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Attenuated total reflection Fourier transform infrared spectra of faceted diamonds

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Abstract

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy has been employed for characterization of faceted diamonds. ATR spectra of round brilliant cut natural diamonds of ~ 0.1 ct were observed with excellent spectral quality. The mirror-flat spectrum of the table facet enables a good contact to the ATR crystal with a minimal applied pressure. The observed ATR spectra agreed very well with the diffuse reflectance and transflectance spectra. The detailed spectral information in the one-phonon region of diamonds with high nitrogen impurities can be clearly observed in the ATR spectra but those in the diffuse reflectance and transflectance spectra were obscured by the saturated absorption. The strong evanescent field under the ATR condition enables spectral acquisition of a thin film on the mirror-flat surface of the faceted diamonds. The spectral signatures of this thin film were not observable in the diffuse reflectance or the transflectance spectra. © 2006 Elsevier B.V. All rights reserved.

Keywords: Faceted diamond; Diamond; Infrared spectroscopy; ATR FT-IR spectroscopy; Diffuse reflectance; Transflectance; Evanescent field

1. Introduction

Diamond has long been the prime interest in gem and jewelry markets due to its popularity, mystic believes, and commercial values. The gem quality diamonds are the most profitable part of the diamond market [1-3]. Diamonds of low quality were generally treated in order to enhance the optical properties (i.e., color and clarity) or to eliminate inclusions. The treatment techniques include irradiation, thermal, and high temperature-high pressure treatments. The treated diamonds are difficult to detect or to exclude from the un-treated diamonds by the conventional characterization techniques (i.e., refractive index, hardness, color, specific gravity, and light dispersion measurements). Nowadays, gemologists depend strongly on advance characterization techniques that provide chemical structure, composition, and/or detailed treatment information for the diamond grading [1]. Due to its high commercial value, characterization of faceted diamond or diamond on jewelry body is limited to non-destructive techniques, preferably those without additional

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sample preparation, such as Fourier transform infrared (FT-IR) spectroscopy [4–8], Raman spectroscopy [9] electron spin resonance (ESR) spectroscopy [10,11], and photoluminescence spectroscopy [12–14].

In general, natural diamond is classified into four main classes according to amount of nitrogen impurity: the most abundant type Ia with the nitrogen content up to 5000 ppm, type Ib with the nitrogen impurity up to 500 ppm, the very rare type IIa with less than 5 ppm of nitrogen impurity and the extremely rare type IIb without the nitrogen impurity [15]. FT-IR spectroscopy is well known for its unique spectral information directly related to chemical compositions and structures. Impurities (i.e., nitrogen, hydrogen, and boron), lattice defects, and growth structures as well as the treatment processes applied onto the diamond can be identified from the observed FT-IR spectrum [4–8]. Generally, classical transmission technique was employed of spectral acquisition of diamond [5]. To classify a diamond based on the impurities and defects, a fraction of a rough diamond is priorly acquired for infrared analysis. The fraction is polished into a thin slab for the transmission measurement. However, the destructive nature of the sample preparation makes this approach not suitable for commercially faceted diamonds where the leftover fraction from the cutting process is not readily available.

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Recently, the diffuse reflectance and transflectance techniques were successfully employed for infrared spectral acquisition of the faceted diamonds [4,7,8,16]. Although spectra of superb quality suitable for characterization purpose were obtained, several limitations were encountered. The diffuse reflectance spectrum depends strongly on diamond orientation and is not generally reproducible [4,8]. Moreover, the technique is not applicable for mounted diamonds on a jewelry body. The diamonds must be demounted before an analysis. The transflectance spectrum acquired by an infrared microscope is reproducible while the technique is applicable for mounted diamonds [7,8]. However, the transflectance technique cannot be employed for a spectral acquisition of a very large diamonds (i.e., a 5 ct round brilliant cut diamond or bigger).

The attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy is one of a powerful characterization technique using infrared radiation. The obtained molecular information from an ATR spectrum is associated with the physicochemical phenomena at the surface. The ability to provide surface-related information of the ATR FT-IR technique is derived from the unique decay characteristic of the evanescent electromagnetic field generated under the total internal reflection (TIR) phenomenon. The evanescent field is strongest at the internal reflection element (IRE)/sample interface while exponentially decays as a function of the distance from the interface. Due to the fast decay of the evanescent field, the material must be brought into an optical contact with the IRE in order to exploit the strong evanescent field. An air gap between the IRE and a rigid solid sample can deteriorate the spectral quality. If the air gap is thick enough (i.e., at least three times the penetration depth), an ATR FT-IR spectrum cannot be observed as the evanescent field decays to an insignificant level within the air gap [17]. The purpose of this paper is to demonstrate that ATR FT-IR spectroscopy can be employed for spectral acquisition of a faceted diamond. Although diamond is the hardest material known to man, the mirror-flat surface of the faceted diamond favors an ATR spectral acquisition. The observed ATR spectrum will be compared with the corresponding diffuse reflectance and transflectance spectra. Applicability of the technique providing the unique spectral features associated with chemical compositions and impurities of diamond will be discussed.

2. Theory

ATR FT-IR spectroscopy is a highly sensitive surface characterization technique where its unique capabilities are derived from the rapid decay of the evanescent field generated under the TIR phenomenon. As an electromagnetic radiation traveling within an IRE made of a high refractive index material impinges the surface of a material of lower refractive index (i.e., the sample being analyzed) at an angle of incidence greater than the critical angle, a strong electromagnetic filed, so-called the evanescent field, is generated at the IRE/sample interface. The evanescent filed is strongest at the interface while decays exponentially as a function of the distance from the interface. If the sample is absorbing at the coupled frequency, the intensity of the reflected radiation is attenuated and becomes smaller than that of the incident radiation. The magnitude of the reflection loss or the sample absorption is proportional to the integration of the product between the evanescent field amplitude and the imaginary part of the complex dielectric constant of the absorbing material. The absorption A(v) in *absorbance unit* can be expressed in terms of the experimental conditions and material characteristics as [17,18]:

$$A(\theta, \nu) = \frac{(2\pi\nu)^2}{\ln(10)k_{z,\text{IRE}}(\theta, \nu)} \int_0^\infty \text{Im}[\hat{\varepsilon}_{\text{sample}}(\nu)] \langle E_z^2(\theta, \nu) \rangle \, dz$$
(1)

where θ is the angle of incidence, ν is the frequency of the incident radiation, $\hat{\varepsilon}_{sample}(\nu)$ is the complex dielectric constant of the sample, $\langle E_z^2(\theta, \nu) \rangle$ is the mean square evanescent field (MSEvF) at depth *z* from the IRE/sample interface, and $k_{z,IRE}(\theta, \nu)$ is the *z*-component of the wavevector within the IRE. The *z*-wavevector can be expressed in terms of the *x*-wavevector $k_{x,IRE}(\theta, \nu)$ by $k_{z,IRE}(\theta, \nu) = [(2\pi\nu)^2 \varepsilon_{IRE} - k_{x,IRE}(\theta, \nu)]^{1/2}$; $k_{x,IRE}(\theta, \nu) = (2\pi\nu)^2 [\varepsilon_{IRE} \sin^2 \theta]$ and ε_{IRE} is the dielectric constant of the IRE. The detailed calculations of the MSEvF are given elsewhere [19,20].

According to Eq. (1), the rapid decay of the evanescent field makes an ATR spectrum very sensitive to physicochemical phenomena at the surface of the sample. However, if the sample being analyzed is homogenous and isotropic, the observed ATR spectrum becomes that of the bulk. Although the ability to provide the molecular information at the surface and interface is the unique advantage of ATR spectroscopy, the rapid decay of the evanescent field also imposes restriction on the application of the technique. In order to obtain a good quality ATR spectrum by effectively exploiting the strong evanescent field, the sample must be optically contact to the IRE. As a result, under the normal operation, ATR FT-IR spectroscopy is suitable for liquids and soft solids where a good contact can be easily achieved. ATR spectrum of a hard and rigid solid sample is not normally obtained unless an excessive force is applied in order to improve the contact. Although diamond is the hardest material, the physical configuration of the faceted diamond favors ATR spectral acquisition. An extremely small air gap or a perfect contact between the IRE and the table facet of a diamond can easily be achieved since the table facet is mirror flat and small. A minute pressure may be applied onto the diamond against the IRE in order to ensure a good contact.

