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Nitrogen and group-IV (Si, Ge) vacancy color centres in nanodiamonds: photoluminescence study at high temperature (25 °C–600 °C)

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Abstract

Raman scattering and photoluminescence measurements have been carried out on nano-diamonds containing Nitrogen-vacancy (NV−), Silicon-Vacancy (SiV−) and Germanium-vacancy (GeV−) synthesized by high pressure and high temperature method. Optical zero-phonon-line transition of these negatively charged centres were measured from room temperature up to 600 °C under air. The results show that all nano-diamonds are stable at this temperature range and spectra are reproducible for heating and cooling cycles. Thermal behaviors of linewidth and zero phonon line, for SiV− and GeV− centres, are well described by the second-order electron-phonon interactions involving two-phonon and elastic processes.

1. Introduction

In recent years, color centres in diamond have attracted much interest for research due to their new quantum technology applications (information processing, communications, metrology). The most interesting centers are the negatively charged vacancy point defects as the negative nitrogen-vacancy (NV−) and the group-IV vacancies (SiV−, GeV−, SnV− and PbV−). NV− centre is the most popular one due to its photo-physical properties and a large potential application such as bio-imaging, electric and magnetic field sensors and thermometry at nanoscale [1–5].

Thermometry applications are one of the potential applications of color centres in diamonds [6–10]. Most of these applications concern precise temperature sensors around room temperature in living organisms based on the thermal dependence of their photoluminescence spectra [8, 10]. NV centers however suffer of low intensity of its zero-phonon line (ZPL line) notably around room temperature, which complicates line position measurements [8, 10–17]. ZPL line position of NV centres is also dependent on other factors such as strain and impurities. Other color centres having strong ZPL line (SiV−, GeV− and SnV−) could be an alternative to the NV centres for this thermometry applications. Group-IV vacancies in nano-diamonds were reported to be more adequate to be employed in such application [7, 14, 18–26]. High temperature applications could also be considered in small systems for example like rubies used in cell anvil to measure the pressure. All these applications require a good control of the synthesis process and a good understanding of the mechanisms driving the transition energy of the ZPL line in a wide range of temperature. Most thermal line dependence investigations have been done at temperatures lower than 400 K, and to our knowledge the only study making measurements above 400 K (up to 600 K) has been done on NV− centre [27]. Several of them have explained the ZPL line shift and the line broadening by electron-phonon interactions originating from the dynamic Jahn-Teller effect. This thermal behavior is thus determined by the excited state population transfer and the relaxation rates between orbitales. In such a case, linewidth broadening and line shift of the ZPL line vary as T5 for NV− centres [28–31] and as T3 for SiV− and GeV− centres [7, 32, 33] for temperatures lower than room temperature. These different investigations are carried out at temperatures far from the Debye temperature of diamond,
which allow approximations that cannot be valid at higher temperatures. In this sense, we have investigated both Raman phonon of diamond and photoluminescence (PL) spectra for NV\(^{-}\), GeV\(^{-}\) and SiV\(^{-}\) color centres in nano-diamonds for temperatures ranging from 298 K up to 873 K (25 °C–600 °C).

2. Experimental details

Nano-diamonds with NV, SiV and GeV impurity-vacancy color centres were obtained by high pressure - high temperature (HPHT) treatment of the catalyst metals-free hydrocarbon growth system based on homogeneous mixture of Naphthalene—C\(_{10}\)H\(_{8}\) (Chemapol), with hexamethyleneetramine—C\(_{6}\)H\(_{12}\)N\(_{6}\), tetrakis(trimethylsilyl)sylane—C\(_{12}\)H\(_{40}\)Si\(_{6}\) (Stream Chemicals Co) and tetraphenylgermanium—C\(_{24}\)H\(_{20}\)Ge, respectively. Cold-pressed tablets of the initial mixture (5 mm diameter and 4 mm height) were placed into a graphite container, which simultaneously served as a heater of the high pressure Toroid-type apparatus [34–36]. The experimental procedure consisted of loading the high-pressure apparatus to 8.0 GPa at room temperature, heating the sample to the temperature of diamond formation (∼1400 °C) and short (3 s) isothermal exposure of the sample at this temperature. The resulting high-pressure states were quenched to room temperature under pressure. Obtained diamond materials were treated by a mixture of acid (mixture of HNO\(_{3}\), HClO\(_{4}\) and H\(_{2}\)SO\(_{4}\)) at 250 °C for 4 h, then neutralized with NH\(_{4}\)OH and washed with distilled water. The recovered diamond materials were characterized under ambient conditions by means of x–ray diffraction, Raman spectroscopy and scanning and transmission electron microscopies (SEM and TEM).

