

STUDY OF THE PHOTOCONDUCTANCE OF UNINTENTIONALLY DOPED CUBIC BORON NITRIDE CRYSTAL

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ABSTRACT: *Cubic boron nitride (cBN) is a kind of artificial (synthetic) crystal. The band gap of cBN crystal is about 6.3 eV, which has the zinc blende structure and the $\bar{4}3m$ symmetry. The cBN crystal has strong effects of frequency doubling and sum frequency generation which is second order nonlinear optical properties. The Nd: YAG laser with wavelength of 1064 nm is used. After the main beam passing KTP (KTiOPO₄) which is a nonlinear optical crystal, the second harmonic with the wavelength of 532 nm is obtained. When the beam of 532 nm passes through the frequency doubling crystal cBN, it is frequency-doubled to 266 nm. Then the wavelength of 177 nm is obtained after the wavelength of 266 nm is frequency-summed with the wavelength of 532 nm. These light beams of 532, 266 and 177 nm come into the cBN crystal, they are absorbed. The photoconductance of unintentionally doped cBN is studied under the illumination of light rays with wavelength of 266 and 177 nm respectively. The electric signal is measured and analyzed.*

KEYWORDS: Cubic boron nitride, Second order nonlinear optical properties, Photoconductance

INTRODUCTION

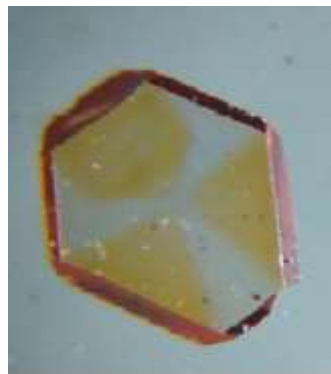
Cubic boron nitride (cBN) is a kind of wide energy gap artificial semiconductor crystal, which has zinc blende structure with $\bar{4}3$ symmetry. Although the cBN crystal is the simplest III-V compound, it has the widest band gap^[1, 2] (about 6.3 eV, indirect) among IV and III-V materials. The cBN crystal has similar properties compared to diamond in terms of mechanical hardness, thermal conductivity^[3], chemical stability, and transparency over a wide optical spectrum. The cBN crystal surpasses diamond in terms of heat resistance, oxidation resistance, and semiconducting characteristics. The cBN crystal can be made into p-type or n-type semiconductors when doped with suitable impurities^[4]. In 1962, the first study describing the potential of cBN as a semiconductor was reported^[5]. According to the intrinsic photoconductance of cBN, UV photoconductor can be made. The cBN crystal is not sensitive to the light of a wavelength more than 197 nm, such as visible light and infrared ray (IR) light. However, it is sensitive to light of wavelength less than 197 nm, as UV light. It is very important to detect UV radiation under background of visible light and IR light. The cBN crystal is an ideal material for designing devices which have high power, short wavelength and high temperature-resistance.

As a light ray is incident through a semiconductor sample, the conductivity of the

semiconductor increases^[6]. It can be divided into two types, intrinsic and impurity photoconductance. In this paper, the photoconductance of unintentionally doped cBN single crystal is investigated. As far as we know, few experiments on the study of the photoconductance of the cBN crystal by short laser pulses has been reported.

EXPERIMENT AND THOERY

The cBN sample and sample preparation



L 400 μm \times d 60 μm

Figure 1. Photograph of the cBN sample

An ideal cBN crystal is a regular octahedron structure. But most crystal samples were irregular octahedra made in laboratory, whose surfaces are all $\{111\}$ planes^[7]. The actual shape of the cBN crystal in our experiment is shown in Figure 1.

For the small size of the crystal, length L and thickness d of the cBN sample were measured with a microscope. We designed a special structure in which the cBN sample is sandwiched between two conducting glass plates. The conducting glass plates used as two electrodes are attached to each other with insulating glue, as in Figure 2.