3. Experimental

The measured samples were round-brilliant-cut natural diamonds with ~ 0.1 ct weight with the table size of ~ 3 mm. The diamonds were analyzed as received without an additional sample preparation except cleaning by water and organic solvents. Three types of spectral acquisition techniques were employed; diffuse reflectance, transflectance, and ATR. All spectra were collected by a Nicolet Magna 750 FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Spectra in the mid-infrared region $(4000-650 \text{ cm}^{-1})$ were collected with 512 co-addition scans at a spectral resolution of 4 cm^{-1} .

A commercial diffuse reflectance accessory (the Collector, Spectra-Tech Inc., USA) was employed for all diffuse reflectance spectral collections. To acquire a diffuse reflectance spectrum, a faceted diamond was placed on the sample holder with the table facet faced down. The infrared radiation was coupled onto the diamond at a near normal incidence. The spectrum was collected from the diffuse reflectance infrared radiation while the spectral intensity was expressed in the Kubelka-Munk unit. Since the observed diffuse reflectance spectra were greatly influenced by the diamond arrangement on the sample holder [4,8], several spectra with different arrangements were collected. The measured spectrum with the best signal-to-noise ratio was employed for further analysis.

The transflectance spectra of the same diamonds were collected by a Nicolet NicPlan infrared microscope attached to the FT-IR spectrometer. The infrared microscope is also equipped with a liquid-nitrogen-cooled MCT detector. A homemade accessory was employed for all spectral acquisitions using the microscope. The diamond was positioned on the sample holder with the table facet faced up. The infrared radiation is coupled into the diamond through the table facet by the built-in $15 \times$ Cassegrain-type infrared objective while the transflected radiation from the pavilion facet was collected by the same objective [7,8]. The observed spectrum was expressed in the absorbance unit.

A commercial ATR accessory (the SeagullTM, Harrick Scientific, USA) was employed of all ATR spectral acquisition. A faceted diamond was placed on a modified sample holder with the table facet faced up, see Fig. 1. The diamond was carefully elevated until the table facet touched the germanium (Ge) IRE. With a small applied pressure, the modified sample holder adjusts the degree of parallelism between the table facet and the IRE regardless of their initial alignments. A great care had been



Fig. 1. A schematic illustration of the experimental setup for ATR spectral acquisition of a round brilliant cut diamond.

taken since the diamond may damage the surface of the IRE. Since the angle of incidence for an ATR spectral acquisition must be greater than the critical angle, the infrared radiation was coupled through the Ge IRE at the angle of 45° (i.e., the critical angle at Ge/diamond interface equals 37.17°).

For ATR spectral acquisition, all the diamonds were analyzed before and after the cleaning procedure. To remove a substance on the diamond surface, the diamond was thoroughly cleaned several times with organic solvents (i.e., acetone, isopropanal, and toluene) with ultrasonic agitation. Further removal of residual contaminant was performed by boiling in a hot alkali solution (saturated NaOH solution), then thoroughly rinsed with water and blown dry with nitrogen gas.

4. Results and discussion

To verify that the ATR technique can be utilized for diamond characterization, a natural diamond type IaB (0.1005 ct) with a low nitrogen impurity was employed. Diffuse reflectance, transflectance and ATR spectra of the diamond are shown in Fig. 2. The diffuse reflectance and transflectance spectra in Fig. 2A and B clearly show the three principle absorption bands of dia-



Fig. 2. FT-IR spectra of a 0.1005 ct round brilliant cut natural diamond type IaB acquired by (A) diffuse reflectance, (B) transflectance, (C) ATR (before cleaning), and (D) ATR (after cleaning) with alkali solution.

