"Subthreshold" defect formation in natural diamond

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Occurrence of vacancies in diamond under bombardment by electrons with energies lower than the threshold energy for elastic discomposition is observed by the cathodoluminescence method. It is suggested that the vacancies develop as a result of decay of unstable ion configurations that include multiply ionized atoms of transition metals.

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Defects in solids may be produced by fast particles as a result of both elastic interaction with the lattice atoms and excitation of the electron system (ionization of inner atomic shells, production of electron-hole pairs, excitons and plasmons). Each of these defect-producing processes corresponds to a fixed particle threshold energy. As applied to diamond-like semiconductors "subthreshold" defect formation is traditionally the occurrence of defects due to bombardment by particles with energies lower than the energy required to knock out an atom from the site (E_d).[1,2] In spite of a large number of papers dealing with defect production in this energy region, convincing evidence has not been offered heretofore to support the occurrence of Frenkel pair

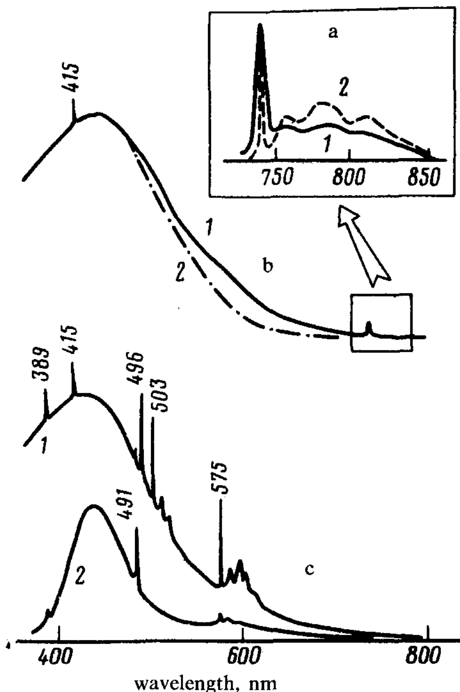

FIG. 1. a—CL spectra of 741-nm center (GR1) produced in diamond under electron bombardment with energy 10 keV (1) and H^+ ions with energy 100 keV (2); b—CL spectrum of type Ia diamond before (2) and after (1) bombardment by 10-keV electrons; c—CL spectra of type Ia (1) and type IIa (2) diamond after bombardment by 10-keV electrons and subsequent annealing at $T = 800$ °C.

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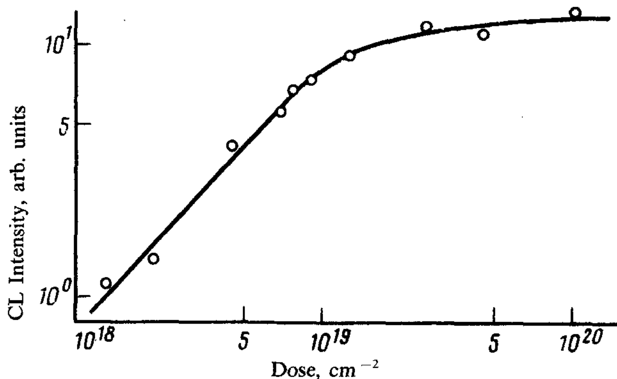

FIG. 2. Dependence of CL intensity of 741-nm (GR1) line on dose for 10-keV electrons.

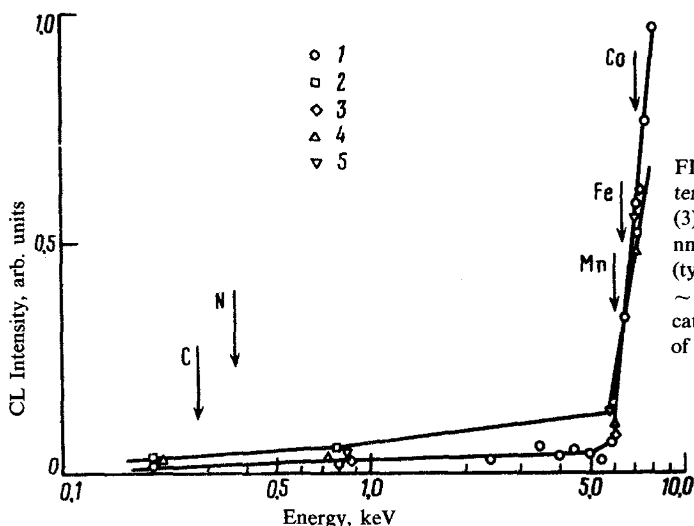

FIG. 3. Dependence of CL intensity of 741 (1), 491 (2), 575 (3), 503 and 496 (4), and 389 (5) nm centers on electron energy (type Ia diamond, exposure dose $\sim 5\times10^{18}$ cm^{-2}). Arrows indicate K-shell ionization energies of certain elements.

components, i.e., vacancies and/or interstitial atoms. This may be explained by the fact that the majority of workers investigate the macroscopic characteristics of a crystal (for example, conductivity), which are incapable of conveying information regarding the nature of the incipient defects. In this work the cathodoluminescence (CL) method was used to obtain, for the first time direct evidence for the occurrence of vacancies in diamond under bombardment by electrons with energies $E = 6$–10 keV (in diamond, E_d for electrons ~ 200 keV[2]).