Raman and fluorescence spectra were recorded between room temperature and 600 °C under air. A 514 nm of Ar–Laser line was used as the excitation source with power of 1 mW. The incident light was focused by x50 lens (spot size ∼2 \(\mu\)m of diameter) and, the scattered and the emitted light were collected in the backscattering configuration. For all samples, after the set temperature was reached, the temperature was stabilized for 10 min before spectrum acquisition.

3. Results

Figure 1 shows spectra obtained at room temperature on nano-diamonds doped with nitrogen (ND-N), silicon (ND-Si) and germanium (ND-Ge). One can observe a narrow peak at about 550 nm in all spectra noted T\(_{2g}\). This peak corresponds to the first-order Raman T\(_{2g}\) phonon line of diamonds. In addition, ND-N, ND-Si and ND-Ge spectra show, respectively, a line at about 638 nm, 738 nm and 602 nm corresponding to the fluorescence (zero-phonon line emission) related respectively to the negative vacancy of nitrogen (NV\(^{-}\)), silicon (SiV\(^{-}\)) and germanium (GeV\(^{-}\)) color centres [7, 20, 37–42]. NV\(^{-}\) centre corresponds to a substitution of a carbon atom by a nitrogen atom, which produces a pair of nitrogen atom and a lattice vacancy. This point defect in diamond has an additional electron and its site symmetry is C\(_{3v}\). The optical transition observed in photoluminescence spectra involves the ground state \(^3\)A\(_2\) and the excited state \(^3\)E [1, 28–30, 43, 44]. GeV\(^{-}\) and SiV\(^{-}\) centres correspond to a
germanium or a silicon atom centered between two neighboring vacant lattice sites. The $D_{5h}$ point defect gives rise to the optical transition occurring between $^2E_g$ ground state and $^2E_u$ excited state [7, 20, 32–38, 42, 45, 46].

3.1. First-order Raman line of diamonds

The thermal behavior of the first-order Raman phonon line of diamonds, between 25 and 600 °C, is shown in figure 2(a) for ND-Si as an example. For ND-N, ND-Ge and ND-Si, the line presents the same evolution for heating and cooling cycles. By increasing the temperature the phonon line softens and broadens. Also, the spectral line profile remains invariant during heating and cooling cycles. This behavior strongly suggests that the nano-diamonds are not affected by heating up to 600 °C. As a result, nano-diamonds are stable at this temperature range and the thermal treatment induces neither order nor disorder in the diamond structure, even after 3 cycles (not shown here). To compare results obtained on the three doped nano-diamonds, Lorentzian fit to the experimental data was chosen to extract line position and linewidth (Full Width at Half Maximum). As shown in figure 2(b), line positions versus temperature for ND-N, ND-Ge and ND-Si are very close, and decreases as the temperature increases corresponding to the standard thermal behavior of phonon mode. This variation is in accordance with several results reported in the literature [47–51].

The line lowering of a phonon mode is essentially due to harmonic contribution of the thermal lattice expansion and to the anharmonic contribution from other phonons called ‘thermal bath’. Firstly, it is known that the harmonic contribution does not affect the linewidth. Thus the linear dependence of the linewidth versus the line position (inset of figure 2(b)) suggests that the lattice expansion does not contribute to the line shift [48, 52]. The line shift could then be attributed to the anharmonic contribution.

In the literature two principle analytical expressions of this effect are commonly used and both are based on the coupling between zone-center phonons and acoustic modes. The first expression, largely adopted and used in several studies, was first proposed by Klemens [53] and Cowley (the cubic anharmonic term) [54] and modified later by Balkanski et al. (the quartic anharmonic term) [55]. The second expression was proposed by Kolesov [47], where the anharmonic contribution also has two contributions. The first one is due to the thermal population of the phonon itself with energy of $\hbar \omega_1$ and a phonon with less energy from the thermal bath with energy of $\hbar \omega_i$. Kolesov [47] reported that the experimental line shift of diamonds is well described including contribution from $T_{3g}$ phonon itself and the transverse acoustic phonon at $L$ point located at 540 cm$^{-1}$. As shown in figure 2(b) (dashed line), the proposed expression and parameters reported by Kolesov ($\omega_0 = 1333$ cm$^{-1}$, $\omega_i = 540$ cm$^{-1}$, $C = -63$ cm$^{-1}$ and $C_i = -7$ cm$^{-1}$) fit our data as well [47].

