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Intensity-dependent dynamics of photoinduced absorption in $CdS_{0.4}Se_{0.6}$ semiconductor doped glasses

Jung-Chul Seo and Dongho Kim

Spectroscopy Group, Korea Research Institute of Standards and Science, Taejon 305-600, Korea

Hong Jin Kong

Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

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Intensity dependent dynamics of photoinduced absorption in $CdS_{0.4}Se_{0.6}$ semiconductor doped glasses below the band gap was investigated by using time-resolved differential transmittance spectroscopy. The carriers populated through ultrafast trapping at semiconductor-glass interfaces give rise to a broad photoinduced absorption below the band gap. The decay time of transient absorption depends strongly on the excitation intensity. Based on our results, the physical mechanism for photoinduced absorption processes was suggested.

I. INTRODUCTION

Semiconductor-doped glasses (SDG), in which CdS_xSe_{1-x} microcrystallites of around 10 nm in diameter are suspended in a borosilicate glass matrix, have attracted considerable attention due to the possible applications as new nonlinear optical materials[1-3]. Recent attention has been paid to understanding the electronic energy states of such microcrystallites at the semiconductor-glass interfaces. The interfaces have strong influence on the photophysical properties including optical nonlinearity, photoluminescence and carrier dynamics[4-13]. At these interfaces, semiconductor clusters can have point defect states due to surface dangling bonds, impurities and vacancies[14,15]. Thus the excited electrons can be deeply trapped into these point defect sites at semiconductor-glass interfaces[14-16]. In addition to these deep trap states, the semiconductor clusters can have intrinsic interface states of semiconductor quantum dots in glasses due to the strained bonds[6,15-17].

Maly' *et al.* studied photoinduced absorption phenomena in CdS_xSe_{1-x} microcrystallites at below the band gap[8]. It was suggested that transient absorption is contributed by the electrons trapped at defect states near the valence band on the surface. They observed that photoinduced absorption shows a single exponential decay and the time constants for both the darkened and the fresh samples are 500 ps at 700 nm. According to their model for photoinduced absorption processes, the decay dynamics of photoinduced absorption is expected to be independent of the excitation intensity. In addition, other research groups reported the photoinduced absorption in microcrystal semiconductors above the band gap. In this case the absorption is attributed to biexciton transitions[18] and carriers trapped on the surface[10]. Though several models for photoinduced absorption phenomena have been suggested, the relevant mechanism has not yet been fully understood[8,10,18-20].

In the present study, we have carried out time resolved photoinduced absorption measurements of $CdS_{0.4}Se_{0.6}$ semiconductor-doped glasses by using a pump/probe spectroscopic technique. We have demonstrated that photoinduced absorption is contributed by the trapped carriers at semiconductor-glass interfaces and its decay dynamics depends strongly on the excitation intensity, in contrast to recent predictions.[8] The motivation for this study is the elucidation of the relaxation dynamics of semiconductor-doped glasses based on the transient absorption measurements under various experimental conditions. Based on our results, a new model for photoinduced absorption was suggested.

II. EXPERIMENT

We have measured the time-resolved differential transmittance spectra (DTS) of SDG in order to gain further information regarding the carrier dynamics of the photoinduced absorption processes. The DTS represents the relative change induced by pump pulse in the transmittance of the sample so that a positive value of $-$DTS corresponds to photoinduced absorption. A schematic diagram of the experimental apparatus to measure DTS by the pump/probe technique is given in Fig. 1. The laser source is a combination system of a cw mode-locked Nd:YAG laser (Coherent Antares 76S) pumping a synchronously mode-locked dye laser with GVD (group velocity dispersion) compensating four-prism pairs, a Nd:YAG regenerative amplifier (Continuum RGA60), and a three stage tunable dye amplifier. The final amplified laser pulses had subpicosecond pulse width with an energy of 0.8 - 1.6 mJ/pulse at 585 nm. The SDG sample was pumped by the laser pulses at 585 nm and probed by white light continuum pulses generated by focusing the 585 nm pu-

