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Analysis of Nickel Defect in Diamond with Photoluminescence upon Excitation near 200 nm

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ABSTRACT: Photoluminescent (PL) spectra of synthetic diamond powders at temperatures between 10 and 300 K were excited with synchrotron radiation in the wavelength range 125−375 nm. Prominent spectral PL features were detected at 484.6 and 489.0 nm (2.559 and 2.535 eV), associated with nickel defect. During our measurement of PL excitation (PLE) spectra of Ni defect in diamond, we observed a distinct PLE line at 215 nm for the first time. We thereby suggest the use of UV-PL spectra excited in the region 200−220 nm to analyze and to identify nickel defect in diamonds.
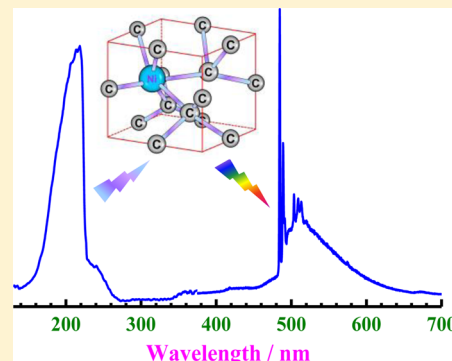
Transition metals and their alloys have served as solvent catalysts in the synthesis of diamonds with techniques involving high pressure and high temperature (HPHT), which transform trigonally bonded carbon atoms in graphite to tetrahedrally bonded carbon atoms in diamond.[1] In particular, a Ni catalyst is commonly employed to fabricate bulk diamonds; in this process, the resulting synthetic diamonds might be contaminated with nickel impurity.[2,3]

The impurities and defects in diamond affect the color, optical, and electrical properties and their applications.[4−6] The contamination by nickel during the HPHT process might generate a substitutional Ni site as a defect in diamonds.[3] This defect has become the subject of many theoretical and experimental investigations applied in various fields for diamond materials. The characterization of this nickel defect in diamond materials is hence of interest. For identification and analysis of the nickel defect in diamonds, several spectral techniques including electron paramagnetic resonance (EPR),[7,8] infrared absorption,[2,9] visible absorption,[10] and cathodoluminescence[3] have been employed. For this purpose, photoluminescence (PL) has also been engaged for the analysis of nickel defect, but with excitation limited to wavelengths beyond 250 nm; a PL emission spectrum excited at wavelengths smaller than 250 nm is hence lacking.[11−14]

Photoluminescence is a sensitive and powerful technique to characterize optically the impurities, defects and absorption edges of diamonds. In previous works, we applied the PL technique with excitation from a synchrotron light source at wavelengths smaller than 250 nm to identify sensitively the nitrogen defects in various diamonds.[15−17] In the present work, we analyzed the nickel defect in diamond by detecting the PL upon excitation at 200−220 nm. On the basis of this UV-PL technique, the detectivity of nickel defect in diamonds has achieved much enhancement, 1000 times as great as before.

■ EXPERIMENTAL SECTION

We recorded the PL spectra at beamline 03A at National Synchrotron Radiation Research Center (NSSRC) in Taiwan; the experiment was similar to that described elsewhere.[18] The intense light for excitation from this beamline attached to the 1.5 GeV storage ring was dispersed with a cylindrical-grating monochromator (CGM, 6 m). The intensity of the synchrotron light was monitored with a gold mesh transmitting about 90% and recorded with an electrometer (Keithley 6512). A CaF_2 or quartz window as a filter was inserted in the beamline to remove light of frequencies multiple of that desired.

The light from the synchrotron transmitted through the gold mesh irradiated the sample, which was arranged at an angle near 45° with respect to both the incident light and the entrance slit of the dispersing monochromator. The PL intensity of the sample was detected with a photomultiplier (Hamamatsu R943-02) in a photon-counting mode. Emission spectra were recorded at resolution 0.5 nm and scanning steps 0.2 nm, unless noted otherwise in particular figures. To measure PL excitation (PLE) spectra, we monitored the dispersed emission at a wavelength selected with a grating (450 lines/mm). All PLE spectra were normalized with respect to the spectral response of the CGM beamline.

