Trace amount of nickel in synthetic diamond and its implication to the abundance of substitutional nitrogen

H. Kagi[a], M. Wakatsuki[a], S. Hayakawa[b], F. Nakamura[b], Y. Gohshi[b],
H. Kanda[c] and J. Isoya[d]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan.

[b] Department of Industrial Chemistry, University of Tokyo, Hongo, Tokyo 113, Japan.

[c] National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan.

[d] University of Library and Information Science, Tsukuba, Ibaraki 305, Japan.

An abundance correlation between Ni^- and C-centers (atomic N) has been obtained for synthetic diamonds grown from Ni-based metallic solvents. The abundance of total nickel in the diamonds was determined by X-ray fluorescence (XRF) analysis and the nitrogen content was determined from electron paramagnetic resonance (EPR) spectra. Electronic configurations of dissolved nickel were investigated with EPR spectra and the amounts of substitutional Ni^- centers (Ni_s^-) were determined. For diamond crystals grown from a nickel solvent, the addition of 2 % Ti (nitrogen getter) into the pure nickel solvent gave rise to a substantial decrease of Ni_s^- and N contents; from 50 to 0.15 atomic (atom.) ppm for Ni_s^- and from 270 to 0.29 atom. ppm for N. On the contrary, the total amount of nickel exhibited a small decrease from 317 to 227 atom. ppm. These results imply a close relationship between the abundances of Ni_s^- and those of N. Furthermore, a nitrogen-reduced diamond crystal was grown from a degassed carbon source without using a nitrogen getter. The nitrogen-reduced diamond showed a decrease of N from 64.7 to 14.9 atom. ppm in addition to a decrease of Ni_s^- from 14.9 to 4.9 atom. ppm which means that Ni_s^- abundance correlated to N abundance. Electron transfer from N to Ni_s^- in the diamond crystal was speculated from our experimental results as a possible physical interpretation of the abundance correlation.

1. INTRODUCTION

Nickel and nitrogen are easily incorporated in synthetic diamonds in the state of solid solution. So far Ni seems to be the only transition-metal ion that gives a well-established EPR signal (g=2.0319) derived from dispersed impurities[1-3]. Substitutional Ni^- with the electronic configuration $3d^7$ ($e^4t_2^3$) and interstitial Ni^+ with $3d^9$ ($e^3t_2^6$) are easy to observe with EPR spectrometry[3]. It has been reported that yellow-colored diamond crystals grown from Ni-based metal solvents show EPR signals of Ni_s^- (substitutional Ni^- centers) in addition to those of isolated neutral nitrogen (C-centers), while green-colored crystals grown from a nickel solvent with addition of a small amount of Ti show a substantial decrease of Ni_s^- and C-centers, in addition to the appearance of Ni_i^+ (interstitial Ni^+). Ti metal, an efficient getter of nitrogen atoms, prevents nitrogen from being incorporated into diamond lattice by its strong chemical affinity to nitrogen. Furthermore, a good correlation between the abundance of Ni_s^- and that of C-centers in synthetic diamond crystals was first reported by Isoya et al (1990)[3]. The abundance correlation between Ni_s^- and C-centers can be open to the following two possibilities. First, the existence of nitrogen getter (Ti metal) in the solvent directly decreased the abundance of Ni_s^-. Second, some charge transfer from N to Ni induced the formation of Ni_s^- which means that the amount of Ni_s^- decreases with the decrease of C-centers. In this study, for understanding the nickel incorporation process, the total amount of nickel atoms (including EPR-inactive species) in the diamond crystal grown from Ni-based metal was determined by the X-ray fluorescence method using the synchrotron radiation (SR) beam in addition to EPR measurements.

Table 1. Concentration of N and Ni. (atom. ppm)

	N	Ni⁻	Ni⁺	Total Ni
Sample-A	270	50	-	317
Sample-B	0.29	0.15	2.4	227

Moreover, the abundance correlation between Ni_s^- and C-centers was investigated for diamond crystals grown from KOV alloy (Fe : Co : Ni = 55 : 16 : 29 wt.%) with various nitrogen concentrations in the crystals.

