In situ optical monitoring of CVD growth and reactive ion etching of nanodiamonds with silicon - vacancy colour centres

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Abstract. A method of in situ optical monitoring of the CVD growth and reactive ion etching of nanodiamonds with silicon-vacancy colour centres is presented. The method is based on measuring the time dependence of the optical reflectivity from a silicon substrate with deposited isolated nanodiamonds. Evolution of the reflectivity due to the light scattering on nanodiamonds is a result of the changes in their size and structure during growth and etching. Optical monitoring of the growth and etching processes allowed reproducible fabrication of high crystalline quality nanodiamonds.

1. Introduction
The nanodiamonds hosting colour centres are attracting attention for applications in quantum information [1, 2] and bio-sensing [3]. Colour centres in nanodiamonds coupled to nanophotonic devices as microcavities [4-6] or antennas [7] could provide strong light-matter interaction and high photon collection efficiencies. The possibility of spatial nanomanipulation of photoluminescent nanodiamonds is important for creating an array of ordered emitters for hybrid photonic platforms [8].

One of the most attractive colour centres in diamond with unique properties is the silicon-vacancy centre (SiV). The negatively charged SiV centre consists of an interstitial silicon atom splitting two vacancies with a strong zero-phonon line (ZPL) at 738 nm and lifetime-limited optical linewidth [1]. It has a high Debye-Waller factor that results in over 70 % of the emitted photons being into the ZPL [9]. Due to its inversion symmetry, the colour centre has weak coupling of the ZPL transitions to charge fluctuations in the SiV centre environment, and therefore demonstrates promising spectral characteristics [10].

One of the most promising techniques for creating nanodiamonds hosting the SiV colour centres is the chemical vapour deposition (CVD) method using a Si doping from gas phase in the course of the deposition process [11]. In [12], it was shown that reactive ion etching (RIE) in an oxygen plasma of CVD diamond particles with SiV colour centres grown on a silicon substrate by the CVD method enable to produce nanodiamonds with crystalline quality close to homoepitaxial diamond films and single-crystal diamond. The method of reactive ion etching is characterized by a high etching rate, anisotropic etching nature, a strong dependence of the etching rate on the substrate temperature and the phase composition of diamond particles. In situ monitoring of the growth and etching of nanodiamonds was used to improve the reproducibility of nanodiamond production.

In the present work, in situ optical monitoring technique has been developed for optical monitoring of the CVD growth and subsequent etching of diamond particles. The technique is based on the in situ measurement of the dependence of the optical reflectivity from a silicon substrate with isolated
nanodiamonds on time. The \textit{in situ} optical monitoring technique provides control of changes in light scattering on diamond particles owing to the evolution of their size and structure.

2. Experimental

The diamond particles were grown by the microwave plasma-assisted CVD in the CH$_4$/H$_2$ gas mixture. Detonation-synthesis nanodiamonds with the characteristic size of $\sim 4$ nm served as nucleation centres and were deposited in controlled way onto a silicon substrate by the aerosol spraying method [13]. The density of nucleation centres was about $\sim 10^7$ cm$^{-2}$ for isolated nanodiamonds fabrication. The CVD growth has been performed at microwave power 600 W (2.45 GHz), substrate temperature 700 ºC, total pressure 15 Torr, hydrogen flow rate 500 sccm, methane concentration 2.8 %. The SiV colour centres were introduced into the diamond particles in the course of their synthesis. The etching of the silicon substrate with atomic hydrogen provided delivery of Si into the gas mixture in the reactor, where from it was incorporated into the crystal lattice of growing diamond particles.

The diamond particles were successively grown and etched in the same reactor without exposure to air. The diamond particles were etched in an oxygen-nitrogen mixture (20 % vol O$_2$ + 80 % vol N$_2$) at the following process parameters: microwave power 250 W, substrate temperature 500 - 600 ºC, oxygen-nitrogen mixture flow rate 100 sccm, total reactor pressure 10 Torr.

The reflectivity from a substrate with diamond particles was measured \textit{in situ} in the course of the CVD growth and RIE at a wavelength of 610 nm. The measured data were subsequently sent to the computer at a sampling rate of 2 s and plotted in real time.

Micro-Raman and micro-photoluminescence measurements were made on a Horiba Jobin Yvon T64000 spectrometer equipped with a confocal microscope. The a frequency doubled Nd:YAG laser operating at a wavelength of 532 nm was used for excitation. Low-temperature µ-PL measurements were made in a closed-cycle helium system for microscopy (Cryo Industries, Inc.).

3. Results and discussion

Figure 1 shows the results of the \textit{in situ} measurements (for three processes) of the normalized specular reflectivity from a silicon substrate with isolated diamond particles on the time in the course of the growth-etching cycle.

