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L. L. Chase
H. W. H. Lee

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Accumulated Surface Damage on ZnS Crystals Produced by Closely Spaced Pairs of Picosecond Laser Pulses*

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L. L. Chase and H. W. H. Lee
Lawrence Livermore National Laboratory
Livermore, CA 94550

Excitation of a transparent ZnS crystal by repetitive picosecond dye laser pulses causes an accumulated surface modification leading to optical damage. The onset of the damage is detected by an abrupt increase in the emission of neutral Zn (and possibly S_2) from the surface. Comparison of the neutral emission thresholds with pulse-pair and single-pulse excitation shows that linear absorption is the dominant laser-surface interaction. In general, this measurement technique shows considerable promise for investigating the possible influence of nonlinear absorption or excitation processes on damage mechanisms. The data suggest that heating of small absorbing regions produces the surface modification that leads to the observed surface ablation. The nature of the damage observed at fluences above the threshold suggests that it is caused by heating of a relatively large (~10 - 100 µm) surface region that has been modified by the accumulation pulses.

Key words: surface damage; accumulation; picosecond; neutral species emission

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1. Introduction

The interaction of intense laser beams with the surfaces of transparent optical materials can involve linear and nonlinear absorption caused by surface states, defects and impurities. Direct measurement and characterization of these interactions is very difficult. It is known, however, that laser excitation of many materials causes the emission of charged and neutral surface constituents and impurities. The characteristics of the emitted products, such as the identity of the emitted species, velocity distributions, absolute and relative yields, and internal excitations, provide useful information regarding the laser-surface interaction.[1,2] In previous work on ZnS with nanosecond lasers at wavelengths above and below the interband absorption threshold, it was found that Zn, S, and possibly S_2 were emitted at laser fluences below the threshold for observable optical damage[1]. In this work we measured the yield of neutral Zn and S from surfaces of ZnS single crystals caused by multiple-pulse excitation with a picosecond dye laser at a wavelength of 580 nm, which is much longer than the interband absorption threshold of about 330 nm. This wavelength is, however, well within the region of two-photon bulk absorption.[3] In this circumstance two photon absorption involving bulk, surface, or defect levels may be a significant factor in optical damage mechanisms, particularly for picosecond pulses, which have high peak intensities at the damage threshold.

2. Experimental procedure

The experimental setup is shown in Fig. 1. The sample was irradiated in a vacuum system at a pressure of about 10^{-9} torr using a picosecond dye laser operating at 10 Hz with a pulsewidth of 1.5 ps and a pulse energy of up to 300 μJ. The laser was focused to a spot diameter of about 150 μm, yielding fluences of up to about 1.3 J/cm^2. A quadrupole mass spectrometer was used with a reduced mass resolution to detect the emitted Zn at masses 64 - 68 amu. It is also possible that S_2 (mostly mass 64 amu and some at 66 amu) is detected, although its presence in the emission is not established with certainty because of its mass overlap with Zn. The output of the mass spectrometer was sampled by a gated integrator for a time interval of 1 ms following the laser pulse. The polished surface of the crystal was cleaned in methanol and heated in vacuum to 300 C to desorb contaminants. Data were collected using multiple excitation on each of a grid of spots separated by about 1 mm on the sample surfaces.