mond (i.e., the three-phonon absorption at $3900-2650 \,\mathrm{cm}^{-1}$, the two-phonon absorption at $2650-1500 \,\mathrm{cm}^{-1}$, and the onephonon absorption at $1400-900 \text{ cm}^{-1}$). The high noise level and the absorption magnitude at the peak maxima of the twophonon indicates saturated absorption. The absorption bands associated with hydrogen and nitrogen impurity in diamond crystal structure are clearly observed. The spectral envelop in the one-phonon region does show unique characteristic of the type IaB natural diamond. The type IaB diamond is associated with a B-center defect (an aggregate consists of four nitrogen atoms surrounding a vacancy), which shows absorption at 1330, 1172 and 1013 cm^{-1} [5,6]. The absorption band at 1360 cm^{-1} assigned to the extended-planar-defect platelet is quite distinct in the observed spectra (Fig. 2A and B). The absorption at $3107 \,\mathrm{cm}^{-1}$ is assigned to the C-H stretching of the vinylidene group. The absorption at 1405 cm^{-1} attributed to the C-H bending is observed as the concentration of the hydrogen impurity is very high. Although the spectral envelop of the diffuse reflectance spectrum was the same as that of the transflectance spectrum, the transflectance spectrum seems to possess a superior spectral quality as the absorptions in all three principle regions are more prominent. It should be noted that the absorp-

the fluctuation of the ambient air during the spectral acquisition. Unlike the diffuse reflectance and transflectance spectra, the ATR spectrum of the same diamond in Fig. 2C revealed entirely different spectral features. The three main characteristic bands of the diamond were not obvious in the observed ATR spectrum before cleaning. The unique spectral envelope of diamond in the one-phonon region was totally obscured by anomalous absorptions of foreign materials. Although the spectrum of the diamond was collected under the ATR condition, the weak absorption associated with the hydrogen impurity at 3107 cm^{-1} was clearly observed. After the diamond was thoroughly cleaned several times with organic solvents, the unique characteristic of the aliphatic hydrocarbon at $3000-2900 \text{ cm}^{-1}$ was still prominent in the observed ATR spectrum. A characteristic absorption of the free hydroxyl group at 3678 cm^{-1} can also be clearly noticed. The strongest absorption of the foreign materials at 1048 cm^{-1} was still persisted and did not decrease after repeated cleaning.

tions of water vapor (3900–3500 and $1800-1400 \, \text{cm}^{-1}$) and

carbon dioxide gas $(2350\,\text{cm}^{-1})$ can be noticed in all measured

spectra. The variations of the absorption magnitudes are due to

ATR spectra of the alkali-cleaned diamond was shown in Fig. 2D. The unique spectral features of diamond in the oneand two-phonon region can be noticed. Due to the weak absorption, the spectral feature in the two-phonon region was quite different from those in the diffuse reflectance and transflectance spectra. However, it did reveal the unique shape of the twophonon absorption. Although the three-phonon absorption of the diamond was obscured by the broad absorption of the hydrogenbonded hydroxyl group, the hydrogen-related absorptions at 3107 and 1405 cm⁻¹ were clearly observed. The absorption of the free hydroxyl group at 3678 cm⁻¹ was not observed in the ATR spectra of the alkali-cleaned diamond but the strong absorption band of molecular water at 3600–3300 cm⁻¹ was prominent. Although the unique absorption of the type IaB diamond at 1330 cm⁻¹ can be clearly observed in the ATR spectra Fig. 3. FT-IR spectra of a 0.1075 ct round brilliant cut natural diamond type IaA acquired by (A) diffuse reflectance, (B) transflectance, (C) ATR (before cleaning), and (D) ATR (after cleaning) with alkali solution.

