PHYSICAL REVIEW B **72**, 024108 (2005)

Carbon self-diffusion in a natural diamond

Kenneth T. Koga,* Micheal J. Walter,† Eizo Nakamura, and Katsura Kobayashi
Institute for Study of the Earth's Interior, Okayama University at Misasa, Tottori 689-0193, Japan

(Received 2 February 2005; revised manuscript received 19 April 2005; published 15 July 2005)

We report experimentally determined self-diffusion coefficients for carbon in a type-IaA diamond at pressure and temperature conditions within diamond stability field at 10 GPa and 2075–2375 K. The activation energy of diffusion is 6.8 ± 1.6 eV and a preexponent constant is of 4.1×10^{-5} m^2/s [$\ln(-10.1 \pm 2.0)$ m^2/s]. The activation energy is approximately 30% lower than results predicted previously from *ab initio* calculations.

DOI: 10.1103/PhysRevB.72.024108 PACS number(s): 66.30.Hs, 91.60.−x, 91.70.−c

INTRODUCTION

The diffusivity of carbon in diamond has been investigated by numerical experiments.[1,2] These studies determined the energies associated with atom migration and vacancy formation, but the jumping frequency of carbon atoms has not been determined due to limitations in computational capability. This prevents the determination of self-diffusion coefficients for carbon in diamond. The direct experimental measurements of carbon diffusivity by physical experiments provide the data that can be compared to theoretical predictions. We have measured a set of carbon self-diffusion coefficients in diamond at the condition within its field of stability: 10 GPa and 2075–2375 K.

Carbon diffusion processes in diamond are generally considered extremely slow but highly temperature dependent (i.e., high activation energy). For this reason, an experimental determination of diffusion coefficients requires high-temperature and -pressure conditions where diamond is stable and an analytical technique that allows concentration profiling at high spatial and analytical resolution. In this experimental study, we used a combination of state-of-the-art experimental and analytical techniques to measure carbon diffusion. We used a multianvil type high-pressure and -temperature apparatus to create the conditions of diamond stability while maintaining extreme high temperatures for an extended period of time in a near-hydrostatic environment. High-resolution concentration profiles of C isotopes in run products were made with a secondary-ion mass spectrometer (SIMS).

The diffusion properties of diamond are of interest in earth sciences, because natural diamonds and their mineral inclusions provide important information about the geochemical character and geotherm of the ancient continental lithosphere. Such diamonds record formation ages as old as 3×10^9 years,[3] although Shimizu *et al.*[4] have shown the juvenile character of syngenetic garnet inclusions in some diamonds and suggested a residence time of only 100 000 years in the mantle. Experimental determination of carbon self-diffusion in diamond constrains the maximum possible residence time of diamond in the mantle, because the time scale of homogenization of C isotope zoning in many natural diamonds can be calculated once C self-diffusion coefficients are determined.

EXPERIMENTAL PROCEDURES

The starting materials for the experiments were chips of a shattered, single-crystal, gem-quality, type-IaA diamond with approximately 200 ppm nitrogen (Fig. 1). The diamond was previously used as an anvil for diamond-anvil-cell (DAC) high-pressure experiments. The defect structure of the diamond consists dominantly of dispersed and paired (*A*-type) nitrogen defects. The roughness of polished surfaces was less than 2 nm, which was determined by a stylus-type surface profilometer (Dektak). Due to the method used to produce diamond chips, crystallographic orientation was not tracked during preparation.

Vitrified glass ^{13}C powder (90% ^{13}C, 10% ^{12}C) was deposited on the polished surface of diamond chips using a pressed pellet of ^{13}C powder that was evaporated under vacuum above the diamonds by electronic current (vapor deposition method). The deposited ^{13}C film was approximately 30 nm thick and was the source for the diffusant. The ^{13}C film converts to diamond upon heating at high pressure, thus providing an ideal ^{13}C source for diffusion experiments.

Prepared diamond chips with the ^{13}C coating were annealed at elevated pressure and temperature within the diamond stability field. Experimental conditions were achieved in a Kawai-type (6–8 configuration) multianvil pressure device with a split-sphere press at ISEI, Okayama University at Misasa. The pressure cell was a Cr-doped MgO octahedron with 14-mm edge lengths, which was compressed using WC cubes with 8-mm corner truncations (so-called 14/8 cell)

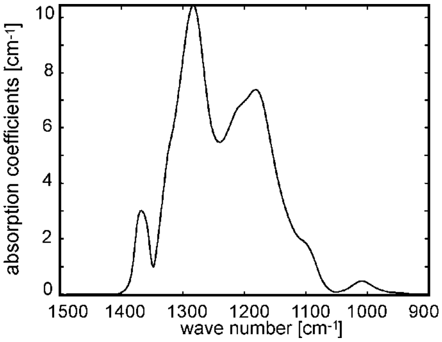

FIG. 1. An IR absorption spectrum of the diamond normalized to 1 cm thickness. Nitrogen concentration was determined using the calibration of Boyd *et al.* (Ref. 5).

