Transflectance Spectra of Faceted Diamonds Acquired by Infrared Microscopy

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A novel transflectance technique using an infrared microscope was employed for spectral acquisition of loose and mounted faceted diamonds. The observed transflectance spectrum shows the same spectral features as those of the well-accepted diffuse reflectance spectrum. Unlike the diffuse reflectance spectrum, the transflectance spectrum was not affected by the diamond arrangements. The technique can be employed for direct spectra acquisition of mounted diamonds without taking the diamonds out of the jewelry bodies. Moreover, an individual diamond on a complex jewelry setting can be selectively measured. Infrared absorption bands unique to the chemical compositions, impurities, and treatment processes of the diamonds are discussed. The observed transflectance spectra can be exploited for diamond classification.

Index Headings: Faceted diamonds; Infrared spectrum; Transflectance; Diffuse reflectance.

INTRODUCTION

Diamond has long been the prime interest of gem and jewelry markets due to its popularity, mystic beliefs surrounding it, and commercial value. Due to its high commercial value, various types of diamond simulants have been produced. Since diamond simulants do not share the same chemical composition as natural diamond, they can be easily distinguished by appearance and/or physical properties. Diamonds are also synthesized by high temperature, high pressure, and chemical vapor deposition processes. Due to the small size of synthetic diamonds, their major utilization is in industrial applications. Recently, large gem-quality synthetic diamonds have also become available in the jewelry market. Beside the synthetics and simulants, various types of treatments (i.e., irradiation, heat, and high pressure-high temperature (HPHT) treatments) are applied to the low-quality diamonds in order to improve their appearance (i.e., inclusion elimination, color enhancement, and clarity improvement). Because they possess the same chemical structure and composition the synthetic or treated diamonds cannot be differentiated from natural gemstones by conventional characterization techniques (i.e., refractive index, hardness, color, specific gravity, and light dispersion measurements).¹⁻⁴ The enhanced or treated diamonds are more difficult to detect or to exclude from their natural untreated counterparts. Due to the large price difference between the synthetic or treated diamonds and natural untreated diamonds, it is important for gemologists to correctly identify the diamonds. As a result, gemologists and jewelry traders are increasingly dependent on chemical-based analytical techniques to defend the integrity of their trade against aggressive tampering.¹

Modern technology is increasing its impact on diamond trading. Methods for changing the color, and consequently the value, of diamonds are becoming more and more advanced and complicated. The treatment processes are difficult to detect via conventional gemological characterization techniques. Detection of treatment processes becomes a major task for diamond grading laboratories, especially those of the faceted diamonds and diamonds on jewelry bodies where nondestructive and/or noninvasive characterization is required. Irradiation and HPHT treatments improve clarity and color of low-quality diamonds by altering defects in the diamond crystal lattice. Advanced analytical techniques such as Fourier transform infrared (FT-IR) spectroscopy,⁵⁻⁸ Raman spectroscopy,⁹ electron spin resonance (ESR) spectroscopy,^{10,11} and photoluminescence spectroscopy^{8,12–14} are employed for diamond characterization. Raman spectroscopy has been employed to identify inclusions within diamond and to separate naturals from simulants,9 and ESR spectroscopy has been employed for detecting the Ni-related centers (i.e., nickel-nitrogen complex) in diamonds, especially those synthesized by the high pressure-high temperature process.¹⁰ Photoluminescence is used to differentiate natural and synthetic diamonds and to detect certain color centers.8,12,13

Fourier transform infrared spectroscopy is well known for obtaining spectral information unique to molecular structure and chemical composition. The technique is widely employed for diamond classification based on impurities (i.e., nitrogen, hydrogen, and boron) in the crystal lattice.^{5,7} Spectral information associated with lattice defects (i.e., changes or transitions of defect centers) and growth structures are determined and employed for differentiating natural, synthetic, and treated diamonds. Different treatment processes can also be identified by FT-IR spectroscopy.^{13,14}

For classical diamond characterization using the transmission technique, a thin slab of diamond is required.⁷ Since the technique is destructive, it is not suitable for faceted diamonds of high commercial value. Transmission measurement of a faceted diamond using a beam condenser is complicated by the sample arrangement and the complex reflections at the cut and polished surfaces.^{17,18} Diffuse reflectance measurements of a faceted diamond, on the other hand, tend to be non-reproducible since the observed spectral intensity depends strongly on the diamond arrangement on the sample holder.^{5,19} Moreover, both transmission and diffuse reflectance techniques are not applicable for mounted diamonds on jewelry bodies.

