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Characterization of Diamond Clusters using TEM and X-ray Diffraction Methods

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Three different kinds of diamond samples (bulk powder (1-4)μm, fine particle (144 and 195) Å and cluster (55-63)Å) were characterized by the Grazing Incidence X-Ray Diffraction (GIXRD) and Transmission Electron Microscopy (TEM) methods. The values of the Debye temperature parameter, B, were found to be in the range of (0.50-0.71)Å^2 for the particle size range of (195-55)Å, respectively, except for two samples of particle size (1-4)μm where the B value was found to be 0.27 Å^2. The observed B values are larger than the diamond bulk value. The strain was calculated in the range of (0.05-0.18)% for different particle sizes that indicates less static lattice distortion. TEM photographs indicate that the clusters are not spherical in shape but mostly rectangular and some are polyhedron. The observed B values increase with decreasing the particle size. This is the first observation of its kind for such a trend of particles size dependence of B-parameter in diamond samples. Thermal vibrations of surface atoms are possibly more responsible than the static lattice distortions in the fine particle and clusters for large B values.

1. INTRODUCTION

In recent years, researchers are paying their great attention to the fundamental study of inorganic, organic, metallic and semiconductor clusters in the size range from 1 to 10 nm because of their actual and potential uses in the integrated circuits, X-ray mirrors, micro electronics, as catalysts etc. [1, 2]. The fundamental study of the metallic clusters is not only for their applications but also for their basic properties. It is still not clear whether the structural and physical properties of metallic clusters are different from those of bulk.

Harada et. al. [3] have reported two times larger Debye temperature parameter (B) value than that of the bulk for 100 Å average diameter Au fine particle. Ohshima et. al. [4] have characterized the Pd cluster with average size of 20Å and reported almost three times larger B value than that of the bulk. These studies strongly suggest that the B value seems to increase when particle size decrease, although the reason for this change in B value is not clear. However, no systematic study has been carried on this problem.

Diamond nano-particles with various sizes are very important commercially. They are widely used for superpolishing various solid surfaces and for chemical and electrochemical coatings. Although the properties of the bulk diamond are well known, those of fine particles and clusters have not been well characterized yet. Since various sizes of diamond particles are commercially available, the changes in properties with particle size can be studied systematically and the above mention problem can be solved by applying the X-ray diffraction technique. The B-Parameter, the average particle size (ε), the mean square atomic displacement ($\langle u^2 \rangle$), the mean square strain ($\langle e^2 \rangle$) etc. are obtainable from the analyses. In this paper the results of observation will be reported.

2. EXPERIMENTAL PROCEDURE

Ten diamond samples with different particle sizes were kindly supplied by Tokyo Diamond Tools Mfg. Co. Ltd., Tokyo, Japan. The particles were prepared by detonation decomposition of explosive TNT [5] in Russia (all C-samples and FP-1), USA (FP-2) and China (BP), where C, FP and BP denote cluster, fine particle and bulk powder, respectively. The colour of samples is different each other. The Grazing

Incidence X-Ray Diffraction (GIXRD) method was used which is suitable for the study of fine particle. The CuKβ radiation, with a primary beam power of 50 kV and 200 mA, was selected by a HOPG monochromator placed between the soller slit and the counter. The reflection mode was used with the incident angle of 2° and a soller slit was placed after the sample. A glass plate with a central groove of 20x20x0.5 mm^3 dimensions was used as a sample holder and the sample was placed in the groove and made its surface smooth. For the Transmission Electron Microscopy (TEM) measurement a JEOL JEM-2010 Electron Microscope was used with an amorphous carbon substrate as a sample substrate. Samples for the TEM measurement were prepared as follows: A very small amount of powder diamond particles (0.005 g) was put into 50 cc of water. The particles were dispersed into water by shaking the solution with an ultrasonic vibrator for 10 minutes, then an amorphous carbon substrate was placed into the solution to collect particles on the substrate. The substrate was dried and used for the TEM observation.

3. RESULTS AND DISCUSSION

Powder patterns of five Debye-Scherrer lines were observed from each sample where the lines 111, 220, 311, 400 and 331 are well indexed by the bulk diamond structure, respectively. Figure 1 shows a typical X-ray diffraction pattern observed from the 55Å cluster sample. The observed integrated intensities ($I_{obs.}$) were analyzed by comparing with their calculated values ($I_{cal.}$) according to equation (1). The B-parameter was obtained by fitting the plot of $\ln(I_{obs.}/I_{cal.})$ versus $(\sin\theta/\lambda)^2$ shown in Figure 2 by a least squares fitting procedure. In the

