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Characterization of single crystal diamond by double crystal X-ray diffraction

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The crystal quality of bulk and epitaxially grown diamond was characterized by double crystal X-ray diffraction for the first time. Synthetic bulk diamond (Ib type) was used as first crystal in a double crystal diffractometer. The extremely small full width at half maximum (FWHM) from 5" to 20" was obtained for synthetic diamond of Ib type crystal, whereas large FWHMs of 200" to 2000" and 6" to 60" were obtained for IIa and Ia tpye natural diamond, respectively. For epitaxial diamond films on synthetic diamond, FWHM broadening from the substrate were only few arc sec.

1. INTRODUCTION

Diamond has excellent optical and electrical properties. In optical properties, diamond is transparent in the range of infrared to ultra-violet region except for the absorption at lattice vibration. In electrical properties, diamond has a wide band gap and high breakdown voltage, which make diamond devices suitable for high temperature [1,2]. Since these properties are dependent on the crystalline quality such as defects, impurities, disorder and strain, high quality crystals are required. Therefore, a single crystal substrate and an epitaxial film should be characterized and be refined.

The crystallinity of diamond is usually characterized by Raman spectroscopy in order to distinguish diamond from graphitic component [3]. The crystalline quality of a polycrystalline diamond is often estimated by FWHM of Raman spectroscopy [4]. Estimating IIa single crystal diamond by Raman spectroscopy, it is found that the spectrum is very sharp, which is believed to have high crystal quality. However, the Raman spectroscopy can not provide informations on crystallographic structure. Thus, it is important to obtain further crystallographic information by X-ray diffraction method, which is usually performed in Si, GaAs and other semiconductors.

In this study, the crystallographic quality of single crystal diamond characterized by the double crystal X-ray diffraction method is reported for the first time. The characterized diamond were synthesized diamond (type Ib) and natural diamond (type Ia, IIa, IIb). Epitaxial diamond films grown by the micro-wave CVD method on synthesized diamond substrates were also characterized.

2. EXPERIMENTAL

The schematic diagram of the double crystal X-ray diffraction method is shown in Fig. 1. Cu $K\alpha$ ray was used as a source of X-ray and a synthesized single crystal (100) plane was used as the first crystal. The size of the first crystal was 4mmx4mmx0.3mmt. As the diffracted beam is collimated, only $K\alpha_1$ is introduced into the crystal specimen. Single

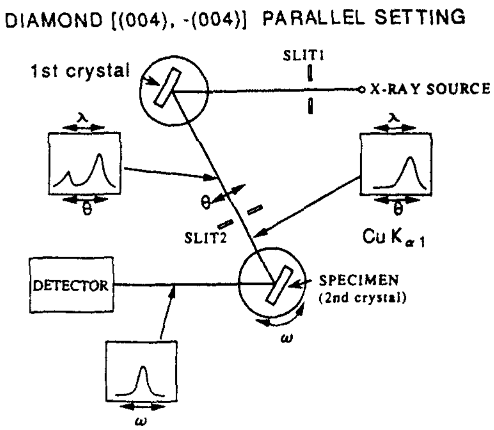

Fig. 1 Schematic of rocking curve measurement of double crystal X-ray diffraction.

crystal diamond (001) of type Ia, IIa, IIb and Ib are characterized. Typical second crystal size is 2mmx2mmx2mmt for the natural diamond and 2mmx1.5mmx0.3mmt for the synthetic diamond.

Epitaxial films are grown on synthetic diamond by the micro-wave plasma CVD method. Preceding deposition, synthetic diamond substrates have been estimated by the double crystal method and the high quality substrates whose FWHM are less than 8 arc sec. have been selected as the substrate of the epitaxial films.

Condition of micro-wave plasma CVD are as follow: CH_4/H_2 is 1-8 %, micro-wave power 400 W, pressure 40 Torr, substrate temperature 870 °C.

3. THEORETICAL FWHM

Theoretical FWHM of the double crystal method include both the width of first crystal and second crystal and the width (Δ) of double crystal diffraction method, as shown in equation (1).

$$(\delta w)^2=(\delta w_1)^2+(\delta w_2)^2+(\Delta)^2 \qquad (1)$$

where,
δw_1: the widening by the 1st crystal
δw_2: the widening by the 2nd crystal

The widening by the first or second crystal include both the fluctuation of the crystal axis and the ideal width. The Δ are given by the equation (2).

$$\Delta=\delta\lambda/\lambda\{\tan(\theta_1)-\tan(\theta_2)\} \qquad (2)$$

where
θ_1: Bragg angle of the 1st crystal
θ_2: Bragg angle of the 2nd crystal

In order to accurately estimate the widening of the second crystal (the specimen), the widening of the first crystal and Δ must be small as posible. However, for diamond evaluation, the Δ is large when Si or Ge is used as the first crystal. Therefore diamond is required for first crystal.

Table 1
Theoretical FWHM for perfect crystal.

1st crystal	Reflection	Bragg angle (°)	FWHM of 1st crystal (")	FWHM of double crystal (")
Diamond(100)	(400)	59.75	2.9	4.1
Si(100)	(400)	34.56	3.6	79.9
Ge(100)	(400)	33.07	7.9	83.1

Table 2
Extinction distance for diamond (100) at Bragg condition.

crystal	Reflection	Bragg angle (°)	Extinction distance (μm)
Diamond(100)	(400)	59.75	11

Next, in order to estimate the crystal strain, we calcuated the ideal width of the perfect crystal. The ideal width of various kind of crystals and FWHM of double crystal rocking curve are shown in Table 1. The increase from the ideal value indicates the strain of the crystal.