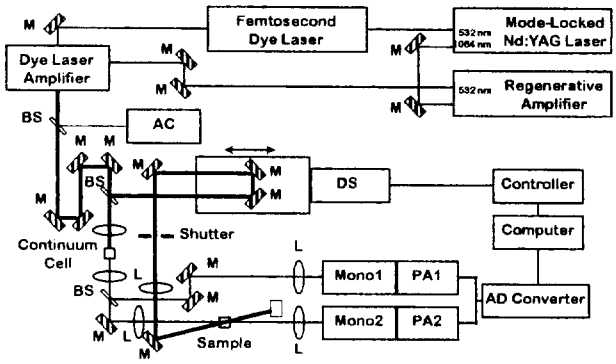

Fig. 1. System configuration for differential transmittance spectra measurement.

lses onto a 1-cm pathlength cell containing water. The probe beam was divided into two beams. One of the two probe beams was passed through the SDG, and then focused onto a 32-cm focal length spectrometer, and finally detected by a 512 channel photodiode array detector (Hamamatsu C4350) interfaced with a computer. The other probe beam was used as a reference signal to compensate the fluctuation in the white light continuum pulses. The time delay between pump and probe pulses was controlled by an optical delay line based on a translation stage with 5 μm resolution (SAR1615T-800 smart actuator). All the experiments were done at room temperature. Our SDG sample is a Schott RG 630 color glass filter with a thickness of 2.5 mm which is essentially transparent above 650 nm. In our pump-probe experiment, the excitation wavelength is 585 nm (2.1 eV) which is close to the excitonic peak of $CdS_{0.4}Se_{0.6}$ microcrystals, and the probe wavelength is in the range of 650-870 nm (1.91-1.43 eV).

III. RESULTS

We recorded the photoinduced absorption spectra of a color glass filter doped by $CdS_{0.4}Se_{0.6}$ microcrystals at wavelengths below the band gap. The differential transmittance spectra in Fig. 2 were obtained with an excitation (pump) intensity of 110 mW/mm^2 in the wavelength range of 650-870 nm at various time delays between pump and probe pulses. The experiment was repeated several times to confirm that the transient absorption dynamics is reversible as excitation intensities increase or decrease. The results were consistent, indicating that photoinduced absorption is contributed by a reversible process. We have observed absorption bleaching below 660 nm with a lifetime of shorter than 500 ps. It is well known that photoexcitation of electrons to the states near the conduction band gives rise to absorption bleaching by band filling effects[11,21]. On the other hand, photoinduced absorption

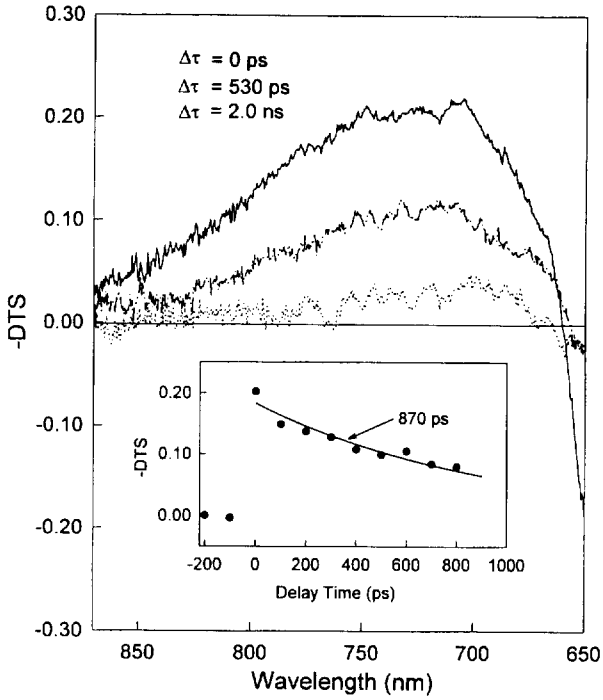

Fig. 2. Differential transmittance spectra (DTS) of color glasses doped by $CdS_{0.4}Se_{0.6}$ microcrystals at various delay times between pump and probe pulses. The inset shows the decay curve of the photoinduced absorption in SDG at 720 nm.