In order to solve the problems associated with characterization of faceted diamonds and diamonds on jew-

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FIG. 1. (A) A schematic drawing of a round brilliant cut diamond. (B) Ray tracing of different radiations inside a round brilliant cut diamond. A summary of angles at the diamond/air interface is shown.

elry, a novel transflectance technique using infrared microscopy is introduced. The technique is applicable for both loose and mounted diamonds. The observed transflectance spectrum will be compared with the corresponding diffuse reflectance spectrum. The unique spectral features associated with chemical compositions, impurities, and treatment processes will also be discussed.

THEORY

A modern brilliant cut diamond consists of 57 + 1facets depending on the presence of the culet (see Fig. 1). Since the refractive index of diamond $(n_{\text{diamond}} =$ 2.417) is greater than that of air $(n_{air} = 1.0)$, total internal reflection at the diamond/air interface is observed when radiation traveling inside the diamond impinges on the interface with an angle greater than the critical angle. The critical angle, $\theta_{\rm C}$, is given in terms of the refractive indices by $\theta_{\rm C} = \sin^{-1}(n_{\rm air}/n_{\rm diamond})$ and is equal 24.44° for the diamond/air interface. In principle, a faceted diamond is cut in such a proportion that the total internal reflection within the diamond is enhanced. To increase the number of total internal reflections, the cutting proportion of the diamond is carefully designed with respect to refractive index, size, shape, and carat weight. The number of total internal reflections depends on the angle and positions at which light enters the diamond. The greater the number of reflections within the diamond, the better the *fire* and brilliance of the faceted diamond.^{20,21}

In order to collect transflectance spectra of a faceted diamond using an infrared microscope, the infrared radiation is coupled into while the transflected radiation is collected from the table facet by the built-in $15 \times$ Cassegrain objective. According to the optical design of the objective, the coupled radiation is inherently converging.²² For the coupled infrared radiation with a normal

incidence to the table facet, the radiation totally reflects at the pavilion facet. Under the employed cut proportion shown in Fig. 1 (i.e., a set of Tolkowsky's recommended cut proportion with pavilion angle of 41° and crown angle of 34°), the reflecting angles at the pavilion facet are 41° and 57°, respectively, for the first and second reflections. The radiation reaches the diamond/air interface at the table facet with a 16° angle of incidence and refracts into air with an angle of 41.77°. Due to the complex cut surfaces of the faceted diamond and the convergence of the coupled radiations, the radiations impinge the table facet with different angles and undergo different reflections before emerging into the air. However, some radiations may not emerge from the table facet but undergo multiple internal reflections before emerging into the air at any other facet.

According to the traveling path of the coupled radiation in Fig. 1, the outgoing radiation from the table facet is defined as the *transflected radiation*. Since diamond has absorption bands in the mid-infrared region, attenuations of the infrared radiation at characteristic absorption frequencies of diamond are expected. As a result, by collecting the transflected radiation, the absorption spectra of the diamonds can be measured. Since the absorption bands in an infrared spectrum are directly associated with chemical structures and compositions, they can be employed for diamond classification, characterization, and determination of the impurities and/or inclusions in the diamonds. Moreover, the spectrum can be exploited for the determination of the treatment processes applied to the diamond.^{13,14}

EXPERIMENTAL

The measured specimens were gem quality round brilliant cut diamonds with carat weights of 0.08 to 0.45 ct. The diamonds were characterized as received without additional sample preparation except cleaning. All FT-IR spectra were collected using a Nicolet Magna 750 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. A spectral resolution of 4 cm⁻¹ with 512 coadded scans was employed. The observed spectra in the mid-infrared region were baseline corrected before further analysis.

The transflectance spectrum of a faceted diamond was collected by a NICPLAN infrared microscope (also equipped with an MCT detector) attached to the FT-IR spectrometer. A homemade accessory was employed for all spectral acquisitions using the microscope. For the spectral acquisition of a loose diamond, the specimen was positioned on the sample holder with the table facet face up. For the spectral acquisition of mounted diamonds on jewelry (i.e., ring, pendant, necklace, earring, etc.), the whole piece of jewelry is placed on the sample holder without removing the diamonds from the jewelry body. The infrared radiation is coupled into the diamond through the table facet by a built-in 15× Cassegrain objective while the transflected radiation was collected by the same objective. The observed spectrum was expressed in absorbance units.

For comparison purposes, a commercial diffuse reflectance accessory (the Collector, Spectra-Tech Inc.) was employed for all diffuse reflectance spectral acquisitions.



