Growth and annealing study of hydrogen-doped single diamond crystals under high pressure and high temperature*

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A series of diamond crystals doped with hydrogen is successfully synthesized using LiH as the hydrogen source in a catalyst-carbon system at a pressure of 6.0 GPa and temperature ranging from 1255 °C to 1350 °C. It is shown that the high temperature plays a key role in the incorporation of hydrogen atoms during diamond crystallization. Fourier transform infrared micro-spectroscopy reveals that most of the hydrogen atoms in the synthesized diamond are incorporated into the crystal structure as sp^3 –CH_2-symmetric (2850 cm^{-1}) and sp^3 CH_2-antisymmetric vibrations (2920 cm^{-1}). The intensities of these peaks increase gradually with an increase in the content of the hydrogen source in the catalyst. The incorporation of hydrogen impurity leads to a significant shift towards higher frequencies of the Raman peak from 1332.06 cm^{-1} to 1333.05 cm^{-1} and gives rise to some compressive stress in the diamond crystal lattice. Furthermore, hydrogen to carbon bonds are evident in the annealed diamond, indicating that the bonds that remain throughout the annealing process and the vibration frequencies centred at 2850 and 2920 cm^{-1} have no observable shift. Therefore, we suggest that the sp^3 C–H bond is rather stable in diamond crystals.

Keywords: high pressure and high temperature, hydrogen-doped diamond crystals, annealing, LiH additives

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1. Introduction

Due to the unique physical, chemical, mechanical, and electrical properties of diamond, natural and synthetic diamonds have been widely used for a long time.[1−3] As is well known, hydrogen is one of the most common impurities in natural diamond.[4−7] Theoretical studies have shown that semiconductor properties could be endowed by attaching hydrogen to diamond.[8] In 1989, it was reported that a natural diamond single crystal subjected to the action of atomic hydrogen in hydrogen plasma could remarkably reduce its resistivity from a high value of 10^{16} $\Omega \cdot$ cm to about 10^5 $\Omega \cdot$ cm.[9]

In recent years, investigations into hydrogen in the chemical vapour deposition (CVD) of diamond have been extensively performed.[10−12] However, the measurement results have shown that hydrogen exists mainly at the grain boundaries of the CVD diamond film. Whether hydrogen exists in diamond film structures is still under argument.[13]

Nevertheless, so far, there have been hardly any reports on synthetic diamond doped with hydrogen under high pressure and high temperature (HPHT). Considering this, we now attempt to prepare single diamond crystals doped with hydrogen and study the behaviours of hydrogen in synthesized diamond.

In the present investigation, hydrogen is intentionally incorporated into synthesized diamond. In order to obtain a better understanding of the defects involved, the experiments doped with LiH additive in a range from 0.0% to 0.3 % (the weight ratio in the crystal) are performed in an $Fe_{59}Ni_{25}Co_{16}$–C system at a pressure of 6.0 GPa and temperature ranging from 1255 °C to 1350 °C. Moreover, the effects of hydrogen incorporation are investigated in detail. Our results may benefit the further study of the incorporation of hydrogen and nitrogen into natural diamond.

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2. Experimental procedure

All experimental runs were performed in a China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1200).[14,15] The sample assembly for the synthesis of diamond using the temperature gradient method (TGM) has been reported previously.[16−21] The temperature was calibrated using a Pt-6% Rh/Pt-30% RH thermocouple, whose junction was placed near the crystallization sample. Pressure was measured at room temperature by the change in resistance of the standard substances and at the temperature when the graphite-diamond equilibrium was reached. The {100} face of a high-quality diamond crystal was selected as the growth facet. High-purity graphite powder (99.9% purity) was employed as the carbon source, and single diamonds were grown in the $Fe_{59}Ni_{25}Co_{16}$–C system. Then, LiH powder was directly added into the catalyst as the hydrogen source, and the sample selected was annealed in a solid-state cell at a temperature of 1870 °C and a pressure of 6.8 GPa for 30 min.

After synthesis, the crystallization samples were dissolved in hot acids mixed with H_2SO_4 and HNO_3 to remove the remaining graphite and metal catalyst from the crystal surface. After annealing, synthetic diamond was removed from the sample chamber and cleaned in boiling acids (HCl,HNO_3). Then, the infrared spectra were measured with a Perkin–Elmer 2000 Fourier-transform infrared (FTIR) spectrometer in a spectral range between 400 and 4000 cm^{-1} with a spectral resolution of 2 cm^{-1} in transmittance mode. X-ray photoelectron spectroscopy (XPS) was used to detect the state of Li in the diamond structure. Furthermore, the synthesized products were characterized by Raman spectra to analyse the stress in the diamond lattice.