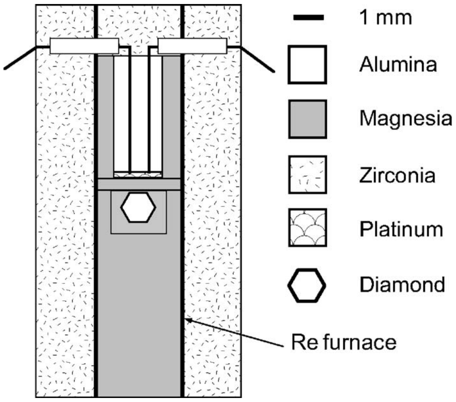

FIG. 2. A schematic cross-section illustration of the experimental assembly.

and pyropholite gaskets. Room-temperature and high-temperature pressure calibration was made using a set of fixed-point phase transitions, as described in Walter *et al.*[6] The sample was centrally located within cell, surrounded by MgO spacers, a cylindrical Re foil heater (~40–80 μm wall thicknesses) and an outer Zr_2O_3 insulating sleeve (Fig. 2). Temperature was measured using an axially positioned $W_{95}Re_5$–$W_{70}Re_{30}$ thermocouple insulated from the heater by a two-bore alumina sleeve.

To obtain a measurable diffusion profile, it was critical to conduct high-temperature experiments for the longest possible duration. For example, a stable condition (e.g., ±10 K) could be maintained for as long as 6 days at 2073 K. However, for temperatures above 2273 K, deformation of the Re heater was significant and led to heater failure after only a few hours, and also the deterioration of thermocouples was significant. To mitigate thermocouple degradation we chose to hold experiments at constant power after an appropriately long settling in time (~30 min). We monitored the resistance of the heater to detect drift. When the resistance varied by more than 15% of the initial value, we terminated the experiments. In our laboratory, the normal procedure is to regulate temperature within ±1 K by controlling the heater power. Comparing our experience with resistance-temperature systematics in shorter experiments, our constant-power method suggests a precision better than ±20 K in long duration runs.

ANALYTICAL PROCEDURES

After annealing, diamonds were recovered by dissolving surrounding MgO spacers using 6 mol L^{-1}HCl solution at 50 °C. Then they were delicately pressed into soft indium mounts. Prior to SIMS analysis, the mount was coated with 300 Å-thick Au.

Samples were analyzed with a Cameca ims 5*f* ion microprobe at the Pheasant memorial lab, ISEI, Okayama University at Misasa.[7] Tuning of the instrument was achieved as follows: the acceleration voltage of a $^{16}O^-$ primary beam was 12.5 kV, and with a current of 6 nA; the focused beam diameter was approximately 10 μm. A 50×50 μm area was rastered and the electronic gate was set between 20×20 and 30×30 μm. The secondary acceleration voltage was 4.5 kV and the energy offset was −20 V. An electron multiplier was used for counting the incoming carbon ions. The "depth profiling" analytical mode was employed to measure isotopic variation of diffusion profiles.[8]

TABLE I. Experimental conditions and determined diffusion coefficients.

T^a [K]	t^b [min]	$D^c[m^2/s]$
2073	1401	1.4×10^{-21}
2073	1506	2.5×10^{-21}
2073	2884	1.5×10^{-21}
2073	4130	1.6×10^{-21}
2073	4595	1.5×10^{-21}
2273^d	480	2.4×10^{-20}
2373	10	2.3×10^{-19}
2373	75	2.2×10^{-19}

[a] Temperature conditions of diffusion anneal. Pressure conditions were at 10 GPa.
[b] Experiment duration.
[c] Diffusion coefficients.
[d] Temperature is determined by power consumption.

In this study, we chose a relatively small energy offset to obtain maximum signal. The mass interference by $^{12}C^1H$ (Ref. 9) was sufficiently negligible for the determination of diffusion coefficients, because of the drastic difference of the initial isotopic composition from 90% ^{13}C to 1.1% ^{13}C. Furthermore, the measurement reproducibility of the natural $^{12}C/^{13}C$ abundance ratio was within 1%.