To record the spectra of samples below 300 K, we attached the sample holder to the cold head of a cryostat (helium closed-cycle system, APD HC-DE204S) mounted on a flange; the sample was then rotatable to about 45° with respect to both the incident light and the entrance slit of the monochromator. The temperature of the cold head at the sample was controlled better than ±1 K during the collection of the data.
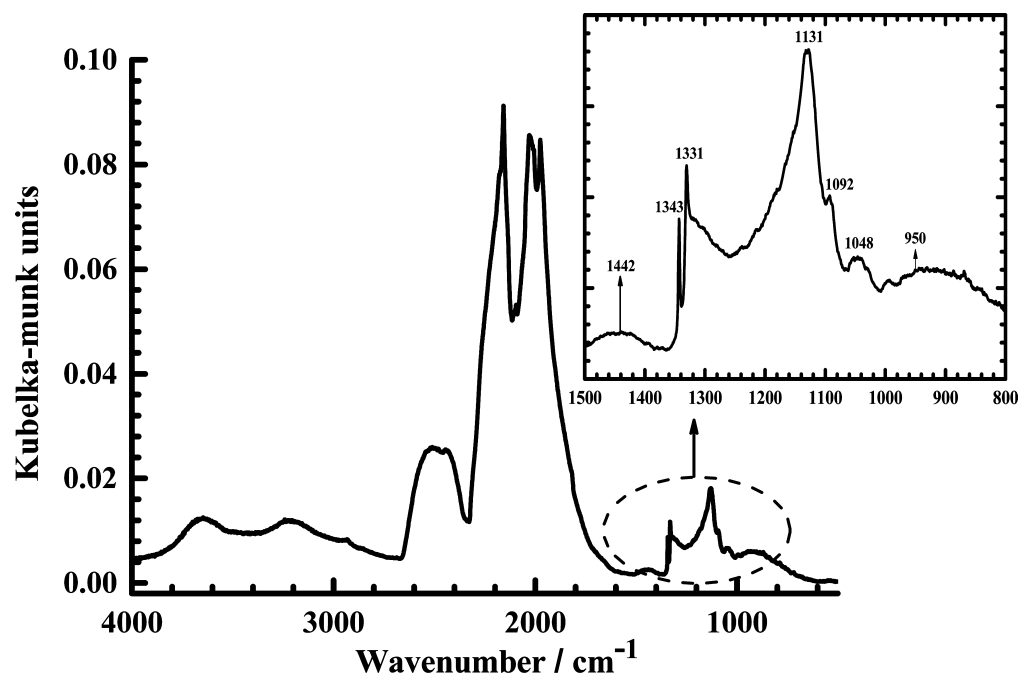
Figure 1. Diffuse reflectance infrared spectrum of synthetic diamond powder (50 μm) at 300 K. The spectrum was recorded at resolution 1 cm^{-1} with 200 scans in the spectral range 4000−500 cm^{-1}.

Infrared spectra of diamond powders were recorded with an interferometric spectrometer (Bomem DA8, KBr beamsplitter, HgCdTe detector) equipped with a diffuse reflectance (DRIFT) accessory (Spectra-Tech). The interferometer was evacuated to eliminate the absorption of water vapor and carbon dioxide from the spectra. For DRIFT measurements, KBr powder served as a reference. Typical spectra were measured with resolution 1 cm^{-1} and 200 scans.

Synthetic diamond powders (size 50 μm) were purchased (Well Expediting Ent. Co., Ltd.).

■ RESULTS AND DISCUSSION

To identify the defects and impurities in diamonds as powder samples with infrared spectra, we applied a diffuse-reflectance technique to avoid further sample preparation. Figure 1 shows the characteristic diffuse-reflectance infrared spectrum of that synthetic diamond powder. Seventeen lines were measured, appearing in three zones; their positions and assignments are listed in Table 1.

Perfect diamond possesses a tetrahedral structure and reveals no intrinsic infrared absorption in its one-phonon region, but diamond has strong absorption at 1975, 2030, 2094, 2157, 2175, 2444, and 2511 cm^{-1} associated with two- and three-phonon intrinsic absorptions in the central region of the spectrum.[19,20] Two broad bumps appeared near 3240 and 3700 cm^{-1},[21,22] and two further weak lines at 2912 and 2933 cm^{-1} were barely discernible.[22,23] The weak absorptions at wavenumbers beyond 2800 cm^{-1} are all attributed to hydrogen impurities, as assigned and listed in Table 1.

