One Photon and Two Photon Process in Photo-Decomposition of Germanium Oxygen Deficient Centres

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Introduction: There has been much debate on the fundamental mechanism of photosensitivity in germanium-doped silica optical fibres. The importance of the effect, which was discovered by K.O. Hill in 1978 [1], has been well demonstrated by the still rapidly increasing application areas that it has in fibre optics. Photo-induced index changes as high as $\sim 10^{-3}$ [2,3] and $\sim 10^{-2}$ in H_2 loaded fibres [4] have enabled very strong gratings to be written conveniently into optical fibres to produce filters, wavelength defining reflectors, dispersion compensators, and sensors. However, the connection between the photosensitivity and the germanium-related oxygen deficient centre (GODC), first proposed by Hand and Russell [5], is well recognised. Despite uncertainty on the exact microscopic structure of the GODC, the energy levels of the centre is well understood through spectroscopic studies of the centre. A diagram of such an energy level system is depicted in figure 1, with singlet states marked by S and triplet states T. Despite the fact there has been much work been done on the photo-decomposition of GODCs, there is still work to be done for a thorough understanding the process. Potentially there are two possible reaction path ways. One is a direct two photon reaction producing a photoelectron in the conduction band. Most of the photoelectrons will recombine with no net effect and some will be trapped at various sites to create a net change. The second one is a single photon process involving the long lived triplet state and a near by trapping site, probably situated at the next co-ordination sphere. The two situations are shown in figure 1. Here we report an experimental study on the reaction path way of the GODCs, demonstrating that there are both single photon and two photon process existing under different conditions.

Experiments: All the samples used in the experiment were made by MCVD process. The first experiment was a measurement of photo-currents in different silica samples and germanium-doped silica samples. A KrF excimer laser (248 nm, 25 ns pulse width) was used. The sample with an area ~5 mm X 5 mm with polished faces was placed between two electrodes smaller than the sample to minimise background photo-current caused by ionisation of air. Simultaneously, the laser induced luminescence was collected into a monochromator, monitored by a photo-multiplier and displayed on an oscilloscope. The temporal resolution of the our photo-current measurement (10 μs) was much longer than the lifetime of the free carriers (1 - 0.01 ns), the amplitude of the photo-current is proportional to the total number of displaced elementary charges, $P \sim \delta Q$. Figure 2a gives the fluence dependence of photo-current signal $P(\Phi)$ and yield of silicone oxygen deficient centres (SODC) decomposition per single pulse $\beta(\Phi)$ on sample S1 (Cl~10 ppm, OH~1 ppm, Al,Na<1 ppm, thickness 8 mm) and figure 2b gives the fluence dependence of photo-current $P(\Phi)$ and photo luminescence $I(\Phi)$ of GODC on sample G1 (OH~200 ppm, Al, Na~10 ppm, Ge 100 ppm, thickness 14 mm). For SODC in S1, there is a good correlation between P(Φ) and β(Φ). The dependence below 0.3 J/cm^2 is square law and above that is linear. For the GODC in G1, this change of slope happens at ~0.1 J/cm^2. For I(Φ) in G1, it increases linearly with Φ below 0.2 J/cm^2 and then reaches a saturation before actually falling at higher fluence (Φ>0.5 J/cm^2). The change of slope from 2 to 1 in both cases is due the depletion of the ground states S_0 population. The photo-current is a two photon effect despite the linear dependence at high pulse intensity.

In another experiment, yield of photo-reaction was measured in a range of germanium-doped silica samples with different concentrations. Two types of exposures were used, one being a Hg lamp (5 mW/cm^2) for 10 minutes and the other being a KrF laser (250 mJ/cm^2) for 40 pulses. The results were shown in figure 3. For the exposure to Hg lamp, a monotonic increase of yield with germanium concentration was seen. This is a strong indication that the electron traps is some germanium related sites, increasing with germanium concentration. For the exposure to KrF Excimer laser, two regimes obviously exist. The transition seems to happen at ~10 mol%. In each regime, the yield increases with germanium concentration, again due to an increase in the number of trapping sites. At low concentration, a higher yield is actually seen. We believe that the two photon reaction path way is dominate at low germanium concentration, due to the small likely hood of a nearby trapping sites to enable the single photon reaction. The photoelectrons generated in this case can access more stable trapping sites further away and therefore higher yield. At high germanium concentration (>10 mol%), the single photon process dominates due the availability of nearby trapping centres to react with the long lived triplet state. The low overall yield is due to the unstable nature of the centres. This effect seems to correlate well with some works done in low germanium doped fibres which can achieved ~10^{-3} photo-induced index change much higher that was demonstrated in highly doped germanium fibres[6].

