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Linear–supralinear–sublinear beta-ray dose dependences of TL, OSL and afterglow in undoped CVD diamond

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The thermoluminescence (TL), optically stimulated luminescence (OSL) and afterglow (AG) properties of chemical vapour deposition (CVD) diamond film irradiated by beta rays with doses from 0.5 to 1000 Gy have been studied. The film (23 μm) was grown for 47 h on monocrystalline silicon. The TL dose responses are similar for all the peaks and exhibit the typical linear–supralinear–sublinear behaviour. The supralinear growth starts at about 1.0 Gy and goes up to 100 Gy. At higher doses the dose responses go to saturation. The AG and OSL dose responses are similar to the TL one and exhibit the supralinear–sublinear behaviour. The linear part (if it exists) is not observed due to low AG and OSL intensity at doses lower than 2.0 Gy. The diamond film that had been irradiated with high doses, partially preheated and irradiated again with low test dose, exhibits increased TL, OSL and AG sensitivity that can be considered as a mixture of the supralinearity and sensitization. Pure sensitization is observed for the 350 and 400 K TL peaks and AG after preheating the sample to temperatures higher than 500 K. This sensitization gradually decreases from 10 to 1 as the preheating increases from 500 to 770 K.

1 Introduction Chemical vapour deposition (CVD) synthetic diamond exhibits intense thermally and optically stimulated luminescence (TL and OSL, respectively) created by ionizing radiation or UV light, and is therefore considered as a promising dosimetric material for biomedical applications. The most important characteristic of any dosimeter is the dose response which should be linear for the broadest dose range. There are a number of publications where the TL and OSL dose dependences for undoped CVD diamonds have been investigated. The observed dependences are linear at low doses, but sublinear at higher doses until they finally reach saturation [1–4]. Several dependences [5–7], however, exhibit a supralinear behaviour which is manifested as an increase of the sensitivity (intensity divided by dose) as the dose increases. Similar linear–supralinear–sublinear dose response curves have been observed in many other thermoluminophors (the best known example of which is LiF:Mg,Ti [8]). The origin of the supralinearity is usually explained by a competition between traps during the excitation or readout stages (see Ref. [9] and references therein).

In this work we report the dose dependences of TL, OSL and afterglow (AG) of an undoped microcrystalline diamond film exposed to beta rays from 0.5 to 1000 Gy.

2 Experimental The studied diamond film was grown for 47 h on a monocrystalline silicon substrate by the CVD method in a hot filament diamond reactor using 1%CH_4/H_2 as process gases. The substrate was (100) oriented and had dimensions of about $0.5 \times 5 \times 5\ mm^3$. The thickness of the grown film was 24 μm and consisted of a polycrystalline layer with a columnar structure, with grain size at the surface of ~5 μm.

All measurements and procedures on the substrate covered with the diamond film were performed inside a Risø TL/OSL reader (model TL/OSL-DA-15). In this device, a cup with the sample is placed on a rotating table and automatically moved to several positions at which beta irradiation at room temperature (RT) and AG, TL and OSL measurements are performed. The time between the end of irradiation and the start of the measurements was equal to

40 s. The fixed position of the sample in the cup guarantees a good reproducibility of the experiments. The device is equipped with a 33 mCi ^{90}Sr-^{90}Y source for the beta irradiations and an IR laser (830 nm, ~0.36 W) for the OSL stimulation. According to the Risø device specifications, the indicated activity of the beta source corresponds to a dose rate of about 300 Gy/h in quartz. The stopping powers (in units of MeV cm^2/g) of diamond and quartz are closer than 5% for electron energies between 0.3 and 2.5 MeV [10], so that the absorbed dose rate in diamond could be taken as equivalent to that in quartz. AG and OSL decay curves were recorded at RT in the same way without and with IR light stimulation, respectively. The heating rate of the TL readouts was 2 K/s. To protect the photomultiplier the luminescence measurements were performed with a Schott BG-39 band-pass filter (transmission between 330 and 620 nm) in front of the photomultiplier.