2. EXPERIMENTAL METHOD
2.1. Sample preparation
Synthetic diamond crystals were grown by the temperature gradient method using three types of metal solvents, Ni, Ni + 2 wt.% Ti and KOV alloy, at high pressure. Sample-A was grown in the solvent of Ni without any additives, while Sample-B was grown in Ni with additive of 2 wt.% of Ti and showed a green-color. The green color of Sample-B seemed to derive from the presence of some nickel centers in the diamond crystal. The pressure and the temperature of the growths of Sample-A and B were about 6 GPa and 1700 K. Sample-C and D were grown in KOV alloy at about 5.5 GPa and 1620 K. For the purpose of reducing the nitrogen content, Sample-D was grown from degassed graphite [4]. The decrease in the nitrogen content (abundance of C-centers) was confirmed with EPR spectra as described later.

2.2. XRF analysis
For XRF analysis, the diamond crystals were sliced to thin sections through the middle of a diamond crystal with thickness of 500 μm for Sample-A and 300 μm for Sample-B. The XRF measurements were carried out at the Photon Factory on beamline 4A using monochromatized 9 keV SR x-rays. Nickel distributions were measured with the same system described previously using an incident beam of size 300 μm square [5]. An absorption correction method was employed for nickel quantification in diamond using a nickel foil of thickness 12.8 nm as a reference sample [6].

For analysis of Ti, the sample chamber was evacuated with a rotary pump for preventing the X-ray fluorescence from being absorbed in air, and 6 keV SR x-rays were used for excitation.

2.3. EPR measurements
Concentrations of paramagnetic impurities (C-centers and Ni_s^-) in the samples were determined with EPR measurements. The EPR spectra were recorded on a Bruker ESP300 x-band spectrometer. For the determination of Ni_s^- abundance, the EPR measurements were carried out at 77K by using an insertion Dewar with liquid nitrogen. The absolute number of nitrogen atoms was calibrated against a primary standard of $CuSO_4 \cdot 5H_2O$ crystal. Spin concentrations were calculated by a double integration of the derivative signals generated by the spectrometer. The number of Ni_s^- was determined by the signal intensity ratio of Ni_s^- to C-centers at liquid N_2 temperature.

3. RESULTS AND DISCUSSION
3.1. Abundances of total Ni and N
Spatially averaged concentrations of total nickel, EPR-active Ni_s^- and neutral nitrogen (C-centers) for Sample-A and B are listed in Table 1. It is proved that the total amounts of nickel for the two samples are much larger than that of the EPR-active nickel, and show a close similarity between Sample-A and Sample-B, while the concentrations of EPR-active Ni_s^- and C-centers show a substantial decrease in Sample-B. From the similarity in the total amounts of nickel, one can speculate that the total amount of incorporated nickel is determined at the growing interface of diamond; on the other hand, the states of nickel (Ni^0, Ni_s^-, Ni_i^+ etc.) are determined inside the diamond crystal depending on the nitrogen

Table 2. Concentration of N and Ni. (atom. ppm)

	N	Ni $^-$
Sample-C	149	14.9
Sample-D	64.7	4.9

concentration. These results lead us to the following two implications.

The first one is that the major nickel impurity in the diamonds grown from Ni-based metallic solvents is EPR-inactive. The second one is that the amount of EPR-active nickel (Ni_s^-) shows a good correlation with that of neutral nitrogen, which suggests an occurrence of certain charge transfer between nitrogen and nickel. One can speculate that electrons might migrate from nitrogen atoms to neutral Ni to form the EPR-active Ni_s^- centers, which means the substituted nitrogen atoms serve as electron donors.

3.2. Ti abundance in Sample-B

We must take into consideration that micro inclusions of metallic nickel in the crystal might make a contribution to the total amount of nickel observed with XRF. The amount of Ni in metallic inclusions would make a considerable contribution to the amount of Ni^0. But this possibility can be excluded, because the crystal grown from Ni plus 2% of Ti showed no incorporated Ti judging from the XRF spectrum as shown in Fig.1. X-ray fluorescence from Ti at 4.5 keV cannot be observed. If the metallic inclusions were incorporated in the diamond crystal, the XRF spectra should show the existence of Ti. Furthermore, XANES (X-ray absorption near edge structure) of nickel in the crystal exhibited a spectral feature distinct from that of metallic nickel [7]. This preliminary result suggests the absence of metallic inclusions.

