Chapter 12
Modification of Diamond by Irradiation and Heat

More optical centers are observed in modified diamond than in natural diamond. An example is given by the 75 centers of intrinsic defects and associates in Chap. 8, where only 24 occur in natural diamond.

An important method in creating additional defect centers in diamond is the irradiation with X-rays, high energy electrons, or fast neutrons (Sect. 12.1).

Ion implantation is used to introduce specific impurities with simultaneous radiation damage (Sect. 12.2).

With heat treatment, the migration of intrinsic defects and of impurities is activated. Both aggregation and dissociation can occur, i.e., new defect centers are created or annealed out (Sect. 12.3).

12.1 High Energy Irradiation by X-rays, Electrons, or Neutrons

The basic radiation damage is the displacement of a carbon atom from its lattice site, leaving behind one vacancy and one self-interstitial. Also some lattice disorder occurs. The three types of irradiation differ by their penetration depth and by the resulting lattice disorder.

12.2 Ion Implantation

With ion implantation and subsequent annealing at 800–1,400 °C, optically active centers of He, Li, Ti, Cr, Zn, Ag, Xe, and Tl have been successfully produced (see Tables 8.1.7.1 and 8.1.7.2). All these centers are associated with one or two vacancies. Nitrogen ion implantation is very efficient in producing nitrogen containing optical centers in diamond. One example is the $^{*}(C_2)_iN_I^-$ center at

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3.188 eV (see Table 8.2.3). With carbon ion implantation the just mentioned center can also be obtained. For many ions the implantation did not produce optical centers (Be, F, Na, S, Cu, Ga, Y, Nb, Mo, Pd, Cd, Sb, and Au) [Zai00a].

12.3 Heat Treatment

Heat treatment is a powerful tool to remove lattice disorder after irradiation or ion implantation. The self-interstitial $(C_2)_i^\circ$ with a migration activation energy of 1.7 eV anneals out at temperatures of 420–700 °C. At slightly higher temperatures, i.e., 500–1,000 °C the single vacancy anneals out, having a migration activation energy of 2.4 eV [Mai94b].

At higher temperatures, a protecting pressure is necessary during anneal to avoid graphitization. This is usually accomplished by using the same apparatus as for HPHT diamond growth.

The heat (1,500–1,900 °C) induced nitrogen aggregation (N_1° (C center) to N_2° (A center) to $V_1N_4^\circ$ (B center)) is described in Sect. 9.1.6.1 for *nonirradiated* samples. In the presence of vacancies (*irradiated* samples), association with nitrogen centers starts above 600 °C and centers are formed, which also occur naturally: NV ($= V_1N_1^\circ$) from N_1° (C center), H3 ($= V_1N_2^\circ$) from N_2° (A center), and H4 ($= V_2N_4^\circ$) from $V_1N_4^\circ$ (B center) (see Sect. 9.1.6.2).

For nickel centers in nitrogen-rich samples, interesting annealing effects occur in the range 1,500–1,900 °C (see Sect. 9.5.6 and Table 9.5.6). The quantitative transformation of $^*(V_3Ni_2)^\circ$ at 1.883 eV into $^*V_1Ni_2^+$ at 1.693 eV (at $T <$ 1,800 °C) has been documented [Law93a].

In a forthcoming book [Zai10] the optical changes, which result from HPHT treatment of diamond, are described in detail.