3. Experimental results and discussion

At low fluences with 10 Hz excitation the neutral emission from the surface is very weak and is not detectable at the sensitivities used for this work. This is consistent with the behavior of the Zn emission yields observed below the optical damage threshold in our previous experiments[1], which showed that the surface sites from which atoms are desorbed at low fluences are bleached after a few laser pulses. At a rather well-defined threshold fluence, however, a large flux of neutrals is observed after several hundred pulses, and the number of pulses required to initiate the emission decreases very rapidly with increasing fluence. This is illustrated in Figs. 2 and 3. In Fig. 2 the emission yields from each of several different sites are plotted as a function of time in traces (a) - (e). The abscissa is labeled by the cumulative number of excitation pulses. The fluence per pulse was increased at successive spots. At the lowest fluence, 0.38 J/cm^2, no emission was observed for up to 3800 pulses. On the next site, the fluence per pulse was increased to 0.4 J/cm^2, and emission was observed after about 300 pulses. Traces (c) - (e) show that the number of pulses required to initiate emission decreases rapidly with increasing fluence. This is evident in Fig. 3, where the number of required pulses is plotted as a function of pulse fluence for a series of initially virgin spots. This procedure was repeated several times, and it was found that the threshold fluence was repeatable to within about 20 - 30 percent. For this case of excitation by a single pulse every 100 ms, we define the single-pulse threshold fluence $F_t(1)$ for which the emission increase is observed after at most 1000 pulses. We found visible damage on each grid spot for which the threshold fluence was attained. The form of this damage will be discussed below. The important point is that the neutral emission threshold corresponds to the multiple-pulse optical damage threshold.

The threshold fluence was measured for excitation by pairs of identical picosecond pulses separated by various time delays, τ. $F_t(2,\tau)$ is defined as the sum of the fluences of the two pulses. The threshold fluence for the pulse pair (twice the fluence of each pulse) was compared with the threshold fluence for a single pulse. The ratio $R = F_t(2,\tau)/F_t(1)$ is plotted in Fig.4 as a function of τ. For $\tau < 2$ ps, the two pulses form interference fringes on the surface, and the peak fluence in the fringe maxima is twice as large as for a single pulse of the same fluence. This accounts for the value of $R \sim 0.5$ for small time delays.

For 2 ps $< \tau <$ 1 ns, R is approximately unity. This result implies that the threshold is determined by the total fluence of the pulse pair. When the pulses have no temporal overlap, which is the case in this range of time delays, emission resulting from multiphoton or other superlinear interaction processes would occur at a higher fluence than for a single pulse, since the intensity of each pulse of the pulse pair is half as large as for the single pulse. For example, the total absorbed energy due to two-photon absorption is proportional to the number of pulses times the square of the peak intensity. If this absorbed energy determines the emission threshold, we should find $R = \sqrt{2}$. For nonlinear absorption proportional to I^n the appropriate value of R is $R = 2^{1-1/n}$.

For $\tau >$ 1 ns, the ratio R increases toward the value R = 2 that is expected if the pulses act independently on the surface, and <u>each</u> pulse must exceed the single-pulse threshold fluence. The simplest model that accounts for the changes with pulse separation is that the cooperative effects caused by the two pulses decay exponentially with increasing pulse separation with a time constant τ_m. This is equivalent to assuming that the relevant surface excitation produced by the first pulse decays with this time constant and its effective fluence is reduced by $\exp(-\tau/\tau_m)$. Then the ratio R is determined from the condition that the effective fluence of the two pulses at the emission threshold be equal to that of the single pulse threshold:

$$F_t(2,\tau) \exp(-\tau/\tau_m)/2 + F_t(2,\tau)/2 = F_t(1) \qquad (1)$$

The ratio R obtained from Eq. 1 is

$$R = [1 + \exp(-\tau/\tau_m)]^{-1}. \qquad (2)$$

The dotted curve in Fig. 4 gives a reasonable fit of this function to the data for a "memory time" $\tau_m = 5$ ns.

Heating is a possible explanation for this "memory time" in the double-pulse threshold behavior. The approximate distance over which heat diffuses in a time τ_m is $d = (\kappa\tau_m)^{1/2}$, where κ is assumed to be the bulk thermal diffusivity of ZnS. For $\tau_m = 5$ ns, this assumption yields $d = 0.1$ µm as the approximate dimension of the heated regions of the sample surface. This could correspond to the size of absorbing inclusions or it could be the depth of an absorbing region near the surface produced by damage introduced in the polishing process. It is possibly significant that a similar size estimate was made based on surface temperatures obtained from Doppler shifts of ablated Zn atoms caused by laser excitation above the bandgap of ZnS[2]. In Ref. 2, much higher effective particle temperatures were observed than could be accounted for using the known interband absorption coefficient and the bulk thermal diffusivity of ZnS. It was suggested that these high temperatures resulted from heating of a thermally isolated region of 0.1 µm dimensions by the interband absorption. In the present experiments, bulk interband absorption does not, of course, play a role. It is possible that some form of surface absorption, rather than bulk interband absorption, is also responsible for the emission observed in Ref. 2.

