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EFFECTS OF THERMOLUMINESCENCE EXCITATION IN SEMICONDUCTING DIAMONDS

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ABSTRACT

Results are presented which indicate a clear connection between the excitation mechanisms of the 260 K and 150 K glow peaks in semiconducting diamond when excited at 80 K by λ=360 nm. Excitations in this wavelength region and with λ=225 nm at $T \geq 150$ K, however, seem to indicate that under these conditions, different mechanisms are involved. A model is discussed which takes into account the new observations.

INTRODUCTION

Thermoluminescence (TL) of semiconducting diamonds was first investigated by Halperin and Nahum (1). After excitation at 80 K (LNT) with uv light of 225 nm (5.5 eV), corresponding to the band to band transition, they found an intense blue glow peak at 250-260 K and a blue peak at ~150 K, both depending linearly on the radiation dose. The activation energies of these peaks were found to be 0.2 eV and 0.35 eV for the lower and higher temperature peak respectively. The latter value was in good agreement with 0.37 eV, the activation energy for release of holes in semiconducting diamonds as measured by electrical methods (2).

Halperin and Chen (3) showed that the two TL peaks could be excited also in the 300-400 nm region by employing higher light doses for excitation. For this wavelength range, the dependence of the 260 K peak on the radiation dose (D) was found to be super-linear at low doses. The maximum intensity of this peak increased

with D^n, where n depended on the excitation wavelength λ and showed values of up to 3. The 150 K peak depended linearly on the excitation dose.

The superlinear excitation was explained by assuming a multi-stage transition of electrons excited from the valence to the conduction band before being trapped at the center. This model was supported by the results of pre-excitation experiments (4). Emission spectra of the band to band excited TL in semiconducting diamonds have recently been measured by Walsh, Lightowlers, and Collins (5).

In the present work, a connection is established between the excitation of the 150 and 260 K peaks at different exciting wavelengths. The processes involved are discussed.

EXPERIMENTAL

The samples used were the C_2, C_3 and C_4 semiconducting diamonds (II_b) mentioned in the previous work (3). The crystal was mounted in a metal vacuum cryostat and was excited at LNT or at higher temperatures up to 300 K. A 900 Watt xenon arc lamp in conjunction with a Hilger and Watts D285 quartz monochromator was used for uv excitation. The emission was measured with a thermo-electrically cooled EMI9558 QB (S 20) photomultiplier. The signal was amplified by a Keithley 414S picoammeter and fed into the Y axis of a YEW 3073 X-Y recorder. The reading of a copper-constantan thermocouple attached to the crystal holder was fed into the X channel. The intensity of the exciting light was kept constant in each series of measurements. The time of irradiation was 1 minute for λ=225 nm and 10 minutes for 360 nm.

RESULTS AND DISCUSSION

The experiments consisted mainly of exciting the sample at various temperatures. Curve a of Fig. 1 is a typical blue glow curve excited with 360 nm light at LNT. The TL peaks appear at 155 K and 260 K, the height of the latter depending superlinearly on the excitation dose (3). Normally, the intensity of a peak is reduced substantially when excited at temperatures close to its maximum. This is indeed how the low temperature peak behaved as the temperature of excitation approached 150 K. This is shown in curve b, c and d which were obtained after excitation at 130, 140 and 150 K respectively. Excitation at temperatures below 110 K resulted in the same glow curve as 1 a. The behavior of the 260 K peak was surprising: it fell rather sharply as the temperature of excitation approached 150 K. When the temperature of excitation was above 150 K, the 260 K peak did not appear at all.

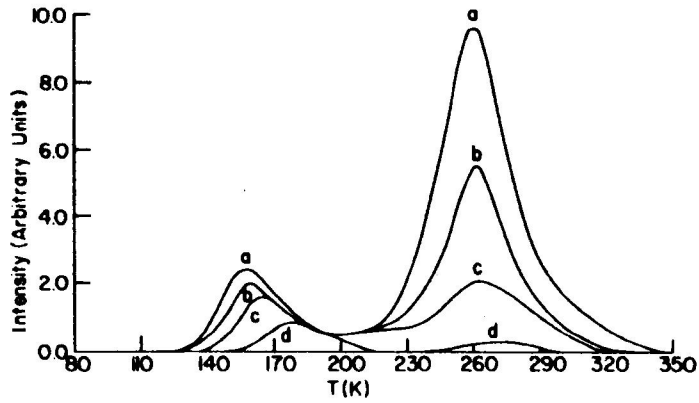

Fig. 1 Glow curves of semiconducting diamonds excited by 360 nm at LNT (curve a), 130 K (curve b), 140 K (curve c) and 150 K (curve d).

