

# Magnetic Levitation of Diamond Modified with Manganese and Bismuth

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# Abstract

Operating diamond grits to produce a precise grind tool is need. In order to lift up a diamond grit by magnetic force, the magnetic flux was estimated to be 100  $\mu$ T/g. Diamond (110) surface was modified with manganese powder at 450°C (720 K) then with bismuth powder at 270°C (540 K) due to its low melting temperature. Manganese carbides were formed on the diamond surface which was confirmed by an X-ray diffraction. A magnet that exhibits ferrimagnetism was formed on the surface, it had a spontaneous magnetism. We conducted to form six small disk magnets at hexagonal apex positions on the diamond (110) by using gold film mask. The magnetic flux measured at the center of the hexagon magnets on was 232  $\mu$ T at room temperature, and the surface modified diamond grid could be lifted up in the magnetic field between two solenoid coils.

# **Keywords**

Manganese Carbide, MnBi, Magnet, Levitation, Diamond

# **1. Introduction**

As known anti ferrous magnetism of MnO, manganese compounds exhibit various magnetic properties. The manganese compounds of MnAs and MnBi are known as ferrimagnetism materials [1]. P. Karen *et al.* [2] reported the manganese carbide  $Mn_7C_3$  and  $Mn_5C_2$  microstructure and paramagnetic property. On the other hand, bismuth exhibits diamagnetism. Manganese and carbon react to be formed carbide easily. A mixture of a fine diamond powder and manganese powder reacted not to remain the diamond powder. Infrared ray heating has less damage to diamond due to the transparency into diamond. The three surfaces of (111), (100) and (110) of diamond were attempted to be surface modification using diamond powder by infrared ray irradiation [3] [4]. Diamond (110) was modified with manganese powder by infrared ray irradiation to form lamellar manganese carbide. An alloy of MnBi has been utilized as permanent magnet under room temperature. The deposited films of MnBi on glass or mica by fabricated by vapor deposition exhibit magneto-optical effect. The deposition series were manganese then bismuth to form epitaxial growth of an ally of MnBi [5]. When the composite of MnBi are formed on diamond (110), the magnetic flux would be more than the manganese carbides. We propose thin MnBi magnets on lamellar manganese carbide modified the (110) surface of the diamond using infrared ray heating.

Six disk magnets at the sites of hexagonal apex on the diamond surface were conducted to be formed in order to obtain a high density magnetic flux at the center of the hexagonal magnets than each magnet. This method was used in levitation technology to slide precisely [6].

Magnetic flux was measured by Hall effect probe. The probe was utilized as a positioning sensor with magnets. Using Hall effect sensor at the edge of a solenoid coil, the modified diamond would be lifted up stably at level.

# 2. Experimental Procedures

# 2.1. Differential Thermal Analysis for the Magnet Formation Process

Manganese and Bismuth were materials which did not damage the diamond at a temperature with a rage where the Mn-Bi alloys were formed although the manganese reacts diamond quickly. Differential thermal analysis (DTA) for a diamond powder was conducted to confirm a magnet formation process by using manganese and bismuth. A commercially available diamond powder passed through 30  $\mu$ m sieve grids was used. Manganese powder and manganese powder for DTA test were produced respectively by a ball mill using alumina balls for hour to be a sample of 45  $\mu$ m or less in diameter. These powders were mixed at a molar ratio of C:Mn:Bi = 3:7:1, based on the molar ratio to form Mn<sub>7</sub>C<sub>3</sub> and MnBi. The mixed powder with 30 mg in mass were placed in a platinum cell of DTA/DTG sensor. This cell and sample alumina cell were heated from 30°C to 800°C (300 K to 1070 K) at the heating rate of 10 K/min with Argon gas flowed at 60 ml/min.

