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Hydrogen impurity in natural gem diamond

P. R. W. HUDSON, I. S. T. TSONG*
Physics Department, Monash University, Clayton, Victoria, Australia

Five natural gem diamonds which included type I_A, I_B and II_A specimens, have been investigated by ion beam spectrochemical analysis (IBSCA) to determine the total hydrogen impurity concentration in the diamonds. These data were compared with that obtained from other "conventional" techniques such as infrared and ultraviolet absorption spectroscopy, electron spin resonance and transmission electron microscopy (TEM). IBSCA indicated that all the specimens appeared to contain ~ 1 at. % of hydrogen contrary to the infrared evidence. The highest hydrogen concentration was recorded by a type I_B specimen which contained small (~ 3 nm) bubbles. The hydrogen concentration did not correlate with any defect within the specimens, for example the {1 0 0} planar faults, and appeared to be a general impurity. No evidence was found to suggest that inclusions were responsible for the impurity.

1. Introduction

Hydrogen impurity is of relevance to the unsolved problem of {1 0 0} planar defects in type I_A diamond. It is possible that these defects or 'platelets' could contain hydrogen to a significant extent. Considerable evidence has been obtained since 1969 which indicates that nitrogen is not the majority constituent of the 'platelet' structure. The lack of correlation between the nitrogen concentration and the integrated platelet X-ray spike intensity [1, 2], coupled with the strong point defect phonon scattering mechanism which only exists in I_A diamond and which is approximately proportional to the nitrogen concentration [3], are the major pieces of evidence which do not favour a nitrogen platelet model. The first direct measurement of the platelet structure has been obtained recently [4], and the presence of hydrogen within the platelet is quite compatible with this evidence. The interested reader is referred to the review [5] for further information.

To the Geologist trying to specify the conditions of diamond genesis the presence of hydrogen and its compounds are important. Many analytical techniques such as X-ray fluorescence and electron probe microanalysis cannot detect hydrogen easily. Prior to this work only mass spectroscopical determinations have been reported in the case of diamond [6, 7], but neither of these reports quantify the hydrogen concentration.

Indirect evidence has been found by infrared absorption measurements. Chrenko *et al.* [8] investigated the spectrum of diamond coat, that material which is often found surrounding the core of diamond. Diamond coat is especially prevalent in Congo stones and is filled with sub-micron size particles [9]. Broad absorption bands were found at 3400 and 1640 cm^{-1} which were assigned to water of hydration. Sharp absorption features were also found at 3107 and 1405 cm^{-1} which were assigned to carbon–hydrogen vibrations. These well defined absorptions were also detected by Runciman and Carter [10] in gem quality I_A diamonds. These workers estimated the hydrogen concentration to be ~ 10^{19} atoms cm^{-3}, which was confirmed by vacuum fusion measurements. Seal [10] was reported to have found evidence of the C–H stretching vibration in 6 out of 182 diamonds. Sellschop [11] has found strong evidence using neutron activation analysis of submicroscopic inclusions containing the parental melt in which diamond is formed. Liquids rich in H_2O are expected to be present at diamond genesis as evidenced by the results of Melton and Giardini [7, 12, 13].

The ion beam spectrochemical analyser (IBSCA)

*Present address: Materials Research Laboratory, Pensylvania State University, University Park, Pa. 16802, U.S.A.

has been developed to perform rapid and accurate elemental analysis of solid surfaces. Qualitative and quantitative analyses of solids using this method have been described by Tsong and McLaren [14, 15] and a similar method has been used by White *et al.* [16, 17] for the same purpose. Tsong *et al.* [18] have shown that IBSCA provides a new method for the detection of hydrogen in a variety of silicate samples. The absolute concentration of hydrogen in synthetic quartz crystals determined by IBSCA appeared to be considerably higher than previous measurements by infrared absorption spectroscopy. IBSCA measures hydrogen with a similar efficiency, whatever its chemical bonding within the solid sample. Lateral and depth profiles can also be obtained, thereby eliminating the ambiguity of inclusion-derived signals which other bulk measurement techniques experience.

