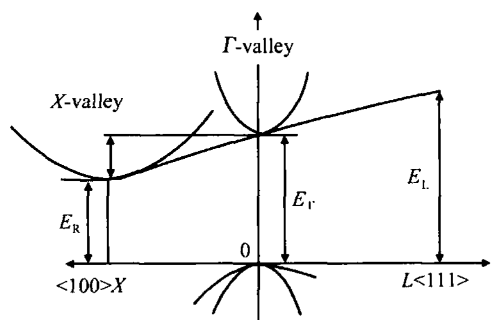

Fig. 4 Scheme of the energy band of cBN crystal At 300K: $E_g \approx 6.1 \sim 6.3eV$, $E_\Gamma \approx 8.5 \sim 10eV$, $E_L > 12eV$

According to the energy-band structure of the cBN crystal (Fig. 4), when the electrons transfer between the *X* and Γ valleys of the conduction band, the wavelength of the emitted light should be about 400nm, which is in the blue-violet range. This agrees with our experimental observations.

4 Conclusion

We measured the current-voltage (I-V) curves of cBN crystal sandwiched between two metallic electrodes. The curves are nonlinear. The SCLC plays a role in the cBN crystal. The carrier concentration of the cBN crystal used here is calculated. The light emission from the cBN crystal becomes visible to the naked eye when the voltage applied to the cBN crystal reaches about 560V. The electrons in the cBN crystal produce a radiative transition, leading to the luminescence of the crystal. The experimental observations are well in accord with our theoretical analysis.

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立方氮化硼晶体的非线性伏安特性及电致发光*

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摘要: 测量了夹在两个金属电极间的非故意掺杂的 n 型立方氮化硼(cBN)晶体的伏安特性,它们为非线性曲线. 使用不同的电极测量了 20 多个 cBN 晶体的伏安特性,曲线的形状非常相似. 在样品两端的电压值大约为 560V 时, cBN 晶体发生电致发光现象. 利用空间电荷限制电流和能谷间的电子跃迁解释了上述实验现象.

关键词: n 型立方氮化硼; 非线性伏安特性; 空间电荷限制电流; 能谷间电子跃迁

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