of the cleaned diamond, the absorption in the low wavenumber region of the one-phonon region was still obscured by the absorption of the foreign materials. In comparison to the ATR spectrum in Fig. 2C, the relative absorption intensity at 1048 cm^{-1} in Fig. 2D is drastically decreased. However, the strong absorption at $1170 \,\mathrm{cm}^{-1}$ of the foreign materials still interfered with the one-phonon absorption. Although the one-phonon absorption at 1172 cm^{-1} was obscured, the nitrogen-related absorption at 1360, 1330, and 1280 cm⁻¹ were clearly distinct. Due to the rapid decay of the evanescent electromagnetic field under the ATR condition, diamond must be brought into contact or very close to the IRE in order to obtain a good quality spectrum. Since the penetration depth at $3107 \,\mathrm{cm}^{-1}$ is very small under the employed condition (i.e., 0.193 µm for Ge/air and 0.348 µm for Ge/diamond interface), the clearly distinct absorption at 3107 cm⁻¹ in Fig. 2C and D suggested that the table facet of diamond had a good contact with the IRE. The strong absorption at $3107 \,\mathrm{cm}^{-1}$ of the cleaned diamond suggests that a better contact between the diamond and the IRE was obtained after the alkali cleaning.

Fig. 3 shows spectra of a natural diamond type IaA (0.1075 ct). Due to the relatively high nitrogen impurity and



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different types of defects in the crystal lattice, spectral feature of the type IaA diamond is distinctively difference from that of the type IaB diamond. The type IaA diamond is associated with the A-center defect (i.e., a defect consists of a pair of adjacent nitrogen atoms in the diamond lattice). The diamond has absorption bands in the one-phonon region with a strong absorption at 1282 cm^{-1} and additional weak absorption at 1362, 1208, and 1011 cm^{-1} [4,21]. Similar to those observed in the type IaB dia-

1011 cm⁻¹ [4,21]. Similar to those observed in the type IaB diamond, the ATR spectra in Fig. 3C of the type IaA diamond before cleaning is dominated by the same foreign materials. The free hydroxyl absorption at 3768 cm^{-1} was disappeared after cleaning. After boiling in the hot alkali solution, ATR spectrum in Fig. 3D did reveal the unique characteristic of the type IaA natural diamond. However, the fraction at the lower wavenumber region of the one-phonon absorption was still obscured by the absorption of un-removed foreign materials.

Fig. 4 shows spectra of a natural diamond (0.1105 ct) with an extremely high nitrogen impurity. Due to the saturated absorption in the one-phonon region when measured by the diffuse reflectance and the transflectance techniques (Fig. 4A and B), classification of the diamond cannot be performed. The diamond might be mistakenly classified as type IaA based on the diffuse reflectance and/or the transflectance spectra. Although the one-phonon absorption in the ATR spectra of the un-cleaned and alkali-cleaned diamond (Fig. 4C and D) was partially obscured by the absorption of the same foreign material as that in Figs. 2 and 4, the ATR spectra did reveal the unique absorption signature at 1330 cm^{-1} of the B-center defect (Fig. 4D). Due to the extremely high nitrogen impurity and the presence of the B-center defect, the diamond is classified as type IaAB. The problem associated with the over absorption will be more pronounced for a larger diamond with a greater nitrogen impurity. Similar to those in Figs. 2 and 3, ATR spectra of the diamonds were obscured by the same foreign material. In comparison to that observed in Fig. 2D, the C-H stretching absorption of hydrogen impurity was absent in the ATR spectra of alkali-cleaned diamond in Fig. 4D. This phenomenon suggested that a good contact between the diamond and the IRE was not as good as that in Fig. 2D. As a result, the evanescent field in that region within the diamond is too weak to produce an absorption with a magnitude greater than the noise level.



Fig. 4. FT-IR spectra of a 0.1105 ct round brilliant cut natural diamond type IaAB acquired by (A) diffuse reflectance, (B) transflectance, (C) ATR (before cleaning), and (D) ATR (after cleaning) with alkali solution.