# 2.2. Magnet Formation on Diamond (110)

Surface modification of diamond (110) with Mn-Bi by infrared ray heating was carried out in vacuum to prevent oxidation in order to minimize carbon desorption from diamond surface. Artificial diamond of half cut diamond of 2 mm in thickness was used. The mass of the diamond was 0.069 g. The diamond surface (110) was manufactured by a laser cutting in half cut of the diamond (100). Another rectangular disk shape of diamond was prepared. The dimension was  $3.0 \times 2.5 \times 1.0$  mm. The mass was 0.030 g. The diamond surface was covered with gold spattering film preventing the reaction of manganese except six spots.

Gold spattering by argon ions was carried out for 10 min to become a film of 30  $\mu$ m in thickness. The gold film on diamond (110) was removed off at 6 spots where were the vertexes of the regular hexagon. The spot area was the circle with a diameter of 0.5 mm which was corresponding space for surface modification by manganese powder and bismuth powder as shown in **Figure 1**. The regular circle spots were produced by FIB (Focused Ion Beam) fabrication using Ga ion spattering. The specimen of diamond (110) with gold spattering film and appearance after FIB fabrication are shown in **Figure 2(a)** and **Figure 2(b)**. Manganese powder and bismuth powder were produced as mentioned before was mounted on diamond surface (110) at a selected molar ratio. The weight of manganese was 8.0 mg and it of bismuth was 4.4 mg. The purity of the manganese powder was 98.0 and it of the bismuth powder was 99.999.

Infrared rays emitted by a halogen lamp are focused by gold elliptical mirror. The condensed rays were passed through fused quartz window into a vacuum chamber. The irradiation area on the sample was 20 mm in diameter. The chamber was evacuated by turbo molecular drag pump under  $8.0 \times 10^{-4}$  Pa. Firstly, manganese powder was mounted on diamond and heated at 450°C (720 K) to form manganese carbides for 10 s. Then bismuth powder was mounted on the manganese powder and heated at 270°C (540 K) for 120 s as shown in **Figure 3**.

#### 2.3. Measurement of Magnetic Flux

Low temperature Hall effect sensor was used. In order to measure the magnetic flux density, geomagnetism was taken as 36  $\mu$ T in Tokyo in vertical component. The measurement voltage was  $2.52 \times 10$  mV. The coefficient was  $0.7 \times 10^{-2}$  V/T, and the operating temperature range specification was from 4 to 373 K. The Hall element was protected by two electrical resistances of 50 W and the output signal was amplified by the DC amplifier. The measurement temperatures were room temperature and the measurement value of the magnetic flux at every spot was obtained as shown in **Figure 3**. The distance from a magnet to the sensor was constant by the flat ceramic cover of the sensor.



**Figure 1.** Dimensions of the holes of gold covered film on diamond fabricated by focused ion beam.



**Figure 2.** Artificial diamond sample images after FIB fabrication, (a) Sample 1 diamond (110); (b) Sample 2 diamond (110).



Figure 3. Procedures of surface modification using Mn powder and Bi powder on the gold coated surface of diamond.

A Vibrating Sample Magnetometer (VSM) was used to obtain a magnetization curve of the modified diamond surface. The magnetometer was equipped with the physical properties measurement system, it can apply the magnetic field of 7 T in horizontal direction and the measurement temperature ranges from 1.9 to 400 K. For the diamond specimens, the magnetization-magnetic field curves were measured at 10 K varied magnetic field from -4000 to 4000 kA/m.

#### 3. Results

#### 3.1. Thermal Analysis for Mixed Powder

DTA/DTG curves for the mixed powder are shown in **Figure 4**. Solid line shows DTA curve and dotted line shows DTG curve. Endothermal peak can be observed at 276°C (550 K). The endothermal peak was considered to be a melting point of bismuth. Other endothermal peak around 355°C (628 K) can be observed. It indicates the phase transition from MnBi to  $Mn_{1.08}Bi$  with endothermal reaction. A mark at 450°C (720 K) is sited. One small peak at 420°C (690 K) can be obtained. This temperature is considered to be related with the formation of  $Mn_7C_3$  according to the binary phase diagram of Mn-C. The reason why the temperature of manganese carbide was detected is small amount of bismuth. If amount of the bismuth is large, manganese atoms will be consumed in formation of MnBi at 270°C (540 K). The DTG curves increased with temperature. It

indicates manganese and bismuth have been oxidized gradually. The degree of the increasing mass weight was greater than a sample of C:Mn:Bi = 1:1:1 and the increase of the mass was not detected for a sample non-containing of Bi. The increasing of mass with increasing temperature was considered to be oxidation after Bi molten. The surface modification of diamond was conducted in vacuum without oxidation and using small amount of bismuth to depress the formation of MnBi.