2. Experimental methods

Five natural African gem quality diamonds have been investigated. These consisted of three I_A specimens, one I_B specimen and one II_A specimen. Data from birefringence, infrared and ultraviolet spectroscopy, electron spin resonance (ESR) and transmission electron microscopy (TEM) experiments were taken to complement the IBSCA data.

2.1. Specimen preparation

The specimens were initially $8\,\text{mm}^3$ cubes with polished (1 0 0) or (1 1 0) surfaces. For the IBSCA measurements the specimens were initially cleaned with aqua regia and distilled water and then baked at 140° C for 24 h. The purpose of this preparation was to minimize impurity contamination and adsorption of moisture on the surface of the specimens. During the course of investigation thin slices were cut for TEM, so IBSCA measurements were also taken on the (1 0 0) faces of the remaining diamond. It is planned in the future to measure the hydrogen content of the $80\,\mu\text{m}$ slices prior to ion beam thinning for TEM observations. Optical measurements were taken on the diamond cubes, slices and remainders; ESR was carried out on the cubes only with the exception of an additional experiment on one particular slice (Specimen 2). In this way it was thought possible to overcome the problem of inhomogeneity in diamond samples and to be aware of the imperfections which were present in the surface under investigation.

2.2. Infrared and ultraviolet absorption spectroscopy

The infrared absorption spectrum of all specimens was measured in the frequency range 400 to 4000 cm^{-1} by a Perkin Elmer Model 180 Spectrometer. Absorption coefficents were calculated at the significant frequencies 3107 ($3.22\,\mu\text{m}$), 1370 ($7.3\,\mu\text{m}$) and $1280\,\text{cm}^{-1}$ ($7.8\,\mu\text{m}$). From this data the hydrogen concentration was estimated following Runciman and Carter [10], and the platelet area density [19] and the nitrogen concentration were found [6]. The ratio of A to B infrared spectra has also been determined using the method described by Davies and Summersgill [20]. Ultraviolet absorption spectra were taken in the wavelength range 200 to 320 nm using a Cary Model 17 Spectrophotometer. These data were used to aid classification of the specimens.

2.3. ESR and TEM measurements

ESR experiments were carried out on all specimens at room temperature using a Varian E-line spectrometer. Specimen 2 was responsible for a characteristic spectrum which has been attributed to singly substitutional nitrogen impurity [21]. None of the other specimens produced a significant response.

Two of the five diamonds specimens (2 and 5) were investigated by TEM. Details of this work are given elsewhere [19, 22]. Areas were selected by birefringence and cut from the diamond cube, ground and ion beam thinned to produce suitable specimens for high resolution work. IBSCA was completed on adjacent diamond material to that studied by TEM.

2.4. IBSCA

The IBSCA apparatus used for the detection of hydrogen in diamonds is shown in Fig. 1. Specpure grade argon gas was used to provide the bombarding ions. An intense, stable and nearly monoenergetic ion beam was produced by the duoplasmatron ion source operated at + 12 kV. The double Einzel lens system focussed the beam to a 2 mm diameter spot on the target surface producing an ion current density of about $10\,\mu\text{A}\,\text{mm}^{-2}$. With this beam current, the typical mass of diamond sputtered per minute is about $0.3\,\mu\text{g}$, corresponding to 2 ejected atoms per incident ion. The charge accumulation on the non-conducting surface was alleviated by inserting a metallic mask with a 2 mm diameter