The diffusion coefficient was determined by fitting to the data a diffusion model of a limited source diffusant. We fitted the error function iteratively using a least-squares gradient convergence method and determined the parameters including the diffusion coefficient. The model equation was

$$\frac{C}{C_0} = \frac{1}{2}\left(\operatorname{erfc}\frac{h-x}{2\sqrt{Dt}} + \operatorname{erfc}\frac{h+x}{2\sqrt{Dt}}\right), \tag{1}$$

where the concentration C, corresponding distance x, and duration t are determined from experiments while solving for the diffusion coefficient D, initial boundary concentration C_0, and initial source thickness, h.

RESULTS

Experimental conditions and calculated diffusion coefficients are given in Table I. Figure 3 shows a typical result of the model fit to a concentration profile obtained by SIMS. It demonstrates the agreement between the fit and data.

The calculated diffusion coefficients for a series of experiments at the same *P*-*T* conditions but ranging over a factor of 3 in run duration show a constant value within the uncertainty (Fig. 4). The quality of the model fit to the depth profile data and the constancy of diffusivity over a range of the time duration provide evidences that we have indeed measured the diffusion phenomena.

The main source of uncertainty occurs in the measurement of the depth of the crater made by the SIMS beam,

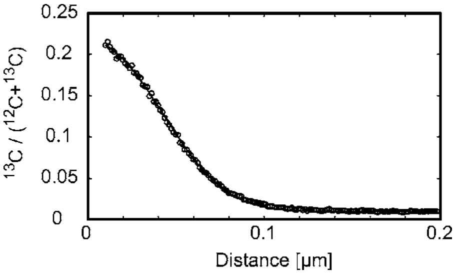

FIG. 3. A diffusion model fit to a concentration profile. Circles are fraction of ^{13}C measured by SIMS. The line is the best-fit model as discussed in the text.

rather than the quality of the fit. The surface of diamond and the bottom of the crater were a slightly nonorthogonal to the trajectory of the primary beam. By propagating the uncertainty, a ±30% variation was expected as the error associated with these measurements. This uncertainty is comparable to the variation of repeated analyses on one sample (1σ ranges from 20% to 40%).

At the pressure condition of 10 GPa, we have determined diffusion coefficient at three temperatures. This allowed us to determine the Arrhenius relationship (Fig. 5)

$$D[\mathrm{m}^2/\mathrm{s}] = 4.1 \times 10^{-5} \exp\left(\frac{-6.8[\mathrm{eV}]}{kT}\right). \qquad (2)$$

The thermal activation energy of diffusion is 6.8 ± 1.6 eV (650 ± 160 kJ/mol) and frequency factor is $D_0=4.1\times10^{-5}\ m^2/\mathrm{s}$ [$\ln(-10.1\pm2.0)\ m^2/\mathrm{s}$]. Due to the limited temperature range of the experiments, the uncertainty of D_0 exceeds an order of magnitude. Extrapolation of the reported Arrhenius relationship shown in Fig. 5 used beyond the range of experimental conditions requires caution.

DISCUSSION

The activation energy of carbon self-diffusion in diamond has been calculated by *ab initio* methods.[1] These studies determined the various types of vacancy formation energies and the energy of migration of an atom. Addition of the vacancy formation and migration energies is the activation energy of intrinsic diffusion. Our experimentally determined activation energy (6.8 eV) is smaller than that of the energy of neutral vacancy formation (7.2 eV) and calculated activation energy for self-diffusion in diamond (9.1 eV).[1] We consider these discrepancies to be reconcilable considering the uncertainty associated with our result and model dependence of *ab initio* calculations. For instance, the activation energy of migration can be reduced by the choice of electron density function and/or consideration of polarizability of atoms.

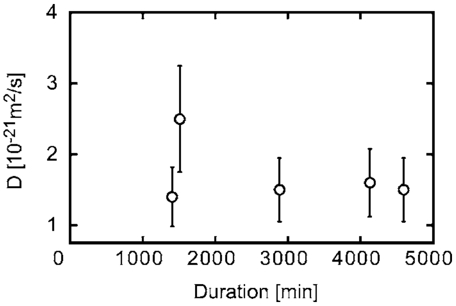

FIG. 4. Diffusion coefficients determined at 2073 K, 10 GPa is plotted against experiment duration. No systematic changes are seen.