![Figure 1](image-url)  

\textbf{Figure 1.} The dependence of the normalized reflectivity from a silicon substrate with nanodiamonds on the time in the course of the growth-etching cycle ($t_g$ - time of growth termination, $t_e$ - etching start time). The nucleation density is $\sim 10^7$ cm$^{-2}$. 


The normalized reflectivity is the measured reflectivity in the experiment divided by the primary reflectivity from the substrate. In order to create isolated diamond particles on the substrate, the density of nucleation centers was less than $10^7$ cm$^{-2}$. At the beginning of growth for about 300 seconds, the reflectivity almost does not change. Then, a decrease in reflectivity is observed, due to the light scattering on individual diamond particles increasing in size. When the reflectivity reaches a plateau, the delivery of methane into the reactor was terminated, which resulted in that the growth ceased because of the removal of carbon-containing species from the reaction zone. Then microwave feed was turned off. The growth stage was followed by a transient stage during which the reflectivity practically did not change.

Further, the plasma was ignited and the RIE process of particles in the oxygen plasma was started. The implementation of the RIE method involves plasma heating of the substrate. In turn, the etching rate depends on the substrate temperature. Therefore, the absence on the initial stages of etching the noticeable change in reflectivity may be due to the low etching rate because of the low substrate temperature. With increasing the etching time, the characteristic particle size decreased, which resulted in an increase in the reflectivity.

The analysis of the results of studying of the structural and optical properties of the nanodiamonds synthesized in the course of the growth-etching cycle showed, the properties of the samples obtained during the same etching time are different. Therefore, the etching time, as a parameter characterizing the change in the size and structure of the nanodiamonds does not provide reproducible results. It can be explained by the strong dependence of the etching rate of diamond particles on the initial size of particles, their phase composition and anisotropic nature of etching. In order to obtain reproducible results as a parameter, upon reaching which the etching process was completed, the value $R_e = (R - R_g)/(R_0 - R_g)100\%$ was used, where $R$ is the reflectivity at the current time, $R_g$ is the reflectivity at the time of termination of the CVD growth process; $R_0$ is the primary reflectivity from the substrate (before the start of the CVD growth). Figure 1 shows the time dependence of the normalized reflectivity for the three processes for which $R_e = 50\%, 70\%, 100\%$.

The average size of as-grown diamond particles (at the time of termination of the CVD growth, $R_e = 0\%$) was about 900 nm. The nanodiamonds obtained by the etching at which $R_e = 50\%$ have average size of 550 nm. It was shown in [12] that during RIE the size of the nanodiamonds decreased, and at $R_e \geq 70\%$ they were partially disintegrated into separate nanocrystallites less than 200 nm in size. As demonstrated by scanning electron microscopy studies the nanodiamonds obtained at $R_e = 100\%$ were not fully etched. In this case, the size of the nanocrystallites was so small that the scattering of light on them practically did not affect the value of the reflectivity.

The shape of the time dependence curve of the reflectivity in the process of the CVD growth can be described in the framework of the Mie scattering theory in the approximation of elastic scattering of light on individual non-absorbing spherical particles [14]. Such scattering can be considered as the diffraction of a plane wave on the spherical particles, randomly distributed in a homogeneous medium and located at a distance from each other that is longer than the wavelength [15]. For diamond particles on a substrate, the reflectivity can be calculated by the expression [14]:

$$R = R_0 (1 - NQ\pi d^2 / 4)$$  \hspace{1cm} (1)

where $N$ - concentration of diamond particles on the surface, $Q$ - scattering efficiency factor, $d$ - diameter of particles. Figure 2 represents a plot of calculated scattering efficiency factor versus diameter of particle (refractive index $n = 2.41$), calculated by the formulas from [15].

Diamond particles fabricated by the CVD method are not monodisperse in size. Therefore, it is necessary to take into account the distribution of diamond particles in the size when calculating the scattering efficiency factor. Assuming that the particle size distribution obeys the Gaussian distribution law, the average value of the scattering efficiency factor is expressed as:
\[ Q_{av}(d) = \sum_{x=d_i}^{d_f} Q(x) \left( \frac{1}{\sqrt{2\pi}} \right)^{-1} \exp\left( -\frac{(x-d)^2}{2\sigma^2} \right) \]  \hspace{1cm} (2)

where \( \sigma \) - relative standard deviation, \( d_1 = d - 2\sigma d \), \( d_2 = d + 2\sigma d \).