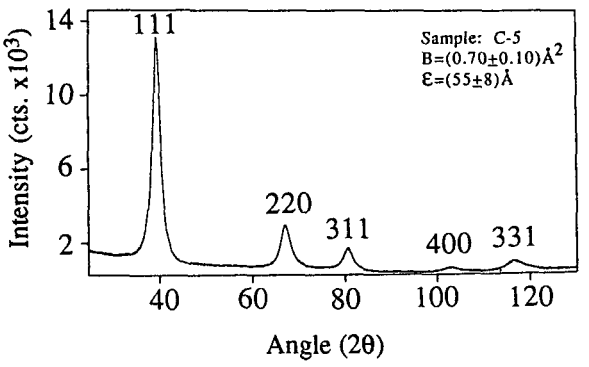

Figure 1. A typical X-ray diffraction pattern observed from 55Å cluster sample using CuKβ radiation.

equation B is the Debye temperature parameter, θ is the Bragg angle and λ is the wavelength. Several examples are shown in Figure 2 where the bulk value is also shown as the reference. The obtained

$$\ln(I_{obs.}/I_{cal.}) = -2B(\sin\theta/\lambda)^2 + \text{const.} \quad (1)$$

values are listed in Table I. The mean square atomic displacement ($\langle u^2 \rangle$), which consists of static lattice distortion and thermal vibrations of atoms, was derived from the measured B-parameters by using equation (2). In Table I the percentage of root mean square atomic displacement with lattice parameter of a_o=3.567Å, $[[\langle u^2 \rangle^{1/2}]/a_o]$x100, are also given.

$$B = 8\pi^2 \langle u^2 \rangle \quad (2)$$

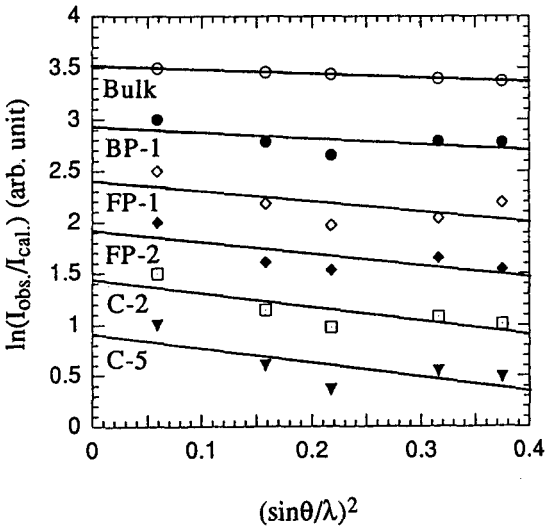

Figure 2. Plots of $\ln(I_{obs.}/I_{cal.})$ versus $(\sin\theta/\lambda)^2$ for several particles.

To estimate the average particle size and strain, Full Width at Half Maximum (FWHM) of the peaks was derived from the diffraction profiles. The instrumental broadening was corrected from each FWHM by the Cauchy method. Using the Hall method [6] average size and strain of the particle were obtained with equation (3), where β is the net FWHM of the

$$\beta\cos\theta/\lambda = 1/\varepsilon + 2\eta \sin\theta/\lambda \quad (3)$$

peak in radian. Figure 3 shows some examples of the Hall plot. The intercept of extrapolated straight line at $\sin\theta/\lambda$=0 is the inverse of particle size ($1/\varepsilon$). The slope of the line gives 2η, from which the mean square strain ($\langle e^2 \rangle$) was calculated using equation

Table I.
Experimental values of the B-parameter, the average particle size, the percentage of root mean square atomic displacement and the percentage of root mean square strain for various diamond particles. (* Determined by the company).

Sample	B-parameter ($Å^2$)	ε (Å) (X-ray data)	ε (Å) (TEM data)	$[<u^2>^{1/2}]/a_o$ (%)	$<e^2>^{1/2}$ (%)
Bulk	0.20	-	-	1.41	-
BP-1	0.27±0.06	(1-4)μm*	-	1.64	-
BP-2	0.27±0.06	(1-4)μm*	-	1.64	-
FP-1	0.50±0.09	195±20	-	2.23	0.06
FP-2	0.56±0.07	144±15	-	2.36	0.05
C-1	0.61±0.06	63±8	70±10	2.46	0.13
C-2	0.66±0.07	61±8	60±10	2.56	0.11
C-3	0.69±0.10	55±8	-	2.62	0.17
C-4	0.69±0.09	56±8	54±10	2.62	0.18
C-5	0.70±0.10	55±8	56±10	2.64	0.16
C-6	0.71±0.09	55±8	-	2.66	0.17

(4). Derived values of average particle size and the percentage of root mean square strain, $[<e^2>^{1/2}]x100$, are listed in Table I.

$$\eta = (2\pi <e^2>)^{1/2} \quad (4)$$

TEM photographs were taken from four different samples to get information of the shape of the particle as well as the size. Figure 4 shows an example of average 55Å particles TEM photograph. The photograph shows that the particles are not spherical in shape but mostly rectangular and some are polyhedron. It was very difficult to separate each particle from the others completely and in fact, an aggregate of many particles in one place was observed. Figure 5 shows the histogram of particles size distribution estimated from figure 4. In the figure, the total number of particles versus particles size are shown. The obtained average particle sizes are also listed in Table I for comparison with the values estimated from X-ray data. The agreement between the two results is very good.

