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Abstract
The distribution of oxygen and nitrogen impurities in diamond single crystals from a variety of origins and qualities was investigated using secondary ion mass spectrometry. A positive correlation between these impurities is observed over a wide concentration range. It is suggested that in diamonds oxygen is present not only in submicroscopic inclusions, but also as a lattice impurity. It appears that the presence of oxygen in a given crystal volume suppresses the IR-activity of nitrogen defects.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Oxygen within the diamond lattice remains an elusive impurity. Mass spectrometry (Melton and Giardini 1981) and nuclear probes (Sellschop *et al* 1980, Mathez *et al* 1993) have documented the presence of oxygen in all diamonds that have been studied, with concentration ranging from <100 to 1000 at. ppm; apparently no correlation with nitrogen exists. Oxygen enters solid and fluid submicroscopic inclusions (e.g. Chrenko *et al* 1967, Galimov *et al* 1979, Melton and Giardini 1974), but the relative amount of this inclusion-related O is unknown and is certainly sample-dependent. Quantitative studies (Sellschop 1992) have shown that in virtually every diamond there exists 'inclusion-independent' oxygen which is believed to be a lattice impurity. Several rare paramagnetic defects have been tentatively assigned to oxygen-containing complexes (Newton and Baker 1989, van Wyk *et al* 1992), though this assignment was recently questioned (Nadolinny *et al* 2009a, 2009b). Implantation of ^{17}O and ^{16}O and subsequent annealing produces a small amount of luminescent (Gippius 1993), paramagnetic (Iakoubovskii and Stesmans 2002) and, possibly, electrically active (Prins 2000) O-related defects. Mori *et al* (1992) showed that CVD films treated with hot CrO_3 possess cathodoluminescence (CL) lines most likely associated with O-related defects. CVD diamond grown in an O-rich atmosphere sometimes shows CL bands tentatively assigned to O in the diamond lattice (Ruan *et al* 1993). A recent study of natural monocrystalline diamonds showing strong absorption by CO_2 in IR spectra (Hainschwang *et al* 2008) suggests that these diamonds contain oxygen as a lattice impurity. Finally, theoretical calculations (Gali *et al* 2001, Lowther 2003) show the plausibility of the existence of significant concentrations of O-related defects in the diamond lattice, perhaps in configurations similar to substitutional nitrogen. However, up until now evidence for the incorporation of O during growth of monocrystalline diamond is scarce and little is known about associated defects. In addition to being of interest to the fields of solid state physics and geosciences, studies of oxygen in diamond could be of technical significance since substitutional oxygen ions may make diamond electrically conductive (n-type conductivity) and may influence emission properties (Prins 2000, Lowther 2003).

The aim of the current study is to resolve the ambiguity as to whether or not O can exist as a growth-related structural impurity in diamond single crystals. Several types of monocrystalline diamonds, both with and without CO_2 IR absorption, were analysed by techniques sensitive to chemical composition (secondary ion mass spectrometry (SIMS)) and to the crystalline perfection (small-angle x-ray scattering and x-ray topography).
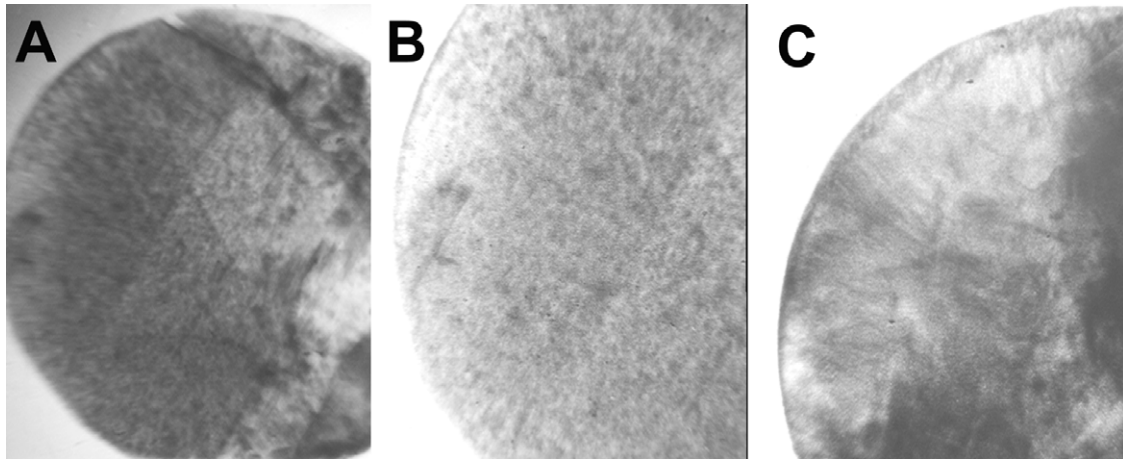
Figure 1. X-ray topographs of several CO_2-rich diamonds. (A)—sample with slip planes and 'patchy' contrast, diameter of the stone is 3 mm; (B)—close up image of the same sample showing spot-like contrast; (C)—another CO_2-rich sample with heterogeneously distributed deformed regions; diameter of the stone is 2.5 mm. All shown topographs are for 111 reflection with the diffraction vector directed vertically.