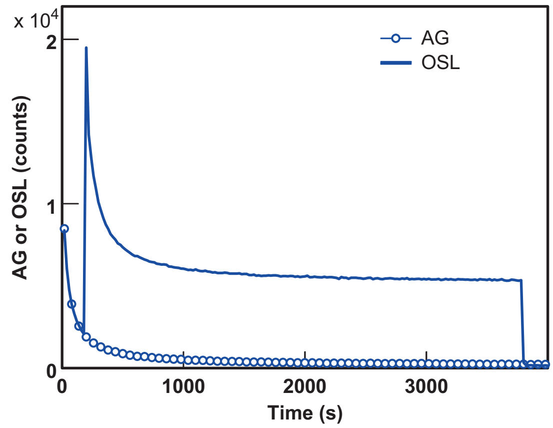

Figure 2 (online colour at: www.pss-a.com) AG and OSL decay curves recorded after beta irradiation with 10 Gy.

3 Results

3.1 TL, AG and OSL The TL glow curve of the CVD diamond film recorded after beta irradiation with 10 Gy is shown in Fig. 1. The glow curve exhibits two broad peaks and an intermediate part in between with unstructured TL. The structure of the glow curve was determined by a simultaneous deconvolution of a set of curves recorded after preliminary heating to various temperatures (see our article in this issue [11]). The TL glow curve was found to consist of five strongly overlapped TL peaks with temperatures of their maxima at 355, 419, 495, 547 and 588 K. The quality of the fitting can be seen in Fig. 1 where the deconvolution of the glow curve is also presented.

Immediately after beta irradiation at RT, the diamond film exhibits luminescence emission that is usually referred to as 'persistent luminescence' or AG.

Figure 2 shows the AG decay curve (points) recorded after the end of irradiation. The curve gradually decreases with time to a background level. The decay curve is fitted well by the phenomenological Becquerel's law [12].

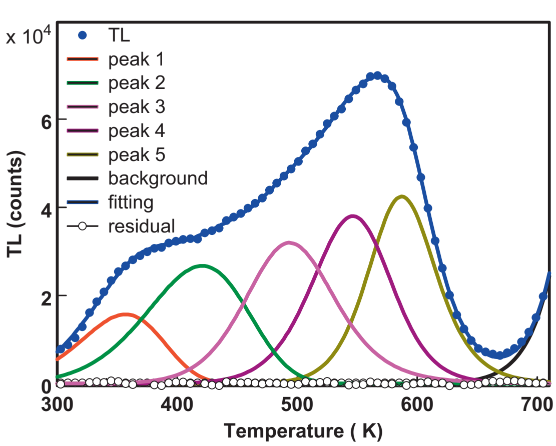

Figure 1 (online colour at: www.pss-a.com) Deconvolution into separate peaks of the TL curve recorded after beta irradiation with 10 Gy. The deconvoluted curves 1 to 5 are labeled sequentially from left to right.

Figure 2 also shows the effect of stimulation with 830 nm light on the luminescence of the beta-irradiated diamond film (solid line). When the IR stimulation is switched on (at 240 s after the end of irradiation), the luminescence intensity increases sharply due to the additional emptying of the traps by light. Further stimulation decreases the luminescence, which decays faster than the AG. Once the stimulation light is switched off, the luminescence intensity drops rapidly down to the background level (It should be mentioned that the background level depends on the IR stimulation power).

3.2 TL dose dependences The TL glow curves and the TL dose response in the beta dose range of 0.5–1000 Gy were obtained with a sequence of irradiations during 6–12 000 s, TL readouts from RT up to 770 K and cooling to RT during 300 s. It should be especially noted that irradiation with high doses followed by TL readout to 770 K does not change the sensitivity of the sample. The selected TL glow curves recorded after beta irradiation are depicted in Fig. 3a. Because of the large variation in intensities, the curves are presented on a semilogarithmic scale.