Below 1600 cm^{-1}, the spectrum consists of lines at 950, 1048, 1092, 1131, 1331, 1343, and 1442 cm^{-1}, as illustrated in enlarged form and marked in the inset of Figure 1.[24−28] Most synthetic diamonds containing single substitutional nitrogen atoms as dominating defects (C center) are classified as type Ib. A prominent absorption line at 1131 cm^{-1} is induced by such single substitutional nitrogen atoms;[25,27,28] a sharp line at 1343

Table 1. Features Observed in the Diffuse-Reflectance IR Spectrum of Synthetic Diamond Powder (50 μm) and Their Assignments

peak (cm^{-1})	assignments	references
3240	induced by the C≡CH group;	21, 22
2933	stretching bending modes of CH$_3$ and CH$_2$ group	22, 23
2912		
2511	diamond intrinsic lines two-phonon lines of diamond associated with C—C bonds	19, 20
2444		
2175		
2157		
2094		
2030		
1975		
1442	a line observed in DRFTI spectra of diamond powders attributed to oxygen-containing groups located at the diamond surface	24
1343	induced by the C center	25, 26
1331	X-center observed in nickel-containing diamonds grown with a temperature-gradient method	2, 25, 26
1131	induced by the C center	25, 27, 28
1092	unknown	
1048	X-center observed in synthetic nickel-containing diamonds grown with the temperature-gradient method.	2, 25, 26
950		

cm^{-1} is another distinct feature associated with a localized vibrational mode in the C center.[25,26] The sharp line at 1331 cm^{-1} is a characteristic feature of an X center, observed in synthetic diamonds containing nickel and grown with the temperature-gradient method.[25,26] Two broad lines about 950 and 1048 cm^{-1} are also associated with the X center.[25,26] The infrared analysis hence indicates that this synthetic diamond might be grown from a nitrogen getter added to a nickel catalyst, so that this diamond contains nickel defect.

That these synthetic diamond powders appear light olive with a yellowish hue indicates that we might characterize this

diamond with visible spectra. For samples of diamond powder, it is difficult to record directly the visible absorption spectrum without further sample preparation, whereas we can detect any visible emission directly upon excitation of diamond powders with appropriate radiation. The absorption of light might excite an impurity or defect so that its excited states become populated; a subsequent radiative transition to the ground state produces a unique spectral feature. A detailed examination of luminescent spectra might yield valuable information about the electronic properties and defects of diamond. The photoluminescence technique is thus a convenient method to identify an impurity or defect in diamonds.

The luminescence of synthetic diamonds containing nickel defect has been studied with cathodoluminescent and photoluminescent techniques. For example, Pereira et al. reported the luminescence spectra of synthetic diamonds, between 2 and 20 K, with Ni substitutional lattice sites excited at 365 nm;[11] they recorded two dominant lines at 2.54 and 2.56 eV. For comparison with their result, we recorded the emission of our synthetic diamond powder, at 10 K, containing nickel defect with excitation at 365 nm. We detected the emission from the target diamond as shown in Figure 2, but the signal
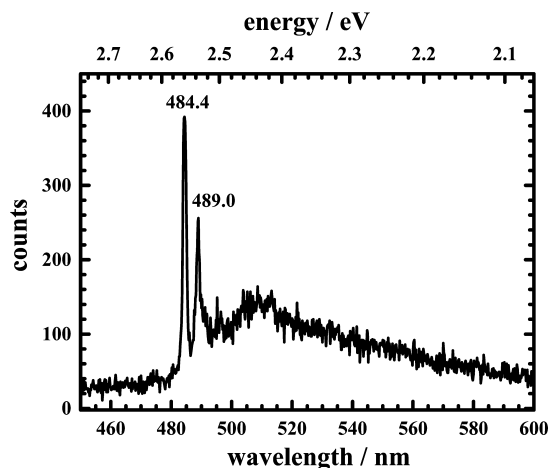

Figure 3. Photoluminescence excitation spectrum (resolution 0.5 nm, scan step 0.5 nm) of synthetic type Ib diamond powder (50 μm) at 10 K monitored with 484.4 nm.

Figure 2. Photoluminescence spectra (resolution 0.2 nm, scan step 0.2 nm) of synthetic type Ib diamond powder (50 μm) at 10 K excited at 365 nm. The spectrum was accumulated for 150 s at each step.

was weak. After accumulating each datum for 150 s, the maximum signal was less than 400 counts, in Figure 2, but the total shape of this emission spectrum is similar to their published result; two distinct dominant lines at 484.4 and 489.0 nm, corresponding to 2.560 and 2.535 eV are associated with substitutional Ni defects.[3,11] This result demonstrates that our PL system can identify the nickel defect in diamonds.