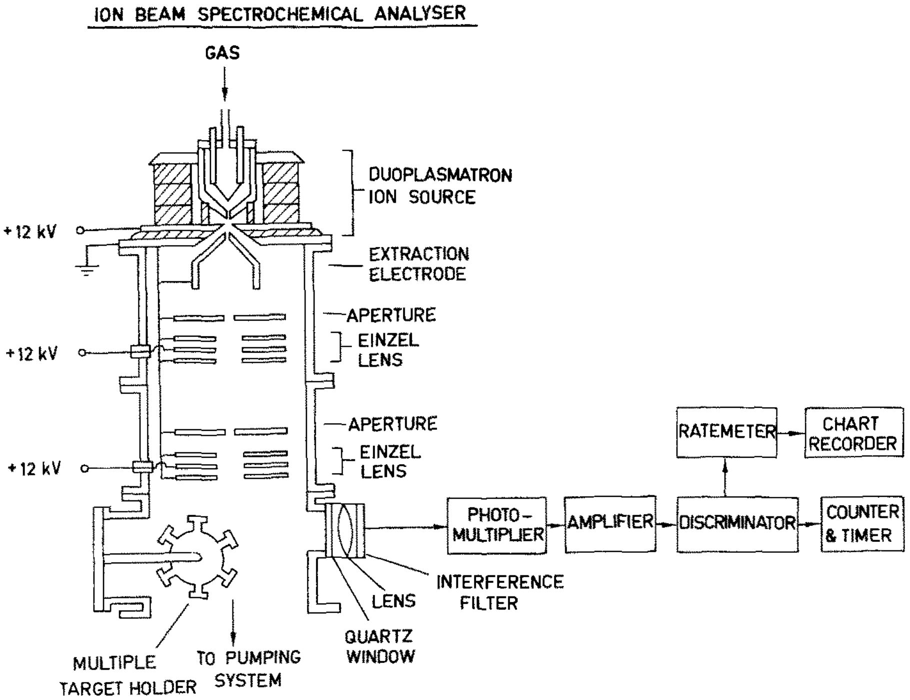

Figure 1 Ion beam spectrochemical analyser.

hole over the target surface. The mask under bombardment acted as a source of secondary elections which neutralised the charge on the surface of the target permitting sputtering to continue.

The multiple target holder can accommodate up to six samples. For the analysis of hydrogen, one target was usually an inert (i.e. hydrogen-free) sample such as copper or brass. Another target was the standard mica sample whose hydrogen (water) content was determined by differential thermal analysis/thermogravimetric analysis techniques.

For maximum sensitivity the light detection system utilized interference filters and photon counting. Two narrow band interference filters (HBW 10 Å) were used to isolate the hydrogen 6563 A line. It must be stated here that the typical signal-to-noise ratio encountered in this work was about 4 : 1, though sometimes as low as 2 : 1. When a monochromator was used, scanning through 6563 A did not indicate the presence of hydrogen in diamond at all. This line was observed, however, with high hydrogen (water) content materials such as opal and other silicate minerals. In view of this, interference filters were used in place of the monochromator as the wavelength selector to improve the sensitivity.

The hydrogen signal was monitored as a function of time as the diamond sample was sputtered. Since the sputtering rate of diamond was very slow, each sample was bombarded for at least 30 min, sometimes as long as 2 h. The mass loss was determined by weighing the sample before and after sputtering with an electronic microbalance (Mettler ME22) capable of measuring to 0.1 μg.

The hydrogen concentration was then determined by comparison with the standard mica sample using a method previously described by Tsong and McLaren [15], who showed that

$$I_{\mathrm{H}} \propto \Delta M W_{\mathrm{H}} \qquad (1)$$

where I_{H} is the relative intensity of the H-6563 line, ΔM is the rate of mass loss of the sample and W_{H} is the concentration of hydrogen by weight.

3. Results

3.1. Standard techniques

The relevant information obtained from all techniques with the exception of IBSCA is presented in Table I. Specimens 2 and 5 were thought to be particularly interesting and were therefore investigated by TEM. Specimen 2 possessed an extremely low birefringence typically that associated with $\mathrm{II_A}$ material. Small spherical defects of ~ 3 nm size were present with a concentration ~ 2×10^{21} m^{-3} [22]. The scattering factor for the defects was less than that of the diamond matrix.

TABLE I

	Diamond				
	2	3	5	7	11
Colour	amber	light amber	colourless	colourless	colourless
Hydrogen Concentration (from infrared)	ND*	ND	ND	1	ND
Nitrogen Concentration					
Total	1.2	8	23 (slice)	> 13	ND
A/B ratio	–	7.5	7	~ 3	–
Homogeneity	Good	–	poor	–	–
Single Substitutional	$\sim 10^{-2}$	ND	ND	ND	ND
U.V. absorption edge	Intermediate	Sharp Secondary	Intermediate	Sharp Secondary	Primary
Platelet area density	ND	4	300†	20	ND
Homogeneity	–	–	very poor	–	–
Classification	$\mathrm{I_B}$	$\mathrm{I_A}$	complex $\mathrm{I_A}$	$\mathrm{I_A}$	$\mathrm{II_A}$

Atomic concentrations are measured in units of $(10^{25}$ atoms$)\ \mathrm{m}^{-3}$. The platelet area density is measured in $(10^{23}\ \mathrm{nm}^2)\ \mathrm{m}^{-3}$.