To identify the foreign material covering the surface of the diamond, the table facet of the diamond in Fig. 2 (i.e. before and after cleaning) was scanned by an energy dispersive X-ray fluorescence (EDX) spectrometer. The results were shown in Fig. 5. The observed EDX spectra showed characteristic peaks of carbon, oxygen and aluminum. The relative intensity of the alu-



Fig. 5. EDX spectra of the table facet of the 0.1005 ct diamond shown in Fig. 2: (A) before cleaning and (B) after cleaning with alkali solution.

minum was drastically decreased after the cleaning. The results implied that the strong absorption band at the 1048 cm^{-1} and weak associated bands at $870-810 \text{ cm}^{-1}$ in the ATR spectrum (Fig. 2C) were due to aluminum compound, possibly aluminum oxide film. The absorption band at 3678 cm^{-1} can be assigned to isolated hydroxyl group on the alumina surface (Al–OH). The board band at $3600-3300 \text{ cm}^{-1}$ in Fig. 2D is the stretching vibration of water involving in hydrogen bonding with oxyhydroxide group on the alumina surface [22–24].

Although the diamonds were obtained from different providers and were measured at different time, ATR spectra of the un-cleaned diamonds in Figs. 2C, 3C, and 4C showed prominent spectral features of aluminum oxide. The deposition of the aluminum oxide on the faceted surfaces of the diamond may initiated by the cutting and polishing processes. The faceting process could create a local hot zone at the surface of the diamond. The localized thermal build-up may induce the deposition of aluminum compound on the surface of diamond since alumina (aluminum oxide, Al_2O_3) is a common composition in the cut and polishing powder. The thermal build-up also initiated deposition of organic compound onto the surfaces of diamond and alumina thin film since paraffin wax is also a common composition in the diamond polishing material. The C-H stretching absorption in the ATR spectra confirms the existing of aliphatic hydrocarbon on the diamond surface. The board absorption band at 1735 cm^{-1} can be assigned to the stretching vibration of the carbonyl (C=O) group while that at 1660 cm^{-1} is due to the hydrogen-bonded COOH and COO⁻ group which adsorbed on the alumina surface [22]. The concentration of the oxyhydroxide surface group on the surface of diamond increased significantly by the alkali cleaning process [22]. As a result, the board OH-stretching band can be observed while the isolated OH-stretching vibration disappeared after the cleaning.

The shown results indicated that an infrared spectrum of a faceted diamond can be acquired by the ATR technique. Although the spectral envelop of the ATR spectrum is significantly different from those of the diffuse reflectance and the transflectance spectra due to the interference of foreign materials on the faceted surface (in this case, alumina), unique spectral features of the diamond were clearly revealed. Thus, the ATR technique can be employed for the classification of faceted diamond. Although the diamonds were cleaned by the hot-alkali solution, some of the alumina film was still un-removed. Only after cleaning, the unique spectral signature of diamonds can be observed. Since the spectral signatures of organic materials and that of the alumina were not observed in the diffuse reflectance and transflectance spectra, the thickness of the foreign material covering the diamond surface must be a very thin.

Although the current operation was applied to the faceted diamonds, the technique can also be applied to any other faceted gemstones with mirror-flat surface. The reflection-based ATR FT-IR spectroscopy can be applied to large, small, opaque, transparent, colored, and highly fractured gemstones with a mirrorflat surface. Since the infrared spectrum is directly correlated to structure and composition of the analyzed material, it can be employed for gemstone identification, classification and/or determination of treatments. The technique will also be very useful for the characterization of gemstones on a jewelry body since the operation can be perform without taking the stone from the jewelry setting (i.e., if the table facet is not obstructed by the jewelry setting).

5. Conclusions

The single-reflection ATR FT-IR technique was successfully employed for spectral acquisition of faceted diamonds. For a diamond with low nitrogen impurity, the observed ATR spectrum agreed with the well-accepted diffuse reflectance spectrum. The detailed absorptions in the one-phonon region of a diamond with high nitrogen impurity can be obtained from the ATR spectrum while those in the diffuse reflectance spectrum and the transflectance spectrum were obscured by the saturated absorption. A minute pressure is required in order to ensure a sufficient contact between the faceted surface of the diamond and the IRE. An air gap or a thin film of foreign materials on the diamond surface prohibits acquisition of good quality spectra. The material must be removed prior to the spectral acquisition with the maximum exploitation of the evanescent field.

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