FIG. 2. (A) Diffuse reflectance and (B) transflectance spectra of a 0.1075 ct round brilliant cut type IaA natural diamond.

The same faceted diamond was placed on the sample holder with the table facet face down, and the infrared beam was coupled into the diamond at the near normal angle of incidence, while the representative spectrum was collected from the diffusely reflected radiation. The spectral intensity of the diffuse reflectance spectrum was expressed in Kubelka-Munk units.²³ Since the diffuse reflectance spectra were greatly influence by the arrangement of the diamond on the sample holder,^{5,19} several spectra with different arrangements were collected. The observed spectrum with the best signal-to-noise ratio was employed for further analysis.

RESULTS

Diffuse reflectance and transflectance spectra of a 0.1075 ct round brilliant cut type IaA natural diamond are shown in Fig. 2. The three principal absorption bands of natural diamonds (i.e., three-phonon absorption at $3900-2650 \text{ cm}^{-1}$, two-phonon absorption at 2650-1500cm⁻¹, and one-phonon absorption at 1400–900 cm⁻¹)²³ are clearly observed. Absorption bands associated with hydrogen (3107 cm⁻¹) and nitrogen impurities (1362, 1281, 1208, 1180, 1095, and 1011 cm⁻¹) in the diamond crystal structure could be clearly identified. Although the spectral envelope of the transflectance spectrum is the same as that of the well-accepted diffuse reflectance spectrum, it seems to possess a superior spectral quality. The absorptions in all three principal regions are more prominent in the transflectance spectrum. It should be noted that the absorption at 2350 cm⁻¹ is due to carbon dioxide in the ambient air. Due to fluctuation of carbon dioxide in the ambient air during spectral acquisition, both positive and negative bands were observed.

It is well known that diffuse reflectance spectra of a faceted diamond are greatly influenced by the diamond arrangement on the sample holder.^{5,19} Diffuse reflectance spectra of the diamond with different arrangements (i.e., different positions and/or angles of placement on the sample holder) are not exactly the same. As shown in Fig. 3, although the observed diffuse reflectance spectra clearly revealed the three principal absorption bands, their normalized spectra were not superimposed. Unlike the diffuse reflectance spectrum, the transflectance spectrum was not affected by the diamond arrangement. Superimpositions of the transflectance spectra with different diamond arrangements are shown in Fig. 4. Due to minor variations in the alignment with respect to the incident



FIG. 3. Normalized diffuse reflectance spectra of the diamond in Fig. 2 under different arrangements. The diamond was rotated: (A) 0° , (B) 45° , (C) 90° , (D) 135° , (E) 180° , (F) 225° , (G) 270° , and (H) 315° with respect to a reference position. Due to a significant variation of absorption magnitudes, the observed spectra were normalized by the absorption at 2493 cm⁻¹. The inset of absorptions in the one-phonon region was added for clarity.



FIG. 4. Transflectance spectra of the diamond in Fig. 2 under different arrangements. The diamond was rotated: (A) 0° , (B) 45° , (C) 90° , (D) 135° , (E) 180° , (F) 225° , (G) 270° , and (H) 315° with respect to a reference position. The inset of absorptions in the one-phonon region was added for clarity.



FIG. 5. Transflectance spectra of round brilliant cut natural colorless diamonds: (A) 0.0910 ct, (B) 0.1030 ct, (C) 0.1105 ct, (D) 0.0960 ct, (E) 0.1135 ct, and (F) 0.0835 ct.

radiation, negligible discrepancies among transflectance spectra can be noticed. It should be noted that the displayed transflectance spectra were not normalized.

The spectral features unique to defects and impurities in diamond crystal structure are clearly observed in the transflectance spectra of six faceted white diamonds shown in Fig. 5. These spectral features could be employed for diamond classification. The natural white diamond in Fig. 5A was identified as a type IaB, while that in Fig. 5B is a type IaA. The type IaB diamond possesses a B-center defect (i.e., an aggregate consists of four nitrogen atoms surrounding a vacancy), which shows absorption bands at 1330, 1172, and 1013 cm^{-1.8} An associated absorption band at 1360 cm⁻¹, which refers to the extended-planar-defect platelets, could also be noted. The unique absorption bands in the one-phonon region of the type IaA diamond are associated with an A-center defect (i.e., a defect consists of a pair of adjacent nitrogen atoms in the diamond lattice). The main absorption has a maximum at 1282 cm⁻¹ and additional weak absorptions at 1362, 1208, and 1015 cm^{-1.5,24} Due to the over absorption in the one-phonon region associated with high nitrogen concentrations in Figs. 5C-5F, classifications of the diamonds based on spectral information in the onephonon region are not possible.

