Japanese Journal of Applied Physics, **39** (11) (2000) 6290-6292

Photodarkening and Photobrightening in Glasses Doped with CdS and CdS_xSe_{1-x} Nanocrystals

Tadaki Miyoshi, Akito Hirano, Tomomi Suenaga, Junya Nagata, Tetsuro Nagai and Naoto Matsuo

Department of Electrical and Electronic Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan

(Received April 10, 2000; accepted June 26, 2000)

The photobrightening of photodarkened CdS- and CdS_xSe_{1-x}-doped glasses has been investigated using luminescence experiments. Photobrightening depends on the wavelength of laser light, and is observed in all samples investigated, when the wavelength of laser light is longer than that of absorption edge. Photobrightening is explained by considering the reexcitation of trapped electrons in glass.

KEYWORDS: semiconductor, nanocrystal, quantum dot, photodarkening, luminescence

1. Introduction

Semiconductor nanocrystals in glasses have large optical nonlinearity with a fast response time. The decay time and intensity of luminescence from CdS_xSe_{1-x}-doped glasses decrease upon light irradiation.[1] This photoinduced irreversible process is called photodarkening. However, we observed that the intensity and decay time of luminescence from photodarkened CdS-doped glass, Toshiba Y-44, increased upon light irradiation with a wavelength of about 500 nm.[2] This result indicates that the reverse process of photodarkening (photobrightening) occurrs in CdS-doped glass upon light irradiation. Fig. 1

Photodarkening and photobrightening are explained by the following processes shown in Fig. 1. Electrons in the valence band of CdS nanocrystals are excited to the conduction band, some of which relax to traps at the glass-semiconductor interface. Laser light reexcites some of these trapped electrons to higher-energy surface states, from which they migrate into the glass. These electrons eventually relax to deep levels (T_1 and T_2) in glass.[3,4] Photogenerated holes in CdS nanocrystals migrate to the interface region between CdS nanocrystals and the glass matrix, and they activate defect centers. The activated defect centers act as nonradiative recombination centers, and they cause a decrease in the intensity and decay time of luminescence (photodarkening). In addition to these processes, laser light reexcites the trapped electrons to the conduction band of glass, and some electrons recombine with holes and passivate the defect centers. The passivation of the activated defect centers causes an increase in the intensity and decay time of luminescence (photobrightening).[2] Light with a wavelength longer than 500 nm cannot generate carriers in CdS nanocrystals in Y-44 and does not activate the defect centers. However, this light may excite the trapped electrons in glass to the conduction band of glass, to passivate the defect centers. Thus, the intensity and the decay time of luminescence increase upon laser irradiation with a wavelength of 500 nm. Here, we report the effect of wavelength of the absorption edge of semiconductor nanocrystals on photobrightening. We also investigated photobrightening as a function of irradiation time and irradiation intensity.

2. Experimental procedure

The samples investigated were commercial CdS-doped filter glasses, Toshiba Y-44, Y-45, Y-46, Y-47 and Y-48, and CdS_xSe_{1-x}-doped filter glasses, Toshiba Y-50, Y-52, O-54 and O-56, since Toshiba glasses showed the most noticeable photobrightening among the following manufacturers: Toshiba, Hoya, Schott and Corning. The absorption edges of these glasses are about 440 nm for Y-44 and 560 nm for O-56. The concentration of CdS or CdS_xSe_{1-x} was about 0.4 wt%. The glasses were exposed to pulsed light from a frequency-tripled Nd:YAG laser (Quanta-Ray GCR-230T-10; wavelength = 355 nm, pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 1.3 or 5 MW/cm^2) for 2 min (first irradiation), and then exposed to pulsed light from an optical parametric oscillator (Quanta-Ray MOPO-700; pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 10 MW/cm^2) for 4 min or the frequency-doubled Nd:YAG laser (Quanta-Ray GCR-230T-10; wavelength = 532 nm, pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 2.5 or 5 MW/cm^2) at 300 K (second irradiation).

