Laser-induced darkening in semiconductor-doped glasses

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We have performed experiments to characterize permanent laser-induced darkening in CdS_xSe_{1-x} semiconductor-doped glasses with picosecond pulses as a function of fluence, repetition rate, and pulse width. We find that the darkening occurs by means of a nonlinear process that exhibits an anomalous dependence on pulse width. Transmission spectra show that the induced darkening is uniform over the spectral range from the absorption edge out to 820 μm. Darkening in a number of different glasses is compared. On the basis of our results we propose a mechanism that involves photoassisted trapping of electrons from the semiconductor microcrystallites into states within the glass host material.

1. INTRODUCTION

Semiconductor-doped glasses, consisting of small microcrystallites of CdS_xSe_{1-x} suspended in a borosilicate glass matrix, have been studied quite extensively as nonlinear-optical materials. They are commercially available as color filters, their cutoff wavelength being adjustable through variation of the sulfur–selenium alloy concentration. These commercial color filters typically have microcrystallite diameters of $\simeq$100 Å.[1] Their nonlinear properties are of interest because they potentially exhibit the large nonlinearities of semiconductors combined with the well-established fabrication technology of glass. In addition, these materials can be made to exhibit a wide range of band gaps. Also, their nonlinear response time may be considerably faster than that of bulk semiconductors. The semiconductor-doped glass system is also of interest because of its potential to permit fabrication of microcrystallites as small as 25 Å in diameter, which may permit three-dimensional quantum confinement effects to be studied. However, the results of previous nonlinear-optical studies are somewhat confusing because many different values of $\chi^{(3)}$, ranging from 10^{-7} to 10^{-11} esu,[2–8] and response times from microseconds to picoseconds have been reported.[8–10] It should be noted that these nonlinearities are saturable band-gap resonant carrier nonlinearities, and quoting a value for $\chi^{(3)}$ is only an approximate way to describe the nonlinear refraction.[11,12]

These large inconsistencies were partly explained by Roussignol *et al.*,[9] who first showed that these materials undergo a permanent photodarkening after long-term illumination by intense laser irradiation. This darkening is accompanied by a permanent decrease in both $\chi^{(3)}$ and response times. Using degenerate four-wave mixing with picosecond laser pulses at 532 nm, they studied the temporal decay of the nonlinearity in Corning 3-68 and Schott OG 530 glasses. Slow decays were observed with time constants of tens of nanoseconds or longer in the fresh samples, while much shorter decay times of 50 and 100 ps were observed in the photodarkened Schott and Corning glasses, respectively. They also studied luminescence in darkened and undarkened (fresh) OG 570 and showed that the darkening is accompanied by the disappearance of the broadband luminescence from midgap levels that dominates the luminescence spectrum of the fresh glass. The interband luminescence is only slightly reduced and thus becomes the dominant recombination process in darkened glass. Similar effects of laser exposure on carrier-recombination times were observed by Mitsunaga *et al.*,[13] who saw a slow decay of a few nanoseconds; the decay became quenched with increasing exposure times, and finally a fast decay, as short as 7 ps, remained, although no darkening was observed. Kull *et al.*[14] also reported similar effects; i.e., darkening decreased the lifetime by 1 order of magnitude and also increased free-carrier absorption.

Although some models for darkening have been suggested, the lack of knowledge about many parameters of these materials, in addition to the lack of experimental data, has kept these models quite vague and sometimes contradictory. For example, Roussignol *et al.*[9] clearly rule out a thermal mechanism, whereas Williams *et al.*[15] suggest that the effect is due to rapid thermal annealing of the crystallite, which removes luminescent traps in the crystallites and creates extra surface states. In Ref. 13 the effects are attributed to a change in the collisional cross section of conduction electrons with donorlike trap states, although the cause for such a change is not sug-

