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Investigation on defects in HPHT-grown diamond single crystals

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In the diamond single crystals synthesized at high temperature and high pressure using FeNi as catalyst, there are usually supersaturated vacancies and inclusions formed during the diamond crystal growth and rapid cooling from high temperature. Some defects such as prismatic dislocation loops, stacking faults and array of dislocations are closely related to such supersaturated vacancies and inclusions. The supersaturated vacancies agglomerate into discs on the (111) close-packed planes, subsequent collapse of the discs forms the dislocation loops and stacking faults. The thermal internal stresses, which are caused by the difference of thermal contraction between the diamond and the inclusions due to the difference of thermal coefficients between them as the diamond is cooled from high temperature, may be relieved by the formation of array of dislocations. In the present paper, these defects in the diamond single crystals were directly examined by transmission electron microscopy (TEM). The characteristics and formation process of these defects were analyzed briefly. © *2001 Kluwer Academic Publishers*

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1. Introduction

Since the first announcement of a reproducible process for synthesis of diamond in 1955, the diamond formation including nucleation and growth mechanism have attracted great interest of scientists in engineering and physics field [1–4]. Diamonds, both natural and synthetic, display a remarkable variety of crystal defects. The defects in the natural and CVD diamonds have been studied extensively [5–8]. As a kind of single crystal synthesized at high temperature-high pressure, there must be imperfections, such as point, line, surface and volume defects in it, which disturb locally the regular arrangement of the atoms of the synthetic diamond. All phenomena associated with the plasticity, strength, electrical resistance, optical absorption and other properties of diamond crystal depend upon the defects in it. Therefore investigation on the defects in the HPHT-grown diamond is very importance and interesting. As an attractive and powerful tool, transmission electron microscopy (TEM) has been widely used to study defects in most materials. However, maybe because of the extremely difficulty of the preparation of the diamond thin foil sample for TEM observation, less information concerning the defects in the HPHT-grown diamonds by TEM is available so far. In the present paper, the prismatic dislocation loops, stacking faults and array of dislocations in the synthetic diamond single crystals grown from Fe-Ni-C system under high temperature-high pressure were directly examined by TEM, whose formation process was analyzed briefly.

2. Experimental

The diamond was synthesized under a high temperature of 1597 K and a high pressure of 5.5 GPa in the presence of $Fe_{70}Ni_{30}$ alloy catalyst in a cubic anvil apparatus. The diamond grown in the solvent metal was recovered by dissolving the metals and the residual graphite in a boiling mixture of H_2SO_4 and HNO_3, followed by extensive washing. The as-grown diamond single crystals of about 0.8 mm in dimension were first observed by JXA-840 scanning electron microscopy (SEM), then the diamond crystals were directly ground by argon-ion beam milling machine until they were suitable for TEM observation. The defects were observed using an H-800 type of transmission electron microscope with an operating voltage of 120 kV. Selected electron area diffraction (SAD) pattern was used to index directions of the plane and the dislocation.

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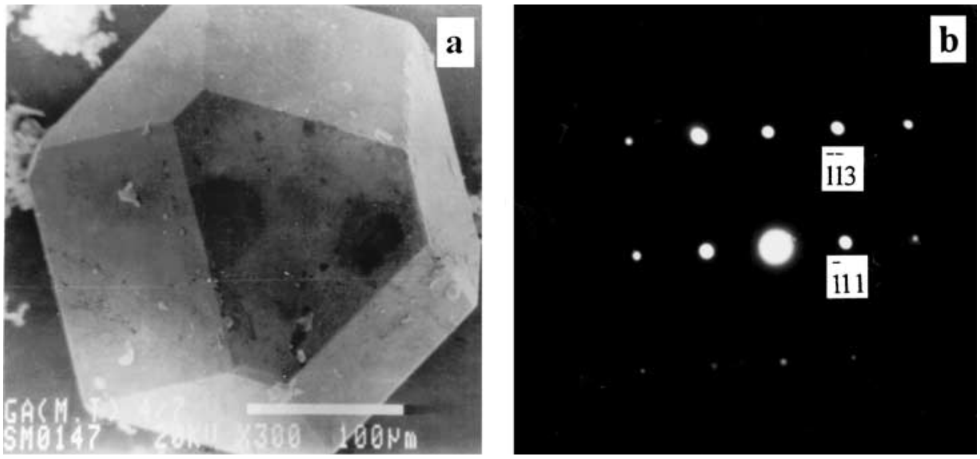