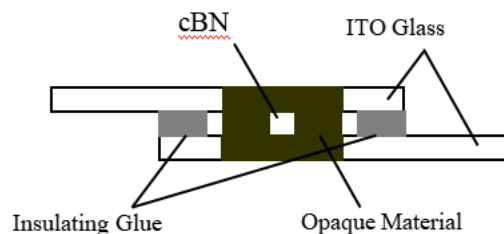


Figure 2. A mount of cBN samples

Measurement of the photoconductance

We use Q-switching Nd: YAG laser, with the wavelength of 1064 nm, the peak power more than 700 W, the repeated frequency of 2 kHz and the pulse wide less than 20 ns. The output light focused on KTP frequency doubling. Figure 3 shows the experimental setup for the photoconductance of unintentionally doped cBN crystal.

The plane mirror optics and detectors provide a reference signal for the lock-in amplifier, it is used to measure the signal voltage on the sampling resistance. In the experiment, the unintentionally doped cBN is a crystal of n-type with amber. Without light, the conductivity σ_0 of cBN crystal is given by equation (1).

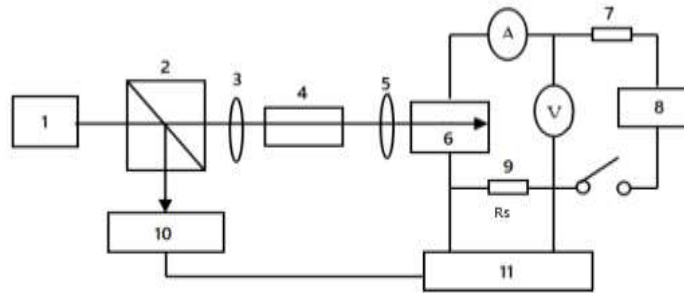
$$\sigma_0 = en_0\mu_n \quad (1)$$

Under light, the conductivity σ of cBN crystal is given by equation (2).

$$\sigma = en\mu_n \quad (2)$$

Where the n_0 and n are the electron concentration with and without illumination respectively, μ_n is the mobility of electron in cBN, and $n = n_0 + \Delta n$. Then the photoconductance is

$$\Delta\sigma = \sigma - \sigma_0 = e\Delta n\mu_n . \quad (3)$$



1. Nd. YAG laser, 2. PBS, 3. Lens, 4. KTP, 5. Lens, 6. cBN sample, 7. Resistor 500 k Ω , 8. Direct-current power, 9. Resistor 1.7 M Ω , 10. Si -Photodetector, 11. Lock-in-Amplifier.

Figure 3. Experimental setup for impurity photoconductance of cBN crystal

The concentration of static photo-induced carrier^[8] is

$$\Delta n = \beta\alpha\Phi\tau_n . \quad (4)$$

Where Φ is light intensity calculated by photon number, α is absorption coefficient of sample, β is quantum yield, τ_n is lifetime of photo-induced electron. On the basis of these discussions, we can obtain

$$\frac{d\sigma}{\sigma} = \frac{e\mu_n}{\sigma} \beta\alpha\Phi\tau_n \quad . \quad (5)$$

Suppose that A and L respectively are area and thickness of the cBN crystal respectively, then its resistance R_C is

$$R_C = \frac{L}{A\sigma} \quad . \quad (6)$$

Then,

$$dR_C = -\frac{L}{A\sigma^2} d\sigma = -R_C \frac{d\sigma}{\sigma} \quad . \quad (7)$$

The minus sign means that the rate of relative change between the resistance and conduction is opposite.

Substitute formula (5) into formula (7), we can obtain the following equation

$$dR_C = -\frac{R_C e\mu_n \beta\alpha\tau_n}{\sigma} \Phi \quad . \quad (8)$$

In order to find the photon induced carrier influence on sample resistance, a voltage should be applied to the sample. Assume the applied voltage is V and the voltage applied to the resistance of the sample is ΔV_s , then we have

$$\Delta V_s = \frac{VR_s}{R_C + R_s} \quad . \quad (9)$$

Then

$$dV_s = \frac{VR_s}{(R_C + R_s)^2} dR_C \quad . \quad (10)$$

We can obtain the voltage on the sample resistant R_s is

$$\Delta V_s = \frac{AR_s R_c^2 e\mu_n}{(R_C + R_s)^2 L} \Delta n V \quad . \quad (11)$$

Where A and L are the area and thickness of the cBN crystal respectively, R_s is the sampling resistance, R_c is the resistance of cBN, μ_n is the mobility of electron in cBN, Δn is the changing value of carrier, V is the applied voltage. From equation (11), we can find a linear relationship between ΔV and V .