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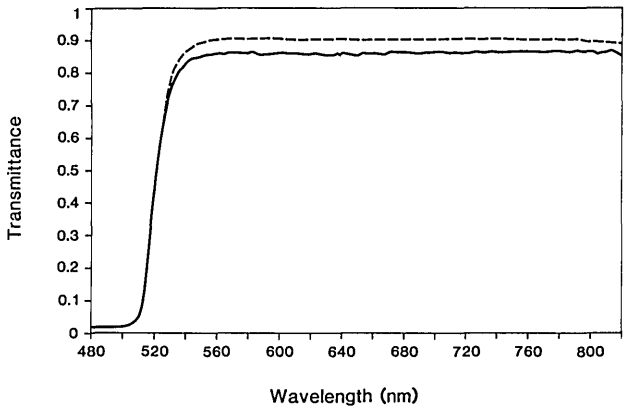

Fig. 1. Spectra of Schott OG 515 glass. The dashed curve represents the spectrum of the undarkened sample, and the solid curve represents the spectrum of the darkened sample.

gested. In any event, the models concentrate on explanations of the change in lifetimes and luminescence spectra while seemingly ignoring the darkening effect. The apparent lack of darkening seen by Mitsunaga *et al.*[13] may be partly due to the small spot sizes (<100 μm) used. We find that the darkening is only barely visible with spot sizes of a few millimeters, while darkening with smaller spot sizes is invisible to the naked eye. It is not clear whether their experiments were sensitive to the small, long-term changes in transmittance that are caused by photodarkening. Because photodarkening strongly affects the performance of semiconductor-doped glasses as nonlinear-optical materials, it is important to understand the processes that cause this effect. Although the maximum transmission change is the order of 5% in our thin (3 mm) sample, it would be substantial and of concern if such materials were used in waveguide device applications when larger interaction lengths are desired.[16] In this paper we describe systematic experiments performed to characterize darkening of a number of commercially available semiconductor-doped glasses with the aim of furthering the understanding of the processes that lead to darkening and its accompanying effects. On the basis of our results we present a modified three-level model that involves trapping of electrons in energy states in the glass in the vicinity of the microcrystallites.

2. EXPERIMENT

A. Change in Transmission Spectrum

Our initial experiments, designed to identify the nature of the photodarkening process, involved the study of the change in the absorption spectrum that is brought about by darkening of the glass. Transmission spectra for samples of Schott OG 515 glass were obtained in both undarkened and darkened areas with a grating spectrometer and vidicon with a white light source. This method proved to be more successful than using a spectrophotometer, which failed to show a clear difference between darkened and undarkened regions because of both the small areas and the small transmittance changes. The darkening was produced by illumination with several thousand pulses of 532-nm light with a 20-ps half-width 1/*e* maximum (HW 1/*e* M) pulse width. As shown in Fig. 1, darkening was observed to reduce the transmittance by ~5% and to be of a broadband nature, with no evidence of distinct spectral features between the fundamental absorption edge and the longest measured wavelength of 820 nm. Although in principle this change in transmittance could be caused by an increase in the Fresnel reflection losses at each surface, this mechanism would require an increase in refractive index from 1.5 to 1.85. Such a large change in index is incompatible with previous experiments on darkening.[9] We further verified that the decrease in transmittance was not due to scattering by observing the effect of passing a helium–neon laser beam through both fresh and darkened regions of the glass. Because the fresh sample produces small amounts of scattered light, a 5% reduction in transmittance arising from scatter ought to give a clearly visible increase in scattered light. However, no difference in scattered-light levels could be seen for the two cases. Thus we conclude that darkening is indeed an absorptive effect.

B. Fluence and Pulse-width Dependence of Darkening

In order to quantify the permanent change in transmittance during irradiation of the glass by a pump laser, a pump–probe configuration was used, as shown in Fig. 2. The pump source was a frequency-doubled hybridly mode-locked Nd:YAG laser with a variable pulse width, in the range of 20 to 140 ps (HW 1/*e* M) at a wavelength of 532 nm, and a variable repetition rate of up to 10 Hz. The pump light was focused on the glass sample with a spot radius of 800 μm (HW 1/e^2 M). A weak cw He–Ne laser, running at 633 nm, was used to probe the change in transmission while the sample was irradiated by the pump beam. This 3-μW probe was focused to a 160-μm (HW 1/e^2 M) radius spot on the sample and was centered on the pump spot. The probe beam was chopped at 1200 Hz, and both input and transmitted signals were fed to a lock-in amplifier. The use of this single wavelength gives us full information for the change in absorption in view of the broadband nature of the darkening, as described above.