The B-parameters were found to be in the range of (0.50-0.71)$Å^2$ for the particle size range of (195-55)Å, respectively, except for two samples with particle size of (1-4)μm where the B value was found 0.27$Å^2$. The bulk B value is 0.20$Å^2$ [7] which

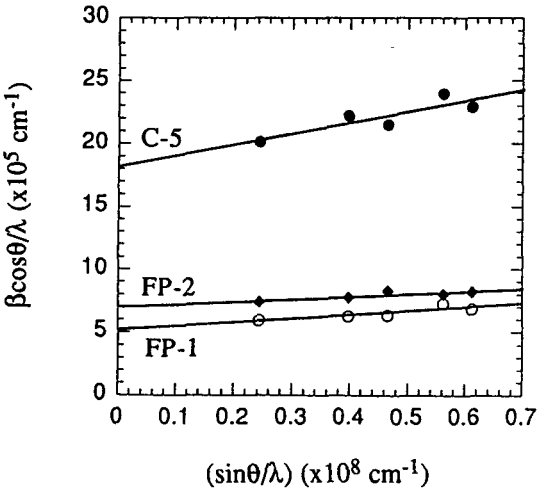

Figure 3. Hall plots of $\beta\cos\theta/\lambda$ versus $\sin\theta/\lambda$ for several diamond particles.

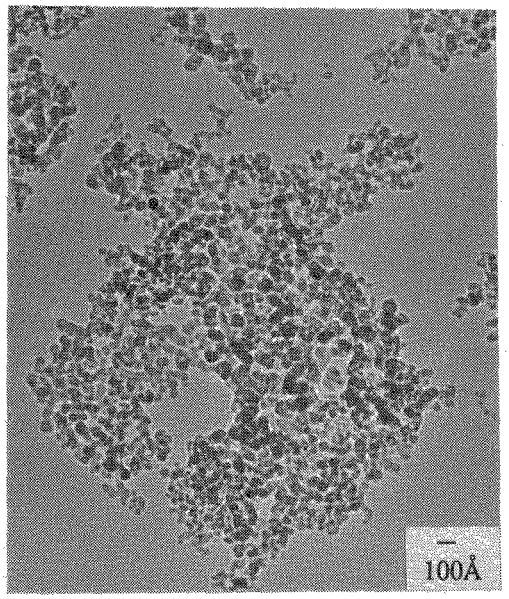

Figure 4. TEM photograph of mean 55Å diamond particles taken from the C-5 sample.

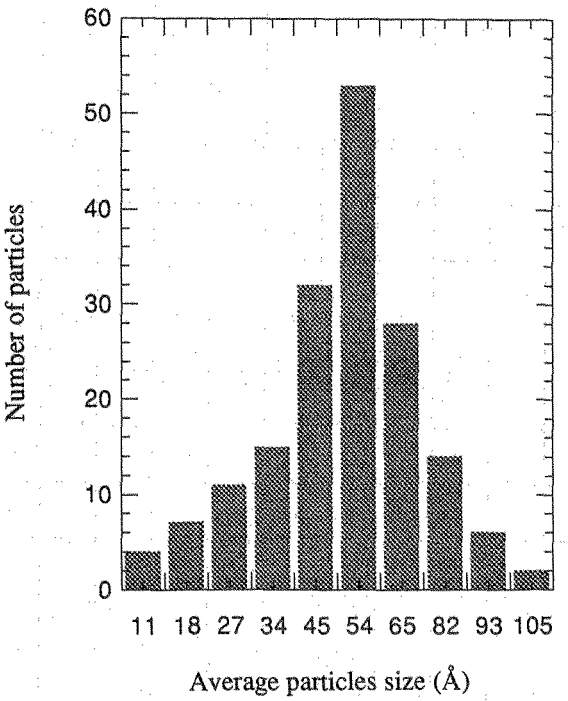

Figure 5. Histogram of the particles size distribution versus total number of particles estimated from figure 4.

is lower than those obtained in this study. The samples investigated are classified into three different classes according to their average sizes; bulk powder, (1-4)μm, fine particle, (144 and 195)Å and cluster, (55-63)Å. The maximum value of the percentage of root mean square atomic displacement was found to be 2.66% for 55Å particle appreciably larger than the bulk value, 1.41%. The percentage of root mean square strain was calculated to be in the range of (0.05-0.18)% for the particles studied.

This is the first observation of the size dependence of B-parameter in diamond samples. The B-parameter contains the contribution from static lattice distortion and the thermal vibrations of atoms. We have observed more than three times large B-value in cluster and that the B-values increase with decreasing the particle size. Moreover the percentage of strain is found to be small in the particle indicating less static lattice distortion. Therefore, thermal vibrations of surface atoms seem to be more responsible than the static lattice distortion for the large B-values of fine particle and clusters. To confirm this fact, a temperature dependent X-ray measurement is necessary and is scheduled in the near future.

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