RESULTS AND DISCUSSION

In practice, the experimental data also fit equation (12) well as shown in Figure 4.

$$\Delta V = -94.33 + 2.25V \quad (12)$$

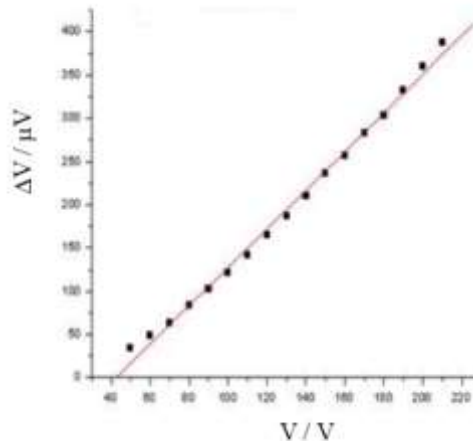


Figure 4. Photoconductance of cBN crystal

When the laser pulse passes through the beam splitter, the sub-beam passes through the silicon detector as a reference signal to be supplied to the lock-in amplifier, and the other the main beam (pulse laser) is focused on the KTP crystal. After the main beam passes KTP, the second harmonic with the wavelength of 532 nm is obtained. The beam of 532 nm passes through the frequency doubling crystal cBN and is frequency-doubled to 266 nm once more. Then the wavelength of 177 nm is obtained after the sum frequency generation of the wavelength of 266 nm with the wavelength of 532 nm. In this process, the cBN crystal produces intrinsic photoconductance of absorbing the wavelength of 177 nm.

From the normalization absorption spectrum^[7] of cBN crystal measured in the Lab, we got that the wavelength of the light which the cBN crystal intrinsic absorption is less than 200 nm^[9]. The second order nonlinear optical conductivity effect of the cBN crystal is strong. We measured the second order nonlinear optical conductivity coefficient in the experiment and the coefficient is higher than other crystal^[10]. And in the previous experiment, the wavelength of 1064 nm passes through the cBN crystal obtained the green light with a wavelength of 532 nm without phase matching^[11]. In conclusion, the cBN crystal is a high-performance frequency doubling crystal.

The cBN crystal has the absorptivity of more than 50% to the light with wavelength less than 500 nm. So the wavelength of 177 nm which is generated by sum frequency of the wavelength of 532 nm and the wavelength of 266 nm made the cBN crystal obtain

intrinsic absorption and produce the intrinsic photoconductivity. In the experiment, using unintentionally doped cBN is n-type crystal wherein oxygen is responsible impurity (energy level is 0.47 eV^[12]). The cBN crystal absorbed the wavelength of 266 nm and obtained the impurity absorption. So the voltage drop we measured is produced by the cBN crystal impurity photoconductance and the intrinsic photoconductance in the sampling resistance. And it has a linear relationship with the applied voltage which fit the matching curve in Figure 4.

CONCLUSION

In conclusion, we have studied the photoconductance of unintentionally doped of cBN crystal. The pulse light with the wavelength of 1064 nm passes through the KDP crystal and the light with wavelength of 532 nm is obtained. The cBN crystal has an effect of frequency doubling and sum-frequency generation. The light with the wavelength of 532 nm illuminates the cBN crystal. The wavelength of 532 nm which passes through the frequency-doubled cBN crystal produces the wavelength of 266 nm. And the wavelength of 177 nm is obtained after the sum frequency generation from the wavelength of 266 nm and the wavelength of 532 nm. Because of absorbing the wavelength of 266 nm and 177 nm, the cBN crystal creates the impurity and intrinsic photoconductance. We measured the second order nonlinear optical conductivity coefficient in the experiment and the coefficient is higher than other crystal.

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