The sample used for most experiments was Schott OG 515 glass. The darkening observed was of a permanent nature and remained unchanged for several months after irradiation. We were unable accurately to calibrate the small transmittance changes; therefore the absolute error of the shown transmittance change may be as much as a factor of 2. However, the relative error among curves in each figure is small. The largest transmittance

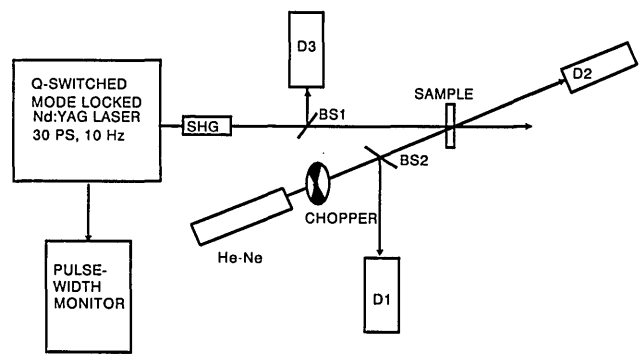

Fig. 2. Experimental apparatus. D1, probe input detector; D2, probe transmission detector; D3, pump energy detector; BS1 and BS2, beam splitters; SHG, second-harmonic generator.

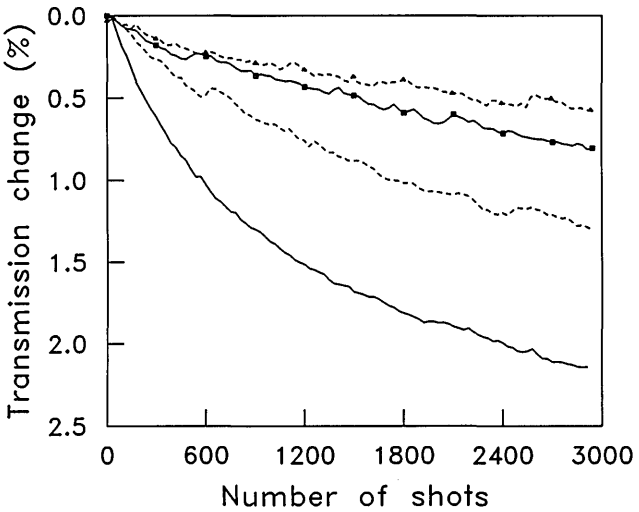

Fig. 3. Transmission change for various pump-beam fluences, all for 3000 shots. Solid curve, 49.2 mJ/cm^2; dashed curve, 34.3 mJ/cm^2; solid curve with squares, 21.2 mJ/cm^2; dashed curve with triangles, 19.2 mJ/cm^2.

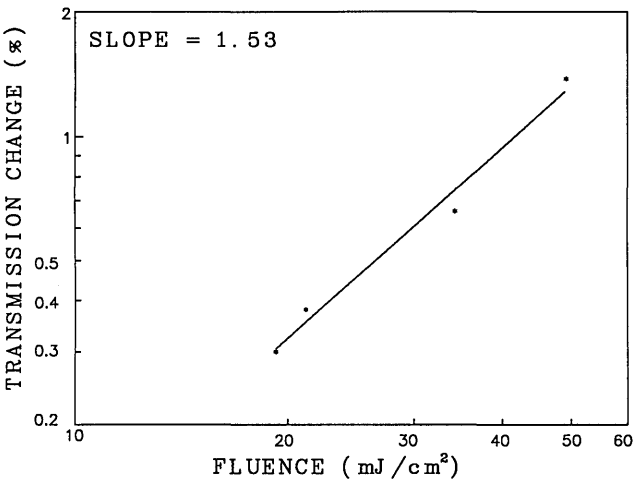

Fig. 4. Plot of transmission change versus fluence at 1000 shots, from Fig. 3, on a logarithmic scale.