How can heating account for the progressive surface modification implied by the accumulation effect involved in the multiple-pulse damage?

It is known that ZnS sublimes at the relatively low temperature of 1200 C. Since the sublimation rate increases very rapidly with increasing temperature, the degree of surface modification caused by this process would have a threshold-like behavior as a function of laser fluence. If the sublimation process is not congruent, it will lead to the production of surface defects through loss of stoichiometry. In our previous experiments with excitation by single nanosecond pulses, we did in fact find evidence that the Zn emission was delayed relative to the S emission following a laser pulse[1]. This time delay provides evidence that the two constituents desorb at different rates, with the likely result being a surface that is deficient in sulfur. This anion deficiency could result in the production of color centers, such as F centers, near the surface. This type of surface modification could produce enough defects to cause a catastrophic runaway in the cycle of absorption of light and the consequent production of additional absorbing defects.

There are other possible causes for the memory effect implied by the data in Fig. 4. Electronic excitation can exist for several nanoseconds after a short pulse, either in the form of localized excitations or as free carriers. Deeply trapped carriers form color centers which could enhance the absorption of the second pulse. Free carriers produced by the first pulse could likewise cause additional absorption and heating during the second pulse. An accumulation effect would appear to be unlikely in either case, since the original absorbing site would be bleached, leading to no net increase in the absorbing sites. A second possibility involves the emitted neutrals produced by the first laser pulse, which travel only a few microns from the surface within the 5 ns memory time. Ionization and heating of these neutrals by the second laser pulse could lead to surface bombardment, resulting in ablation or heating. This process is not a likely cause of the accumulation effect since the ionization of Zn or S requires about 10 eV of energy and would involve a four-photon absorption, which is not consistent with the observed value of R.

After the sample was removed from the vacuum chamber, it was investigated using Nomarski microscopy. A typical damage site is shown in Fig. 5. At this site, laser excitation was halted very soon (several tens of pulses) after neutral emission was observed. The damage spot, which appears elongated because of the excitation at 45° to the surface normal, covers a sizeable fraction of the laser focal spot. We saw no evidence of clearly defined nucleation sites for the damage at most irradiated spots on the crystal. Either the damaged regions spread very rapidly on successive shots or the damage is initiated over a rather large area. The damaged surface acquires a granular structure, which suggests that material is removed either by plasma ablation or by sublimation, rather than by melting.

The accumulation effects observed in this work may well be related to damage caused by single and multiple-pulse excitation at much longer pulse lengths than we have used. Since total fluence is the important parameter determining the threshold for the accumulation process, the same surface modification must also proceed during excitation by longer laser pulses. The important point is that when either prolonged or repetitive excitation creates a critical level of surface defects, optical damage will occur either during a long pulse or on a subsequent short pulse.

4. Conclusions

These experiments show that nonlinear excitation of any type is not involved in the accumulation effect leading to multiple-pulse damage on ZnS despite the very large intensities, > 50 Gw/cm^2, of the picosecond pulses at the threshold fluence. The total fluence of the pulses is the important parameter. It is most likely that the accumulation is caused by the heating of either small absorbing defects or by a thin surface layer, with a typical dimension of 0.1 μm in either case. Efforts are underway to detect changes in surface composition resulting from laser excitation in order to characterize the accumulated surface modification. The use of picosecond pulse-pair excitation to investigate the duration of surface excitations leading to optical damage is a promising technique that is currently being applied to other materials.

Acknowledgement

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FIGURE CAPTIONS

Fig. 1: Schematic of UHV system and picosecond pulse pair excitation setup.