From Fig. 3a, it is clear that as the dose increases the TL intensity increases systematically and goes to saturation. The shape of the curves also changes. This is seen more clearly in Fig. 3b, which displays the TL curves following background subtraction and normalization to the absorbed dose. The curves exhibit a complicated behaviour due to the different dose response and, maybe, a shape change of the individual TL peaks with dose. It is impossible to obtain the correct dose responses of the individual TL peaks without careful deconvolution of the TL glow curves, for which an additional study is needed. Therefore, in this work we will evaluate the behaviour of the TL intensity at 350 and 540 K (averaged over 10 K neighbouring points). These temperatures correspond to the two pronounced maxima on the high-dose curves and should reflect reasonably the behaviour of the low and high temperature TL peaks.

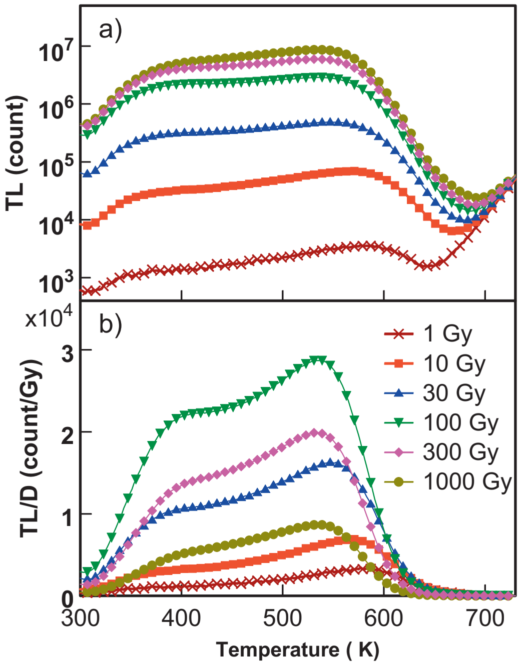

Figure 3 (online colour at: www.pss-a.com) (a) TL curves recorded after beta irradiation with indicated doses (note the semi-logarithmic scale). (b) The curves from (a) after being background subtracted and normalized to dose.

The TL dose responses at 350 and 540 K for beta irradiation (background subtracted) are presented in Fig. 4. The dose response curves are similar for both temperatures, and exhibit the typical linear–supralinear–sublinear behaviour. The supralinear growth starts at about 1.0 Gy and goes up to 100 Gy. At higher doses the dose response goes to saturation. The possible reasons for the saturation are the decay (fading) of the TL peaks during irradiation and/or the saturation of the traps and recombination centres due to their low concentration. The first reason is more probable for the low-temperature peaks. The second one can limit the TL response of any peak. The similarity of the dose responses in the saturation dose range may indicate the same origin for the saturation of all the TL peaks, and probably the saturation of the recombination centres.

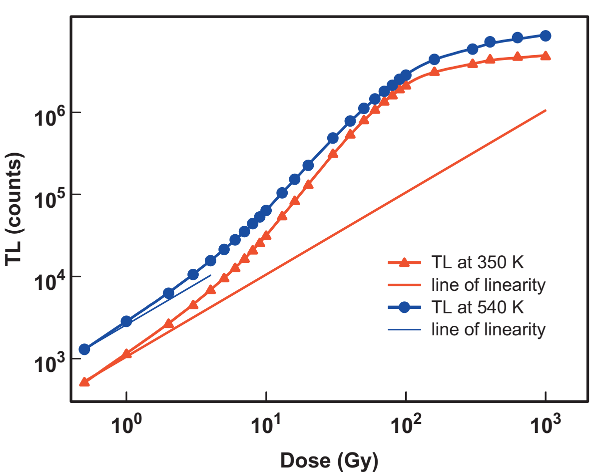

Figure 4 (online colour at: www.pss-a.com) Growth of the TL response at 350 and 540 K as a function of beta dose.

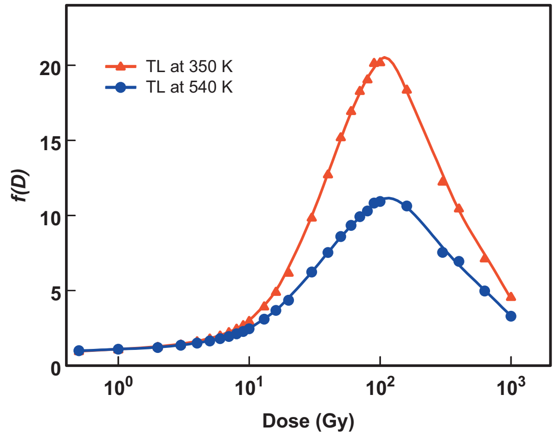

Figure 5 (online colour at: www.pss-a.com) The dependences of the linearity index on beta dose for the TL responses at 350 and 540 K.