The luminescence intensity was measured at 300 K using an N_2 laser (Laser Photonics LN120; wavelength = 337.1 nm, pulse duration = 0.3 ns, repetition rate = 4 Hz, peak power density = 50 kW/cm^2) and a photomultiplier (Hamamatsu R456). The decay time of the luminescene was measured at 300 K using a frequency-doubled Ti:sapphire laser with a pulse selector (Spectra Physics Tsunami 3960 and 3980; wavelength = 390 nm, pulse duration = 200 fs, peak power density = 0.5 MW/cm^2, repetition rate = 4 MHz) and a streak camera (Hamamatsu C4334).

3. Results and discussion

We observed a luminescence band at about 440 nm for CdS-doped glass, Y-44. This band is attributable to the band-to-band or shallow-trapping state-to-band transition. The intensity and decay time of the luminescence decrease upon 355 nm light irradiation, and then increase upon the second irradiation with wavelength of about 500 nm.[2)] Photobrightening depends on the light wavelength for the second irradiation. The increase in the intensity and the decay time of the luminescence is greatest after irradiation of 500 nm light for Y-44. Thus, the most efficient wavelength for photobrightening is 500 nm for Y-

44. Since the absorption edge of semiconductor nanocrystals in other samples is longer than that in Y-44, photodarkening occurs upon light irradiation with longer wavelengths. Thus, the most efficient wavelength for photobrightening shifts to the longer wavelength side: 530 nm (Y-46), 540 nm (Y-48), 560 nm (Y-50), 570 nm (Y-52), 590 nm (O-54) and 620 nm (O-56). Photobrightening occurs, when the wavelength of the laser light for the second irradiation is longer than that of the absorption edge. Fig. 2

We investigated photobrightening as a function of irradiation time of the second irradiation. Figure 2 shows the luminescence intensity of photodarkened CdS-doped glass, Y-46, as a function of irradiation time of 532 nm light. We used pulsed light from the frequency-doubled Nd:YAG laser instead of the optical parametric oscillator, since the light intensity of the former is more stable than that of the latter. The luminescence intensity increases with irradiation time, reaches a maximum, and then decreases. This decrease in the luminescence intensity is considered to be due to photodarkening. Although the absorption coefficient at 532 nm for Y-46 is almost zero according to the transmission spectrum, a small number of electrons may be genarated in semiconductor nanocrystals by the irradiation with 532 nm light. Photogenerated electrons are trapped in glass (T_1 and T_2 in Fig. 1). Although the traps in glass are distributed energeticaly, we classify them in the following manner: T_1 represents shallower traps and T_2 represents deeper traps. Since the energy level of T_1 is shallower, the trapped electrons in T_1 are excited to the conduction band of glass upon irradiation with 532 nm light. The number of trapped electrons, N_1, decreases with irradiation time, and then becomes constant. In addition, the energy level of T_2 is deeper. Thus, the trapped electrons are not excited to the conduction band of glass upon irradiation with 532 nm light. The number of trapped electrons, N_2, increases with irradiation time, since electrons are supplied from semiconductor nanocrystals. Total number of N_1 and N_2 decreases with irradiation time, reaches a minimum, and then increases. Since the intensity and decay time of the luminescence are approximately proportional to the inverse of $(N_1 + N_2)$, they should increase with irradiation time, reach a maximum, and then decrease.

We consider the rate equation for electrons.[5] The rate equation for trapped electrons

is

$$dN/dt = B_1 nJ - B_2 NJ, \tag{3.1}$$

where n is the number of photogenerated electrons in CdS nanocrystals, N is the number of trapped electrons in glass near CdS nanocrystals, J is the irradiation intensity, B_1 and B_2 are rate constants. Since the value of n is proportional to J, the first term on the right-hand side becomes $B_3 J^2$. Thus, rate equations for N_1 and N_2 are