changes reported are estimated to correspond to a change of ~5%. Figure 3 shows the transmittance change in OG 515 for a number of different fluences versus number of laser shots at a 10-Hz repetition rate and 20-ps pulse width. In all cases we observed that the transmission change saturates to some maximum value, although this effect is not shown in Fig. 3. From our data we find for higher fluence that not only was the initial rate of darkening higher but also that the saturation transmission change was greater. By logarithmically plotting the net transmission change at 1000 shots versus the fluence, we determine the fluence dependence of the rate of darkening before saturation. The resulting plot is shown in Fig. 4. From this calculation we establish that the darkening is a nonlinear process with the transmission change proportional to $F^{3/2}$, where F is the pump fluence. It is also worthwhile to note that a small amount of recovery of transmission was observed after the pump irradiation was blocked, as shown in Fig. 5. This recovery occurs over a time period of a few seconds.

Now that it is established that the darkening process is nonlinearly related to the incident fluence, it is of interest to characterize darkening as a function of pulse width. If darkening were due to a purely fluence-dependent mechanism (such as excited-state absorption), we would not expect any change for different pulse widths of the same fluence. However, if the effect were due to a purely irradiance-dependent mechanism (such as two-photon absorption), then more darkening would be seen for decreased pulse widths at a fixed fluence. Figure 6 shows the transmission change for 20-, 64-, and 140-ps (HW 1/*e* M) pulses, all of which have a fluence of 24.6 mJ/cm^2 per pulse. Somewhat surprisingly, we observe that darkening is less for 20 ps than for 64 ps. The 140-ps pulse gives approximately the same amount of darkening as the 64-ps pulse. This result suggests that the darkening process cannot be explained by simple fluence- or irradiance-dependent mechanisms such as excited-state absorption or two-photon absorption. We return to this problem in Section 3 below.

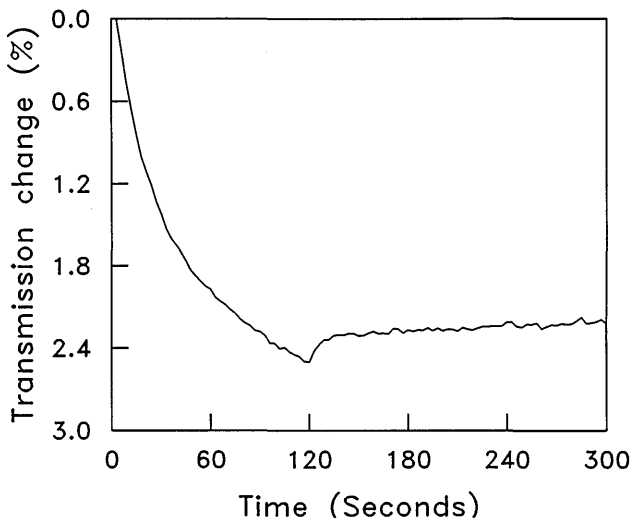

Fig. 5. Recovery from darkening. Sample was exposed to the pump beam at 67.8 mJ/cm^2 for 1200 shots, and then the beam was blocked.

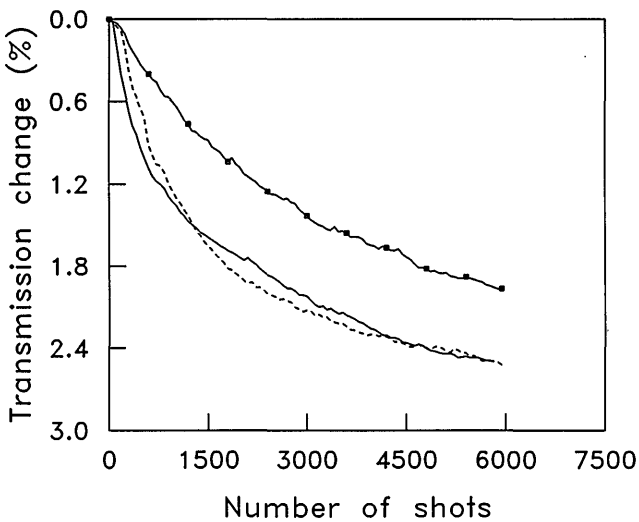

Fig. 6. Transmission change for various pulse widths of the pump beam for 6000 shots at constant fluence of 24.6 mJ/cm^2. Dashed curve, 140 ps; solid curve, 64 ps; solid curve with squares, 20 ps.