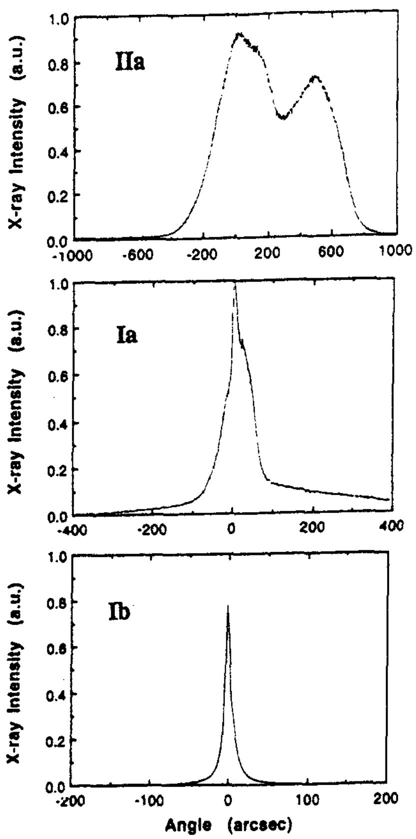

Fig. 2 Typical double crystal rocking curves for various type diamond

For epitaxial film characterization, we should know the extinction distance. According to the dynamical theory of X-ray diffraction, the extinction distance in a single crystal become very small at the Bragg condition. These values are shown in Table 2. It is found that diamond epitaxial film over 10μm thick can be characterized by this method.

4. RESULTS AND DISCUSSION

The typical rocking curves of (400) diffraction of a natural diamond and a synthetic diamond are shown in Fig. 2. The rocking curves for the natural diamond are broad and consist of many peaks. It shows that the natural diamond contain some crystals, which may have tilted grain boundaries. In particular, it seems that type IIa and IIb diamond have poor crystal quality. On the other hand, the synthetic diamond (type Ib) has high crystal quality without any grain boundaries.

Results on a lot of crystals are summarized in Fig. 3. In this figure, it is found that the FWHM of type IIa and IIb diamond are over a thousand arc sec, FWHM of Ia diamond are 6-60 arc sec and FWHM of Ib diamond are 5-20 arc sec. Therefore, in general, it can be concluded that the crystalline quality of a synthetic diamond is higher than that of the natural dia-

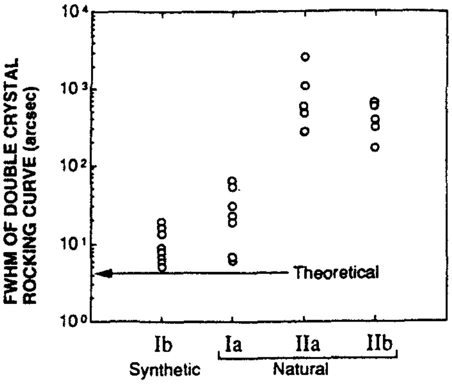

Fig. 3 FWHM of rocking curve for various type diamond.

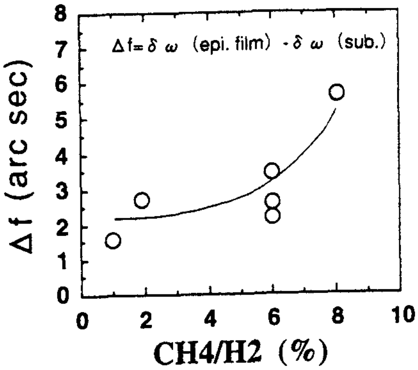

Fig. 4 Broadening of FWHM of double crystal rocking curve for various methane concentration.

mond.

Some of the type Ib diamond have sharp peaks of 5-6 arc sec. This value is as small as that of high quality Si or GaAs single crystals. This indicates that some synthetic diamond have high crystallographic quality of semiconductor material level.

The epitaxial diamond films are grown on the substrates whose FWHM are less than 8 arc sec. The diffraction broadening of the epitaxial films from the substrate are shown in Fig. 4. In the epitaxial films grown at CH_4/H_2 of 1-6 %, FWHM broadening are only a few arc sec. Though the epitaxial film grown by the micro-wave plasma CVD method have room for improvement, CVD epitaxial diamond films on synthetic diamond seem to have higher crystallographic quality compared with type IIa or Ia diamond.

4. CONCLUSION

The crystallographic quality of natural, synthetic and epitaxially grown single crystal diamond was characterized by the double crystal X-ray diffraction method for the first time. It was found that some type Ib diamonds have quality as high as Si and Ge single crystals and that synthetic diamond have higher crystalline quality compared with natural diamond. The FWHM of epitaxial film grown by the micro-wave plasma CVD method become typically broad from 1.5" to 6" compared with that of the synthetic diamond substrate. This indicates that the epitaxially grown diamond films have high crystallographic quality.

REFERENCES

1. A. V. Bogdanov, I. M. Vikulin and T. V. Bogdanova: Sov. Phys. Semicond. 16 (1982) 720.
2. E. A. Konoirova, Yu. A. Kuznetsov, V. F. Sergienko, S. D. Tkachenko, A. V. Tsikanov, A. V. Spitsyn and Yu. Z. Danyushevski: Sov. Phys.-Semicond. 17 (1983) 146.
3. D. S. Knight and W. B. White: J. Mater. Res. 4 (1989) 385.
4. J. Wagner, M. Ramsteiner, Ch. Wild and P. Koidl: Phys. Rev. B 40 (1989) 1817.