$$dN_1/dt = B_3 J^2 - B_2 N_1 J, \tag{3.2}$$

$$dN_2/dt = B_3 J^2, \tag{3.3}$$

The first terms on the right-hand side in eqs. (3.2) and (3.3) express the trapping process of electrons. Since the trapping occurs via the two-step excitation process, as shown in Fig. 1, these terms are proportional to J^2. The second term on the right-hand side in eq. (3.2) expresses the reexcitation of the trapped electrons. The solution of these equations are

$$N_1 = B_3 J/B_2 + (N_{10} - B_3 J/B_2)\exp(-B_2 Jt), \tag{3.4}$$

$$N_2 = N_{20} + B_3 J^2 t, \tag{3.5}$$

where N_{10} is the value of N_1 at $t = 0$ and N_{20} is the value of N_2 at $t = 0$. Figure 3 shows the calculated results for the peak power densities: 2.5 MW/cm^2 and 5 MW/cm^2. Since only a small number of electrons is genarated in semiconductor nanocrystals by irradiation with 532 nm light, the value of B_3 is less than that of B_2. The calculated results reproduce the experimental results.

Fig. 3

Fig. 4

We also measured the decay time and intensity of the luminescence of photodarkened CdS-doped glasses, Y-44, Y-45, Y-46, Y-47 and Y-48, as a function of irradiation time with 532 nm light. Figure 4 shows the decay time of the luminescence of photodarkened CdS-doped glasses: Y-44 and Y-46. The luminescence intensity as a function of irradiation time shows similar behavior to that of the decay time of luminescence shown in Fig. 4. The decay time of the luminescence of Y-46 increases with irradiation time, reaches a maximum, and then decreases. The result for Y-48 is also similar to that for Y-46. In

contrast, we did not observe a decrease in the decay time or intensity of the luminescence for the longer irradiation time for Y-44. We consider that semiconductor nanocrystals in Y-44 do not absorb 532 nm light, since the band gap of semiconductor nanocrystals in Y-44 is larger than that of other samples. Thus, the value of B_3 in eqs. (2) and (3) becomes 0 for Y-44. Figure 5 shows the calculated results for Y-44 and Y-46. The calculated results correspond well with the experimental results. Fig. 5

4. Summary

The intensity and decay time of the luminescence were measured in photodarkened CdS- and CdS_xSe_{1-x}-doped glasses after irradiation of laser light with a wavelength longer than that of the absorption edge. The luminescence intensity increases with irradiation time, reaches a maximum, and then decreases. This result is explained by a model which considers the reexcitation of trapped electrons in glass.

Acknowledgement

This work was performed using the lasers in the Venture Business Laboratory, Yamaguchi University. The authors are grateful to Associate Professor K. Kasatani.

References

1) P. Roussignol, D. Ricard, J. Lukasik and C. Flytzanis: J. Opt. Soc. Am. B **4** (1987) 5.

2) T. Miyoshi, K. Nitta, H. Ohkuni, F. Ikeda and N. Matsuo: Jpn. J. Appl. Phys. **36** (1997) 6726.

3) J. Malhotra, D. J. Hagan and B. G. Potter: J. Opt. Soc. Am. B **8** (1991) 1531.

4) T. Miyoshi, K. Nitta, H. Ohkuni, K. Shiraishi and N. Matsuo: Jpn. J. Appl. Phys. **37** (1998) 4330.

5) T. Kaneda, T. Miyoshi, H. Furukawa, K. Nitta, H. Okuni and N. Matsuo: Nonlinear Opt. **18** (1997) 337.

Figure captions

Fig. 1. Model used for explaining photobrightening.

Fig. 2. Luminescence intensity of photodarkened CdS-doped glass, Toshiba Y-46, as a function of irradiation time with 532 nm light. The peak power density of 355 nm light is 1.3 MW/cm^2, and the peak power density of 532 nm light is 2.5 MW/cm^2 (solid circles) and 5 MW/cm^2 (open triangles). The luminescence intensity is a value relative to that of the unirradiated sample. Curves were drawn through the data points as a visual guide.

