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The effect of phosphorus and nitrogen co-doped on the synthesis of diamond at high pressure and high temperature

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ABSTRACT

The synthesis of phosphorus and nitrogen co-doped diamond is investigated in the NiMnCo–C system by adding P_3N_5 or carbonyl iron powders mixed with phosphorus powders under high pressure and high temperature. Experimental results show that the color distribution in diamond crystals with low concentration of P_3N_5 additive is not uniform. The color becomes deep green with the increase of P_3N_5 additive. The optical images and FTIR spectra reveal that the nitrogen atoms are more easily incorporated via {111} than {100} in the same conditions. In addition, the result of FTIR spectra of synthesized diamond indicates that the hydrogen atoms in the form of sp^3–CH_2– are more likely to enter the diamond lattice in the P/N co-doped system, compared with the single N-doped system. The absorption peak at 3107 cm^{-1} attributed to vibration of H-related point defects (sp^2–CH═CH–) is observed in diamonds, which is often found in natural diamonds. The Raman shifting to lower frequency and FWHM value becoming wider are due to the doping of phosphorus atoms.

1. Introduction

Due to its unique physical, mechanical and electrical properties, the diamond as a promising material has attracted wide research for mechanical and electrical applications. Much of this research reveals that the presence of impurities and defects in diamond can affect its mechanical application such as the morphology, hardness, toughness, etc. For electrical applications, we required the fabrication of low-resistivity n-type and p-type material by doping diamond with donor and acceptor impurities, respectively. However, n-type conduction of diamond is basically more challenging than p-type, which has already been achieved by B-doping [1–4]. In recent years, the researchers have focused on nitrogen, phosphorus and sulfur doping primarily. However, the nitrogen atoms incorporated at substitutional sites in diamond form a deep donor level with activation energy of 1.7 eV [5]. No electrical conduction could be observed at room temperature [6–8]. Theoretical candidates for shallow donors are phosphorus (substitutional) [9–11]. However, phosphorus atoms are difficult to incorporate into the diamond lattice, because its atomic radius is larger than the carbon atom. What is more, the electron mobility of P-doped diamond crystal is low, which makes its application problematic at room temperature. The effect on S-doped diamond is similar with P-doping.

Recently, theoretical studies have indicated that the co-doping might be a universal valence control method to overcome self-compensation in wide-gap and super-wide-gap semiconductors [12]. Experimentally, there was still a lack of investigation on the synthesis of co-doped diamonds. HPHT is a kind of effective method to research the single crystal synthetic diamond [13]. Therefore, it is an interesting work to investigate the synthesis and characterization of diamond crystal co-doped with P and N under HPHT conditions. And we expect to improve the characteristics of diamond crystals by P and N synergistically doped, especially their electrical properties.

In this paper, diamond crystals synergistically doped with P and N are successfully obtained, and the FTIR spectra of synthetic diamond indicated that the hydrogen atoms in the form of sp^3–CH_2– can more easily enter into the diamond lattice in the P/N co-doped system. It will be of help for deep understanding of the genesis of natural diamond.

2. Experiment

The synthetic experiments were carried out in a china-type large volume cubic high-pressure apparatus (CHPA) (SPD-6 × 1200) with sample chamber of 10 mm in diameter. The diamond crystallization was run at pressure of 5.8–6.3 GPa and temperature of 1280–1550 °C. Diamonds were synthesized through both film growth method (FGM) and temperature gradient method (TGM). The sample assemblies for diamond synthesized by HPHT are shown in Fig. 1. Graphite with a purity of 99.9% was used as a source of carbon. The synthesized diamond

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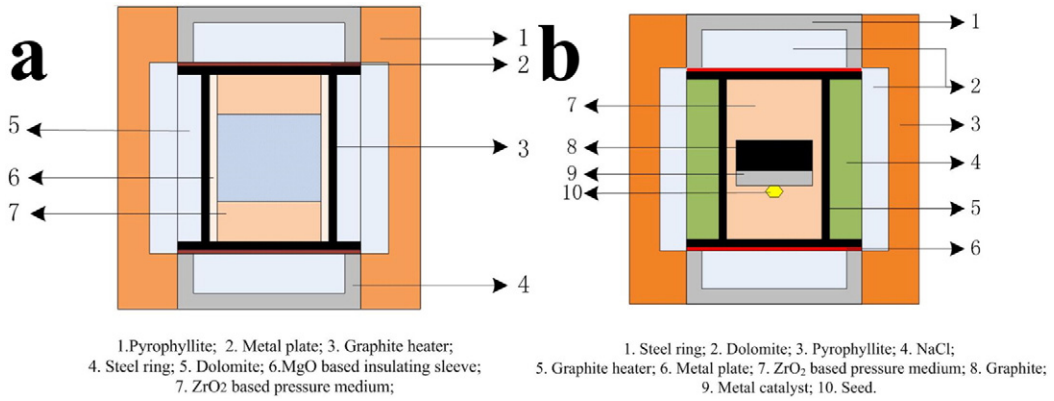

Fig. 1. Sample assembly for diamond synthesized by HPHT. (a) The sample assembly for FGM; (b) the sample assembly for TGM.