3. Results and discussion

3.1. Hydrogen-doped single diamond crystallization

A schematic diagram of the growth cell is shown in Fig. 1. Growth runs were carried out at a fixed pressure of 6.0 GPa and in a temperature range of 1255–1350 °C. The experimental results obtained in the $Fe_{59}Ni_{25}Co_{16}$–C system are summarized in Table 1. As clearly illustrated, the synthesis temperature of the growing high-quality pure diamond single crystal generally increases slightly with the increase in the LiH additive in the system. Otherwise, skeletal crystal would be produced because of the inappropriate synthesis temperature.

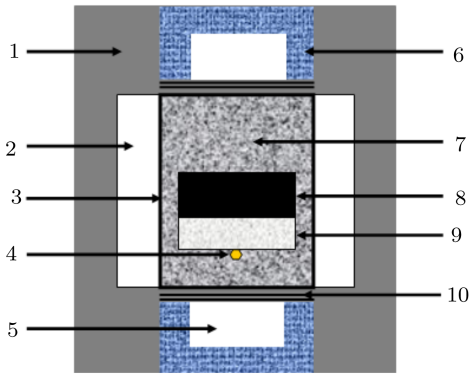


Fig. 1. (colour online) Schematic diagram of the growth cell. 1: pyrophyllite; 2, 5: ceramic cylinder and cover; 3: graphite heater; 4: seed; 6: steel ring; 7: insulator; 8: carbon source; 9: alloy solvent; 10: metal plate.

Table 1. Experimental results of the crystallization of diamond in the $Fe_{59}Ni_{25}Co_{16}$–C system with LiH additive.

Runs	LiH /%	Temperature/°C	Time/h	Colour
N-1	0.0	1255	6	yellow
N-2	0.1	1255	6	–
N-3	0.1	1262	6	yellow
N-4	0.2	1262	6	–
N-5	0.2	1262	6	yellow
N-6	0.3	1262	7	–
N-7	0.3	1273	8	yellow
N-8	¿0.3	1273∼1350	8	–

Figure 2 shows optical images of typical single diamond crystals synthesized under HPHT conditions. Obviously, the obtained diamonds all exhibit cubic or cub-octahedral shapes with dominant {100} faces and minor {111} faces, and display yellowness. The sizes of the four samples are all approximately 2 mm in diameter. However, it is necessary to note that high-quality single crystal is extremely difficult to obtain as the content of additive LiH exceeds 0.3 %, which can be explained as follows. In the system, H can be offered by LiH decomposition under a pressure of 4–4.5 GPa and a temperature of 850 °C,[22] so a rich-hydrogen environment can be established. In addition, it is extremely difficult to completely expel the inherent free-nitrogen, which comes from the air and raw materials, from the chamber. Thus, rich-hydrogen and nitrogen simultaneously introduced into the cell may change the behaviours of the catalyst/solvent, such as the glutinosity, the liquid surface tension, and the

capability of dissolving graphite, and the change restrains the growth of high-quality diamond crystal.[23] Hence, the content of LiH must be controlled strictly in the growth process.

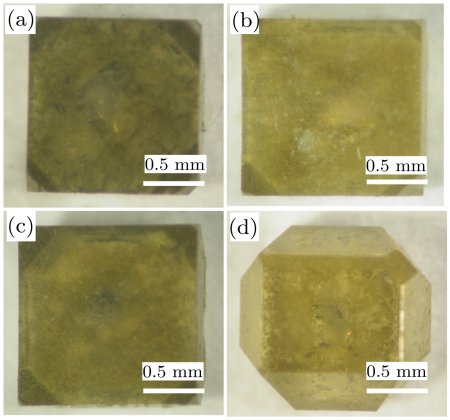


Fig. 2. (colour online) Optical images of diamond doped separately with LiH additive of (a) 0.0%, (b) 0.1%, (c) 0.2%, (d) 0.3%.