2. Samples and methods

The following types of diamonds were studied (see table 1): (a) natural type Ia diamonds with nitrogen concentrations between 200 and 800 at. ppm in the A and B forms; (b) synthetic Ib HPHT diamonds from DeBeers and other producers with N content of 100–250 at. ppm; (c) natural monocrystalline diamonds (type Ia with 20–50 ppm of N) showing CO_2 IR absorption (for detailed spectroscopic information about these crystals see Hainschwang *et al* 2008); (d) natural polycrystalline diamond—ballas (low N content). Nitrogen concentrations were estimated from IR absorption spectra acquired at several spots on each sample. Perfection of the samples was assessed by x-ray topography. Nanosized heterogeneities in several representative CO_2-rich diamonds were also studied using small-angle scattering (SAXS) using monochromatic Cu radiation. The size distribution of the scattering centres was calculated using the Tikhonov regularization method (Svergun 1992) assuming a spherical shape.

SIMS was performed using the Cameca ims 6f instrument at the Helmholtz Centre, Potsdam. Due to the demanding character of the current SIMS study, a detailed description of methodology is given below. Prior to the analysis, the polished diamond samples were mounted in epoxy, ultrasonically cleaned in high purity ethanol, dried at $60\,°C$ in atmosphere and were then sputter coated with a high purity, 35 nm thick conductive gold coat. Due to prolonged storage (several weeks) of the sample mount in high vacuum conditions ($\sim 10^{-7}$ Pa), the O background signal was very low. Both digital mapping of the oxygen lateral and depth distributions and spot analyses were performed. Mapping mode, employing the instrument's dynamic transfer function, examined single growth sectors over $100 \times 100\ \mu m^2$ areas. Mapping was conducted using a 20 nA $^{133}Cs^+$ primary beam focused to a 6 μm diameter, which represents the spatial resolution of our imaging method.

In spot analysis mode a high primary current (100 nA) was employed and the resolving power of the mass-spectrometer was set at $M/\Delta M = 4600$. The beam profile at the sample surface was *circa* $50 \times 75\ \mu m^2$. The domain being analysed was carefully cleaned using a 10 min pre-sputtering, which effectively removed all surface contamination which might have been present. Furthermore, in order to suppress vacuum derived contaminants, a 100 μm diameter field aperture was employed, thereby limiting secondary ion collection from the central 8 μm of the sputtered crater. SIMS spot measurements were performed at random, i.e. spots on individual crystals were not measured sequentially one after another, but rather measurements were interspersed between stones so as to minimize any systematic drift which might have influenced the results. On every specimen several (typically 2–4 spots) randomly selected points were investigated. A single analysis consisted of 25 cycles of ^{13}C–^{14}N–^{16}O measurements which required 8 min of data acquisition. The eight minutes of sputtering during which data were collected for the spot analyses removed $<2\ \mu$m of material from the sample surface. The lowest observed secondary ion intensities were 0.7 counts s^{-1}, which is well above the 0.01 cps dark noise of our digital ion counting system. Hence we conclude that all of our analyses are at least an order of magnitude above the limit of determination of our setup.

Many of the samples were heterogeneous in their N content as determined by IR. In addition, the sample volume probed by SIMS is much smaller than that analysed by FTIR and direct correspondence of the SIMS and IR concentrations of N is not always possible. SIMS is only a comparative method. In order to obtain reliable quantitative data from the SIMS technique it is essential to calibrate the instrument using a well characterized, matrix matched material. As no such reference material is, to the authors' knowledge, available for the quantification of oxygen in diamond, the data are reported only in the form of measured ratios $^{16}O/^{13}C$ and $^{14}N/^{13}C$. Use of an inappropriate reference material would likely lead to a systematic, potentially large error in any quantitative results. As the relative ion yields of C, N and O could not be determined it is not possible to derive absolute concentration values from our results.