Fig. 2: Neutral emission yield for picosecond pulse excitation of ZnS at a 10 Hz repetition rate. Approximate fluences (J/cm^2) are: (a) 0.38, (b) 0.4, (c) 0.43, (d) 0.56, (e) 1.35.

Fig. 3: Number of pulses required to produce neutral emission and damage as a function of pulse fluence.

Fig. 4: Ratio of threshold fluences for pulse-pair and single-pulse excitation as a function of pulse-pair separation. The dotted line is calculated from Eq. 2 with $\tau_m = 5$ ns.

Fig. 5: Nomarski micrograph of optical damage observed at the threshold fluence.

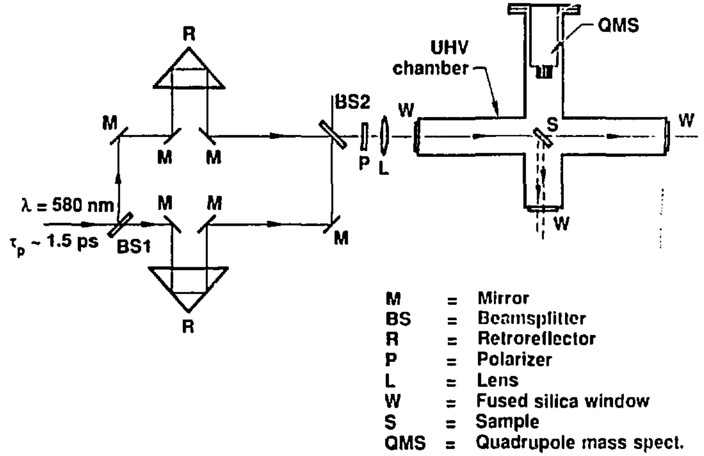

R
UHV chamber
QMS
M
BS2
W
S
W
M
M
P
L
λ = 580 nm
M
M
τp ~ 1.5 ps
BS1
M
W
R
M = Mirror
BS = Beamsplitter
R = Retroreflector
P = Polarizer
L = Lens
W = Fused silica window
S = Sample
QMS = Quadrupole mass spect.

Figure 1

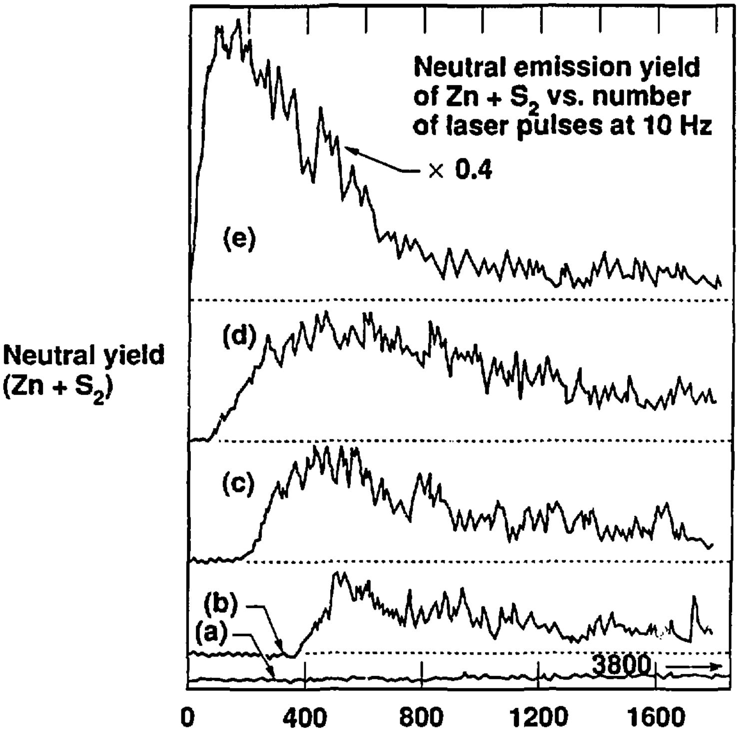

Neutral emission yield of Zn + S_2 vs. number of laser pulses at 10 Hz
× 0.4
(e)
(d)
(c)
(b)
(a)
3800
Neutral yield ($Zn + S_2$)
0
400
800
1200
1600

