Laser induced surface emission of neutral species and its relationship to optical surface damage processes*

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Abstract

The laser-induced emission of neutral constituents and impurities from surfaces of several optical materials is shown to be correlated with optical surface damage thresholds. The characteristics of the emission can be utilized to investigate physical processes involved in the absorption of laser energy at the surface. Examples are given of neutral emission correlated with catastrophic surface heating, changes in surface stoichiometry, and thermally-induced cracking.

Key words: damage; mass spectroscopy; sodium fluoride, surface damage; surfaces; zinc sulfite

Introduction

Two fundamental problems involved in understanding and controlling optical surface damage involve identifying the initial mechanism for deposition of laser energy at the surface and the resulting physical processes that precipitate catastrophic failure. There are several possible interaction mechanisms that could account for the absorption of laser energy at the surface of a nominally transparent optical material. These are illustrated in Fig. 1, which shows the valence and conduction bands of a typical optical material. We shall be concerned here with optical damage to such a material caused by irradiation with laser light having a photon energy much less than the optical bandgap energy. Direct absorption of light by the intrinsic material can result only from multiphoton excitation across the bandgap or by multiphonon absorption. In the first case, electrons and holes are generated, and in the second case, heating of the material results directly from the excitation. Both of these direct excitation processes are very weak, and the energy density deposited in the near-surface region is certainly too low to cause direct thermal failure of the material. It is possible, however, that free carriers produced by the multiphoton process could nucleate an avalanche process. There are also extrinsic absorption processes that produce free carriers or direct heating near the surface of a "real" optical material. These are illustrated in Fig. 1 by the presence of surface states or defects that can supply "cheap" electrons or holes by direct absorption of the laser light, or by highly absorbing particles embedded in the surface region.

The problem of detecting these surface absorption processes is formidable because they may be very localized and cause unobservably small changes in the transmitted or reflected laser intensities and average surface temperatures. In the present work, we have investigated the possibility of observing the interaction of the laser with the surface by detecting neutral atoms or molecules emitted as a result of the laser excitation. It is also possible, and much easier, to detect ions and electrons. In general, however, it is found that, at least for ion beam or electron beam excitation of surfaces, the primary emitted species are neutrals.[1] In previous work on ZnS, we also found this to be the case for laser excitation at 1.06 μm.[2]

There are several characteristics of the emitted neutrals that could, in principle, provide evidence regarding the nature of the interaction of the laser beam with the surface:

(1) Emission yields as a function of laser fluence, photon energy and surface preparation can help to identify the type of optical absorption process.
(2) The identity and relative abundance of the emitted species can be used to infer the physical process causing surface ablation, and to search for changes in surface composition caused by the laser excitation.
(3) The time dependence of the neutral emission following initiation or termination of laser excitation can be significant for a variety of reasons. Temperatures of the emitted particles can be obtained from time-of-flight data, if there is not too large a time delay between laser excitation and emission. On the other hand, a measurable time delay may help to identify the ablation process.
(4) The spatial dependence of the emission can be used to locate regions susceptible to ablation and optical damage.

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If neutral emission is to be a very useful method for surface damage research, it must be established that it is caused by the same interaction of the laser with the surface that precipitates the observable damage event. In addition the emission must be detectable at fluence levels considerably below the threshold for significant optical damage so that it probes the initial interaction of the laser beam with the surface, rather than a catastrophic breakdown of the surface, which will always result in copious neutral, ion and electron emission. To the best of our knowledge, only one previous investigation of neutral or ion emission was successful in establishing these properties. This is the work of Schmid, et.al., who observed multiphoton-induced emission of halogen atoms from alkali-halides using ruby laser excitation.[3] It is the aim of the present work to explore the possibility of utilizing neutral emission as a probe of optical surface damage processes in various types of optical materials. We have therefore selected for study a set of representative types of optical materials. These include fused silica, and single crystals of ZnS, NaF, Al_2O_3, and BaF_2.

Experimental procedure

The experiments are carried out in two UHV systems with base pressures of 5×10^{-10} and 2×10^{-9} torr, respectively. At these pressures, the adsorbed impurities accumulate at a rate very much less than a monolayer between laser shots. The samples were optically polished, cleaned with ethanol, and blown free from dust and other particles just before insertion in the vacuum system. Prior to laser excitation, a heater on the sample holder was used to desorb contaminants from the surfaces at temperatures up to 500C in UHV. The experiments on fused silica were done in the vacuum system with lower ambient pressure using a variable-pulsewidth (1 - 10 ns) Nd:glass laser at a wavelength of 1.05 μm and a beam diameter of 1 mm. A vidicon and calorimeter system provided accurate fluence measurements. For the other materials, the smaller vacuum system with higher base pressure was used, and a Q-switched YAG:Nd laser, providing pulses of 5-8 ns duration at the fundamental and first three harmonics (1.06 μm, 0.532 μm, 0.355 μm, and 0.266 μm), was used for excitation with beam diameters of about 500 μm. Fluence estimates with this second laser system were made by measuring the beam diameter with a travelling knife-edge, and a calorimeter measured the total pulse energy. Optical damage was identified visually by increased scattering of a probe laser beam. The optical damage thresholds quoted in this work are therefore to be regarded as estimates of relative thresholds for the various samples and laser wavelengths.