3.2. FTIR spectra of hydrogen-doped diamond

For the spectroscopic characterization, a number of diamond crystals are selected from runs N-1, N-3, N-5 and N-7 for further analysis. In Fig. 3, the FTIR spectra of these representative diamond crystals are recorded in a range from 1000 to 3500 cm^{-1}. It is revealed that the absorptions at 1130 and 1344 cm^{-1} are typical for synthesized crystals and attributed to the C-centre with a single substitutional nitrogen atom. In addition, the hydrogen-related absorption is hardly found in the diamond (sample A, as shown by curve *a*) without any LiH additive. However, samples B, C, and D all exhibit absorptions at 2850 and 2920 cm^{-1}, as shown by curves *b*, *c*, and *d*, respectively. As discussed in previous reports,[24–26] the two peaks of absorption are attributed to sp^3 $-CH_2$-symmetric vibrations and sp^3 CH_2-antisymmetric vibrations, respectively. Hence, this allows us to conclude that H atoms potentially occupy the lattice sites of the carbon atoms in diamond structure and bond with C atoms, which leads to the formation of H in the form of sp^3. Additionally, the tendency shown clearly in Fig. 3 is that the intensities of the 2850 and 2920 cm^{-1} hydrogen-related peaks increase with an increase in the ratio of LiH additive. It should be noted that so far there has been no reliable method to determine the concentration of H incorporated as an impurity in diamond. Apparently, further investigations on this subject should be carried out.

XPS is used to detect whether Li exists in the diamond structure. The XPS for the diamond with an LiH content of 0.3% is shown in Fig. 4. In Fig. 4, no signal related to Li is observed, which indicates that Li atoms are not trapped in diamond structure. This is possibly because the overwhelming majority of Li elements remain in the catalyst.

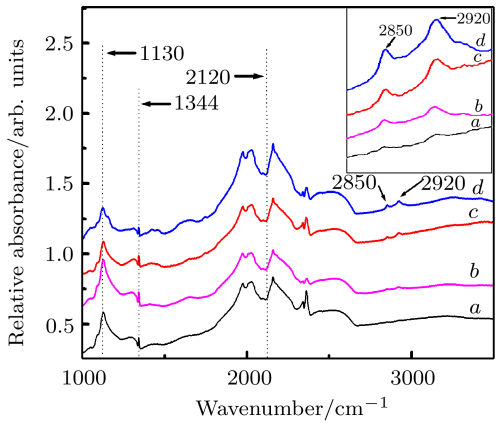


Fig. 3. (colour online) FTIR spectra of diamonds synthesized separately by adding an LiH additive of 0.0%, 0.1%, 0.2%, and 0.3% for curves *a* *b*, *c*, and *d*, respectively.

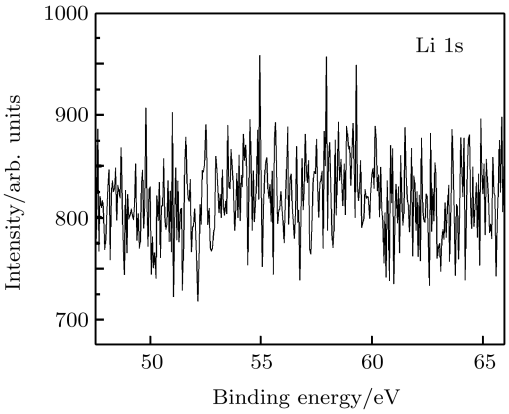


Fig. 4. The XPS of diamond with an Li–H content of 0.3 %.

Furthermore, the corresponding relationship between hydrogen incorporation and the concentration of substitutional nitrogen is investigated in detail. According to the absorption coefficient of the IR spectra, the concentrations of nitrogen impurity can be evaluated.[24,27] Our results indicate that the substitutional nitrogen concentration in diamond decreases from 416 ppm to 80 ppm as LiH content increases from 0.0% to 0.3%. It is a likely explanation that hydrogen

atoms can be effectively incorporated into diamond and hydrogen atoms restrain the nitrogen atoms from entering into the diamond structure.

3.3. The effect of hydrogen on the Raman spectrum of diamond

Raman spectroscopy is used to analyse the residual stress in diamond grown in the $Fe_{59}Ni_{25}Co_{16}$–C system. The typical Raman spectra for these samples are recorded and shown in Fig. 5. Obviously, the Raman spectra of diamond single crystals each show only a very strong and narrow peak with a linear background, which means that each of the diamonds obtained possesses a high-quality single crystal structure. However, we notice that the characteristic peak of diamond shifts from 1332.06 to 1333.05 cm^{-1}. The previous literature[28] show that various impurities, such as nitrogen, oxygen and solvent metal (Ni, Co), and the forms of their existence and distributions in diamond crystals, can affect the stress in diamond crystal. During the growth of diamond, H atoms may bond with C atoms. Furthermore, the bond length of C–H is shorter than the C–C bond. Thus, compressive stresses in the diamond structure could be produced, which leads to Raman peak shifting towards higher frequency. The result that hydrogen is trapped in diamond in the growth process is in good agreement with our FTIR measurement mentioned above.