represents the transient behavior of excited carriers. We have observed a broad and featureless transient photoinduced absorption in the wavelength region extending to 870 nm. We observed the photoinduced absorption at delay times up to 2 ns with no dependence of its dynamics on the wavelength in 680-870 nm region. We can see that the carriers responsible for such absorption are different from those for absorption bleaching because of different dynamics. The inset in Fig. 2 shows the time evolution of the photoinduced signal at 720 nm, which exhibits about 870 ps lifetime based on single exponential decay through the model suggested by Maly' *et al.*[8]. However, the temporal profile for photoinduced absorption is not well described by a single exponential decay. As shown in Fig. 3(a), we can see clearly that the decay profile exhibits two distinct time constants in contrast to the single exponential decay reported previously[8]. Assuming double exponential decay we can extract the time constants of about 50 ps and 3.2 ns. We suppose that such long-lived photoinduced absorption (3.2 ns) is contributed by deeply trapped carriers at semiconductor-glass interfaces where carriers can be populated as suggested by several research groups[14-17]. A detailed discussion of this assignment will be given in the following section. Nevertheless, as shown in Fig. 3(c), at the low excitation intensity of 12 mW/mm^2 only the long-lived photoinduced absorption was observed. As shown in Fig. 3(a) and (b), however, we observed that

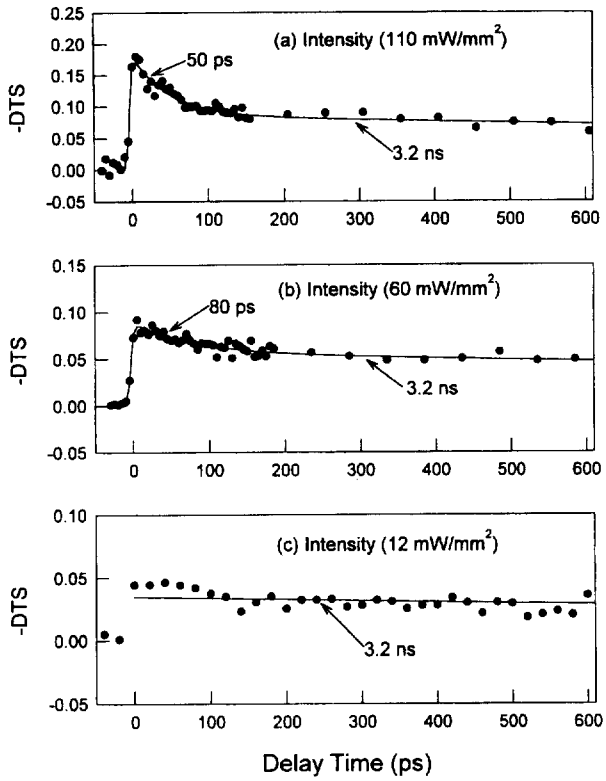

Fig. 3. Excitation intensity dependence of photoinduced absorption dynamics.

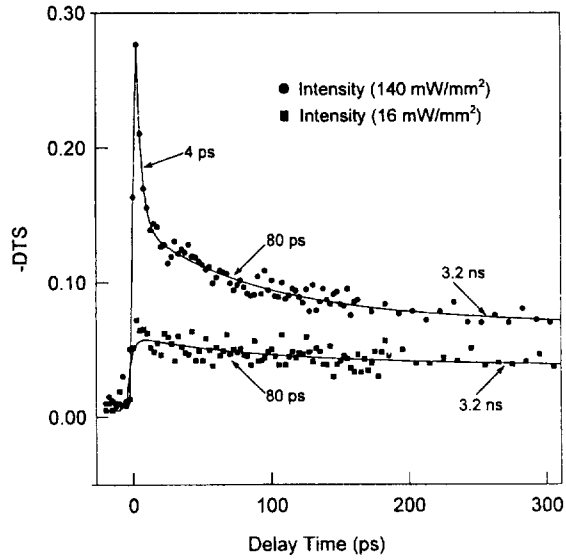

Fig. 4. Dependence of ultrafast photoinduced absorption dynamics on excitation intensities.