A quadrupole mass spectrometer (QMS) was mounted in the line-of-sight to the sample at a distance of 11.3 cm to detect the emitted neutrals. The response time of the detection system was limited to about 10 μs because of the transit-time dispersion in the quadrupole system. Pulse counting and digital storage were used to record the signals from the microchannel plate detector. Data were obtained with increasing fluence on each new spot on the sample, starting from about an order of magnitude below the observed damage threshold. At most, about ten to twenty shots were taken at each spot on the surface before damage occurred or the spot was abandoned.

The time-of-flight from the sample to the ionizer on the QMS is inversely proportional to the particle velocity. For a Maxwellian distribution of particle velocities characterized by a temperature T, the detected signal will have the time-dependence

$$S = K\, t^{-4} \exp[-(t_0/t)^2] \qquad (1)$$

where $t_0 = (M/2kT)^{1/2}d$, M is the particle mass, d is the sample-detector distance, and K is a normalizing constant. This distribution has a maximum at a time delay $t_p = t_0/\sqrt{2} = d(M/4kT)^{1/2}$ This relationship is plotted in Fig. 2 for various masses of interest for the samples studied in this work. We see that for temperatures up to a few thousand K, the time delay provides a sensitive measure of the effective temperature of the particles, particularly for those of large mass. Of course, Eq. 1 is valid only if the emission occurs within a time interval smaller than t_p after the laser pulse.

Experimental Results

Synopsis

A summary of the samples studied, laser wavelengths, and general characteristics of the observed emission is given in Table 1. Al_2O_3 is the only material for which unambiguous evidence of emission of surface constituents below the optical damage threshold could not be obtained. In all cases, of course, desorption of surface contaminants was found, usually at a very low level, after thermal cleaning of the surface. For fused silica, ZnS and NaF, one or more Maxwellian-shaped components were dominant at low fluences. At higher fluences, we also

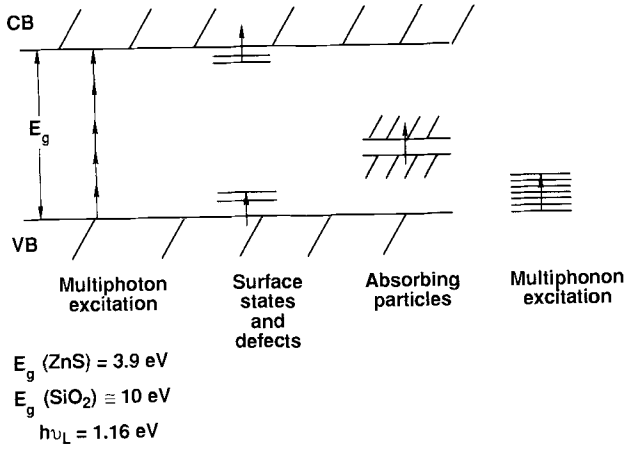

Fig. 1. Possible mechanisms for absorption of light on the surface of a nominally transparent medium.

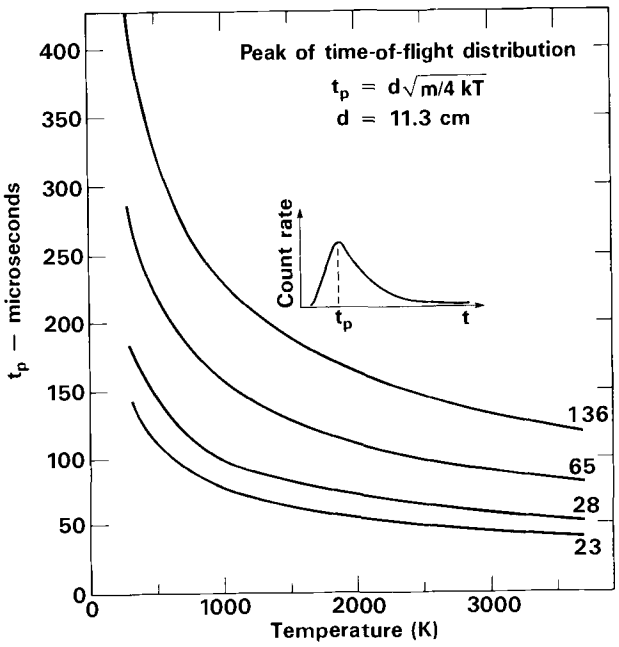

Fig. 2. Relationship between the time delay of the peak of the time-of-flight distribution and the particle temperature. A Maxwellian distribution of particle velocities is assumed. Numbers at the right of each curve are masses, in atomic units.