3.2. Emission line of color centres

Figure 3 shows photoluminescence (PL) spectra at various temperatures for ND-N, ND-Ge and ND-Si for the heating (gray lines) and the cooling (red lines) cycles. PL intensities were normalized after the removing background. Spectra for all nano-diamonds are reproducible for each temperature as was observed for the first-order Raman line corroborating the unchanged structure of diamonds in this temperature range. The temperature dependence of ZPL line, for NV$^-$, GeV$^-$ and SiV$^-$ centres, presents a decrease in intensity, a red
shift and a broadening as the temperature is increased. Note that the PL line is partially masked by the large background emission for ND-Si at 600 °C (figure 3(b)). In addition, spectra collected on ND-N show that NV$^-$ line is no longer visible above 150 °C because of its low intensity and the presence of the broad intense band around 700 nm (figures 3(c) and 1).

In order to quantify these observations, a Lorentzian line-shape was used to fit the lines to extract line position and linewidth. These parameters are of great importance for potential applications in thermometry and in quantum information processing, and equally so for better understanding mechanisms driving the ZPL line. The temperature-dependent evolution of the linewidth (FWHM) is shown in figure 4. At room temperature, NV$^-$, GeV$^-$ and SiV$^-$ centres present comparable widths, which are very close to that reported in the literature for GeV$^-$ and SiV$^-$ [7, 32, 39]. To our knowledge, there is no available data for NV$^-$ centres despite the numerous studies. Due to this lack of published information, we will now focus on linewidth evolution of GeV$^-$ and SiV$^-$ centres for which data are available at low temperature (T < 400 K). Indeed, Jahnke et al [32] and Fan et al [7] have measurements between 4 and 350 K and 80 and 400 K, respectively. They reported that the thermal linewidth evolution scales as $T^2$. Unfortunately attempts to fit our experimental data, using this temperature exponent, failed as it can be seen in figure 4. However, our data are well described by a temperature exponent.

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**Figure 3.** Normalized photoluminescence spectra as a function of temperature for (a) ND-Ge, (b) ND-Si and (c) ND-N during heating (gray lines) and cooling (red line) cycles.

**Figure 4.** Thermal evolution of linewidth for NV$^-$, GeV$^-$ and SiV$^-$ centres. Dashed and dot-dashed lines are the fit using $T^2$ (this work) and $T^3$ (after [7, 32]) behaviors, respectively. Γ$^\circ washer$ corresponds to the linewidth at low temperature (∼0 K).
Figure 5. Transition energies of the ZPL line as a function of temperature for (a) ND-N, (b) ND-Si and (c) ND-Ge. Open symbol stands for experimental data, dashed lines are the fit to equation (2) and dot-dashed lines are the fit after [7, 28, 32]. Dot lines correspond to the calculated lattice contribution.

In general, the ZPL line shift is a result of lattice thermal expansion ($\Delta E_{\text{latt}}$) and electron-phonon interactions ($\Delta E_{\text{e-ph}}$) [7, 28, 32, 39]. Only the later interactions contribute to the linewidth broadening. The overall line redshift is expressed thus as

$$E(T) = E_0 - [\Delta E_{\text{latt}}(T) + \Delta E_{\text{e-ph}}(T)]$$  \hspace{1cm} (1)

where $E_0$ is the line energy at 0 K.

The shift induced by the lattice expansion is $\Delta E_{\text{latt}}(T) = A \times B \times \int_0^T \alpha_V(T')dT'$ where A is the hydrostatic pressure shift of NV', GeV' or SiV', and B and $\alpha_V(T)$ are the bulk modulus and the thermal expansion coefficient of diamond, respectively. Pressure shift A is known for all centres studied here [40, 41, 44], other parameters of diamond are well known, bulk modulus is $B = 442$ GPa [56–60] and thermal expression of $\alpha_V(T)$ can be obtained from the polynomial fit to experimental data. By taking data reported in [58], in the temperature range 50–1000 K, and polynomial function: $\alpha_V(T) = \sum_{i=1}^{4} \epsilon_i T^i$ [28, 61, 62, 63], a set of $\epsilon_i$ coefficient values were obtained (table 1). Note that these coefficients are completely different from those used by Doherty et al [28], taking from [62], to study the PL line evolutions of NV' centres. Indeed, their coefficients

close to 2. As shown in figure 4, both $T^2$ and $T^3$ curves present a small difference up to 400 K; above this temperature, a deviation between them is observed, which becomes more and more important as the temperature is increased.