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Table 1. Description of studied samples.

| Sample #	Nat1	Nat2	Nat3	Nat4	Nat5	Nat6	Nat7	Nat8	Syn1	Syn2	Syn3
Type	IaB	IaA ≫ B	IaAB	IaA > B	n/a	IAB	IaB	n/a	Ib	Ib	Ib + N$^+$
Colour	Medium pinkish brown	Medium dark brown	Medium brown	Medium brown	Black (very dark brown-yellow)	Transparent	Transparent	Black	Yellow	Yellow	Yellow
Colour distribution	Colour banding along (111)	Patchy brown colour	Patchy brown colour zones	Patchy brown colour	Uniform	—	—	Uniform	Sector zonation	Sector zonation	Sector zonation
PL at 365 nm excitation	Medium blue	Medium greenish yellow	Medium bluish yellow	Medium yellow	Inert	n/a	n/a	n/a	n/a	n/a	n/a
PL at 254 nm excitation	Weak blue	Weak greenish yellow	Weak greenish yellow	Weak yellow	Inert	n/a	n/a	n/a	n/a	n/a	n/a
CO_2 peak intensity in IR	0	Extremely low	Low	0	Very strong	0	0	0	0	0	0
Average $^{16}O/^{13}C$ (*n*—number of individual SIMS analyses)	1.68×10^{-3}	5.36×10^{-3} ($n = 3$)	1.40×10^{-3}	5.20×10^{-3}	3.40×10^{-2} ($n = 2$)	6.11×10^{-4} ($n = 2$)	6.61×10^{-4}	6.19×10^{-4}	5×10^{-4} ($n = 2$)	4.85×10^{-4} ($n = 4$)	3.80×10^{-4}
Average $^{14}N/^{13}C$ (*n*—number of individual SIMS analyses)	2.21×10^{-5}	2.81×10^{-5} ($n = 3$)	1.90×10^{-5}	2.90×10^{-5}	5.09×10^{-5} ($n = 2$)	7.75×10^{-6} ($n = 2$)	1.03×10^{-5}	8.29×10^{-6}	7.1×10^{-6} ($n = 2$)	7.45×10^{-6} ($n = 4$)	5.95×10^{-6}
Comments	'Standard' brown	'Pseudo-CO_2' diamond, strong one-phonon absorption	CO_2 diamond	'Pseudo-CO_2' diamond, strong one-phonon absorption	CO_2 diamond, polycrystalline, lonsdaleite-rich	Common natural diamond	Common natural diamond	Ballas; low-quality IR spectrum	HPHT diamond	HPHT diamond	HPHT diamond
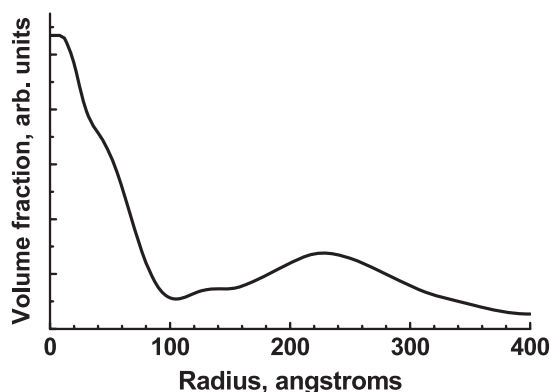
Figure 2. Size distribution of scatterers for a CO_2-rich diamond obtained from small-angle x-ray scattering.

3. Results

3.1. X-ray and spectroscopic data

The synthetic samples that we studied were of high crystalline perfection and x-ray topography revealed only a few dislocations and stacking faults. The white-beam topograph of the ballas diamond was not informative due to a high density of extended defects. The topographs of the CO_2-rich diamonds were highly variable, showing various degrees of deformation. Some of the samples show slip planes and very unusual x-ray contrast (figure 1). This patchy contrast might be due to either stress fields around numerous, micron-sized inclusions or, less likely, from entangled dislocations. Several reflections were employed for topography, but nevertheless no unique interpretations of the observed contrast patterns exist. Other studied CO_2-rich diamonds show heterogeneously distributed deformed regions and dislocations. Note that individual dislocations are often resolved, thus indicating moderate degrees of deformation. This topography work confirms results of previous CL studies (Chinn 1995, Hainschwang *et al* 2008), which documented that heterogeneously distributed, plastically deformed regions are typical for many CO_2-rich diamonds.

IR absorption spectra of some of the CO_2-diamonds show a 'triangular' absorption band in the one-phonon region. A similar band was observed earlier both in lonsdaleite-containing (Klyuev *et al* 1978) and heavily deformed diamonds (Shiryaev 2007), which has been tentatively ascribed to absorption due to lonsdaleite, twins and/or stacking faults. IR spectra of other diamonds were rather typical for corresponding diamond types, showing nitrogen-related bands in the one-phonon range and lattice absorption.