Table 1. Summary of optical materials and neutral emission characteristics

Sample	Wavelengths	Emitted Species	Characteristics
Fused silica	1064 nm	Si, SiO, O, O_2, OH	Maxwellian, HE neutrals
ZnS crystal	1064, 532 355, 266	Zn, S, S_2	Complex HE neutrals
NaF crystal	1064, 532 355, 266	Na, F	Maxwellian, cleaving, cracking, HE neutrals
Al_2O_3 crystal	1064, 532 355, 266	No predamage emission observed	
BaF_2 crystal	1064, 532 355, 266	Ba, F	HE neutrals only

observed emission of high-energy (HE) neutrals from these materials, as well as BaF_2. The results obtained for BaF_2 are interesting, because of the contrast with the work of Matthias, et. al., who observed copious emission of fluorine neutrals and Ba^+ ions from vacuum-cleaved surfaces of BaF_2 excited by a dye laser.[4,5,6] By contrast, we have investigated emission from polished and air-cleaved surfaces, from which these laser-induced emission components are completely absent, despite the fact that one of our wavelengths, 0.532 μm, is close to one of the resonant peaks for the desorption identified by Matthias, et. al.[5] Presumably, the

surface states that are active on the vacuum-cleaved surface are neutralized by exposure to air and polishing procedures. This demonstrates the sensitivity of the laser-induced emission to surface conditions. The remainder of this discussion will be focused on fused silica, ZnS and NaF, since the most significant results have been obtained for those materials.

Fused silica

Figure 3 shows a set of oscilloscope photographs giving the time-of-flight (TOF) characteristics of the emission of Si and SiO from four different spots on fused silica following 1 ns laser pulses at 1.05 μm. (It is worth mentioning that common surface contaminants, CO, N_2, and CO_2 have the same masses as Si and SiO. By introducing these gases into the chamber, we were able to do control experiments which verified that they were not responsible for the observed emission.) Occasionally, two distinct Maxwellian components were found in a single shot for fused silica; these presumably result from emission from different regions in the laser spot. At fluences near the damage threshold the number of high energy particles (i.e., at small time delays) increases, and a "spike" develops near zero time delay. By comparing data taken with the QMS ionizer on and off, we found that this spike consisted mostly of neutrals, although a fraction are ions. These high energy (HE) neutrals are a common feature of several of the materials studied at fluences close to the threshold for observable damage. In the trace on the lower right of Fig. 3 the damage threshold has been exceeded, and copious emission of energetic ions and neutrals is observed. The damage morphology produced in such events consists of a number of small craters, typical of nanosecond-pulse damage on fused silica.

Two examples of fits to time-of-flight profiles of SiO with assumed Maxwellian velocity distributions are shown in Fig. 4 for different fluences and sample temperatures. There is no reason why a single effective particle temperature should characterize emission from a $1mm^2$ region. Nevertheless, the fits to a single Maxwellian are quite reasonable. The most interesting aspect of these results is the low effective temperatures, in some cases well below the temperature at which the surfaces were cleaned prior to laser excitation. This shows that the emission process does not result primarily from heating of the surface by the laser beam. This common feature of the emission from several of the materials will be discussed later.

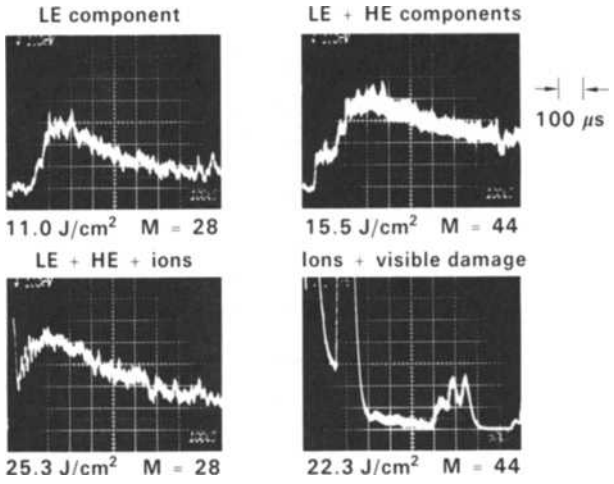

Fig. 3. Some typical TOF distributions for Si and SiO emitted from a fused silica surface following excitation with a 1.05 μm, 1 ns laser pulse. LE and HE refer to the Maxwellian ("low energy") and "high energy" components, respectively.