The temperature-dependent evolution of the transition energies are shown in figure 5. As the temperature is increased, energies present a redshift in agreement with studies done at lower temperatures. Note that the redshift of lines of SiV' and GeV' centres is more than 30 meV, between 25 °C and 600 °C, which is 3 times higher than the variation reported at low temperatures [7, 32, 39].

4. Discussion

In general, the ZPL line shift is a result of lattice thermal expansion ($\Delta E_{\text{latt}}$) and electron-phonon interactions ($\Delta E_{\text{e-ph}}$) [7, 28, 32, 39]. Only the later interactions contribute to the linewidth broadening. The overall line redshift is expressed thus as

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are only valid in the temperature range of 0–300 K and do not correctly describe experimental thermal expansion coefficient data above 300 K.

The thermal line lowering and also linewidth broadening dependences were well described by the electron-phonon interactions resulting from the linear Jahn-Teller interactions between electronic states and E-symmetric acoustic phonon modes [28–30, 33, 46]. The contribution of electron-phonon interactions is defect symmetry dependent. For NV$^-$ centre (C$3v$ symmetry), inelastic Raman processes dominate that scales as $T^3$ [28–30]. Elastic Raman processes however is dominant for SiV$^-$ and GeV$^-$ centres (D$_{3d}$ symmetry), which predicts a $T^4$ dependence [7, 32, 33] at low temperature ($T \ll T_D$, $T_D$ corresponds to the Debye temperature).

On the one hand and due to a lack of data at high temperatures for line shift of NV$^-$ centre, we used the same equation and parameter values reported by Doherty et al [28]. As shown in figure 5(a), our data are in accordance with those of [28]. However, we observe a certain discrepancy at high temperatures, which is better described if we use parameters of the thermal expansion of diamonds reported in this work. This result validates our choice of the coefficients of the thermal expansion expression.

On the other hand, for SiV$^-$ and GeV$^-$ centres, the electron-phonon contributions to the line shift follow $T^2$, $T^3$ or $T^4$ dependence as reported by some authors. Considering these possibilities, we have therefore expressed this contribution as $E_{\text{e-ph}}(T) = b_m T^m$. The overall line shift is then

$$E(T) = E_0 - A \times B \times \left\{ \frac{1}{2} e_1 T^2 + \frac{1}{3} e_2 T^3 + \frac{1}{4} e_3 T^4 + \frac{1}{5} e_4 T^5 \right\} - b_m T^m$$

(2)

Firstly, experimental data were fitted to equation (2) with $m$ and $b_m$ as adjustable parameters after removing lattice contribution. Energy $E_0$ values were set at values after [7, 32]. Obtained values for $m$ were found to be very close to 2 [2.12 (8) and 2.04 (4) for GeV$^-$ and SiV$^-$, respectively]. This suggests that electron-phonon contribution to the line shift scales as $T^2$ rather than $T^3$ reported for temperatures lower than 400 K [7, 32]. Assuming that $m = 2$, a new fit was carried out in order to extract $b_m$ values shown in table 2. Other parameters, $A$ and $E_0$, values, used in the fit procedure are also added in this table. The corresponding curves were added to figures 5(b) and (c) together with the calculated Lattice expansion contribution and fit curves reported in [7, 32], for temperatures lower than 400 K using $T^3$ dependence. Note that in both references, the authors have neglected the lattice thermal expansion contribution in their fit procedure.

The obtained $b_m$ values for SiV$^-$ and GeV$^-$ are very close, suggesting comparable contribution of the electron-phonon interactions to the line shift for both centres. This result corroborates the same thermal linewidth evolutions for both centres (figure 4). As mentioned above, the linewidth broadening and the line position shift of the ZPL transition are essentially due to the second-order electron-phonon interactions. Jahneke et al have proposed a model where the electron-phonon process results from the linear Jahn-Teller interactions between the electronic states and acoustic modes [32]. In SiV$^-$ and GeV$^-$ centres, the elastic two-phonon Raman processes are dominate and the scattering rate, after thermal average over the initial states and the sum over all final states, is given by [32]

$$\gamma_d \propto \frac{1}{\Omega_D} \int_{0}^{\Omega_D} n(\omega, T) [n(\omega, T) + 1] \omega^2 d\omega$$

(3)

where $\Omega_D$ is the Debye frequency of diamond and $n(\omega, T)$ is the thermal distribution of vibrational occupations ($n(\omega, T) = 1/\left[e^{\mu/\hbar}\omega/kT - 1\right]$). The substitution of $x$ for $\hbar\omega/kT$ into equation (3) gives

$$\gamma_d \propto T^3 \int_{0}^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} dx$$