* N.D. = Not Detected.

† Infrared correlation violated by giant platelets [19]. In this case the density was estimated from TEM.

The defects could be bubbles of gas or liquid, voids, amorphous material or low density crystalline material. It is quite possible that hydrogen and nitrogen were contained within the defects. The largest of the defects was ~8 nm in diameter and some of these appeared to be similar to the platelets which are found in type $\mathrm{I_A}$ diamond [22].

Specimen 5 was an inhomogeneous specimen which possessed considerable birefringence. Giant {1 0 0} platelets of up to ~ 5 μm in length existed in well defined growth layers in the diamond. Intermediate sized (~ 300 nm) platelets with ⟨1 1 0⟩ boundaries were found in other regions. No normal platelets were found while other parts of the crystal were definitely $\mathrm{II_A}$ material [19]. IBSCA measured the average hydrogen content over a surface which almost certainly contained all three regions so described.

3.2. IBSCA

Typical intensity–time graphs are presented in Fig. 2. The large initial signal was most likely due to the surface absorption of water and hydrogen which occurs not only in air but also in the vacuum chamber due to contamination from the pumps, outgassing from rubber seals and metal fittings etc. All the hydrogen signals, except for diamond No. 2, reached equilibrium values after a few minutes of sputtering which is consistent with the expected behaviour of removal of surface contaminants containing hydrogen.

The hydrogen concentrations are represented in Table II. Allowing for the uncertainties in the experiment one is justified to conclude that specimen 2 possessed most hydrogen; 7 and 11 have similar concentrations which are in excess of that in 3 and 5. All specimens appeared to possess ~ 1 at.% of hydrogen.

TABLE II Hydrogen content

Diamond	Type	Experiment (wt.%)				
		i	ii	iii	iv	v
No 2	Ib	0.28	0.31	0.17		
No 3	Ia				0.13	0.17
No 5	Ia	0.21			0.12	0.15
No 7	Ia	0.26	0.22	0.12		
No 11	IIa	0.25			0.14	

4. Discussion

The relatively high hydrogen concentration of diamond No. 2 is consistent with the suggestion that all small defects in that crystal are gas or liquid bubbles containing hydrogen and/or its compounds.

No correlation was found between infrared and IBSCA determinations of hydrogen concentration. IBSCA does not indicate in what form the impurity is present in the material. Consequently one would expect a higher concentration than that derived from infrared studies. Furthermore hydrogen was found in all diamonds which contained quite varied crystal imperfections, and this result does not favour (although it does not exclude) hydrogen as an important platelet consitutent. Rather, hydrogen would appear to be a general impurity of gem diamond. It is difficult to understand in this case