The non-linearity of a TL dose dependence is usually described by the relative dose response or linearity (supralinearity) index $f(D)$, which is defined as the ratio of the measured TL signal TL(D) per absorbed dose D, normalized to this ratio at a dose D_{lin} taken from the dose range where the response is linear [13]:

$$f(D) = \frac{\mathrm{TL}(D)/D}{\mathrm{TL}(D_{\mathrm{lin}})/D_{\mathrm{lin}}}. \tag{1}$$

The linearity indexes corresponding to the dose responses at 350 and 540 K were calculated with $D_{lin} = 0.5$ Gy and are plotted in Fig. 5. The indexes underline the strong supralinearity of the TL response for the CVD diamond film, which reaches the maximum values of 20 and 11 at 100 Gy for 350 and 540 K, respectively.

3.3 AG and OSL dose dependences The AG and OSL decay curves and the AG and OSL dose responses in the beta dose range of 0.5–630 Gy were obtained with a sequence of irradiations during 6–7500 s, AG or OSL readout at RT during 250 s, TL readouts from RT up to 770 K and cooling to RT during 300 s. To obtain a clear difference between the luminescence stimulated with heat (AG curves) and those with light (OSL curves), the IR stimulation was switched on after 10 s of the start of the readout and was switched off 10 s before the end of the readout. The TL readouts up to 770 K were used to empty the traps filled by beta irradiation and to return the sample to its initial state.

The selected AG decay curves (AG background subtracted and normalized to the absorbed dose) are depicted in Fig. 6. The normalized-to-dose OSL decay curves are show in Fig. 7. To show a pure OSL signal, the OSL

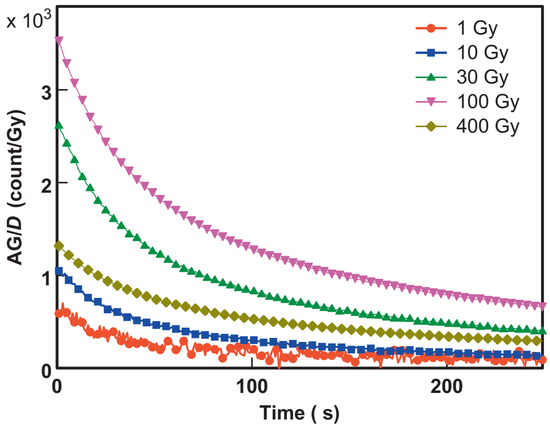

Figure 6 (online colour at: www.pss-a.com) The normalized-to-dose background-subtracted AG decay curves recorded after irradiation with indicated doses.

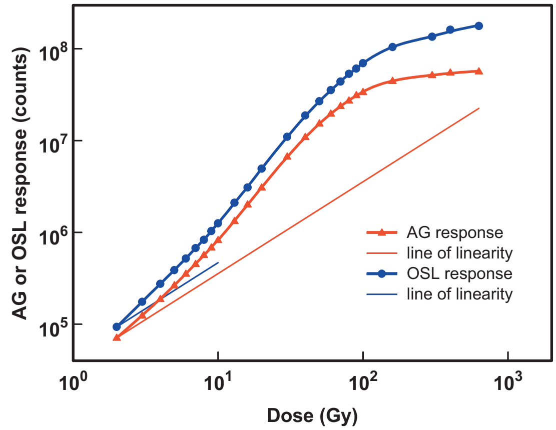

Figure 8 (online colour at: www.pss-a.com) Growth of the AG and OSL response with beta dose.

background and corresponding AG intensity were subtracted from the measured OSL curves. As in the case of TL, the AG and OSL sensitivities increase up to 100 Gy and then decrease. The shapes of the AG and OSL decay curves also change slightly. The AG and OSL dose responses were evaluated as the areas under the curves presented in Figs. 6 and 7. Both dose responses are similar to that from TL and exhibit supralinear–sublinear behaviour. The linear part (if it exists) is not observed due to low AG and OSL intensity at doses lower than 2 Gy.