Fig. 3. Calculated results of $1/(N_1 + N_2)$ as a function of irradiation time. $(N_1 + N_2)$ is the number of trapped electrons in glass. The parameters used for this calculation are as follows: $J = 20$ (5 MW/cm^2) and 10 (2.5 MW/cm^2), $N_{10} = 100$, $N_{20} = 30$, $B_2 = 0.03$ and $B_3 = 0.003$.

Fig. 4. Decay time of the luminescence of photodarkened CdS-doped glasses, Toshiba Y-44 and Y-46, as a function of irradiation time of 532 nm light. The peak power density of 355 nm light is 1.3 MW/cm^2, and the peak power density of 532 nm light is 5 MW/cm^2. Curves were drawn through the data points as a visual.

Fig. 5. Calculated results of $1/(N_1 + N_2)$ as a function of irradiation time. The parameters used for this calculation are as follows: $J = 20$, $N_{10} = 100$, $N_{20} = 30$, $B_2 = 0.03$ and $B_3 = 0$ (Y-44) and 0.003 (Y-46).

Fig. 1

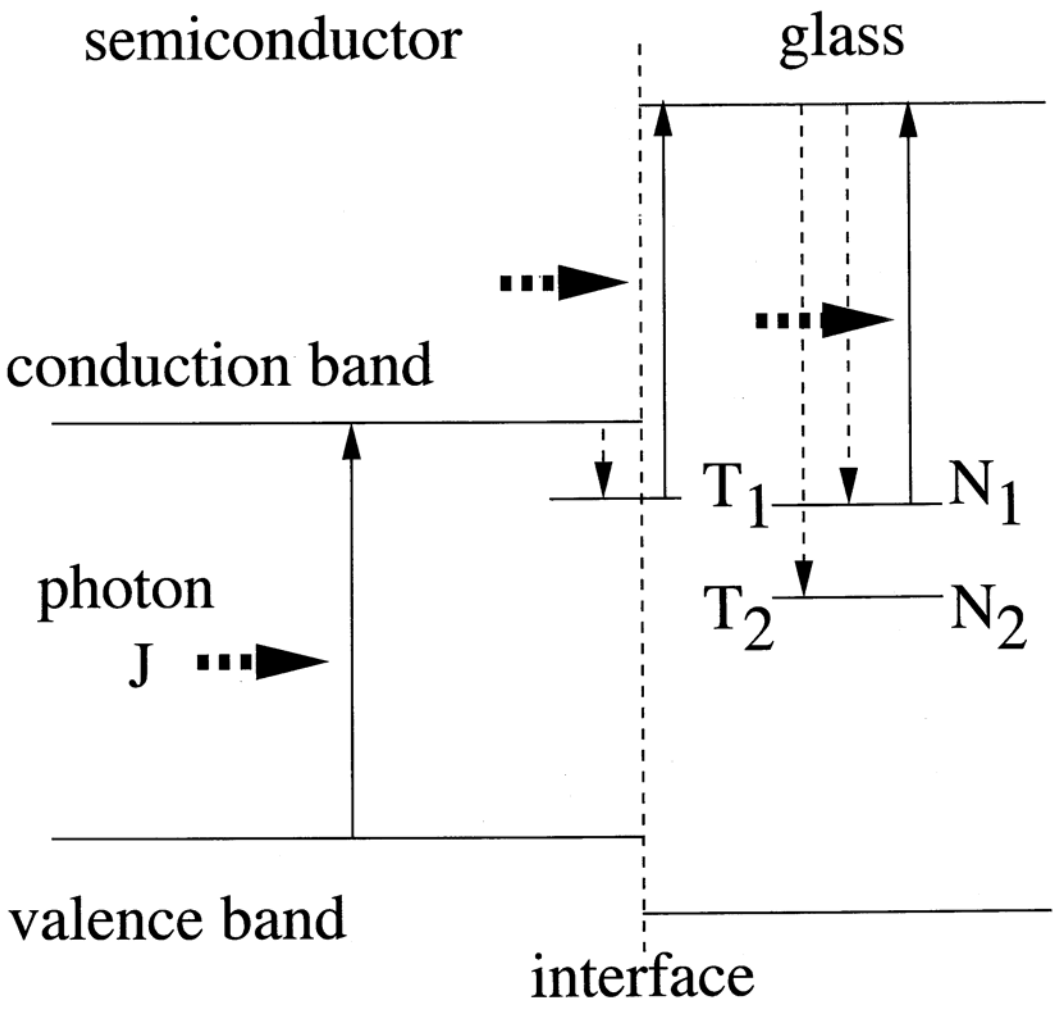

semiconductor
glass
conduction band
T_1
N_1
photon
J
T_2
N_2
valence band
interface