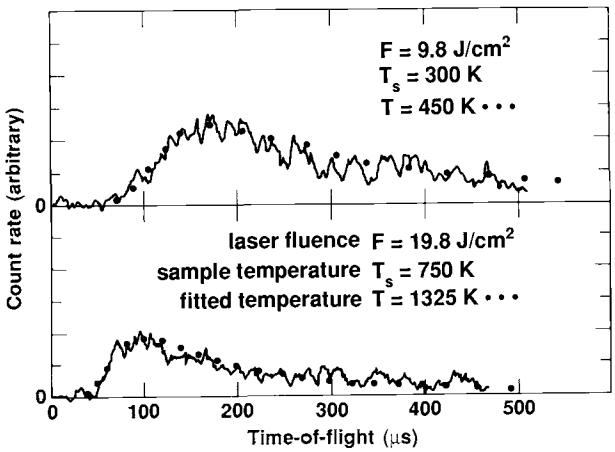

Fig. 4. TOF distributions for SiO emitted from fused silica following a one ns laser pulse at 1.05 μm. The dotted curves are fits to Eq. 1.

Zinc sulphide

ZnS was selected for these studies because it is an example of a wide-bandgap semiconductor, which is used as a material for optical coating, but also because it has a small enough optical bandgap, E_g = 3.9 eV, that measurements can be made with photon energies both above and below E_g using Nd:YAG laser wavelengths up to the fourth harmonic. In addition, we previously investigated ion and electron emission from ZnS and conjectured that the primary emission

component must be neutrals;[2] the present work confirms that hypothesis. TOF data for the emission of Zn from a ZnS single crystal is shown in Fig. 5 for excitation with an 8 ns pulse at 1.064 μm. Near the threshold for observation of neutral Zn emission, about 4 J/cm^2, a gradual onset of the signal suggests that the emission occurs for a time interval of several hundred microseconds, and then the signal decreases due to pumping and adsorption on the chamber walls. At fluences above about 8 J/cm^2, however, a peak develops at a time delay of about 250 μs, which we attribute to promptly emitted Zn particles with a kinetic temperature < 1000K. This behavior is also observed for the emission of S and S_2 and shows that very little surface heating is required in order for the emission to occur. As the damage threshold is approached, however, this peak shifts very rapidly to shorter time delays, indicating characteristic temperatures of several thousand Kelvin. Simultaneously, a spike, due to HE neutrals, appears. Even after the laser shots in the two upper traces in Fig. 5, no visible evidence of optical damage could be detected, although the apparent particle temperature of ~ 10^4K suggests that either the sample surface or the emitted gas of Zn atoms is hot enough to cause local surface modification. This spot on the sample did, in fact, damage catastrophically on the next shot at 11 J/cm^2.

Similar data has been obtained at 532 nm, 355 nm, and 266 nm. As the wavelength decreases, the general characteristics of the TOF distributions are unchanged, which suggests that the same processes are involved in the emission at all four laser wavelengths. On the other hand, the threshold fluences at which emission is observed, and at which optical damage occurs, gradually decrease. We have compared the thresholds for observable neutral Zn emission with the observed optical damage thresholds obtained by taking shots at successively higher fluences on a single site until optical damage occurred. This comparison is shown in Fig. 6, in which the two thresholds for each wavelength are plotted on separate axes. This figure shows that there is a rough correlation between these two thresholds for wavelengths that span the region of optical transparency of ZnS. At 266 nm, however, the emission threshold is very low, below 10 mJ/cm^2, while there is still a measurable optical damage threshold of about 0.5 J/cm^2.

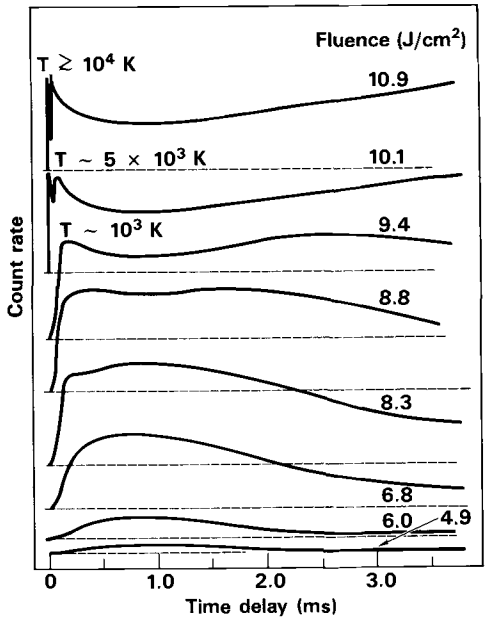

Fig. 5 TOF data for Zn emission from ZnS following a series of 1.06 μm, 8 ns long laser pulses with the indicated fluences. Labelled temperatures are estimates based on the time delay t_d of the peak of the "Maxwellian" emission component. The sharp spike near zero time delay in the two upper curves is the HE neutral emission.