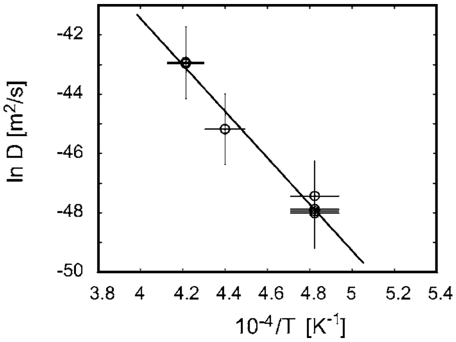

FIG. 5. An Arrhenius plot of carbon self-diffusion coefficient at 10 GPa. The solid line is the best-fit regression accounting for the uncertainty in temperature and diffusion coefficients.

Nitrogen atoms are incorporated in the natural diamond matrix as impurities and form various clusters of nitrogen-associated vacancies.[10] The kinetics of nitrogen migration in diamond may be compared to that of carbon, since the rate of nitrogen migration may be limited by the mobility of carbon atoms. Migration and reorganization of nitrogen associated defects in diamond has been well studied and its activation energy for *A*-center formation is determined experimentally: 6.5 (Ref. 10) and 4.4–6.0 eV (Ref. 11). The variation of activation energy from 4.4 to 6.0 eV (Ref. 11) is attributed to the difference in the growth sector studied (cubic and octahedral).

It is expected that the abundance and nature of nitrogen vacancies are important parameters controlling the diffusion process, considering the quantity of nitrogen in the diamond (200 ppm). For example, the presence of nitrogen atoms may reduce the energies of vacancy formation and migration. The broadly identical activation energies between nitrogen and carbon diffusion suggest that the *A*-center formation is likely rate limited by carbon self-diffusion but this observation does not preclude the possibility that the diffusion kinetics of carbon in diamond is related to nitrogen. Further investigation is necessary to determine the relationship between carbon self-diffusion and nitrogen diffusion processes in diamond with various concentration and vacancy states of nitrogen atoms.

Last, the diffusion data can constrain the maximum possible age of diamonds. A typical length scale of carbon isotopic zoning (5–50 μm) in a majority of diamonds, which are from the continental lithosphere, gives the maximum age more than the age of the Earth (4.5×10^9 years). In contrast, we predict that the rare diamonds originating from the mantle transition zone should have developed the order of the mm length scale of isotopic zoning over 4.5×10^9 years.[12].

ACKNOWLEDGMENTS

This study was supported by JSPS (K.T.K.), JSPS grant-in-aide (M.J.W., K.T.K.), and the program of Center of Excellence for the 21st Century in Japan (E.N.). The authors acknowledge helpful advice from E. Ito, T. Katsura, and A. Yoneda for high-pressure experiments and S. Yamashita for the Fourier transform infrared analysis.

---

*Corresponding author. Present address: Laboratoire Magmas et Volcans UMR-CNRS 6524, 63038 Clermont-Ferrand cedex, France. Electronic address: K.Koga@opgc.univ-bpclermont.fr

†Present address: Department of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK.

[1] J. Bernholc, A. Antonelli, T. M. Del Sole, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **61**, 2689 (1988).

[2] J. Bernholc, S. A. Kajihara, C. Wang, A. Antonelli, and R. F. Davis, Mater. Sci. Eng., B **11**, 265 (1992).

[3] S. H. Richardson, J. J. Gurney, A. J. Erklank, and J. W. Harris, Nature (London) **310**, 198 (1984).

[4] N. Shimizu, N. V. Sobolev, and E. S. Yefimova, Russ. Geol. Geophys. 38, 356 (1997).

[5] S. R. Boyd, I. Kiflawi, G. S. Woods, Philos. Mag. B **69**, 1149 (1994).

[6] M. J. Walter, Y. Thibault, K. Wei, and R. W. Luth, Can. J. Phys. **73**, 273 (1995).

[7] E. Nakamura, A. Makishima, T. Moriguti, K. Kobayashi, C. Sakaguchi, T. Yokoyama, R. Tanaka, T. Kuritani, and H. Takei, Inst. Space Astronaut. Sci. Rep. SP. 16, 49 (2003).

[8] A. Benninghoven, F. G. Rüdenauer, and H. W. Werner, *Secondary Ion Mass Spectrometry: Basic concepts, instrumental aspects, applications, and trends*, (Wiley, New York, 1987).

[9] B. Harte and M. Otter, Chem. Geol. **101**, 177 (1992).

[10] T. Evans and Z. Qi, Proc. R. Soc. London, Ser. A **381**, 159 (1982).

[11] W. R. Taylor, D. Canil, and H. J. Milledge, Geochim. Cosmochim. Acta **60**, 4725 (1996).

[12] K. T. Koga, J. A. Van Orman, and M. J. Walter, Phys. Earth Planet. Inter. **139**, 35 (2003).