3.4 Sensitization of TL, AG and OSL The supralinear behaviour of the dose response is often related to the phenomenon know as sensitization. Sensitization manifests itself as the sensitivity increasing after irradiation with high dose followed by an appropriate thermal treatment that removes the signal generated by the initial high dose. The cause of sensitization is an incomplete restoration of material

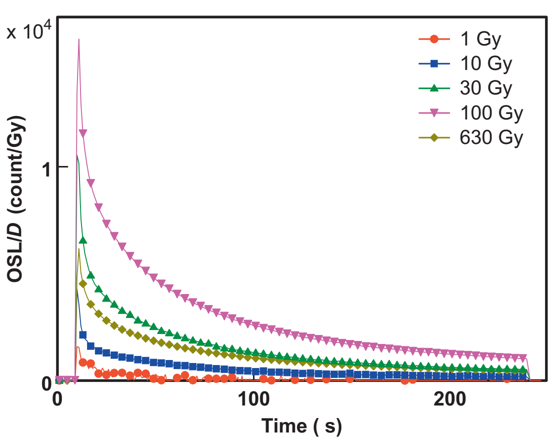

Figure 7 (online colour at: www.pss-a.com) The normalized-to-dose background-subtracted OSL decay curves recorded after irradiation with indicated doses.

properties, which were modified by the irradiation with high dose. As mentioned above, the TL, AG and OSL properties do not change after irradiation with doses up to 1000 Gy followed by TL readout from RT up to 770 K. Therefore, the sensitizations related to the observed supralinearity of the TL, AG and OSL dose responses (if they exist) should disappear at lower temperature.

To see the recovery of the initial TL sensitivity (desensitization) the following sequence of measurements was carried out:

(a) irradiation with 50 Gy at RT;
(b) TL readout from RT up to temperature T_{end};
(c) cooling to RT during 300 s;
(d) TL readout from RT to 770 K (preheated TL curve);
(e) cooling to RT during 300 s;
(f) irradiation with 50 Gy at RT;
(g) TL readout from RT up to T_{end};
(h) cooling to RT during 300 s;
(i) irradiation with 1 Gy (test dose) at RT;
(j) TL readout from RT up to 770 K (preheated and test dose irradiated TL curve);
(k) cooling to RT during 300 s.

The end temperature T_{end} was changed from 320 to 770 K with a step size of 50 K.

Figure 9 presents several TL curves recorded at steps (d) and (j). The curves recorded at step (d) show the effect of the thermal cleaning procedure (see our work in Ref. [12]) on subsequent empting of 5 traps responsible for the TL peaks. The curves corresponding to step (j) show the TL intensity created by the test-dose irradiation. The result of the test-dose irradiation depends on the final filling of the traps after 50 Gy irradiation, preliminary heating to T_{end} and test-dose irradiation. The TL curves recorded after irradiation with 1 and 51 Gy of the film subjected to the standard TL readout with $T_{end} = 770$ K are also shown. These two curves demonstrate the effect of the test-dose irradiation on the

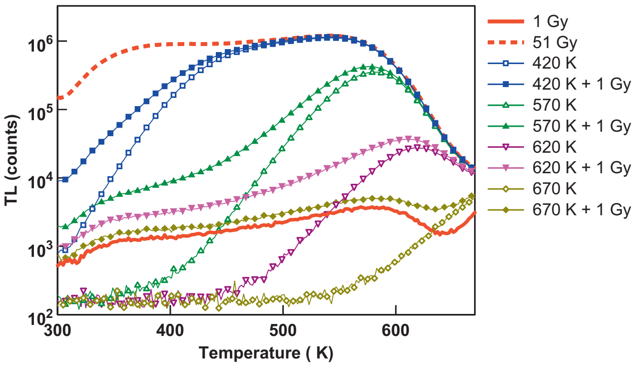

Figure 9 (online colour at: www.pss-a.com) TL glow curves recorded after irradiation with 50 Gy followed by the TL readouts to indicated temperatures (open circles) and after the additional irradiation with 1 Gy (solid circles). The curves drawn with the solid and dashed lines were recorded after 1 and 51 Gy irradiation of the film subjected to the standard TL readout to 770 K.