Type IIa (nitrogen-free) and type Ia (nitrogen concentration $\sim 10^{19}$ cm^{-3}) diamonds were bombarded (and CL was excited) by electrons with E from 0.2 to 10 keV at the temperature $T \approx 80$ K, and were annealed at temperatures $T \leqslant 1400$ °C. Inasmuch as the exposure dose sustained by a specimen during the spectral registration ($\sim 10^{15}$ cm^{-2}) was much smaller than the dose required to introduce defects ($\gtrsim 10^{17}$ cm^{-2}), we shall neglect defect production during the measurement period.

In the CL spectra of irradiated diamonds beginning with doses of $\sim 10^{17}$ cm^{-2},

luminescence lines and bands are observed, a portion of which is attributable to the known optical centers in diamond (Fig. 1). The 741-nm line and the bands A_s ($\lambda_{max} \sim 500$ nm) and B_s ($\lambda_{max} \sim 580$ nm) occur immediately after bombardment; the 491-nm line occurs after heating to room temperature, and lines associated with the nitrogen centers (389, 575, 496, 503 nm) occur after annealing at $T \gg 500$–600 °C. It may be taken for granted that the 741-nm line—observed in any diamond—is associated with a vacancy (the so-called GR1 center), and the 503-nm line—observed in nitrogen-containing diamonds only—with a compound defect that includes two neighboring substituting nitrogen atoms (the so-called A-form) and two vacancies.[3-5] The occurrence of these lines confirms the fact that the vacancies actually occur in a diamond bombarded by electrons with energies considerably below E_d.

The intensity dependence of all the lines excited by bombardment on the exposure dose is characterized by a well-defined saturation (Fig. 2).

The line intensity strongly varies from specimen to specimen for the same dose. This indicates that the vacancies are formed with the participation of some impurity. Furthermore, dependence of line intensity (for the same dose) on electron energy has a distinct threshold at 6–7 keV (Fig. 3). The presence of a threshold in this energy region is characteristic of the ionization mechanism of defect formation,[6] whereby as a result of ionization of the deep-seated atom shell and the subsequent Auger process. There occurs an unstable ion configuration that disintegrates into defects. In germanium crystals,[7] the latter consists of a multiply ionized Ge atom and a singly ionized donor. In diamond, the impurity and not the host lattice atom is ionized; moreover, the impurity is relatively heavy since the ionization energy of the K-shell of a C or N atom is substantially lower than the observed threshold energy (Fig. 3). Inasmuch as the latter is nearly equal the K-shell ionization energy of the transition elements Mn, Co, Fe (~ 6.5 keV) that, as a rule, are present in diamond, it is natural to suppose that these impurities indeed take part in the process of defect formation (indirectly, this is confirmed by the amplification of the 491-nm line in crystals containing implanted Fe atoms). The ionized carbon atom clearly cannot be the other partner in the unstable ion configuration, since this would indicate the occurrence of a hole (free carrier) alongside a multiply changed ion, with the dwell time—because of high hole mobility—much shorter than the time required for atom displacement. The most likely partner is some ionized donor residing near a transition metal atom. Thus, "subthreshold" defect formation observed in our experiments requires the participation of more than one impurity atom. The formation of nitrogen centers requires that the vacancies occur alongside nitrogen atoms or their complexes, since the temperature ~ 600 °C is inadequate for activating the vacancy mobility.[3]

The 741, 503, 496 nm vacancy center luminescence lines produced by electrons with energies $E < E_d$, are broader than those due to electron bombardment with $E > E_d$ (Fig. 1). Evidently, this is due to interaction between vacancies and both the transition metals and the nearest interstitial atoms. Broadening of the 741-nm line—observed for a low temperature bombardment by electrons with $E > E_d$[3]—may be similarly explained. We note that the broadening disappeared after annealing at $T \gtrsim 500$ °C, i.e., at a temperature close to the temperature at which annealing of the

GR1 centers, produced by subthreshold bombardment, takes place. Vacancy recombination with the nearest interstitial atom evidently occurs at these temperatures.

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