Fig. 2

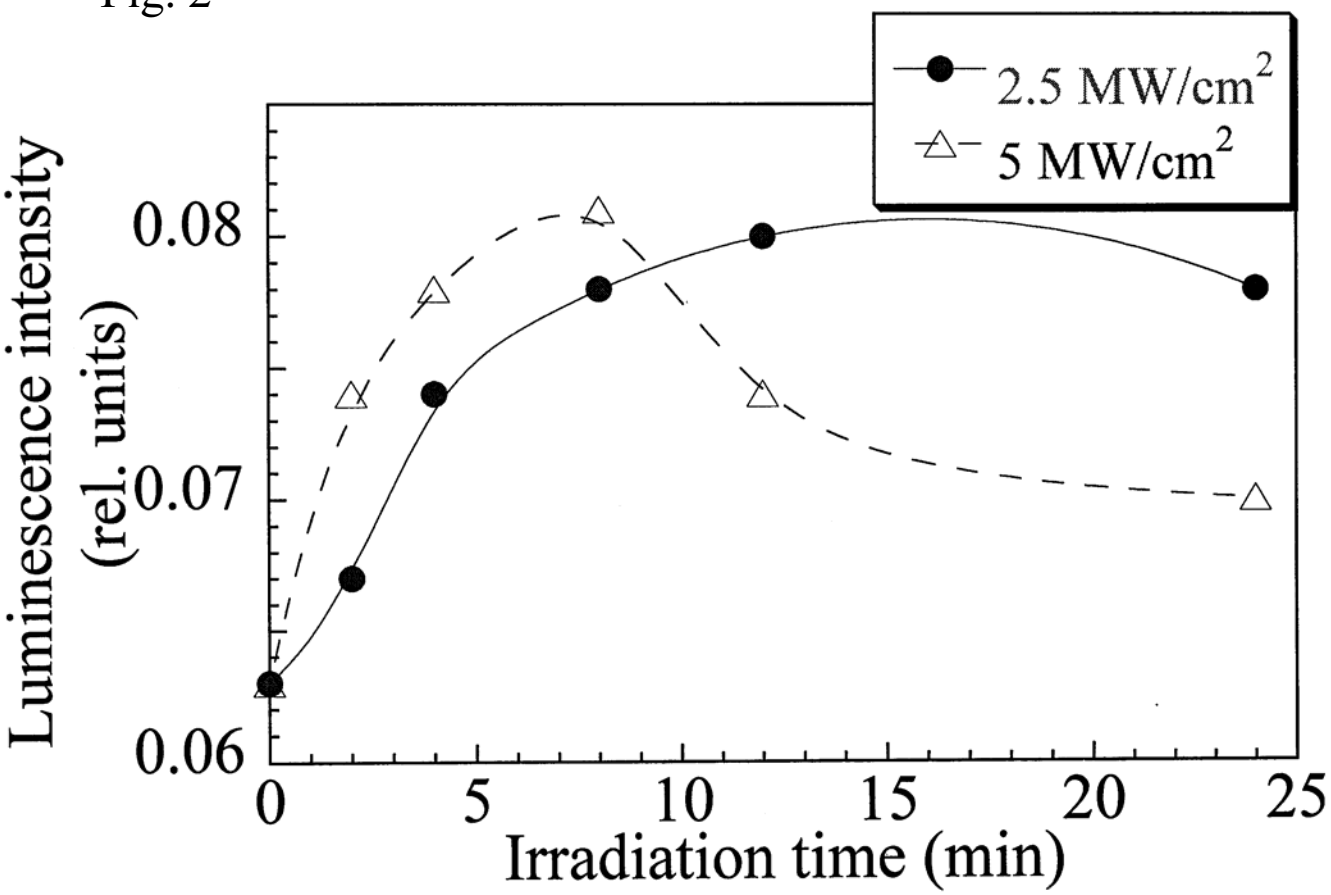

2.5 MW/cm2
5 MW/cm2
Luminescence intensity
(rel. units)
0.08
0.07
0.06
0
5
10
15