#### 3.2. Magnet Formation

Surface modification of a diamond specimen coated with gold after heating at 450°C (720 K) with Mn powder is shown in **Figure 5** and the diamond specimen after heating at 270°C (540 K) with Bi powder is shown in **Figure 6**. Manganese installed area on coated gold film and areas on six removed off gold film where diamond (110) bared look different. In the center of the regular hexagon, remaining gold film and manganese powder show black color. In the apex of the regular hexagon where the gold film was removed shows white color. It is considered to be formed manganese carbide and MnBi.

The X-ray diffraction pattern of the modified diamond (110) is shown in **Figure 7**. The peak of diamond (110) at 76° is detected. Peaks of pure gold and pure bismuth peaks are observed at near angles, 39° and 65°. The peak at 26° is considered to be Bi (012), graphite, and AuMn. Manganese carbide peak Mn<sub>7</sub>C<sub>3</sub> at 39.5° may be overlapped with Bi (110). From the result of X-ray diffraction pattern, Bi has a lot of peaks. Their peaks are overlapped with other materials as pure gold. Focusing on the peak at 41° and 50° as shown in **Figure 7**, it can predict that MnBi was formed.



Figure 4. Differential thermal analysis curve for diamond powder and manganese powder and bismuth powder.



**Figure 5.** Optical microscope image of diamond (110) sample 2 by using manganese powder after the surface modification in the vacuum infrared ray heating furnace.



**Figure 6.** Optical microscope image of diamond (110) sample 2 with Bi powder after heating at 540 K (270°C).



Figure 7. X-ray diffraction pattern of the modified diamond (110) with the manganese and bismuth powder.

#### **3.3. Evaluation of Magnetic Flux**

The measured results of magnetic flux density from the (1) to (6) formed magnets at the six apex of the regular hexagon and at the center around marked (7) as shown in **Figure 3** using a Hall effect sensor were presented in **Table 1**. The

measurement was conducted at room temperature. Two diamond samples of diamond (110) were different shapes and one control sample was diamond (100) that was numbered 3. In the magnet formation process, the diamond surface coated with gold was modified by manganese powder, then the sample was measured the magnetic field by a Hall effect sensor. The values are sited in Table 1. The values of the magnetic flux density after the magnet formation process are sited at the lines of then Bi. The values of the surface magnetic flux density became greater after the formation MnBi than that fabricated with only manganese powder. The small values of the sample 3: diamond (100) at the hexagon apex sites were considered to be related with the magnetization direction. The magnetization direction of MnBi formed on diamond (110) were ordered related to the spontaneous magnetization of Mn<sub>7</sub>C<sub>3</sub>. The maximum magnetic flux densities were measured near the center of the hexagonal spots, around 7 of every samples, the measured magnetic flux density was 408.7, 232.1 and 70.0 µT. Surveying with the Hall effect probe (1.02 mm in diameter) along diagonal lines of the hexagon spots revealed the center of a hexagon on diamond (110).