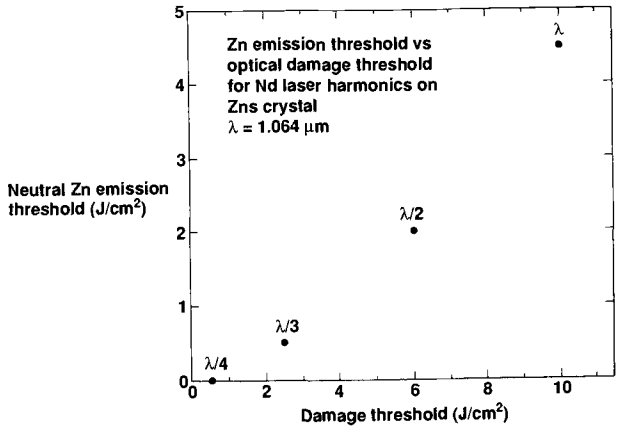

Fig. 6 The threshold for observable neutral Zn emission from ZnS plotted against the optical damage threshold for the four Nd:YAG laser wavelengths.

A potentially important characteristic of the neutral emission is its effects on the surface composition. In Fig. 7a, the signals recorded on successive shots at 266nm with the mass spectrometer set to masses of 68 (Zn), 64 (Zn + S_2), and 32 (S) are compared. The presence of a prompt TOF peak in the mass 64 and 32 data, and the absence of such a feature in the m = 68 trace, suggest that the Zn emission is time-delayed after the laser pulse, but the sulfur emission is not. At fluences close to the damage threshold a prompt TOF peak appears even on the Zn emission signal, as shown in Fig. 7b, although the apparent temperature indicated by the time delay of this peak is lower than the temperature obtained from the corresponding peaks in the S or S_2 data. This suggests that during, and possibly after, a laser pulse the surface composition can be altered by the laser ablation. A possibly related effect is shown in Fig. 8, which shows that the emission observed on consecutive shots on the same site decreases ("bleaches") by an amount that varies with the fluence. As the fluence approaches the damage threshold the bleaching is greatly reduced, if not eliminated. We also observed this bleaching behavior for fused silica and, to a lesser extent, for NaF.

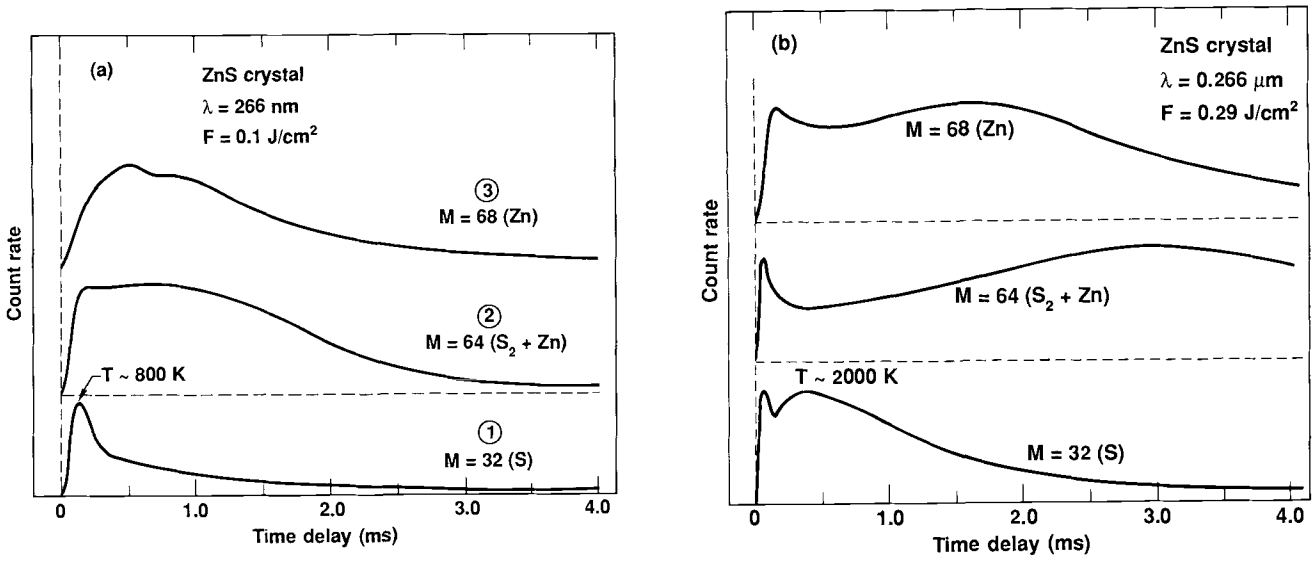

Fig. 7 TOF data for emission of Zn, S, and S_2 from ZnS following laser excitation at 266 nm. Fluences are (a) 0.1 J/cm^2 and (b) 0.29 J/cm^2.