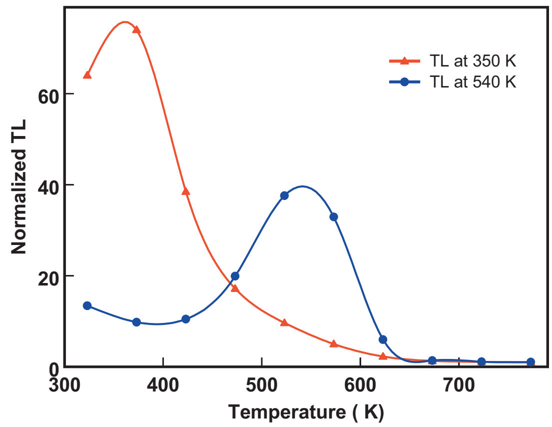

Figure 11 (online colour at: www.pss-a.com) The evolution of the 350 and 540 K TL intensities (normalized to those of the 1-Gy-irradiated 'clean' film) with T_{end} increasing.

'clean' and 50-Gy-irradiated diamond film. Because of the strong peak overlap, a careful deconvolution is needed for a quantitative analysis of the behaviour of the individual TL peaks after high-dose irradiation. In this paper we will restrict ourselves to an analysis that can be done without using the deconvolution.

Figure 10 shows the differences between the TL curves recorded with and without the test irradiation dose. The difference curves corresponding to $T_{end} = 720$ and 770 K (not presented in Fig. 10) coincide fully with the 1-Gy-irradiated TL curve recorded on the clean diamond film.

Figures 9 and 10 demonstrate clearly that 1 Gy test dose irradiation creates much more TL in the irradiated and partially preheated film than in the clean film. This means that 50 Gy irradiation increases drastically the sensitivity of the diamond film. A possible reason for the sensitivity

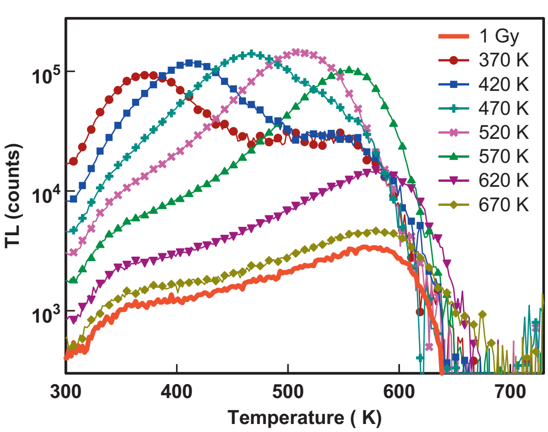

Figure 10 (online colour at: www.pss-a.com) The differences between the TL curves recorded at steps (d) and (j) with and without the test-dose irradiation on the film previously irradiated with 50 Gy and subjected to the TL readouts up to the indicated temperatures. The red curve was recorded after 1 Gy irradiation of the film subjected to the standard TL readout to 770 K.

increase is the competition during excitation or heating between traps responsible for the TL peaks [9]. The TL glow curves consist of 5 strongly overlapped TL peaks (Fig. 1) and all of them, as follows from Fig. 10, exhibit supralinear behaviour.

Figure 11 shows the evolution of the 350 and 540 K TL intensity (normalized to those of the 1-Gy-irradiated clean film) with T_{end} increasing. In fact, these curves are a mixture of the TL peak sensitization and supralinearity depending on the final filling of the traps after 50 Gy irradiation, preliminary heating to T_{end} and test-dose irradiation. The TL intensity at 350 K belongs to the 350 and 400 K peaks, which are removed fully by the preheat with $T_{end} > 500$ K. Therefore, the 350 K curve in Fig. 11 shows (at temperatures higher than 500 K) the decrease of the sensitization of the 350 K TL. The initial part of the 540 K curve (up to 500 K) shows the supralinearity of the 540 K TL intensity. Both the curves go to 1 with T_{end} increasing to 770 K which corresponds to the full emptying of the traps responsible for the supralinearity and sensitization.