The absorption of light excites an impurity or defect in diamond to populate its excited states; a subsequent radiative transition to the ground state produces emission. To understand the PL of the impurity or defect subjected to absorption, we recorded its PL excitation spectrum. For the synthetic diamond containing a nickel defect, no such PL excitation spectrum is reported in the UV region. For this purpose, we measured PL excitation spectra for synthetic diamond powders on detecting emission at 484.4 and 489.0 nm; the spectra obtained on monitoring those two features are identical. Figure 3 displays a typical PL excitation spectrum of synthetic diamond powder (50 μm) at 10 K in the wavelength region 120−375 nm monitored at 484.4 nm. This PLE
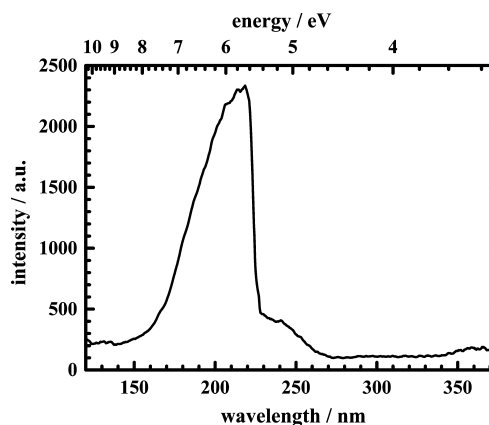
spectrum corresponds to a weak absorption in the wavelength region 250−375 nm; a strong absorption appears near 215 nm with width about 40 nm.

On the basis of this PLE spectrum, we subjected the synthetic diamond powder with nickel defect to strong excitation in the wavelength range 177−225 nm; as a result, this wavelength range is the most suitable region for excitation of the Ni defect in diamond with the PL technique. To confirm this observation, we studied the emission of the target diamond upon excitation with radiation in this region. Figure 4 shows emission spectra of target synthetic diamond powders at temperatures 10, 50, 100, 150, 200, and 300 K upon excitation at 215 nm. The intensity of these zero phonon line (ZPL) signals depends strongly on temperature; as the temperature decreases, the signals become more intense. The PL spectrum of the sample at 10 K reveals distinct lines, as displayed in the inset of Figure 4.

The emission spectra of the target diamond upon excitation at 215 nm and temperatures below 150 K are similar to that at 10 K with excitation at 365 nm. The intensity with excitation at 215 nm is about 1000 times that of the signals of the most distinct lines at 365 nm and 10 K. As a result, the PL spectrum excited at 215 nm and 10 K produces strong signals and detailed features, as displayed in the inset of Figure 4. According to the previous work,[3,11,24] the prominent emission line at 484.6 nm (2.559 eV) could be identified as a zero-phonon line of nickel optical center in HPHT synthetic diamonds. Collins pointed out that the line 484 nm could be produced by implanting diamonds with Ni^+ ions;[6] consequently, this line is associated with nickel defect involving an interstitial Ni^+ atom.[29] The lines at 489.0 (2.535 eV) and 491.2 nm (2.524 eV) are attributed to a quasilocal vibration involving a Ni atom; whereas, the lines at 509.0 (2.436 eV) and 513.2 nm (2.416 eV) are replicas due to coupling with optical phonons of energy about 100 meV.