We also performed studies to determine whether the photodarkening could be removed by long-term low-power illumination. Such an effect has been seen, for example, with color centers in yttrium-stablized cubic zirconia,[17] in which the color centers were formed at high intensity by two-photon absorption, whereas long-term illumination at low intensity caused removal of the color centers. For our experiment the He–Ne laser was focused on a darkened area of the sample in the absence of the Nd:YAG pump radiation. However, no recovery was observed after many hours of illumination. This is not particularly surprising, since we have observed no change in the darkened material after a period of several months despite continuous irradiation by room light.

C. Comparison of Darkening in Different Glasses

We compared darkening between several samples of both Schott and Corning glasses with various cutoff wavelengths. Darkening in Schott OG 475, OG 495, OG 515, OG 530, and OG 570 and in Corning 3-67, 3-68, 3-69, 3-70, and 3-71 was evaluated for a fluence of $\simeq$40 mJ/cm^2 and a 140-ps pulse width. We observed various extents of darkening in different samples with no clear relation to the cutoff wavelength. This is somewhat surprising, because the linear absorption at 532 nm varies by more than an order of magnitude among these samples. Although glasses OG 475, 495, and 515 have similar absorption coefficients below 1 cm^{-1}, OG 530 showed slightly more absorption, and the absorption in OG 570 was so large that no transmitted radiation at 532 nm could be detected. However, in general Schott samples darkened considerably more than did Corning samples. Figure 7 clearly demonstrates this effect in a direct comparison of Schott OG 515 and Corning 3-69 samples, both of which have their cutoff point near 515 nm.

Experiments at 1.06 μm revealed that we could not darken Schott OG 515 with this wavelength, even with the considerably higher fluences that were required for darkening with the second harmonic. Both 30-ps and 18-ns pulses were used.

3. DISCUSSION

There can be little doubt that the darkening effect in these glasses is not due to the glass host matrix alone but must in some way be due to the semiconductor microcrystallites. This is apparent from the previous studies that were reviewed in the Introduction, which showed that the darkening process strongly alters luminescence spectra and lifetimes, properties that are clearly related to the semiconductor material. Thus we see that this process is not related to solarization effects, which are known to occur in optical-grade glasses under intense laser radiation. Of course, we do not see such darkening effects in bulk semiconductors either, so it is apparent that this unusual effect is due to either the particular structure of the crystallites or the semiconductor–glass interface at the surface of the microcrystallites. Therefore in an analysis of the darkening effect we may concentrate our attention on the physics of the interaction of light with the microcrystallites and their surfaces.

The first conclusion we reach from the data presented here is that thermal annealing effects, as proposed in Ref. 15, can be ruled out. For example, in OG 515 we have seen darkening at fluences as low as 4 mJ/cm^2. An estimate for the peak rise in temperature, with no heat diffusion within the pulse width assumed, can be calculated to be $\Delta T = \alpha F/c\rho$, where α is the linear absorption coefficient of the crystallite material, F is the incident fluence, c is the specific heat capacity of the semiconductor, and ρ is the density. Using F = 10 mJ/cm^2, c = 0.27 J K^{-1} g^{-1},[17] ρ = 5.81 g-cm^{-1},[18] and $\alpha = 10^2$ cm^{-1}, we obtain ΔT = 0.2 K. The value of α was obtained by dividing our measured value of 0.1 cm^{-1} for the composite glass by the volumetric fill fraction of 10^{-3}, determined in Ref. 1. Even for those glasses with $\alpha \simeq 10^4$ at 532 nm, such as Schott OG 570, the maximum temperature rise at these fluences is only $\simeq$20 K, too small for any thermally induced change in the material.