In a third experiment, we studied the effect of H_2 loading. Three samples of different germanium concentrations was measured for the triplet life times both H_2 loaded and not H_2 loaded. The excitation is a direct one with a N_2 laser at 337 nm. The results are shown in figure 4. The increase of decomposition yield in the highly doped sample is clearly shown by the reduction in the luminescence life time for not H_2 loaded samples. However a further increase was seen in H_2 loaded samples. In fact the yield for the H_2 loaded samples is independent of the germanium concentration, showing the decomposition of GODC centres is dominated by a H_2 related effect.

To summarise, we have found that photo-current is created through a two photon effect in germanium doped silica glass. Both single and two photon process can be involved in the decomposition of GODCs. At highly doped glass or at low intensity, single photon process dominates. In the lowly doped glass and at high intensity, a two photon process dominates. In H_2 loaded glass, GODC decomposition is dominated by a H_2 related effect.

References:

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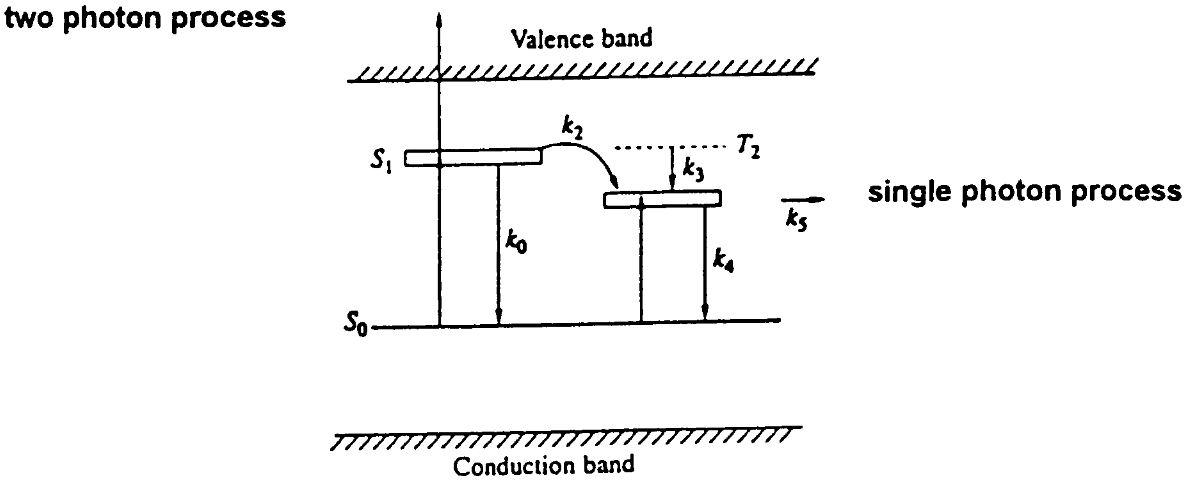

Figure 1. Energy level diagram of GODC and possible photo-decomposition path ways.

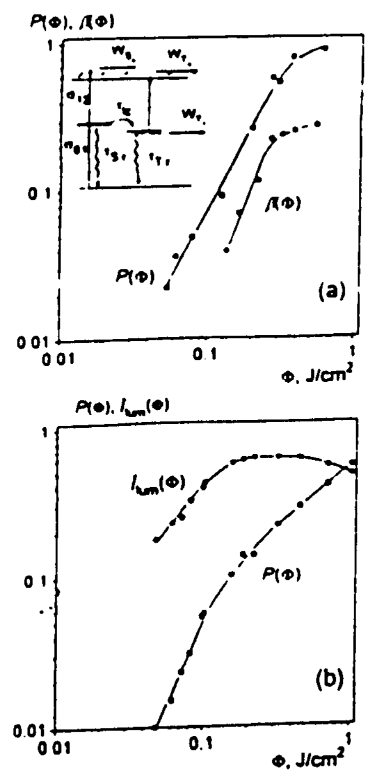

Figure 2 (a) Fluence dependence of photo-current signal P and photo-decomposition yield of SODC β in a silica sample. (b) Fluence dependence of photo-current signal P and photo-luminescence I for GODC in a germanium-doped silica sample.