The SAXS signal from the synthetic diamonds was negligible, as expected from previous works (Shiryaev *et al* 2003, Shiryaev 2007). In contrast, scattering from the CO_2-rich diamonds was strong and is qualitatively comparable with scattering from diamonds with voidites. The size distribution of scattering centres in these diamonds is generally similar and can be represented by superposition of two or three subpopulations with average radii of ∼50 and ∼220 Å (figure 2). Most likely, the scattering is due to clusters of

point defects and the larger populations of the scatterers are microscopic inclusions.

3.2. SIMS results

Ion mapping provided qualitative information about the spatial distributions of ^{13}C, ^{16}O, ^{28}Si with a ∼6 μm spatial resolution. Silicon was included in our peak-stepping sequence in order to test for the presence of microscopic silicate inclusions which are common in natural diamonds. With the exception of a single, clearly observed micron-size spot, interpreted as a small silicate inclusion, no significant signal was found on the ^{28}Si$^-$ peak.

In 'normal' natural and synthetic diamonds, oxygen is distributed homogeneously and the concentration is low. The CO_2-rich diamonds are distinctly richer in oxygen. Mapping of two such specimens revealed a uniform oxygen distribution. Since our mapping mode investigated only small regions of individual growth sectors, we interpret the observed spatial homogeneity as indicative of oxygen being present as a lattice impurity. However, in one of the samples oxygen is distributed as spots with irregular shapes (figure 3) and in the CO_2 sample with the highest O content its distribution versus sputtering time was highly non-uniform. Such behaviour suggests that a fraction of O resides in submicroscopic inclusions. Nevertheless, a relatively high, homogeneous O 'background' distribution was observed which, in conjunction with spot analyses (see below), suggests that oxygen is partitioned between lattice and inclusions.

On every sample several individual locations were analysed for their O and N contents. The values normalized for ^{13}C counts (representative of the diamond matrix) are presented in figure 4. We discovered that a strong correlation exists between nitrogen and oxygen contents. Importantly, the correlation is obeyed both for individual spots on a specimen and for the whole suite of investigated diamonds. As mentioned above, the CO_2-rich sample (Nat5) with the highest O and N content is characterized by an irregular spatial distribution of oxygen, suggesting that a considerable fraction of the oxygen resides in inclusions. For this specimen the positive N–O correlation holds for two independent analysis points.

4. Discussion

For the majority of natural and synthetic diamonds almost all nitrogen present in a crystal is present as point defects in the crystalline lattice and can be quantitatively assessed by IR absorption spectroscopy. Several exceptions to this general fact are known: some inclusion-rich diamonds (De Corte *et al* 1998, Melton and Giardini 1981), and, possibly, diamonds with voidites (Bruley and Brown 1989). In these crystals a fraction of nitrogen resides in fluid inclusions and does not contribute to defect-related IR absorption. However, the presence of a significant population of N-containing submicroscopic inclusions in the high-quality synthetic and monocrystalline natural diamonds studied by us is highly unlikely. Therefore, both the homogeneity of the O spatial
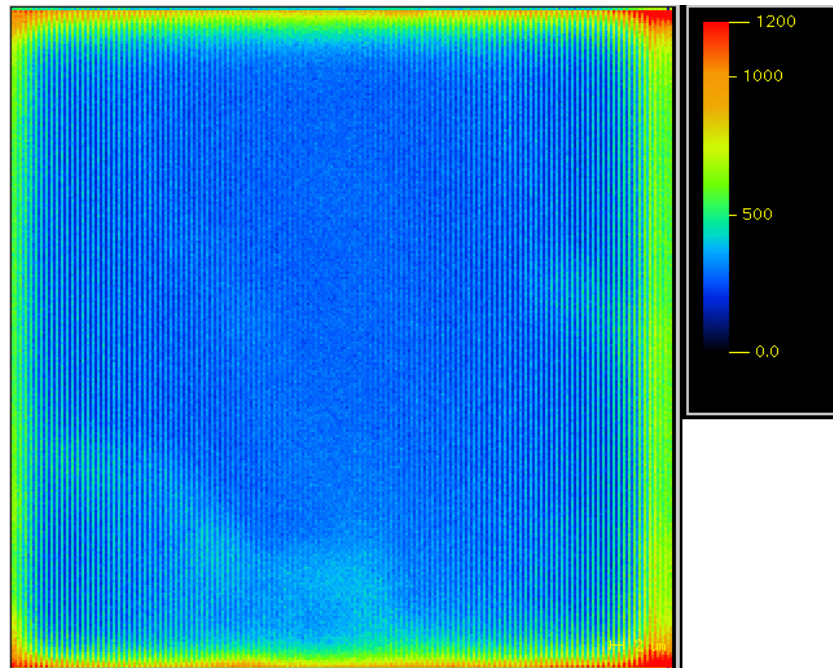
Figure 3. Example of a digital ion map of the $^{16}O^-$ distribution, in this case from sample Nat5 (see table 1 and also figure 4). Linear scale with field of view of 100×100 μm^2. This image shows both a patchy distribution as well as a quite homogeneous 'background' distribution of oxygen. The scale bar indicates the total counts per pixel over a total integration time for the image of 400 s. Intense regions at the very margin of the image are analytical artefacts.
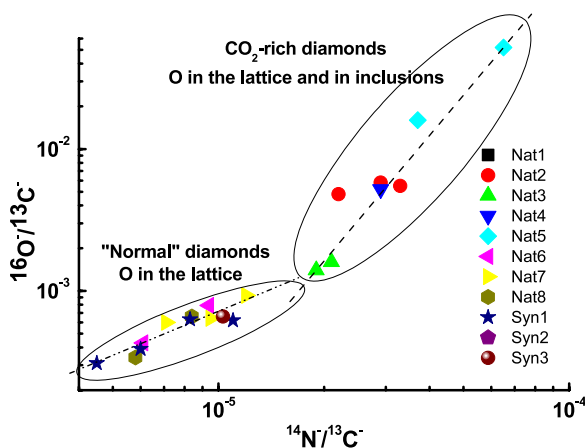