Figure 1 (a) SEM image of HPHT-grown diamond crystal. (b) Corresponding SAD pattern from [211] zone axis indicates the cubic diamond.

3. Results and discussion

Fig. 1a shows a SEM image of the HPHT-grown diamond single crystal with perfect cub-octahedral shape, they were about 0.6–0.8 mm in dimension, their color is yellowish. Fig. 1b is the corresponding electron diffraction pattern from [211] zone axis of the diamond, which indicates the crystal structure of the diamond is cubic.

Fig. 2 illustrates a TEM image of a kind of dislocation loop in an as-grown diamond taken with reflection of $g = 110$ on the (111) close-packed plane. Fig. 3a demonstrates the same kind of dislocation loop at another site of the same diamond as in Fig. 2 taken with reflection of $g = 2\bar{2}0$. If the foil sample was tilted, most of the loops were almost invisible, as shown in Fig. 3b, which further confirmed the existence of the dislocation loops. Similar results on this kind of dislocation have been reported by TEM by Frank, Boss and Jones [9–11] in other materials. This dislocation is called prismatic dislocation, which is related to the excess saturated vacancies in the diamond.

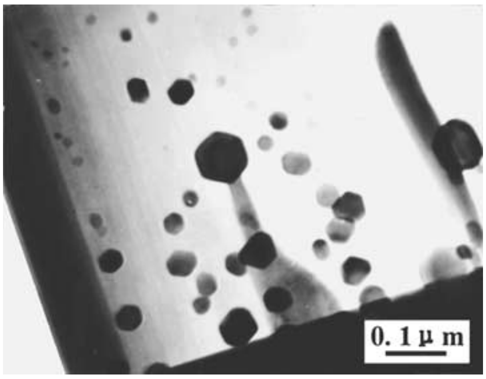

Figure 2 TEM image of prismatic dislocation loops without fringes of stacking faults in them taken with reflection of $g = 110$.

The formation process of the prismatic dislocation loops can be described as follows. In the diamond single crystal synthesized by high temperature-high pressure method, point defect called vacancy is possible, a large numbers of supersaturated vacancies can be retained in the crystal by rapid cooling from a high temperature. From corrected P-T phase diagram of carbon in 1989 by Bundy [12], it is also strongly suggested that vacancies exist in diamond as in most metals, and vacancies are expected to aggregate when diamond is cooled rapidly from a high temperature to room temperature. During diamond growth, crystal may trap vacancies in numbers exceeding the thermodynamic equilibrium numbers at high temperature. After the diamond synthesis finished, because the temperature in the synthesis cell was decreased rapidly, cooling a diamond crystal in such manner increased the supersaturation of the vacancies. Excess saturated vacancies in the diamond resulting from rapid cooling from high temperature can agglomerate into vacancy discs on the (111) closed-packed plane, because the surface energy on the close-packed plane