We can conclude thus that the Ni detected with the XRF method can be assigned to ESR-inactive Ni. Although no optical observations of absorption bands assigned to the EPR-inactive Ni states have been made, our result would throw light on the assignment of unidentified spectral lines for the diamond crystals.
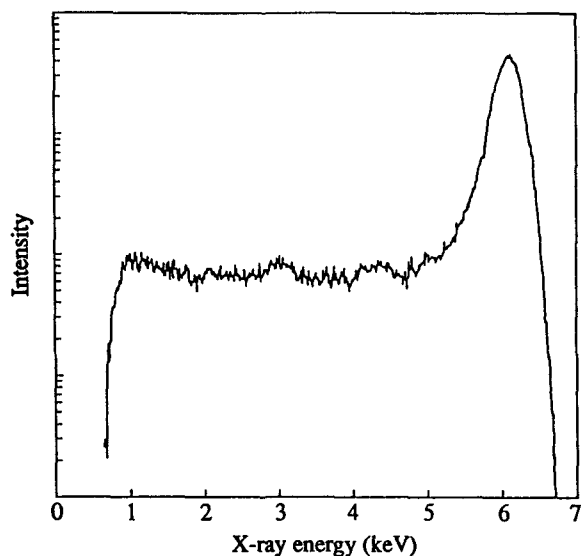

Fig.1. XRF spectrum of diamond grown from Ni-Ti metallic alloy

3.3. The abundance of Ni_s^- and C-centers in the N-reduced diamond

To clarify the speculation attributing the abundance correlation between Ni_s^- and N to the charge transfer from Ni to N, we investigated the abundances of Ni_s^- centers and C-centers contained in the nitrogen-eliminated diamond crystals synthesized without employing Ti (nitrogen getter). In Table 2 are shown the preliminary results on the concentrations of Ni_s^- and C-centers contained in Sample-C and Sample-D grown from KOV alloy. (The reason we denoted here "preliminary" is because we have not been able to grow well-crystallized single crystals of diamond without metallic inclusions when we eliminate the nitrogen content.

The presence of metallic inclusion interferences with the EPR measurement.) One can, however, recognize that the concentration of substitutional Ni_s^- decreases with the decrease of C-centers. This result strongly suggests the second implication, an occurrence of charge transfer between nitrogen and nickel.

4. CONCLUSIONS

(1) Diamond crystals grown from Ni with the addition of 2% of Ti (Sample-B) showed a substantial decrease in the abundance of EPR-active Ni_s^- together with N (C-centers) compared with the crystal grown from pure Ni (Sample-A).

(2) Total amounts of Ni metal for Sample-A and Sample B gave comparable values. This means that the major part of Ni incorporated in the diamond crystals was EPR-inactive.

(3) Sample-B showed the absence of Ti from the XRF spectrum, which suggests that the major part of Ni is incorporated in an atomic state, not in metallic inclusions.

(4) Nitrogen-reduced diamond grown from a degassed carbon source revealed a decrease of Ni_s^- centers, which suggests a charge interaction between Ni and N in diamond lattice.

It is likely that some interactions between the impurity-derived centers exist in diamond crystals. This interaction will determine the electronic configuration of the centers. Further study on the correlation between the abundances of substitutional Ni_s^- and C-centers are required for understanding the behavior of these impurities in diamond.

REFERENCES
1. J. N. Loubser and W. P. van Ryneveld, Nature 211 (1966) 517 .
2. J. Isoya, H. Kanda, J. R. Norris, J. Tang, M. K. Bowman, Phys. Rev. B 41, (1990) 3905.
3. J. Isoya, H. Kanda and Y. Uchida, Phys. Rev. B 42, (1990) 9843.
4. *unpublished data*
5. M. Wakatsuki. S. Hayakawa, S. Aoki, Y. Gohshi and A. Iida, 1991 MRS Int. Conf. Proc. (1992) 143.
6. S. Hayakawa, A. Iida and Y. Gohshi, Anal. Sci., 7 (1991) 509.
7. *unpublished data*