Arlinghaus, et. al.,[7] have investigated the laser-induced emission of Zn from ZnS using laser fluorescence detection. In that experiment, which is performed with a repetitively-pulsed excimer laser at a wavelength of 308 nm, the apparent surface temperatures at the lowest fluences are over 2000K, much higher than those observed near threshold in the present work, and there is no evidence of delayed Zn emission. At this time it is not clear why the laser fluorescence and mass spectrometer measurements differ in those two respects. The major difference between the two measurements is the total number of laser pulses involved in making the measurements. It is likely, however, that, if the ablation causes a change in surface composition, this process reaches a steady state in the repetitively-pulsed experiment, whereas it may not in the measurements with the mass spectrometric detection, where not more than ten to fifteen pulses are used on a single spot. This difference can be resolved with the mass spectrometer experiments by studying a surface area that has undergone many shots.

Sodium fluoride

The experiments were done on single crystals of NaF that were cleaved and subsequently polished. The neutral emission characteristics were similar at all four Nd laser wavelengths, except for a gradual decrease in the threshold fluence with decreasing wavelength, which was similar to the behavior observed for ZnS. The same two characteristic features found for fused silica and ZnS were also present in NaF. Figure 9 shows a TOF distribution of the neutral Na emission following a 266 nm pulse at a fluence of 3.8 J/cm^2, about one-half the observed optical damage threshold. An approximately Maxwellian distribution with a maximum at t_p = 200 μs is indicative of a particle temperature of about 300K, very close to the sample temperature. This cold emission is accompanied by a feature at a very short time delay, which was recorded on the same shot by a second transient recorder with a time resolution of 10 μs. This peak is shown in the inset of Fig. 9, from which the transit time (9.6 μs) in the mass spectometer has been subtracted. This feature was not present when the mass spectrometer was set to transmit other masses, and it was absent or greatly reduced when the ionizer filament was turned off, so

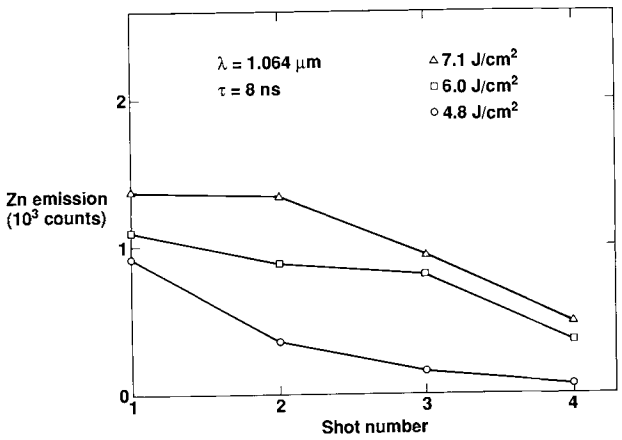

Fig. 8 Total yield of Zn emission for successive laser excitation pulses at 1.064 μm and at three laser fluences.

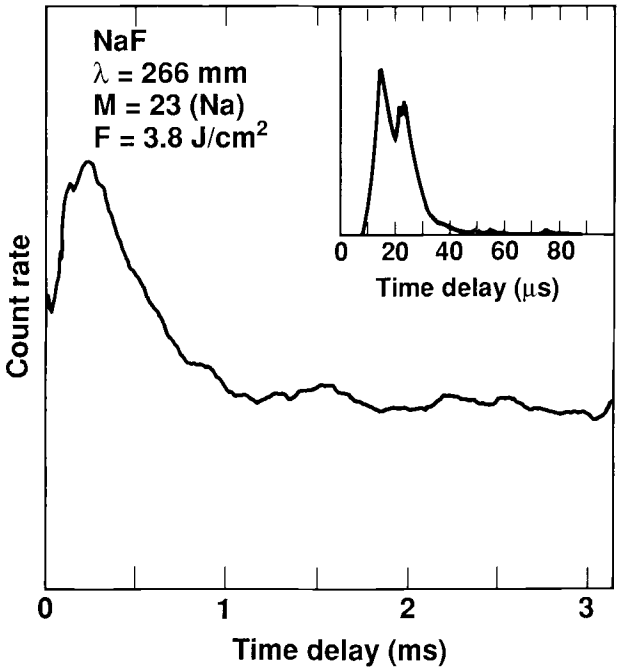

Fig. 9 Time dependence of Na emission from NaF following excitation at 266 nm at a fluence of 3.8 J/cm^2. Inset is the initial 100 μs portion of the data.