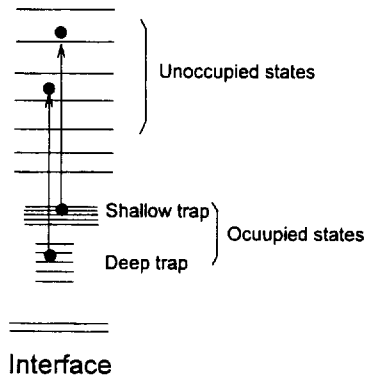

Fig. 5. Schematic representation of photoinduced absorption processes in SDG near microcrystal-glass interfaces. The arrows correspond to the photoinduced absorption.

the decay time constants of short-lived photoinduced absorption decrease as excitation intensities increase. To gain further information on the short-lived photoinduced absorption, we investigated excitation intensity dependence of photoexcitation dynamics with picosecond time resolution. As shown in Fig. 4, we observed a strong dependence of dynamics on excitation intensities. At the excitation intensity of 16 mW/mm^2, the temporal profile of photoinduced absorption is well described by a single-exponential decay with a time constant of 80 ps and a nearly constant long-lived component. However, at the high intensity of 140 mW/mm^2, a new ultrafast decay component was observed. Assuming an exponential decay we find a time constant of about 4 ps for this component which depends on excitation intensities.

IV. DISCUSSION

We can see that carriers responsible for photoinduced absorption are different from those populated at volume states because of different dynamics as shown in Fig. 2. Also, it is well known that the lifetime of carriers populated at volume states is shorter than 100 ps[11]. Recently, one model was suggested in which photoinduced absorption is attributed to electrons populating the surface (so-called L state) near the valence band[8]. However, our results which show an ultrafast trapping phenomena and strong intensity dependence of photoinduced absorption cannot be explained in terms of such model. On the other hand, several research groups proposed the microcrystal-glass interface states to explain the photoexcitation dynamics of semiconductor doped glasses[4-17]. The semiconductor clusters can have point defect states due to surface dangling bonds, impurities and vacancies at these interfaces[10,14,15]. The excited carriers can be deeply trapped into these point defect sites at semiconductor-glass interfaces within less than 1 ps after photoexcitation[10]. Based on our experimental results, we have presented a model for photoinduced absorption processes as shown in Fig. 5. We can suppose that the long-lived photoinduced absorption is due to carriers trapped at such deeply trapped states which are located at the semiconductor-glass interfaces. The amplitude of the long-

lived photoinduced absorption exhibits a saturation behavior with an increase in excitation intensity due to the saturation of the electrons populating the deep trap states[22]. This behavior is similar to the feature observed in the photoluminescence measurements[7,15]. On the other hand, the photoinduced absorption with a short decay time is considered to be due to carriers populated at shallow trap states[1,15-17] formed at the microcrystal-glass interfaces. It is considered that high excitation intensities lead to high concentrations of carriers so that the probability for electrons to recombine with neighboring holes increases[23]. Therefore, we can suggest that the ultrafast decay phenomena is attributed to nongeminate electron-hole recombination of carriers at shallow trap states so that its dynamics depends strongly on excitation intensities. As shown in Fig. 4, the decay of photoinduced absorption at low excitation intensity is well described by a nearly constant long-lived component (3.2 ns) and a single-exponential component with a time constant of 80 ps which is due to the geminate electron-hole recombination at the semiconductor-glass interfaces. However, the nongeminate recombination decay of carriers at semiconductor-glass interfaces becomes the dominant process at high excitation intensities. Based on the experimental observations, we have proposed a model for the photoinduced absorption process assuming that the states at semiconductor-glass interfaces consist of two different trap states. The deep trap states are mainly responsible for the long-lived photoinduced absorption with a lifetime of 3.2 ns. On the other hand, the shallow trap states give rise to the short-lived photoinduced absorption with a lifetime of 80 ps arising from the geminate electron-hole recombination processes. In addition, the ultrafast component with a lifetime of about 4 ps was observed to strongly depend on excitation intensity due to nongeminate electron-hole recombination. We can suggest that photoinduced absorption is related to the transition from these two types of trapping centers to the higher states at semiconductor-glass interfaces(Fig. 5).