The averaged value of the scattering efficiency factor depending on the diameter of particles at \( \sigma = 0.15 \) is presented in figure 2 (dash line). The size distribution of particles leads to blurring of the narrow resonance lines (figure 2). Let us express the diameter of diamond particles as \( d = \upsilon t \), where \( \upsilon \) is the growth rate of diamond particles. From equation (1) we have:

\[ Q_{exp} = 4(1 - R / R_0)(\pi(\upsilon t)^2 N)^{-1} \]  \hspace{1cm} (3)

We can express \( Q_{exp} \) from the experimental time-dependence of reflectivity, using expression (3). The growth rate (\( \upsilon \sim 1 \mu m/h \)) and the concentration of diamond particles can be considered practically unchanged during growth. The light scattering on diamond particles with a size much smaller than the wavelength corresponds to the region of Rayleigh scattering. The reason for the weak change in the reflectivity during the initial stages of growth (up to \( \sim 400 \) s) is the small value of the \( Q \) for Rayleigh scattering (figure 2).

Figure 2. Calculated scattering efficiency factor of spherical particles (for a wavelength of 610 nm) versus diameter of particles in the case of monodispersed particles (solid lines) and in the case of particles size distribution (dash line).

Figure 3. Time dependence of the scattering efficiency factor evaluated from experiment. Characteristic particle sizes corresponding to extremes on the curve are shown.

The curves of the calculated dependence of \( Q_{av} \) on the particle diameter and the experimentally obtained dependence of \( Q_{exp} \) on the growth time are similar to each other. The maxima at \( t = 1050 \) s and \( t = 1900 \) s on the curve shown in figure 3 are due to Mie resonance scattering. Correlation of the positions of the maxima on the calculated (figure 2) and experimental curves (figure 3) makes it possible to determine the particle size at the time instant corresponding to the extremum on the experimental reflectivity curve (\( d = 320 \) nm at \( t = 1050 \) s and \( d = 780 \) nm at \( t = 1900 \) s). This allows using the time dependence of the reflectivity to control the growth rate and the change in particle size.

Figure 4 shows the Raman spectra of the as-grown diamond particles (at the time of termination of the CVD growth, \( R_e = 0 \% \)) and the nanodiamonds formed for etching time at which \( R_e = 50 \% \) and \( R_e = 70 \% \). The Raman spectra display a narrow diamond line at about 1333 cm\(^{-1}\), weak band at 1350 cm\(^{-1}\) and band at 1560 cm\(^{-1}\) belonging to D and G modes of sp\(^2\)-hybridized carbon. The bands at 1490 cm\(^{-1}\) are related to the presence of transpolyacetylene inclusions in the nanodiamonds. A Lorentzian fit was used to obtain the full width at half-maximum (FWHM) and position of the diamond line.
The FWHM of the diamond line for as-grown CVD diamond particles is 4.2 cm\(^{-1}\) and its position, 1334.1 cm\(^{-1}\). For the nanodiamonds formed for the etching time at which \(R_e = 50\%\), the FWHM of the diamond line decreased to 3.6 cm\(^{-1}\), with its position becoming 1332.9 cm\(^{-1}\). For the nanodiamonds formed for the etching time at which \(R_e = 70\%\) the position of Raman line of diamond is about 1332.5 cm\(^{-1}\) and the FWHM at room temperature does not exceed 2.5 cm\(^{-1}\). The RIE results in that the diamond line is shifted to lower frequencies and becomes narrower. The shift and narrowing of the Raman line of diamond suggests that the RIE is responsible for the narrowing of the strain distribution and removing highly defective regions [12].

The RIE led to a significant decrease in the inhomogeneous broadening of the ZPL of an ensemble of SiV colour centres [12]. As a result, at a temperature of 10 K, a ZPL doublet appears in the photoluminescence spectra (figure 5). This fine structure of the ZPL of the SiV centre are formed due to the splitting of the ground and excited states [16]. Observation of the fine structure of ZPL of the SiV centre in the spectra confirms that the SiV centres are situated in low-strain and high crystalline quality nanodiamonds.

### 4. Conclusions

The technique of in situ optical monitoring in the course of the CVD growth and subsequent reactive ion etching of nanodiamonds based on measuring the time dependence of the optical reflectivity from a silicon substrate with spatially isolated nanodiamonds is presented. The shape of the time dependence curve of the reflectivity in the process of the CVD growth is described in the framework of the Mie scattering on the diamond particles. The presence of characteristic resonances on the time dependence of the reflectivity curve enable to monitor the CVD growth rate and the change in the diamond particle sizes. The nanodiamonds produced by reactive ion etching of diamond particles are characterized by a narrow Raman line of diamond at 1332.5 cm\(^{-1}\), the FWHM of which does not exceed 2.4 cm\(^{-1}\). Reactive ion etching in oxygen plasma removes from nanodiamonds the most defective parts having inner strains responsible for the inhomogeneous broadening of the ZPL of SiV colour centres. We have shown that in situ optical monitoring of the growth and etching processes provide reproducible fabrication of high crystalline quality nanodiamonds.

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