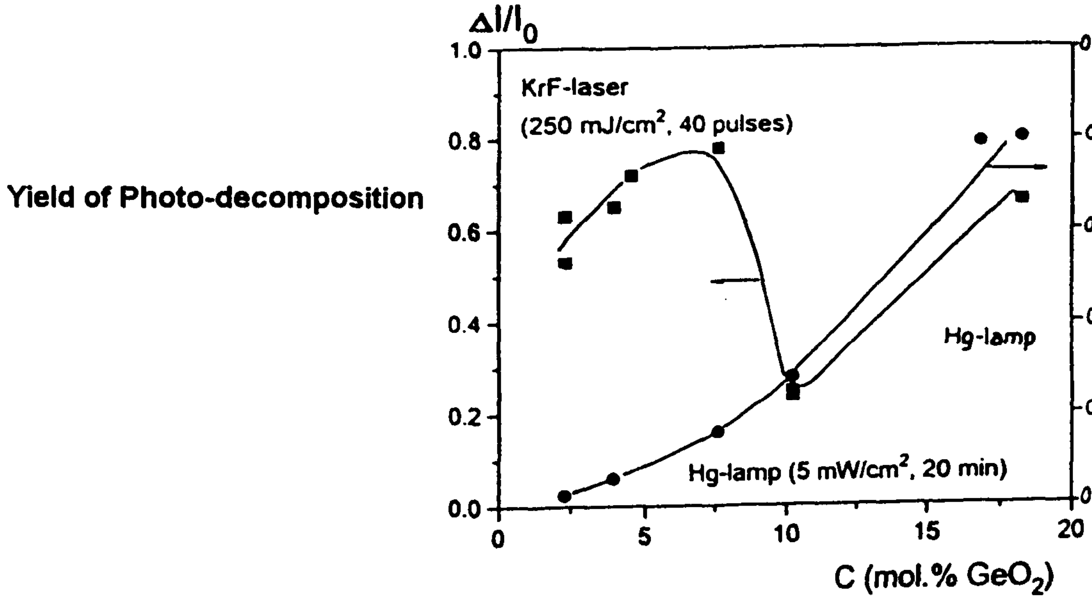

Figure 3 Germanium concentration dependence of the photo-reaction yield with Hg lamp and KrF excimer laser irradiation.

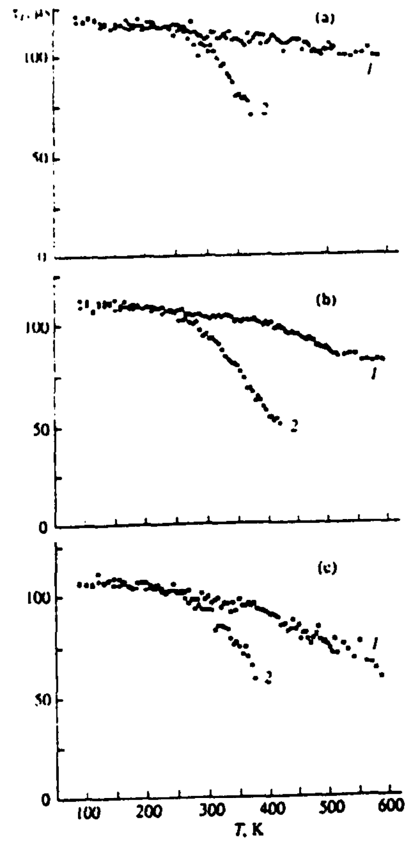

Figure 4 Triplet life time quenching of GODC in original samples (curve 1) and H_2 loaded sample 2 (curve 2).