Table 1
The corresponding experimental parameters of diamond synthesis with P_3N_5 additive at HPHT conditions.

Run	P_3N_5 (wt.%)	Temperature (°C)	Time (h)	Method
N-a	0.1	1350–1450	0.5	FGM
N-b	0.4	1450–1550	0.5	FGM
N-c	0	1280	15	TGM
N-d	0.15	1300	15	TGM
N-e	0.25	1320	15	TGM
N-f	0.4	1330	15	TGM

(0.8 mm in size) was selected as seed crystal. A NiMnCo alloy was used as the solvent–catalyst. We took the P_3N_5 powders (99.99%), carbonyl iron powders (the special iron with 99 wt.% in purity and 5-10 μm in size) and phosphorus powders as the nitrogen and phosphorus source, respectively. These carbonyl iron powders were synthesized from carbonyl iron with a purity of 99.999 wt.% deoxidizing by iron powders in a stream of ammonia (NH_3) in a running quartz reactor at 300–400 °C. Then the carbonyl iron powders were deoxidized under hydrogen for 1 h. As a result, the major impurities in the carbonyl iron

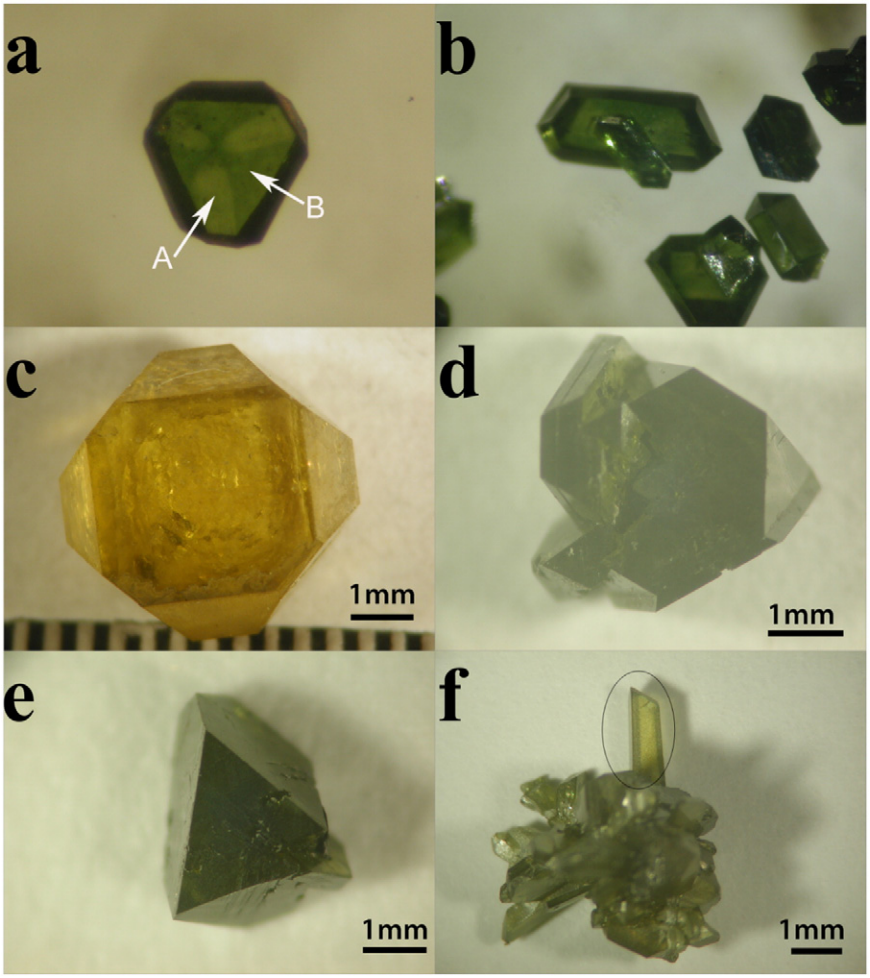

Fig. 2. Optical images of the diamond crystals synthesized from the NiMnCo–C system with P_3N_5 additive: (a) 0.15 wt.%, (b) 0.4 wt.%, (c) 0 wt.%, (d) 0.15 wt.%, (e) 0.20 wt.%, (f) 0.4 wt.%.