Thermal processes being eliminated, it seems apparent that prolonged intense laser radiation cannot influence the structure of the crystallites or the semiconductor–glass interface. This conclusion implies that traps are not created or destroyed, as has been suggested in much of the previous literature. Instead we propose that the darkening mechanism is due to permanent trapping of photoexcited electrons in traps that already exist in the semiconductor-doped glass. One possible mechanism is that electrons excited into the conduction band (CB) of the microcrystallite then decay into permanent traps below the CB in a manner similar to color-center formation. As described above, a similar type of mechanism was observed in cubic zirconia where the color centers were created by two-photon absorption.[17] However, the fact that neither irradiation at 1.06 μm nor long-term illumination at low intensities reverses the darkening process leads us to believe that this is not the mechanism, because absorption from a trap into the CB should be followed by a finite probability of recombination to the valence band, thus eventually reversing the darkening. The fluence and pulse-width dependencies are also not explained by this mechanism.

We suggest another model, which predicts a similar fluence and pulse-width dependence. This is a modified

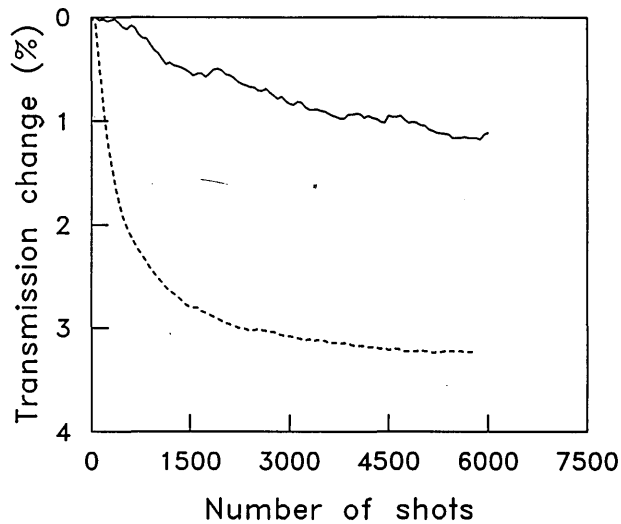

Fig. 7. Comparison of darkening in two samples at 140 ps and 40 mJ/cm^2. Solid curve, Corning 3-69; dashed curve, Schott OG 515.

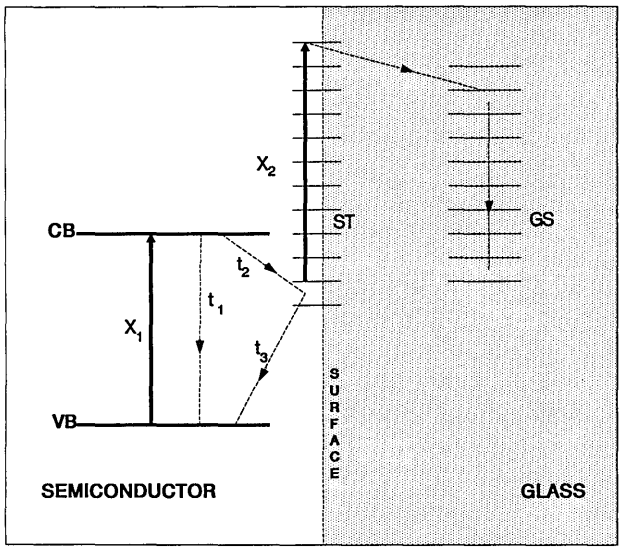

Fig. 8. Band picture of suggested model. X_1 and X_2 represent the sequential laser excitations, and ST and GS represent the surface and glass trapping centers, respectively. The dashed lines represent decay paths, where t_1, t_2, and t_3 are the direct recombination, trapping, and trap-decay times, respectively.

