paper or a jeweler's saw. The sanded powder sample showed 25 ppm Fe, 17 ppm Ti, and 14 ppm V (by weight). The saw-cut powder showed 41 ppm Fe, <5 ppm Ti, and 13 ppm V. When expressed as volume percent, these numbers become two to three times smaller. Our crude estimate of the fractional volume occupied by the metal inclusions (from the scanning electron microscope photographs) is somewhat higher, but the difference is not significant.

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Phosphorus: An Elemental Catalyst for Diamond Synthesis and Growth

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As diamond-producing catalysts, 12 transition metals such as iron, cobalt, and nickel were first reported by General Electric researchers more than 30 years ago. Since then, no additional elemental catalyst has been reported. An investigation of the catalytic action of group V elements is of great interest from the viewpoint of producing an n-type semiconducting diamond crystal. In the present study, diamond was synthesized from graphite in the presence of elemental phosphorus at high pressure and temperature (7.7 gigapascals and 1800°C). Furthermore, single-crystal diamond was grown on a diamond seed crystal.

Diamond can be synthesized from graphite in the presence of any one of 12 transition metal elements (1, 2), such as Fe, Ni, or Co, or in the presence of binary alloys (3), such as Nb-Cu alloy, carbonates (4), hydroxides (5), or sulfates (5, 6) under highpressure and high-temperature conditions in the thermodynamically stable region of diamond. The pressure and temperature conditions required for the synthesis of diamond are strongly dependent on the nature of the catalyst. For example, CaCO₂ does not appear to dissolve any carbon at temperatures of 1600°C (7), but the carbonate acts as a diamond-forming catalyst at higher temperature, above 2000°C (3). Some elements may therefore act as dia-

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mond-forming catalysts only at higher temperature (above 2000°C) in the thermodynamically stable region of diamond.

With respect to efforts being made to synthesize *n*-type semiconducting diamond crystal, it is very important to investigate the catalytic action of the group V elements such as P, As, Sb, and Bi in the synthesis of diamond, because these five-valent elements are considered to have donor properties in diamond. Although diamond growth experiments have been done with Sb, no diamond has been grown on a seed crystal (8). To the best of our knowledge, there have been no reports on the successful synthesis and growth of diamond with these five-valent elements.

Among these group V elements, P has the smallest atomic radius and is considered to be favored for accommodation in the small diamond lattice. We were able to synthesize

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Fig. 1. Sample assembly for the high-pressure synthesis of diamond using a P catalyst: 1, steel ring; 2, Mo foil; 3, Mo capsule; 4, red P; 5, graphite capsule; 6, graphite heater; 7, NaCI-10% ZrO₂ by weight pressure medium; 8, NaCl-20% ZrO, by weight pressure medium.

diamond in the presence of elemental P under comparatively high pressure and temperature conditions (6.5 to 7.7 GPa and 1800° to 2200°C). Furthermore, diamond single crystal was successfully grown on a natural singlecrystal diamond at a lower pressure and temperature (6.5 GPa and 1750° to 1800°C) in the presence of elemental P.

Synthesis experiments were carried out with a modified belt type high-pressure apparatus with a bore diameter of 32 mm (9). Pressure was calibrated at room temperature by means of the known pressure-induced phase transitions of Bi, Tl, and Ba. Temperature was estimated from the extrapolated relations between the input power and the temperature, which we had obtained in advance by measuring the temperature up to 1800° and 2100°C with Pt6%Rh-Pt30%Rh and W5%Re-W26%Re thermocouples, respectively. The pressure effect on the electromotive force of the thermocouple was not corrected.

The starting materials were graphite rod (high-purity graphite, Tokai Carbon Company) and elemental P (red P grains, High Purity Company; stated purity, 99.9999%). The P was pulverized with an agate mortar, and the powder was dried at 110°C in an oven before use. The graphite rod was machined into the desired shape as shown in Fig. 1. The P powder was put into a capsule made of graphite and loaded in a capsule made of Mo at 200 MPa. The encapsulated sample was then placed in an outer Mo capsule made of Mo foil. The sample was maintained at 7.7 GPa and 2200°C for 10 min.