Figure 4. Nitrogen–oxygen correlation determined by spot analysis by SIMS. Note that values are not calibrated and, therefore, the information is largely qualitative. The dashed lines are just to guide the eye and show plausible correlations between N and O. For a description of the samples see table 1.

distribution and the existence of the linear N–O correlation suggest that a substantial fraction of the oxygen atoms in diamond is present as a lattice impurity.

In the CO_2-diamonds the CO_2 IR absorption is the most intense in those regions showing minimal concentrations of N-related defects (Hainschwang *et al* 2008). It was, therefore, suggested that N and O are either mutually exclusive impurities or that they form spectroscopically inactive complexes. The current SIMS study seems to support the latter model. The SIMS spot analyses reveal that oxygen contents are not correlated with nitrogen in a unique way, which suggests that N–O complexes *sensu stricto* are not abundant. Most likely the coexistence of these two impurities in a given volume and their interaction prevents formation and/or hinders IR manifestations of well-known N defects and of CO_2 moieties. The formation of nanosized N–O-containing inclusions is an example of such a mechanism.

Interestingly, previous spectroscopic studies of oxygen in diamond (Gippius 1993, Iakoubovskii and Stesmans 2002) show that this impurity becomes observable only after annealing. Theoretical calculations of relative stabilities of oxygen in diamond show a very strong dependence on the position of the Fermi level in the crystal (Gali *et al* 2001, Lowther 2003). According to these results oxygen behaviour in diamond and, in particular, its diffusivity strongly depends on the nitrogen concentration and speciation. Although the O–N pair appears to be a stable defect at low temperatures, mutual repulsion of positively charged N and O ions creates a vacancy-like state in between them (Lowther 2003). Since most impurities in diamond diffuse by a vacancy-assisted mechanism, such a configuration may be destroyed by annealing. The calculated strength of the C–O bond in diamond is lower than the C–C bond and preferential breaking of the C–O bond seems plausible. Therefore, despite its relatively common presence, oxygen is not always detected by spectroscopic methods if no annealing has been performed.

5. Conclusions

Oxygen and nitrogen content of a suite of natural and synthetic diamonds was measured using secondary ions mass

spectrometry. It is shown that the oxygen impurity correlates positively with nitrogen over a very wide concentration range. We believe that this correlation may serve as indicative of oxygen being present as a lattice impurity in diamond, though in some cases it is also hosted in microinclusions. Diamond single crystals showing strong infrared absorption due to CO_2 sometimes show oxygen distributed heterogeneously at the $<10~\mu$m scale. Annealing may convert IR-inactive O to CO_2-moieties. Apparently, the presence of O hinders IR-activity of N-related defects.

Our work also reports results of the investigation of CO_2-rich diamonds by x-ray topography and small-angle scattering. In line with earlier studies, we show moderate degrees of deformation where the deformed areas are distributed very irregularly. Heterogeneities with sizes ∼50 nm are abundant.

Acknowledgments

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