(4)

with $x_D = T_D/T$ and $T_D = 2230$ K corresponding to the Debye temperature of diamond.

| Table 1. Fit Parameters of the thermal expansion of diamond, $e_i$. Experimental data are taken from [38]. |
|---------------------------------------------------------------|
| $e_1$(K$^{-2}$) | $e_2$(K$^{-2}$) | $e_3$(K$^{-4}$) | $e_4$(K$^{-4}$) |
| Diamond | $-5.36(28) \times 10^{-9}$ | $7.59(15) \times 10^{-11}$ | $-8.98(24) \times 10^{-14}$ | $3.27(13) \times 10^{-17}$ |

| Table 2. Fit parameters for GeV$^-$ and SiV$^-$ obtained from the fit of experimental data to equations (2) and (6), a, b, c and d correspond to [7, 32, 40, 41, 44]. |
|---------------------------------------------------------------|
| Parameter | GeV$^-$ | SiV$^-$ | NV$^-$ |
| A (meV.GPa$^{-1}$) | 3.11(3)$^a$ | 1.09(3)$^a$ | 5.75(7)$^a$ |
| $b_m$ ($10^{-5}$ meV.K$^{-2}$) | 4.7(1) | 5.9(2) | — |
| $b_3$ ($10^{-8}$ meV.K$^{-4}$) | 2.41(4) | 2.29(4) | — |
| $E_0$ (eV) | 2.062$^b$ | 1.683$^a$ | 1.946 |


At lower temperature limit, \( T \ll T_D \), the upper limit of the integral tends to infinity and the integral becomes equal to a constant. The rate is thus proportional to \( T^3 \), which explains thermal behavior of the linewidth and line energy for temperatures lower than 300 K \([7, 32]\). At higher temperature limit, \( T \gg T_D \), \( x_D \ll 1 \) and justifies the approximation of the exponential \( e^x \sim 1 + x \). The integral is then proportional to \( (1/T + 1/T^2) \) and the rate scattering is proportional to \( (T^2 + T) \). It can thus be assumed that the rate may roughly scales as \( T^2 \) since this term will dominate at high temperatures.

For intermediate temperature, which is the case in this work, numerical calculations could be performed to evaluate temperature dependence of the integral. Doing so, the calculated integral was established to vary as \( (1/T - 1/T^2) \) in the temperature range 400–1000 K. Therefore, the rate scattering can be considered as proportional to \( \sim T^2 \) at the first approximation. This could explain thermal behavior of the linewidth and the line shift of our experimental results obtained for SiV\(^-\) and GeV\(^-\) centres. Moreover, complete calculations can be performed using exact numerical values of the integral at each temperature to evaluate electron-phonon interactions to both parameters.

Figure 6 compares, for SiV\(^-\) and GeV\(^-\) centres, the temperature dependence of the measured and the calculated electron-phonon contribution to the ZPL line shift. Experimental and calculated values are shown in insets of figure 6. The values of b\(_3\) parameter used for the calculations are shown in table 2. The experimental data are well described by this model and show that the line broadening has only electron-phonon contribution. Our results corroborate thus the microscopic model established by Jahnke et al \([32]\). Temperature dependence of both linewidth and line shift are thoroughly explained by a two-phonon Raman process where the elastic Raman-type scattering processes dominate for the relaxation rates. Otherwise, one can
observe that b values for SiV− and GeV− centres are very close indicating the same electron-phonon interactions for both centres, which accentuated by the same thermal evolution of their linewidth.

5. Conclusion

Temperature-dependence of Raman scattering and photoluminescence measurements were made on nano-diamond, containing NV−, GeV− and SiV− color centres, obtained by a high pressure and high temperature method. Raman phonon mode of diamond showed the same thermal behavior in peak position and linewidth for all nano-diamonds. The transition associated with the zero-phonon line of NV−, GeV− and SiV− centres presents a red shift and a broadening as the temperature is increased. This behavior is explained by cell expansion and electron-phonon interactions. For SiV− and GeV− centres and for temperature range of 25 °C–600 °C, linewidth and line shift were found to scale as T² rather than T observed at temperatures lower than 25 °C. A complete analysis, however, based on a second-order electron-phonon interactions has been performed and the predictions are consistent with these temperature-dependence. Our results also demonstrate that electron-phonon interactions are of comparable contribution for both GeV− and SiV− color centres.

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