In addition to the nitrogen-related absorptions, the diamonds also exhibited sharp absorption bands related to hydrogen impurities at 4495, 3236, 3107, 2785, and 1405 cm⁻¹. A sharp peak at 3107 cm⁻¹, which is attributed to



FIG. 6. Transflectance spectra of colored and treated diamonds: (A) 0.2845 ct type IaA brown diamond, (B) 0.4440 ct type IaB brown diamond, (C) 0.0750 ct HPHT type Ib diamond, and (D) 0.1440 ct irradiated and annealed diamonds.

the C-H stretching vibration of a vinylidene group,⁸ is present in the transflectance spectra of all diamonds examined. The intensity of this band varied considerably depending on the concentration of the hydrogen impurity. The C-H bending absorption at 1405 cm⁻¹ was detected when the concentration of hydrogen was very high. The band can be clearly observed when interference from water vapor in the ambient air does not obscure the absorption band. For spectra with a strong absorption at 3107 cm⁻¹ (i.e., Figs. 5E and 5F), weak absorptions at 3236 and 2785 cm⁻¹ were noticed. Both absorption bands are commonly observed as minor features in infrared spectra of hydrogen-containing natural diamonds. The absorption at 2785 cm⁻¹ is believed to be the first overtone of the absorption at 1405 cm⁻¹ while the sharp peak at 3236 cm⁻¹ was assigned to the N–H stretching absorption.^{8,25}

All transflectance spectra of brown diamonds and treated diamonds shown in Fig. 6 exhibited absorptions associated with nitrogen-defect-induced one-phonon absorption. According to the absorption in the one-phonon region, the diamond in Fig. 6A is classified as a type IaA diamond while that in Fig. 6B is a type IaB diamond. Both spectra contain a well-defined amber center with an absorption at 4166 cm⁻¹, which is a typical absorption for natural brown diamonds.²⁶ Absorption bands associated with hydrogen impurity in the three-phonon region can also be observed.

The absorption bands in the one-phonon region of the HPHT-treated diamond in Fig. 6C indicate that the diamond is type Ib. A sharp peak at 1344 cm^{-1} is the char-

acteristic absorption of HPHT-treated diamond, attributed to the local vibration induced by the C-centered single nitrogen substitution. A broad absorption band at 1128 cm⁻¹ implies the presence of low-concentration B-centered substitution.^{5,7,27}

Due to the over absorption in the one-phonon region associated with high nitrogen concentration of the irradiated and annealed diamond in Fig. 6D, classification of the diamond based on the spectral information in the onephonon region is not possible. However, absorption bands in the high wavenumber region associated with defect centers can be exploited for characterization purposes. The H1a absorption at 1450 cm⁻¹ is the local vibrational mode associated with interstitial nitrogen. The H1b absorption at 4931 cm⁻¹ seen in type IaA diamonds, on the other hand, is related to the A-center.²⁸ The absorption centers, H1a and H1b, observed in the figure are the unique characteristics of irradiated-and-annealed type I diamond.^{16,26–30} It should be noted that absorption bands in this region are not observed in un-irradiated type I natural diamonds. The sharp absorption bands associated with vinylidene at 3107 cm⁻¹ and that with N-H stretching at 3236 cm⁻¹ are clearly observed. Another vinylidene-related absorption at 1405 cm⁻¹ is observed as a shoulder of the strong absorption at 1372 cm⁻¹.^{10,15}

For diamonds with complex settings on jewelry, a spectrum of an individual diamond can be selectively measured by the novel transflectance technique. As shown in Fig. 7, there are five diamonds on the ring: four small diamonds (0.05 ct) and a big diamond (0.20 ct). According to the ring design, the four small diamonds are embedded in the metal body. The only observable parts of the diamonds are the table facet, the star facet, and parts of the upper girdle facet. As a result, their infrared spectra cannot be acquired by the diffuse reflectance or transmission technique. However, the novel transflectance technique enables the collection of all FT-IR spectra of the mounted diamonds. Similar to spectral features of the loose diamond, the three principal absorption bands of the mounted diamonds are clearly observed. Since the spectra in Fig. 7A were collected without cleaning, strong absorptions of accumulated substances on the surface of the diamonds due to prolonged wearing were clearly observed. When the big diamond (diamond number 3) was carefully cleaned, the absorptions associated with aliphatic hydrocarbon at 2954, 2917, 2848, 1645, 1541, and 1468 cm⁻¹ disappeared. The small diamonds were more difficult to clean due to the ring design, having only a small opening near the culet. The uncleaned surfaces of faceted diamonds are responsible for residual absorptions in the C-H stretching region in Fig. 7B. According to the spectral features in the one-phonon region, all diamonds are of different types. The over absorption in the one-phonon region of diamond number 1 indicates that the diamond contains high levels of nitrogen impurity. Although other weak absorption bands associated with hydrogen and nitrogen impurities can be clearly observed, the type of the diamond cannot be identified. According to spectral envelopes in the one-phonon region, diamonds number 2-5 are classified as type IaA, IaA/B, IaA/B, and IaB, respectively.