20
25
Irradiation time (min)

Fig. 3

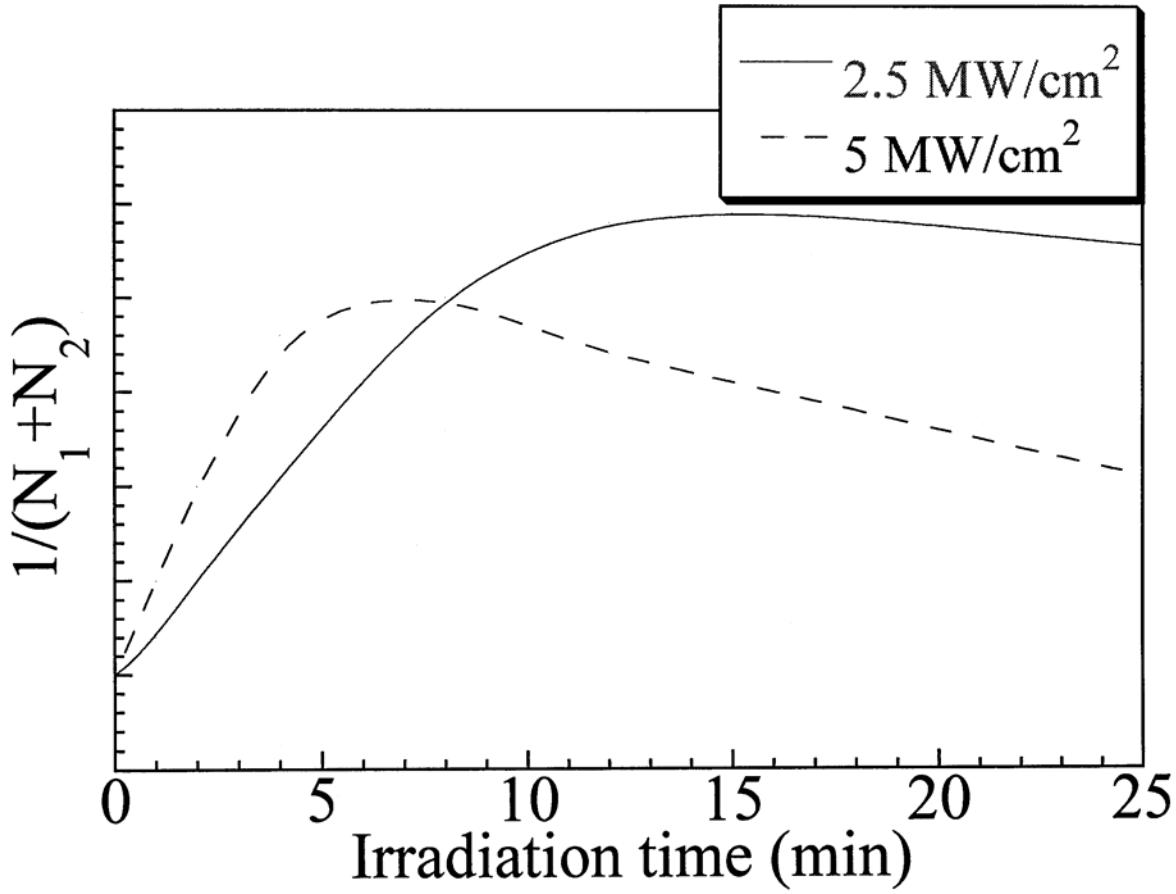

2.5 MW/cm2
5 MW/cm2
1/(N1+N2)
0
5
10
15
20
25