In the PL process, the material might emit light independent of the form, shape, size or state of the sample; for analysis, the greatest advantage of PL technique is the lack of necessity of further sample preparation. During the PL analysis, the tested sample can thus remain intact and entirely undamaged. Diamond possesses extreme properties: it is the hardest natural material, and almost completely resists dissolution with solvents. Further treatment of a diamond material is difficult in preparation for an analysis; the PL technique is hence useful
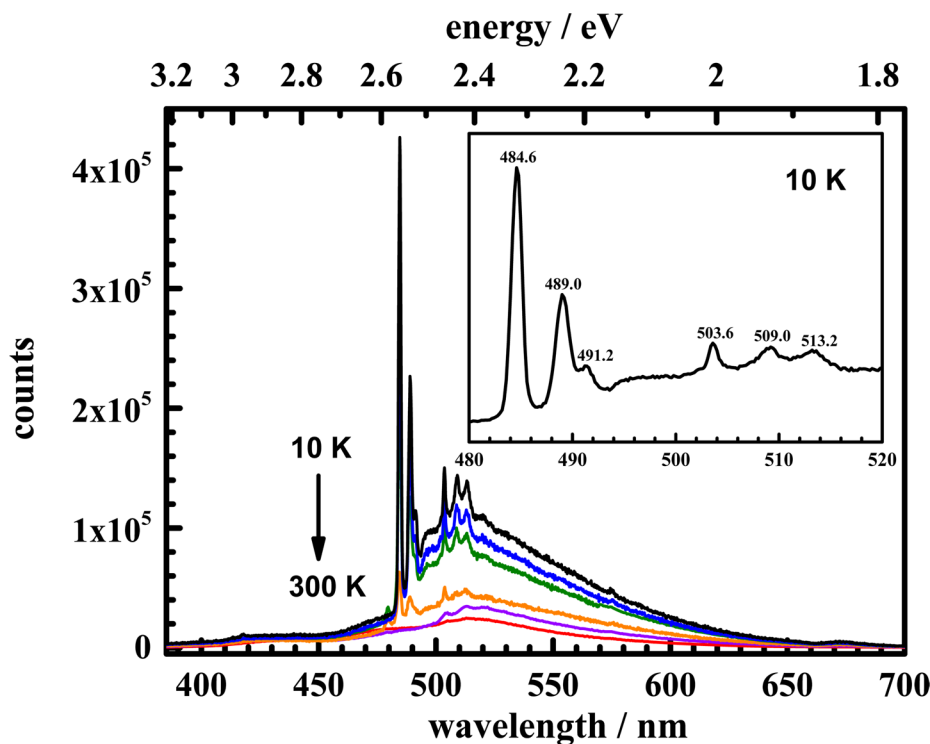
Figure 4. Photoluminescence spectra (resolution 0.2 nm, scan step 0.2 nm) of synthetic type Ib diamond powder (50 μm) excited at 215 nm at temperatures 10, 50, 100, 150, 200, and 300 K; the spectra were accumulated for 10 s at each step.

and convenient for analysis of diamond samples in various forms. This work proves that the PL technique is applicable also to identify the nickel defect in diamond; the emissions at 484.6 and 490.0 nm are two features of that Ni defect.[3,11,24] Figure 1 and Figure 3 display the PL emission spectra upon excitation at 365 and 215 nm, respectively; compared to the signals of the most distinct lines, the intensity upon 215 nm is 3 orders higher than that at 365 nm. In addition, the intensity of the distinct PLE band at 215 nm is 3 orders higher than that in the wavelength region 300−375 nm, as shown in Figure 3. These results indicate PL spectra excited at wavelengths in the range 200−220 nm provide sensitivity 1000 times higher than the previous works with excitation in the region 300−375 nm.

For the characterization of defects in various forms of diamonds, the infrared spectral technique has been advantageously developed to identify various centers; to detect the Ni defect in diamonds, we compare the sensitivity of the infrared method to that with UV-based luminescence. For the purpose of comparison, one can estimate the relative sensitivity from the levels of signal-to-noise (S/N) levels in both methods. For the infrared analysis, the level of signal-to-noise of the Ni defect line at 1331 cm^{-1} is, from Figure 1, about 120 ($S/N = 0.012/0.0001 = 120$), whereas that of the PL line at 484.6 nm is about 8520 ($S/N = 42\,600/5 = 8520$) as displayed in Figure 4. The detectivity of the nickel defect in diamond based on the UV-PL technique is about 70 times that with the infrared method. This estimate yields an idea as a comparison of these two methods; to achieve more quantitative information, we can develop the detection information from our previous work.[17] Similar to this work, the UV-PL technique upon excitation at 170−240 nm was applied to analyze quantitatively the B center as a N4 nitrogen defect in diamonds previously. In our previous work, we obtained that the least detectable concentration of the N4 nitrogen defect was about 13 ppb; in which, the sensitivity of

the UV-PL technique was about 30 times than that practicable with infrared absorption spectra. In present work, we concluded that the detectivity of the nickel defect in diamond using with the UV-PL technique is about 70 times higher than the infrared method. This conclusion hints that the least detectable concentration of the nickel defect in diamonds can reach to about 10 ppb with the UV-PL technique. Notably, although in this work we utilized synchrotron radiation as a source in the UV-PL technique, wavelengths in the range 200−220 nm are located in the near UV region such that conventional lamps and equipment could be applied.

In summary, photoluminescence signals associated with the nickel defect in synthetic diamond were obtained upon excitation with radiation in the wavelength region 125−375 nm from a synchrotron for the first time. PL spectra excited at wavelengths 200−220 nm for a sample at 10 K exhibit prominent characteristic emission lines that provide sensitivity a thousand times that at wavelengths in the range 250−375 nm. The sensitivity to detect the Ni defect in diamond with the UV-PL technique is about 70 times that of the infrared spectral method. Our work thus extends the capability to identify the nickel defect in diamonds.

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Notes
The authors declare no competing financial interest.

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