Figure 2

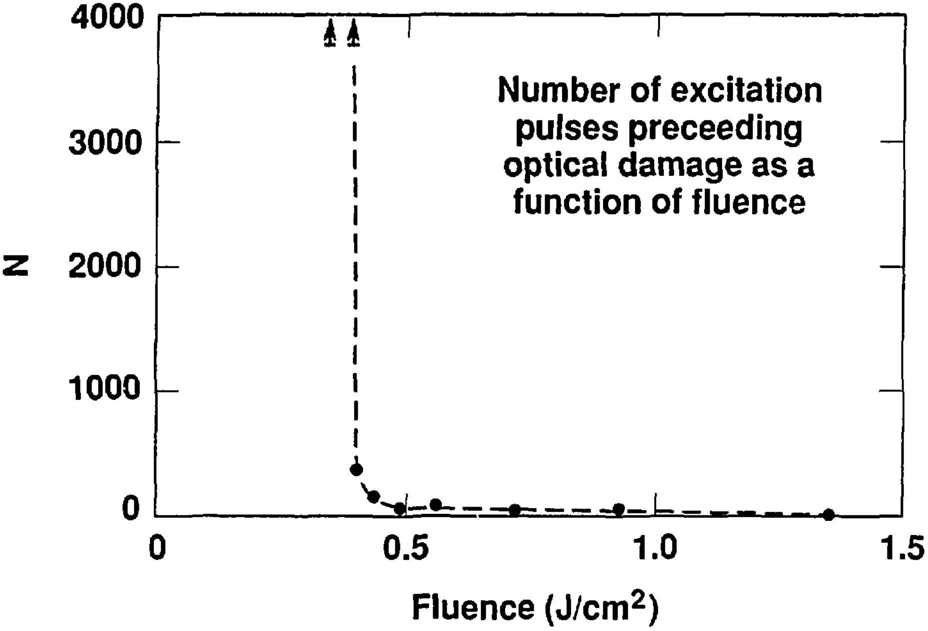
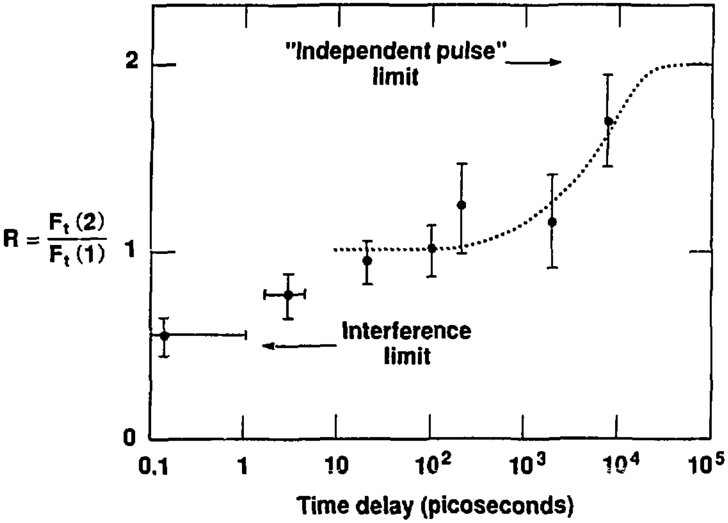

4000
3000
2000
1000
0
N
0
0.5
1.0
1.5
Fluence (J/cm²)
Number of excitation pulses preceeding optical damage as a function of fluence

Figure 3



$R = \frac{F_t(2)}{F_t(1)}$
2
1
0
0.1
1
10
10^2
10^3
10^4
10^5
Time delay (picoseconds)
"Independent pulse" limit
Interference limit

Figure 4

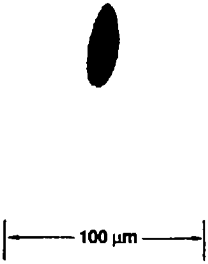


Figure 5