three-level model that involves trapping in the structure of the glass by means of a two-step excitation process. Our model is diagramatically represented in Fig. 8. Valence-to-CB absorption is known to behave as in an inhomogeneously broadened two-level saturable absorber,[11] i.e., $\alpha(I) = \alpha_0/(1 + I/I_s)^{1/2}$. Electrons in the valence band are excited to the CB, some of which relax to trap levels at the glass–semiconductor interface. Before the electrons can recombine, light at later times in the pulse reexcites some of these trapped electrons to higher-energy surface states, from which they may migrate into the bulk of the glass. These electrons eventually relax to deep levels, in which they are permanently trapped. Such mechanisms can be quite likely, because the random glass structure contains many available trapping sites below its fundamental absorption edge. At high intensities ($I \gg I_s$) the rate of excitation from the valence band to the CB is proportional to $F^{1/2}$ owing to the inhomogeneously broadened absorption saturation behavior. The second excitation from the trap level is directly proportional to F, explaining why our results show that the darkening is proportional to $F^{3/2}$.

There are two possible explanations for the anomalous pulse-width dependence associated with this model. Because there is a finite time for electrons to relax from the CB to trap levels, there will be a strong pulse-width dependence for laser pulse widths that are comparable to the trapping time. Pulse widths that were long relative to trapping time would show no such dependence. While this can explain our result for pulse-width dependence, the trapping time would have to be of the order of 10 ps, which is longer than that indicated by luminescence studies.[9] A more plausible explanation is that the pulse-width dependence is caused by the saturation of the interband absorption. Since the interband absorption saturates as $\alpha_0/(1 + I/I_s)^{1/2}$, longer pulses of the same fluence cause less saturation than shorter pulses, resulting in the transfer of more carriers to trap states. This argument relies on the saturation's being a function of the irradiance rather than of the fluence, which is true in this case if we maintain the assumption that the trapping time t_2 is much less than the pulse width.

We have numerically modeled these effects with a simple rate-equation approach. However, we have been unable to demonstrate a quantitative fit owing to our lack of knowledge about several parameters, such as the exact crystallite size, the nature of defects in the crystallites or at the surfaces, and the nature and density of trapping sites in the glass. Nevertheless, our model shows behavior that is qualitatively similar to our experimental results and can also explain the results of previous studies. The saturation of the darkening can be attributed to filling of the available traps in the vicinity of each microcrystallite, which may be only a small number per microcrystallite. The model may also explain why the maximum amount of darkening is fluence dependent in that the electrostatic repulsion of these filled traps may inhibit migration of more electrons to the surface. Additionally, this possibility could explain the disappearance of trap-assisted recombination seen by Roussignol *et al.*[9] where such repulsion makes surface traps unavailable to act as recombination centers.

Finally, the comparative study of darkening in different glasses does not necessarily detract from our model, although it does serve to highlight many of the uncertainties we face when attempting a rigorous explanation of the darkening effect. Clearly the darkening responses of the various Schott or Corning glasses do not show a strong correlation with the linear absorption coefficient. Although our model predicts such a correlation, it is probable that other factors, such as the structure of the host glass, may play as important a role as the absorption coefficient of the microcrystallites. Therefore it may not be meaningful for us to compare different glasses solely in terms of their absorption coefficient. However, for applications of these materials in nonlinear-optical devices, Corning glasses maintain the advantage of having a lower attenuation when darkened, while Schott glasses more readily exhibit faster recombination times.

4. CONCLUSIONS

We have shown that darkening is a broadband effect that is nonlinearly dependent on the fluence of the exciting laser. From our results we have proposed a model that suggests that darkening is due to removal of the electrons from the microcrystallites to states in the amorphous glass host. While the evidence to support this model is not yet complete and further experimental studies are required, this model is to our knowledge the only one to date that can explain our data along with all the previously reported data on lifetimes, luminescence spectra, and darkening. This study indicates that, in order to conclusively identify the darkening process, similar studies, in addition to spectroscopic and lifetime studies, would have to be performed systematically in a large number of different glasses according to the absorption edge, wavelength, and fabrication process of each.

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