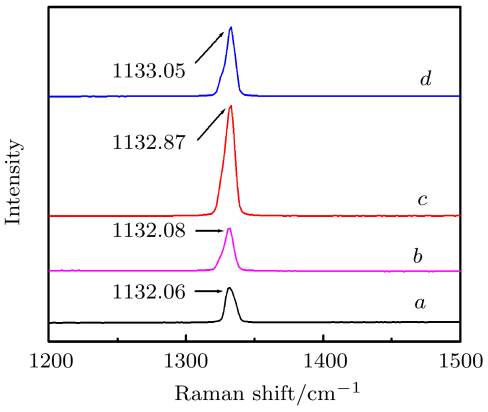


Fig. 5. (colour online) Raman peak shifts of hydrogen-doped diamond separately at an LiH content of 0.0%, 0.1%, 0.2% and 0.3% for curves *a*, *b*, *c*, and *d*, respectively.

3.4. Annealing study of hydrogen-doped diamond

The classical work of Chrenko *et al.*[29] reported that dispersed single substitutional nitrogen could be translated to form pairs of neighbouring nitrogen atoms after HPHT annealing treatment. Importantly, it is also interesting to take into account the stability of the C–H bond in synthesized diamond. In view of this, the D sample was selected to be annealed in the reaction vessel. We compare the behaviours of hydrogen in the same sample before and after annealing, where the FTIR spectra before and after annealing at 6.8 GPa and 1870 °C for 0.5 h are recorded in Fig. 6. It is proved that the physical and chemical properties of many materials can be affected by pressure.[30–33] Herein, the purpose of using higher pressure is to prevent diamond crystal from being graphitized under higher temperature.

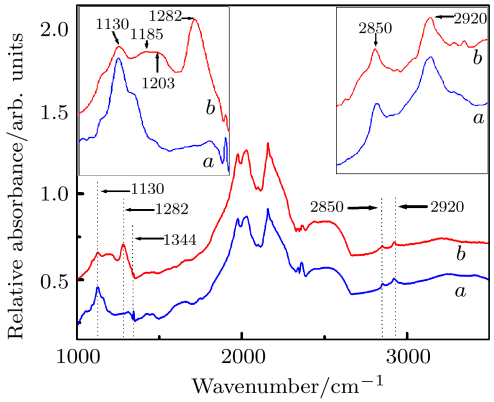


Fig. 6. (colour online) The FTIR spectra of sample D before (curve *a*) and after (curve *b*) annealing.

In Fig. 6, the typical FTIR reveals that after annealing the diamond contains nitrogen in the form of a C-centre with absorption peaks at 1130 and 1344 cm^{-1}. However, the intensities of the peaks at 1130 and 1344 cm^{-1} decrease and even vanish, respectively. This means that the dispersed nitrogen concentration (C-centre) declines. In addition, nitrogen in the form of an A-centre, owing to annealing, gives rise to absorption peaks at 1282 and 1203 cm^{-1}.[34] After annealing, a weak absorption band appears at 1185 cm^{-1}, which confirms that a minority of nitrogen exists in the form of B aggregation in diamond. For all this, it is interesting to investigate whether the state of hydrogen changes after annealing treatment. According to our measurements, no peak shifts towards lower or higher frequency are observed at the 2850 and 2920 cm^{-1} positions. Furthermore, the intensities of the two peaks do not significantly change. Therefore, our experimental results indicate that sp^3 C–H bonds are rather stable in synthesized diamond.

4. Conclusion

In this paper, the results presented provide evidence that hydrogen may be incorporated into synthesized diamond single crystals during growth under HPHT conditions. FTIR measurements show that the absorptions associated with hydrogen peaked at 2850 and 2920 cm^{-1}. Furthermore, it has been observed that the intensities of hydrogen-related absorptions are enhanced when the content of the hydrogen source is increased. Due to the production of compressive stress in the as-grown specimens, the Raman peak shifts towards higher frequency. Finally, annealing experiments suggest that the 2850 and 2920 cm^{-1} positions shift towards neither lower nor higher frequency. The result indicates that the sp^3 C–H bond is rather stable.

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