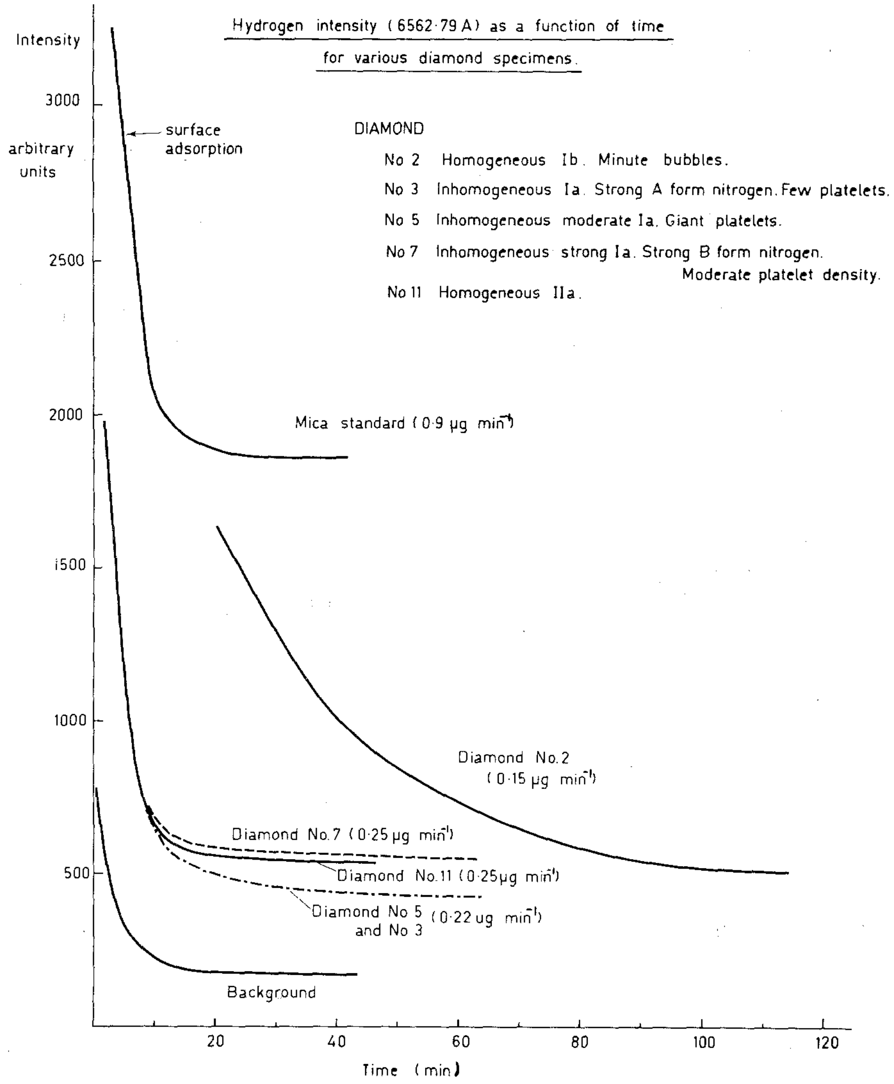

Figure 2 The intensity of the 6563 hydrogen line as a function of time of ion bombardment. The background signal is due to bombardment of a brass target.

why vacuum fusion and mass spectrometry have not detected such hydrogen impurity.

It is possible that the impurity was contained in inclusions. The samples were examined by optical microscopy (x 125) prior to analysis. Generally no inclusions were visible in the areas which were analysed. Sub-micron inclusions were not detected in the two samples investigated by TEM. Nevertheless a programme of low magnification TEM is planned in future to check more rigorously for sub-micron particles in the areas under investigation. The uniformity of the IBSCA signal with time does not encourage an explanation in terms of such inclusions. One is left with the most likely explanation that the hydrogen is in non-paramagnetic arrangements within the lattice and yet does not contribute significantly to characteristic C–H vibrations.

Such a large concentration of hydrogen in the lattice would be expected to influence the physical properties of diamond. Although the thermal conductivity of these specimens has not been measured, the results are sufficiently uniform with regard to diamond classification that a comparison may be made with diamonds for which the conductivity has been determined [3]. The various phonon scattering mechanisms responsible for the conductivity of diamond have been determined and explained exactly by inherent processes plus nitrogen cluster and planar defect scattering centres. I_B diamond is the only type for which some ambiguity exists in the explanation of the thermal conductivity [22]. A concentration of ~ 1 at.% of hydrogen is inconsistent with the phonon scattering strength if the hydrogen is assumed to be present as a "point defect", unless the vibrational frequencies of this point defect are truly localized modes lying outside the normal diamond phonon spectrum. If this were the case one might expect to observe infrared evidence somewhere above $1400\,cm^{-1}$. Considerable absorption does exist in the region $1400 < \nu < 4000\,cm^{-1}$ but it has been explained reasonably well by two phonon absorption processes in the diamond lattice [23]. These absorption bands also have the same strength in all specimens [24, 25]. Alternatively, if the hydrogen is assumed to be present in large possible gaseous or liquid clusters (~ nm size) no explanation can be provided to interpret the thermal conductivity and futhermore such defects have not generally been found by TEM.