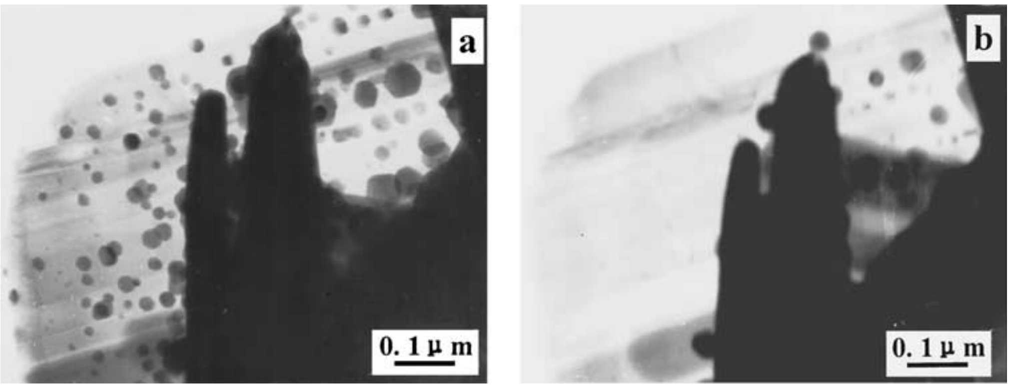

Figure 3 (a) TEM image of prismatic dislocation loops taken with $g = 2\bar{2}0$. (b) TEM image taken with reflection of $g = 22\bar{4}$ for the same field of the view, which corresponds to the invisibility criterion of $g \cdot b = 0$.

is the lowest. As the disc size attains tens of atom space, it will be unstable and collapse. If the vacancy disc is large enough, it is energetically favorable for it to collapse to produce a Frank partial dislocation loop and Shockley partial dislocation, and they can interact with each other to form a perfect dislocation with Burgers vector of 1/2 $\langle 1\bar{1}0\rangle$, as illustrated in Figs 2 and 3a.

The Burgers vector of the prismatic dislocation loop was determined by diffraction contrast, i.e. invisibility criterion of $g \cdot b = 0$. Fig. 3a and b show two bright field images taken with reflections of $g = 2\bar{2}0$ and $g = 22\bar{4}$ from the same field of view, respectively. The image in Fig. 3b corresponds to the invisibility condition of $g \cdot b = 0$ after the foil sample was tilted, therefore the dislocation loops in it are almost at extension. The Burgers vector of the dislocation loops may be determined by diffraction contrast as 1/2 $\langle 1\bar{1}0\rangle$.

From the TEM images shown in Figs 2 and 3a, it may be found that the average size of the prismatic dislocation loops is about 30–70 nm, and the shape of the loops is hexagonal, there are no interference fault fringes in the loops observed. However, it should be noted that the prismatic dislocation loops may have stacking faults in it, as shown in Fig. 4. In the HPHT as-grown diamond single crystal, the saturated vacancies may first form Frank partial dislocation with Burgers vector of 1/3 $\langle 1\bar{1}\bar{1}\rangle$ and Shockley partial dislocation with Burgers vector of 1/6 $\langle 1\bar{1}\bar{2}\rangle$, and they interact with each other to form a perfect dislocation of 1/2 $\langle 1\bar{1}0\rangle$ according to the reaction as follow: $1/3\langle 1\bar{1}1\rangle + 1/6\langle 1\bar{1}\bar{2}\rangle = 1/2\langle 1\bar{1}0\rangle$. So the fringes of stacking fault in the dislocation loops disappear. The Burgers vector of the dislocation loops is normal to the plane of the loop, so that an edge dislocation formed, the dislocation can only climb within the plane. In the presence of excess concentration of vacancies, the loops will expand by positive climb. Alternatively if there is a nearby sink for vacancies, the loops will emit vacancies and shrink by negative climb.

Fig. 5 shows a TEM image of stacking faults in the diamond, from which interference fringes of stacking faults can be found. Because the stacking faults have a higher density in the HPHT-grown diamond, it is of great significance to the HPHT-grown diamond. As is known, the cubic diamond crystal may be considered to be composed of (111) close-packed planes stacking in a sequence of ABCABC. The stacking faults are caused by vacancy collapsing. As described above, there exist larger amount of supersaturated vacancies in the HPHT-grown diamond, the supersaturated vacancies generated by cooling rapidly from high temperature will agglomerate on the (111) close-packed planes because of the low energy associated with such closed-packed planes. Their subsequent collapse provides an intrinsic-fault-formation mechanism that is equivalent to the removal of a close-packed layer, which leads to the change of the regular stacking sequence. The removal of a close-packed layer gives rise to the formation of low-energy stacking faults. The intrinsic stacking faults can be formed by removing the B plane above A plane. So the intrinsic stacking faults along [110] deflection on the (111) close-packed plane form. The existence of the stacking faults destroys the regular stacking sequence of the crystal.