The product that we obtained was tightly covered with Mo, which was removed with a nipper. The recovered sample was examined with an optical microscope and an x-ray diffractometer. Diamond was formed and no graphite was detected in the sample according to the x-ray diffraction patterns, which were the same as those of natural or synthetic samples. Many tiny crystals were observed around the P with an optical microscope. This result suggests that the graphite capsule

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Fig. 2. SEM micrographs of diamonds synthesized at 7.7 GPa and 2200°C for 10 min. The diamonds were treated with a hot mixture of HCI and HNO₂ before SEM observation. (A) Diamond crystals obtained in the region near the P; (B) diamond crystals obtained in the region near the Mo capsule.

was completely transformed to diamond by the catalytic action of P.

To investigate the morphology of the diamond crystals, we examined the sample by scanning electron microscopy (SEM) after treatment with hot aqua regia. The morphology of the diamond crystals obtained in the region near the P was quite different from that of the crystals obtained in the region near the Mo capsule, as shown in Fig. 2. The former crystals were blocky in shape, whereas the latter were dendritic. This difference may arise because diamond crystals near the P were grown in a sufficient quantity of the liquid P to become blocky.

The graphite capsule was completely transformed to diamond when maintained at 7.7 GPa and 2200°C for 10 min. To investigate the lower temperature and pressure limits of diamond synthesis regions in the graphite-P system, we exposed the sample to a pressure of 7.7 GPa and a temperature of 1800°C for 10 min and examined the recovered sample with an optical microscope and SEM. Diamond crystals with a euhedral shape were observed at the interface with the P (Fig. 3). No diamond was found in the graphite adjacent to the Mo capsule. This result confirms that the P acts as a catalyst in the transformation from graphite to diamond and that Mo metal does not. At the lower pressure condition of 6.5 GPa, no diamond was detected in the samples treated at 1800°C for 60 min. Because only a small



Fig. 3. (A) SEM micrograph of the product obtained after exposure of the sample to 7.7 GPa and 1800°C for 10 min and (B) an enlargement of (A). Diamond crystals with a euhedral shape were grown on the surface of P. The P was indexed to black P" by x-ray powder diffraction

amount of graphite transforms to diamond at 7.7 GPa and 1800°C, we consider that these pressure and temperature conditions are the lower limits for diamond production.

We were unable to measure the physical properties of the diamonds that we synthesized from graphite in the presence of P after exposure to conditions of 7.7 GPa and 1800°C for 10 min because the diamond crystals were too small, 20 to 30 µm. In an effort to grow a large diamond crystal, we used a previously reported method (10) in which P powder was packed into a cylindrical graphite capsule with a few natural octahedral diamond crystals (about 2 mg), which acted as seed crystals. The graphite capsule was placed in a Ta capsule, rather than in the Mo capsule shown in Fig. 1, and was then maintained at 6.5 GPa and 1800°C for 12 hours. Then the diamond seed crystals embedded in the P were recovered from the Ta capsule. They were first treated in hot aqua regia to remove P and then were examined with the optical microscope and SEM.

The diamond crystals showed a weight increase of about 10%. The new growth layer was observed on all the surfaces of the seed crystals. The morphology also changed from rounded corners and edges to sharp ones, as shown in Fig. 4, but the crystals were transparent and colorless or pale blue in color. Distinct growth steps and numerous small pits were seen (Fig. 5) when the surface morphol-

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Fig. 4. SEM micrograph of the diamond crystal grown at 6.5 GPa and 1800°C for 12 hours.



Fig. 5. Surface morphology of the diamond crystal that was obtained under conditions of 1800°C and 6.5 GPa for 12 hours in the presence of a P catalyst (reflection differential interference micros-CODV).

ogy of the crystals was examined by reflection differential interference microscopy. The surface morphology of these crystals is quite different from that of crystals grown with metal catalysts. We were not able to examine whether the crystals are *n*-type semiconductors because these diamond crystals (~1 mm in diameter) were too small for an accurate measurement of physical properties such as electrical resistivity, Hall coefficient, and impurity analysis by secondary ion mass spectroscopy.

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