**Figure 8** shows the magnetization curve measured for sample 2. The outer magnet applied the magnetic field to the sample from 4000 to 0 to -4000 to 4000 kA/m at 10 K. There is a difference of the saturated magnetization applied a magnetic field of 4000 kA/m because of the six thin magnets on the diamond (110). The Magnetic susceptibility and coercive force obtained by the VSM measurements and the value of the sample 3 obtained by SQUID are sited in **Table 2**. The value of 0.2 kA/m for the diamond (100) is smaller than those of diamond (110). B-H curves obtained by SQUID, the spontaneous magnetic flux was not remained. Thin layer of the manganese carbide of Mn<sub>7</sub>C<sub>3</sub> on diamond (110) generated spontaneous magnetism to perpendicular axis, then the low temperature formation process formed the MnBi laminated layer on the Mn<sub>7</sub>C<sub>3</sub>. The MnBi layer magnetize along to the perpendicular axis due to the spontaneous magnetism of Mn<sub>7</sub>C<sub>3</sub> on the diamond (110). The result of VSM revealed the ferri-magnetism of Mn<sub>7</sub>C<sub>3</sub> and ferro-magnetism of MnBi.



Figure 8. M-H curve of sample 2 measured at 10 K.

Sample No.	Modification element	1	2	3	4	5	6	Ø
1	Mn	62.1	67.2	66.8	49	71.1	68.6	138.2
D (110)	Then Bi	233.2	218	293.1	298.5	258.2	391.4	408.7
2	Mn	26.4	31.6	43.4	24.5	48.8	61.1	104.1
D (110)	Then Bi	125	139.5	132.4	124.1	171.7	155.2	232.1
3 cntl	Mn	24.2	53.2	21.8	7.4	0.1	5.0	14.6
D (100)	Then Bi	43.5	72.4	82.1	48.3	45.9	38.7	70.0

**Table 1.** Results of the surface magnetic flux density  $[\mu T]$ .

Table 2. Magnetic properties of each sample derived from VSM measurement results.

Sample No.	Modified surface	Magnetic susceptibility	Coercive force [kA/m]
1	(110)	2.64	21.2
2	(110)	2.91	15.0
3 cntl	(100)	3.76	0.2

# 4. Discussion

Higher magnetic flux on the diamond (110) modified with manganese and bismuth than manganese carbide modified surface was detected by the Hall effect element. The difference in the magnetic flux density at the locations of six hexagonal spots on modified diamond is due to the amount of manganese at the rate of C:Mn:Bi = 3:7:1. The lowest magnetic flux value after manganese modification at spot 4 among six spots was measured. The irradiation of infrared ray around spot 4 was slight difficult in the heating. In the manganese carbide formation process, manganese powder did not react with diamond then in the MnBi formation process, the remained manganese reacted with the bismuth to provide the ferro-magnetism.

The surface magnetic flux values in the center of the hexagonal apex magnet disk on the modified diamond (110) were enough to perform magnetic levitation of the diamonds. **Figure 9** shows the flowchart of magnetic levitation with measuring magnetic force using a Hall effect sensor. **Figure 10** show the photograph of the magnetic levitation of diamond sample 2 between the solenoid coils. The floating of diamond maintained by the feedback control using the sensor signal.



**Figure 9.** Flow chart of the levitation by measuring the magnetic flux by Hall effect sensor attached to upper solenoid coil.



**Figure 10.** Magnetic levitation of the diamond sample 2 using two solenoid coils.

# 5. Summary

Diamond (110) was surface modified with manganese firstly then with bismuth to produce magnet disks. A regular hexagon magnet disks were formed using FIB process and covered diamond surface with gold. The temperature of formation of MnBi alloy was 270°C (540 K), and it of  $Mn_{1.08}Bi$  alloy are formed at 360°C (630 K). If the  $Mn_{1.08}Bi$  was formed, magnetic force was not lost due to ferromagnetism. Surface modification of diamond (110) with manganese at 450°C in vacuum then heating at 270°C for 5 minutes in vacuum with bismuth produces MnBi on surface of diamond surface. It gives 100 µT magnetic flux density in partially could move diamond grains by Neodymium magnet.

Using Hall effect sensor and VSM, the spontaneous magnetization with a surface magnetic flux density of 232  $\mu$ T was measured. The diamond (110) sample of which weight was 0.030 g, modified with about 0.010 g of MnBi was lifted between the two solenoid coil controlled using a Hall effect sensor.

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# **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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