The recovery of the initial AG and OSL sensitivity was determined in the same manner as for the TL desensitization. The only difference was the measurement of the AG or OSL decay curves after steps (c) and (i). As in the case of the TL desensitization, the test irradiation dose creates much more AG and OSL in the irradiated and partially preheated film than in the clean film. The evolution of the AG and OSL responses (normalized to those of the 1-Gy-irradiated clean film) with T_{end} increasing is shown in Fig. 12.

AG in the beta-irradiated diamond film is directly related to the low temperature TL peaks [12]. Therefore, the behaviour of the AG response and the 350 K TL intensity should be similar. The comparison of the corresponding curves in Figs. 11 and 12 demonstrate clearly this similarity. As was shown in our article [12], the OSL signal is caused by the simultaneous optical emptying of the traps responsible for the 350, 400, 480 and 540 K TL peaks. So, the OSL decay

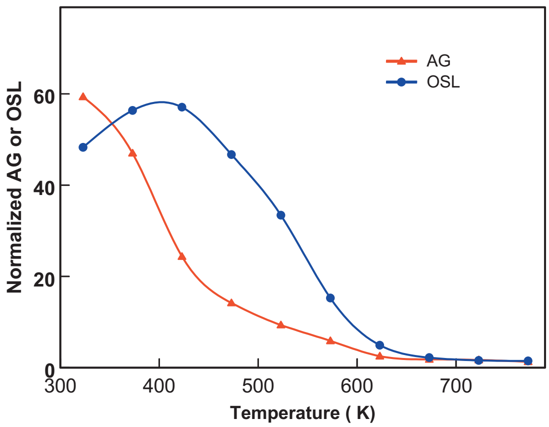

Figure 12 (online colour at: www.pss-a.com) The evolution of the AG and OSL response (normalized to those of the 1-Gy-irradiated 'clean' film) with increasing T_{end}.

curve is composed of four components, whose contributions are determined by the final filling of the corresponding traps after 50 Gy irradiation, preliminary heating to T_{end} and test-dose irradiation. The evolution of the OSL response with increasing T_{end} reflects the change of some averaged sensitivity and seems to be too complicated for an analysis. As in the case of TL, the normalized AG and OSL responses go to 1 as T_{end} increases to 770 K due to the full emptying of the traps.

4 Conclusions The properties of TL, OSL and AG created by beta radiation in a CVD diamond film grown on a silicon substrate have been investigated.

There are at least five traps in the studied undoped CVD diamond film that are responsible for the TL peaks at temperatures at about 350, 400, 480, 540 and 580 K. The traps related to the first four TL peaks are sensitive to IR light and are responsible for the OSL signal. The traps related to the 350 and 400 K TL peaks are emptied by heat at RT (thermal fading) and are responsible for the AG signal.

The TL dose responses are similar for all the peaks and exhibit a typical linear–supralinear–sublinear behaviour. The supralinear growth starts at doses of about 1 Gy and goes up to 100 Gy. At higher doses the dose responses go to saturation. The AG and OSL dose responses are similar to those from TL and exhibit supralinear–sublinear behaviour. The linear part (if it exists) is not observed due to low AG and OSL intensity at doses lower than 2 Gy.

The supralinear behaviour of TL, OSL and AG can be explained by a competition between the traps, either during filling of the traps under beta irradiation or during emptying of the filled traps under heat or light stimulation.

The diamond film sample that was irradiated with high dose, partially preheated and irradiated again with low test-dose, exhibited increased TL, OSL and AG sensitivity, which can be considered as a mixture of the supralinearity and sensitization. Pure sensitization is observed for the 350 and 400 K TL peaks and AG after preheating with a T_{end} value higher than 500 K which empties fully the corresponding traps. This sensitization gradually decreases to 1 as T_{end} increases to 770 K. For the higher temperature peaks and OSL the supralinearity and sensitization cannot be divided into separate parts without an additional study.

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