it is not caused by scattered or emitted light, and there are very few emitted ions. The very short time delay of this pulse is indicative of very high energies, on the order of 10 - 100 eV. The TOF data shown in Fig. 10 suggests a likely explanation for the emission of the HE neutrals. The lower trace was taken at a laser fluence just below the optical damage threshold at the wavelength of 266 nm. The Maxwellian emission and the HE emission at small time delays were both observed on this shot. The upper trace was the next shot, at a slightly higher fluence, on the same spot. The surface was optically damaged, and a large emission of Na was observed at small time delays. In addition, there is a series of aperiodic spikes that persist for at least tens of milliseconds after the laser pulse. These spikes are often followed by Maxwellian-like tails. In the damaged region, many large and small cleavage cracks were observed after this shot. The similarity of these sharp spikes to the HE neutral components observed immediately after the laser pulse at lower fluences shows that microscopic cleaving of the surface is a very likely origin for the HE neutrals.

Since the neutral emission from NaF had only a slight tendency to bleach on consecutive shots, it is meaningful to examine the dependence of the emission yield on the laser fluence for consecutive shots on the same spot. (Ideally, it would be preferable to move to a different spot for each shot, but the total useable surface area of the samples was not adequate for this.) The yield of Na as a function of fluence for excitation at 266 nm is shown in Fig. 11. Emission starts fairly abruptly at a threshold of 1.5 - 2.0 J/cm^2 and rises nearly linearly up to the damage threshold at 7.5 J/cm^2. This behavior is qualitatively similar to that observed for fused silica and ZnS, although the bleaching effect was too pronounced for those materials to give a meaningful plot of yield versus fluence.

Discussion

A central question regarding the observed neutral emission is that of its relationship to optical damage mechanisms. Strictly speaking, any emission of surface constituents <u>is</u> optical damage. If, however, the emission involves desorption of atoms more or less uniformly distributed over the surface, it is not necessarily related to the type of damage that impairs the optical quality of the surface. The ubiquitous correlation observed between the threshold for observable neutral emission and the threshold for observable optical damage is the strongest evidence that these two phenomena are related. For all of the materials studied, with the exception of Al_2O_3, the emission threshold fluence is about 10 - 40 percent of the optical damage threshold for all laser wavelengths at which the materials are transparent and for the two pulse widths (1 ns and 10 ns) used with fused silica. In fused silica and ZnS the rapid

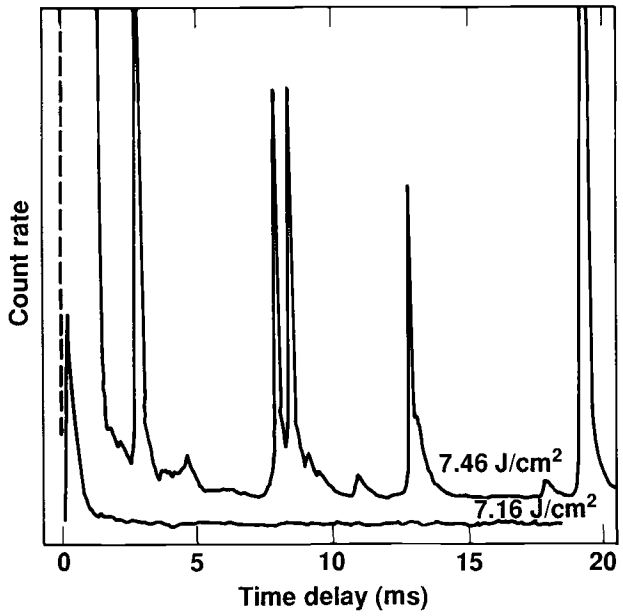

Fig. 10 Time dependence of the emission of Na from NaF after two laser shots. On the second of the two shots, at 7.46 J/cm^2, the sample damaged catastrophically.

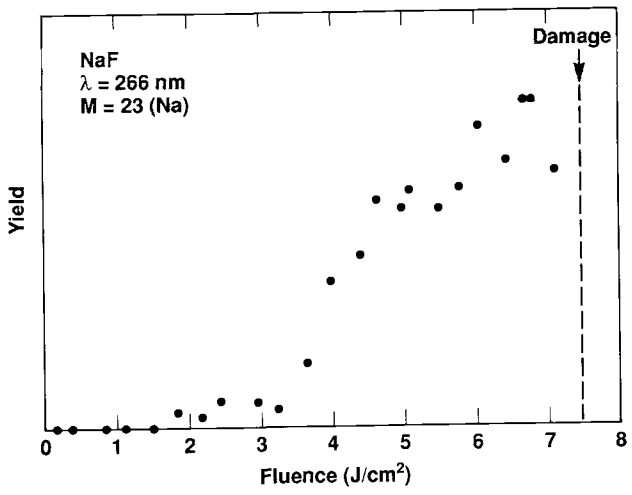

Fig. 11 Yield of laser-induced emission of Na from NaF as a function of fluence with excitation at 266 nm for successive shots of increasing fluence on a single spot.