The presence of such a large hydrogen concentration is sufficiently unattractive (with the exception of specimen 2) to look for other possibilities to explain the data. Firstly could the signal be due to contamination of the diamond surface by hydrocarbons because of a poor vacuum? The specimen chamber was evacuated to 1×10^{-7} torr using an oil diffusion pump and sentovac pump oil was used to minimize the amount of hydrocarbon backstreaming. When the ion beam was in operation, the partial pressure of argon was 1×10^{-5} torr. At this pressure gas molecules would collide with a surface at a rate that would deposit roughly one atomic monolayer (~ 10^{15} atoms cm^{-2}) per second assuming a realistic sticking probability. The ion beam current density was $1\,mA\,cm^{-2}$ or 1.6×10^{16} ions $cm^{-2}\,s^{-1}$. Since the sputtering yield of diamond is approximately 2 atoms per ion, there were always more atoms ejected from the surface than impurity atoms adsorbed. It appears unlikely, therefore, that the H-signal observed would be entirely due to adsorbed hydrogen or hydrocarbon impurities on the surface. Some degree of surface adsorption must be taking place, however, because of the way the H-signals decay to equilibrium values. Such decay behaviour was not observed when analysing for other elements in other materials [15].

Another possibility is that the emission or excitation efficiency (defined as the number of photons emitted per sputtered atom) for sputtered hydrogen atoms from diamond might be considerably higher (~ a factor 100) than for hydrogen in various silicates. It has been found for a system of silicates that the excitation efficiency is a characteristic only of a particular element and is independent of its environment inside the solid [18]. Because of this it is not suspected that hydrogen in diamond would be widely different from hydrogen in silicates. If this is not the case, it does mean that IBSCA possesses an extremely high sensitivity for hydrogen in diamond.

Alternatively the photon emission may derive from broad-band emission or luminescence in the solid surface or in the amorphous carbon layer which appears to coat the diamond once sputtering has progressed. Although broad-band emission, thought to be due to excited clusters, has been observed for a number of metals under ion bombardment [26–29], none has been reported for the case of insulators. Cathodoluminescence studies of diamond have recently become popular means of studying defects [30–32]. One centre has been found at 640 nm by photoluminescence. The emission spectra of this centre, thought to be due to a radiation damage centre trapped at a single nitrogen atom, certainly encompasses the hydrogen line frequency. However this centre is only produced by strong electron irradiation of I_B diamond Specimen 2 is the only I_B diamond out of the five measure. The necessity of electron irradiation of the diamond does not favour this explanation. The 12 KeV Ar^+ ion beam was not energetic enough to cause defects such as colour centres in the diamond samples. Such luminescence effects in ionic crystals are caused by MeV particle irradiation. Nevertheless although no luminescence has been observed by such low energy ion bombardment, the possibility of a luminescence centre in the solid or amorphous surface cannot be ignored. Unfortunately it has not proved possible (in this investigation) to achieve a significant signal–noise ratio with the use of a monochromator rather than filters. Thus the photon intensity cannot be measured as a function of wavelength which would distinguish between a discrete hydrogen line and broad band luminescence emission.

5. Conclusion

Various techniques have been used to discover and numerate the defect structures in a range of natural gem diamonds. The data so obtained have been compared with the determination of the hydrogen impurity concentration as measured by ion beam spectrochemical analysis (IBSCA). One at.% appeared to be a typical hydrogen concentration. The IBSCA-determined hdyrogen concentration conflicts with that derived from infrared absorption spectroscopy. A type I_B specimen which contained small ($\sim$3 nm) bubbles, possessed the highest density of hydrogen. These results in general do not favour the concept of hydrogen as an important platelet constituent although they certainly do not exclude this possibility. They are also difficult to accept in the light of thermal conductivity studies of diamond. It is not impossible that the IBSCA signal could be the result of an anomalously high excitation efficiency and/or luminescence centres.

6. Note added in proof

Further experiments have shown a clear hydrogen line and luminescence can now be eliminated as a possible source of 6563 Å radiation. However, recent infrared absorption, chemical analysis and nuclear reaction determinations of the hydrogen content of quartzs indicate that IBSCA is correctly determining the hydrogen content in the surface layers ($\sim$200 nm), but this concentration may be as much as thirty times higher than the average concentration in the bulk.

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