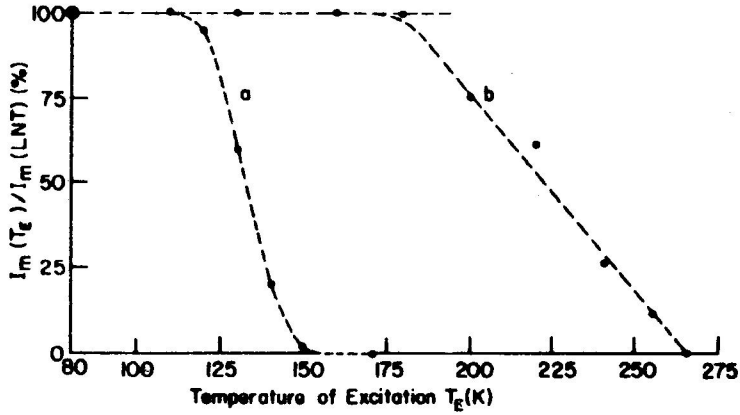

Fig. 2 The maximum intensity of the 260 K glow peak obtained at temperatures T_E divided by the maximum intensity found after excitation at LNT. Curve a gives the results for excitation with 360 nm and curve b for 225 nm.

The dependence of the maximum intensity of the 260 K peak on the temperature of excitation, (T_E) between 80 and 170 K is shown in curve a of Fig. 2 for excitation with 360 nm. In this curve, the Y axis represents the ratio (in percents) of the maximum intensity obtained at T_E, to that obtained after excitation at LNT. This ratio reduces sharply from 100% at 110 K to practically zero at 155 K.

The results of similar series of measurements but with excitation wavelength of 225 nm are shown in curve b of Fig. 2. In this case, the maximum intensity I_m remains constant up to 180 K and decreases rather slowly as the temperature of excitation approaches the temperature of the peak, 260 K.

The difference between the behavior of the 260 K peak excited by 360 nm and 225 nm is readily seen in Fig. 2. As explained before (1,3), the 225 nm light raises electrons from the valence band directly to the conduction band. These electrons are trapped at a level which acts later as a recombination center for thermally released holes. If T_E is relatively high, recombination may occur during the excitation due to the thermal release of trapped holes from the 0.35 eV trap. The occupation of the recombination center is thus expected to be lower than after excitation at LNT, resulting in a less intense glow peak.

The situation is different after excitations with 360 nm. It seems that this is due to the fact that one of the levels involved in the superlinear excitation (3,4) is unstable above 150 K. This may result from the relatively large number of free holes in the valence band at temperatures approaching 150 K. These holes are probably released from the 0.2 eV trap which is the one responsible for the 150 K peak. Since this intermediate state is unstable above 150 K, electrons cannot accumulate at this level and therefore electrons cannot reach the recombination center. This explains the connection between the change in the 150 K peak and the impossibility of exciting the 260 K peak above 150 K.

Although the 260 K peak could not be excited by 360 nm at $T_E>150$ K, irradiation at $150<T_E<200$ K prior to LNT excitation was found to substantially enhance the TL peak, compared to that produced by LNT excitation alone. This indicates that it is probably the second intermediate level of the multistage excitation proposed by Halperin and Chen (3,4) which is temperature unstable. This point is being further investigated presently.

In order to verify that it is one of the intermediate states which is unstable above 150 K and not the recombination center itself, the following measurements have been performed. The sample was irradiated at LNT with 360 nm for a certain period of time, then heated to 180 K and held at this temperature for 15 minutes, then cooled to LNT and heated as usual. The 260 K peak had then the same intensity as without intermediate heating. This supports the assumption that the instability above 150 K is related only to an intermediate state involved in the excitation and not to the recombination center.

The results described and discussed here give an additional

proof to the fact that excitation of the blue glow peak in semiconducting diamonds by light in the 300-400 nm range is due to an entirely different mechanism than the band to band excitation, with 225 nm.

ACKNOWLEDGMENT

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