FIG. 7. Normalized transflectance spectra of mounted round brilliant cut diamonds on a ring (**A**) before cleaning and (**B**) after cleaning. The observed spectra were normalized by the absorption in the two-phonon region at 2493 cm⁻¹. The inset of absorptions in the C–H stretching region was added for clarity.

DISCUSSION

In general, infrared spectra of faceted diamonds are nondestructively acquired by the diffuse reflectance technique or transmission technique using a beam condenser. However, the techniques suffer from the difficulties associated with the measurement processes. The transmission of the faceted diamonds is not always applicable due to complex reflections at the cut and polished surfaces. Moreover, the technique is not normally applicable to mounted diamonds, where the metal part of the jewelry body covers most of the faceted surfaces except the table facet, the star facet, and part of the bezel facet. The observed diffuse reflectance spectra, on the other hand, are greatly influenced by diamond arrangements on the sample holder. Since a concentric rotational axis of a symmetrically faceted diamond and the sample holder is difficult to achieve, exact diffuse reflection patterns under different diamond arrangements cannot be obtained. As a result, a superimposition of diffuse reflectance spectra from the same faceted diamond is not normally observed.

The novel transflectance technique using an infrared microscope to acquire an infrared spectrum by collecting the transflected radiation from the pavilion facets of cut diamonds was exploited. The quality of the transflectance spectrum is comparable to or better than that of the wellaccepted diffuse reflectance spectrum. Unlike the diffuse reflectance spectrum, the transflectance spectrum was not affected by the diamond arrangements. The coupled radiation from the microscope is non-polarized while the incident radiation covers a wide range of angles due to the focusing optics of the built-in $15 \times$ Cassegrain objective. The radiation undergoes transmission-like travel through the faceted diamonds. Since the position at which the coupled radiation entering the diamond can be controlled while the transflected radiation through the symmetrical table facet can be collected, the influences of diamond orientations are eliminated. Thus, the observed transflectance spectra of a diamond are reproducible and are superimposed.

The diffuse reflectance and transflectance spectra of diamonds suffer from over absorption in the one-phonon and two-phonon regions. The magnitude of absorption is associated with size and concentration of nitrogen impurities in the diamond crystal structure. However, a large diamond with an inherently long transflected path length enhances the weak absorption bands. The weak absorption bands unique to defect centers can be clearly observed in the transflectance spectra. As a result, the treatment history and/or unique characters of the faceted diamonds can be drawn from the observed transflectance spectra.

The distinct advantage of the transflectance technique over the diffuse reflectance or transmission technique is its ability to acquire infrared spectra from mounted diamonds on jewelry without taking the diamond out of the jewelry body. An infrared spectrum of an individual diamond on a complex jewelry setting can be selectively measured. Moreover, the spectral features of the mounted diamonds were not interfered with by the metal body.

CONCLUSION

The novel transflectance technique using an infrared microscope was successfully employed for spectral acquisition of loose and mounted faceted diamonds. The technique is nondestructive, provides unambiguous results, requires no sample preparation, and has a short analysis time. The incident radiation is coupled to the diamond via the table facet while the transflectance radiation is collected by the built-in 15× Cassegrain objective. The same spectral features with better quality as those from the well-accepted diffuse reflectance technique are observed. Unlike the diffuse reflectance spectrum, the transflectance spectrum is not altered by the diamond arrangements. Absorption bands unique to impurities, defects in the crystal structures, and treatment processes can be clearly observed. The measured spectrum can be exploited for classification and/or determination of the treatment history of the diamond. Although the shown results are those of the loose diamonds and mounted round brilliant cut diamonds on a ring, the technique is applicable for other types of gemstones, jewelries, and/or cut shape.

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