V. CONCLUSIONS

We observed the strong intensity dependence of photoinduced absorption dynamics below the band gap of a color glass filter doped by $CdS_{0.4}Se_{0.6}$ microcrystals. Our results indicate that carriers at the microcrystal-glass interfaces are trapped very fast after photoexcitation. The deep trap states are mainly responsible for the long-lived photoinduced absorption with a lifetime of 3.2 ns. On the other hand, carriers shallowly trapped at semiconductor-glass interfaces give rise to short-lived photoinduced absorption with time constants of 80 and 4 ps which depend strongly on the excitation intensity. Such ultrafast decay phenomena of photoinduced absorption are attributed to the nongeminate electron-hole recombination processes.

REFERENCES

[1] P. Roussignol, D. Ricard, and C. Flytzanis, Appl. Phys. **A 44**, 285(1987).
[2] H. Shinojima, J. Yumoto, and N. Uesugi, Appl. Phys. Lett. **60**, 298(1992).
[3] K. S. Bindra, S. M. Oak, and K. C. Rustagi, Opt. Commun. **124**, 452(1996).
[4] N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61**, 5399(1987).
[5] Y. R. Wang, and C. B. Duke, Phys. Rev. **B 37**, 6417(1988).
[6] G. Scamarcio, M. Lugara', and D. Manno, Phys. Rev. **B 45**, 13792(1992).
[7] F. Hache, M. C. Klein, D. Ricard, and C. Flytzanis, J. Opt. Soc. Am. **B 8**, 1802(1991).
[8] P. Maly', F. Troja'nek, and A. Svoboda, J. Opt. Soc. Am. **B 10**, 1890(1993).
[9] S. Hunsche, T. Dekorsy, V. Klimov, and H. Kurz, Appl. Phys. **B 62**, 3(1996).
[10] M. G. Bawendi, W. L. Wilson, L. Rothberg, P. J. Carroll, T. M. Jedju, and M. L. Steigerwald, L. E. Brus, Phys. Rev. Lett. **65**, 1623(1990).
[11] M. C. Nuss, W. Zinth, and W. Kaiser, Appl. Phys. Lett. **49**, 1717(1986).
[12] D. M. Mittleman, R. W. Schoenlein, J. J. Shiang, V. L. Colvin, A. P. Alivisatos, and C. V. Shank, Phys. Rev. **B 49**, 14435(1994).
[13] J. Malhotra, D. J. Hagan, and B. G. Potter, J. Opt. Soc. Am. **B 8**, 1531(1991).
[14] J. Warnock, and D. D. Awschalom, Phys. Rev. **B 32**, 5529(1985).
[15] J. P. Zheng, L. Shi, F. S. Choa, P. L. Liu, and H. S. Kwok, Appl. Phys. Lett. **53**, 645(1988).
[16] N. Chestnoy, T. D. Harris, R. Hull, and L. E. Brus, J. Phys. Chem. **90**, 3393(1986).
[17] M. O'Neil, J. Marohn, and G. McLendon, J. Phys. Chem. **94**, 4356(1990).
[18] Y. Z. Hu. S. W. Koch, M. Lindberg, N. Peyghambarian, E. L. Pollock, and Farid F. Abraham, Phys. Rev. Lett. **64**, 1805(1990).
[19] K. V. Yumashev, V. P. Mikhailov, P. V. Prokoshin, M. V. Artemyev, and V. S. Gurin, Opt. Commun. **125**, 59(1996).
[20] Y. Z. Hu, M. Lindberg, and S. W. Koch: Phys. Rev. **B 42**, 1713(1990).
[21] D. W. Hall and N. F. Borrelli, J. Opt. Soc. Am. **B 5**, 1650(1988).
[22] J.-C. Seo, D. Kim, and H. J. Kong, Appl. Phys. A, in the press.
[23] M. Kull and J.-L. Coutaz, J. Opt. Soc. Am. **B 7**, 1463(1990).