Accelerated aggregation of donor nitrogen in diamond containing NV centers

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The aggregation of donor nitrogen (C centers) into nitrogen pairs (A centers) is considered to be a second-order chemical reaction and the kinetics of this reaction can be written as follows:

$$K_t = \frac{1}{C_t} - \frac{1}{C_0}$$

where $K$ is the aggregation rate constant that depends exponentially on temperature and activation energy

$$K = A exp(-E_a/kT)$$

and $C_0$ and $C_T$ are C center concentrations before and after the aggregation. The activation energy $E_a$ in natural diamonds is equal to 5\pm0.3 eV. However, it was shown by Vins (2004) that $E_a$ varied in synthetic diamonds depending on Ni concentration from 3 to 6 eV; and in synthetic diamonds containing cobalt the activation energy exceeded 4 eV. The aggregation rate of C centers also increased dramatically in diamonds irradiated with high-energy electrons (Collins, 1980).

An HPHT diamond single crystal grown in the Fe-Co-C system using the TGG method was studied. The initial C center concentration determined from the intensity of the 1130 cm$^{-1}$ IR absorption band was equal to 118 ppm. In order to determine the influence of NV centers on the activation energy of aggregation, the crystal was first irradiated with high-energy electrons (3MeV, $2\times10^{18}$ cm$^{-2}$) and annealed in a quartz ampoule in vacuum (800°C, 2 hrs). This led to the formation of over 5 ppm of NV centers. After that the sample was annealed at high temperatures in the argon flow (1530°C, 30 minutes). The IR absorption spectra revealed an absorption band due to A centers with an intensity of 5.3 cm$^{-1}$. The concentration of C centers ($C_1$) was 36 ppm and the absorption attributed to NV centers completely disappeared. Then the crystal was repeatedly irradiated with the same dose (3MeV, $2\times10^{18}$ cm$^{-2}$) and annealed in vacuum (800°C, 2 hrs), which led to the formation of NV centers and defects that derived from nitrogen pairs: H3 and 4568 cm$^{-1}$. Subsequent high temperature annealing in the argon flow (1630°C, 10 minutes) resulted in further nitrogen aggregation, with the concentration of C centers decreasing to $C_2=22$ ppm. Only absorption due to A and H3 centers was also observed in the spectra.

Assuming that A, H3 and 4568 cm$^{-1}$ defects do not significantly influence the kinetics of C-center aggregation, which is to be proved, the equations defining the aggregation will be as follows: after the first HT annealing $K_1 \cdot t_1 = 1/C_1 - 1/C_0$, and after the second $K_2 \cdot t_2 = 1/C_2 - 1/C_1$. Dividing one equation by another and finding the logarithm of both parts, we get:

$$E_a = k \times [(T_1 \times T_2)/(T_2 - T_1)] \times \ln\left[\frac{1}{3} \times \left(\frac{C_0 - C_1}{C_1 - C_2}\right) \times (C_2/C_0)\right] = 2.9 \pm 0.5\text{eV}.$$
The calculated activation energy is substantially lower than $E_a$ of C center aggregation in Co-containing diamonds which were not exposed to high-energy electron irradiation. Therefore, NV centers substantially decrease the energy barrier of C center aggregation.