Irradiation time (min)

Fig. 4

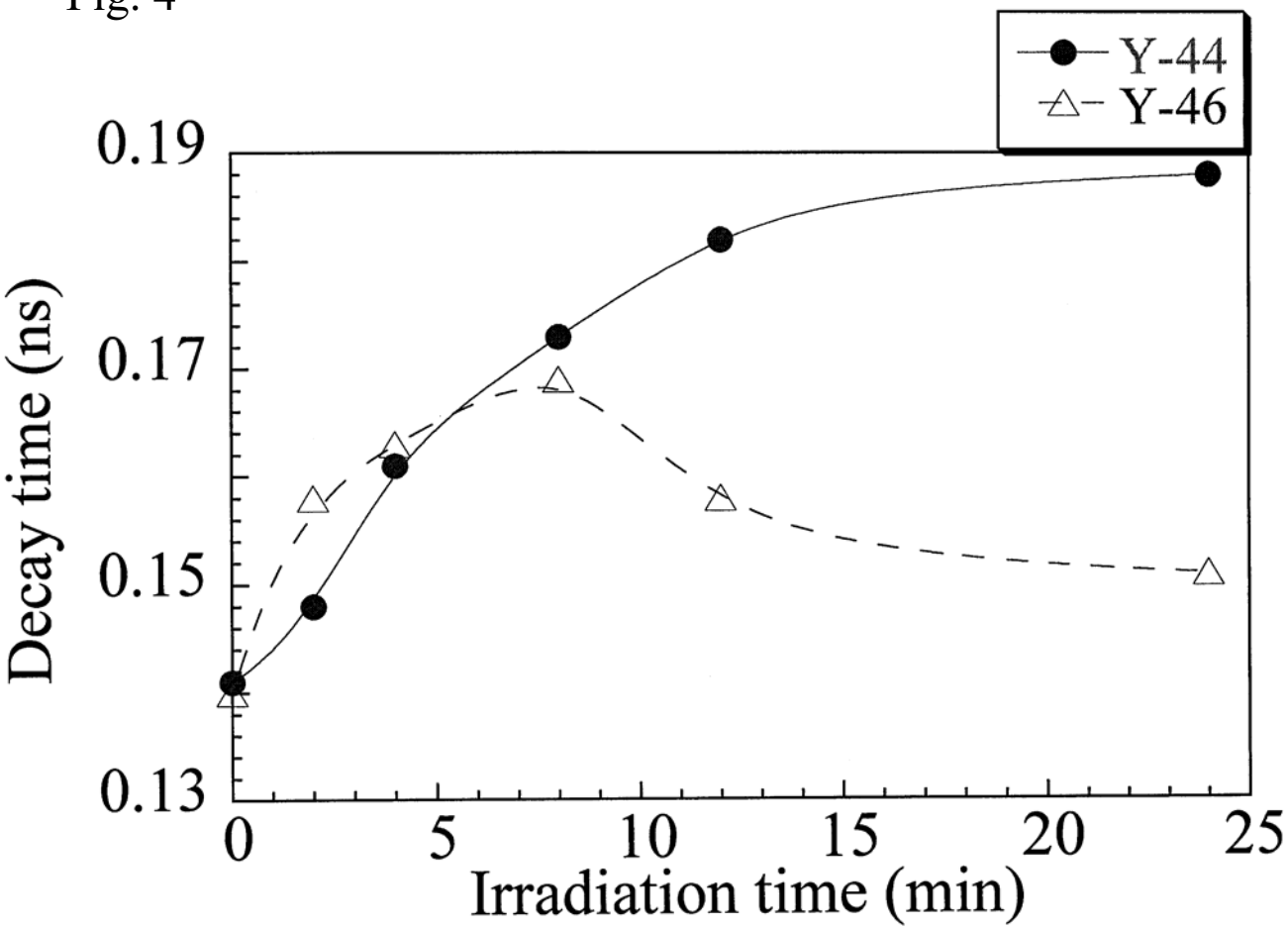
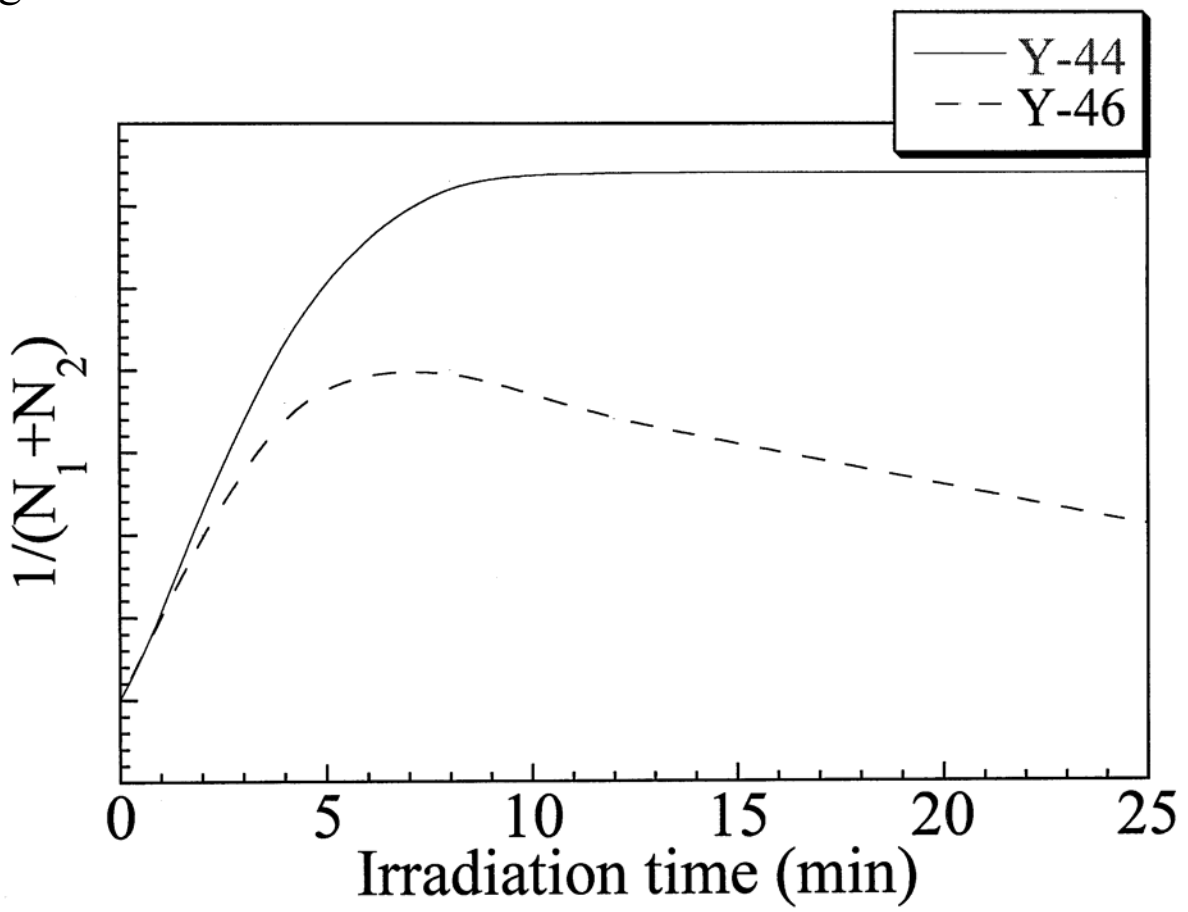

Y-44
Y-46
0.19
0.17
0.15
0.13
Decay time (ns)
0
5
10
15
20
25
Irradiation time (min)

Fig. 5


Y-44
Y-46
1/(N1+N2)
0
5
10
15
20
25
Irradiation time (min)