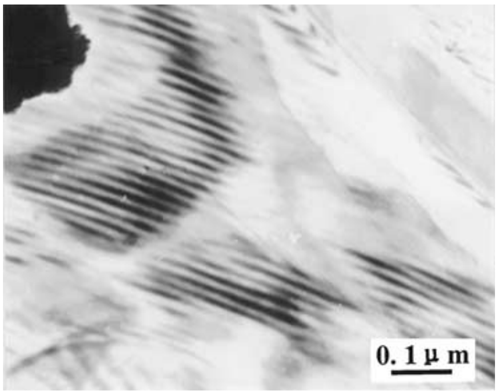

Figure 5 TEM image of stacking faults taken with reflection of $g = 110$ on the (111) close-packed plane.

From available theory on dislocation, defects in a crystal are associated with not only supersaturated vacancies but also the inclusions in it. Fig. 6 shows TEM image of an array of dislocations taken with reflection of $g = 110$, which is related to the thermal stress resulted from the inclusions in the diamond. The arrays of dislocations always lie on the (111) close-packed plane in order to minimize its energy. It is well known that inclusions are trapped in the HPHT-grown diamond single crystal during the diamond synthesis, these inclusions are related to the catalyst and medium for transmitting pressure and they can cause thermal internal

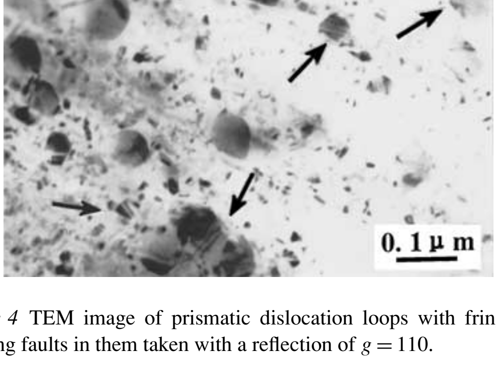

Figure 4 TEM image of prismatic dislocation loops with fringes of stacking faults in them taken with a reflection of $g = 110$.

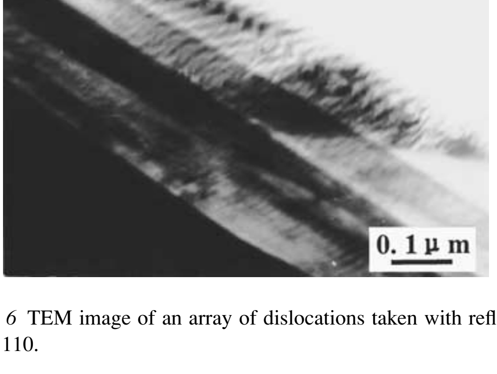

Figure 6 TEM image of an array of dislocations taken with reflection of $g = 110$.

stresses in the diamond due to the differences of thermal contraction between the diamond and the inclusions due to the thermal coefficients difference between them when the diamond is cooled from high temperature [13–15]. The stresses near the inclusions may exceed the average stresses by many tens of percent, so a large elastic strain will be generated near the inclusions. Therefore such stress concentrators are the most possible sites for the nucleation of the dislocations. The strain field may be relieved by the dislocations. Dislocation generation at local regions of stress concentration is common. When the stress reaches a critical value G/30, dislocations are nucleated in the diamond single crystal.

4. Conclusion

The above examination by TEM and analyses demonstrates the presence of prismatic dislocation loops, stacking faults and array of dislocations in an HPHT-grown diamond single crystal. The characteristics and formation process of the three types of defects were analyzed. These defects may be derived from the supersaturated vacancies and inclusions generated during the diamond growth and rapid cooling from high temperature to room temperature.

Acknowledgements

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