increase in the effective particle temperature, to values typical of an optical breakdown plasma just below the optical damage threshold, also suggests a connection with damage events. In NaF and BaF_2 neutral emission has always been observed to include the HE neutrals that are most likely the result of cracking or cleaving, which means that some degree of damage occurs on each laser shot. We conclude from these observations that the neutral emission results from the same interaction of the laser with the surface that precipitates optical damage.

Although these investigations are still far from complete because of the small number of materials studied and the lack of information concerning the effects of surface treatment and other variables, it is possible to draw some conclusions regarding the cause of the emission. Consider first the multiphoton interband excitation mechanism in Fig. 1. The dependence of the Zn emission threshold on laser wavelength in Fig. 6 is far too slow to be consistent with multiphoton absorption, since the absorption at 1.06 μm would correspond to a five-photon process, and at 0.355 μm to a two-photon process. At the peak intensities (~ 10^8 W/cm^2) involved in these experiments, these multiphoton transition rates would differ by many orders of magnitude.[8] Data similar to that in Fig. 6 is obtained for NaF, BaF_2, and fused silica.

Desorption caused by thermal excitation (evaporation or sublimation) is also an unlikely cause of the neutral emission. The most straightforward argument in support of this conclusion is that the characteristic temperatures of the Maxwellian emission components of fused silica, ZnS, and NaF are in the range 300K to 800K at the lowest fluences for which they are detectable. Not only are these temperatures far below the melting (or sublimation, for ZnS) temperatures, but they are comparable with the temperatures at which the surfaces are cleaned, and no emission is observed during the cleaning. It is conceivable, however, that the time-of-flight distributions are not an accurate measure of surface temperature. The experiments on ZnS at the fourth harmonic provide some additional evidence that the surface temperature rise is very small. The absorption coefficient of ZnS at 266 nm is known, as are its relevant thermal properties. We have modelled the temperature rise of ZnS due to illumination at 266nm by using the solutions of the thermal diffusion equations including the presence of bulk heating by the laser.[9] We conclude that, at the threshold fluence (10 mJ/cm^2) for observation of Zn neutrals, the temperature rise at the surface is at most 50K, assuming that all of the energy absorbed from the laser is converted immediately into heat. Since the carrier lifetime in ZnS is on the order of a millisecond, it is possible that only the photon energy in excess of the bandgap energy is effective in heating the surface during the duration of the laser pulse, so the temperature rise may be as small as 20K.

It has been suggested that microscopic cleaving or cracking can result from rather small increases in surface temperature because of the large surface stresses accompanying differential thermal expansion.[10] This is a likely cause of the high energy neutrals observed just below the damage threshold in most of the materials that we studied. Indeed, copious charged and neutral emission ("fractoemission"), as well as visible discharge, has been observed to accompany the fracture of numerous materials.[11] Although no measurements of their energy distributions have been reported, the very rapid spikes in Fig. 9, which undoubtedly result from cleavage of the NaF sample, are evidence of very high velocities, since most of the neutrals reach the detector in a time interval much shorter than the width of the Maxwellian component in the lower trace. Presumably, this emission can also result from the growth of existing cracks near the surface. In addition to the direct damage caused by the crack initiation and propagation, the high gas densities and ionization levels produced by this localized phenomenon can also precipitate local optical breakdown, which could grow catastrophically due to surface bombardment.

The Maxwellian-like emission from fused silica and ZnS is clearly observed even without the HE neutrals at low fluences, so it cannot be attributed to any mechanism of thermal origin, including cracking. It is most likely that this emission results from electronic excitation of defects or surface states. The carriers released by this process can cause bond breaking, followed by desorption of atoms. There is a large body of literature documenting this type of desorption, from semiconductors and insulators, resulting from ion and electron bombardment, and from excitation by photons at frequencies above the optical bandgap.[12] It is not unreasonable to presume that if there is a distribution of defect levels within the bandgap of materials like fused silica, ZnS and NaF, the carriers released from these defects by excitation at photon energies below the bandgap will also cause desorption, although the yield will be much lower. The wavelength dependence of the threshold fluence for observable emission, exemplified by the ZnS data in Fig. 6, is consistent with this assumption. The F-center, which is a singly-charged sulfur vacancy, is an example of a defect in ZnS that absorbs throughout the visible, and photoconductivity measurements show that free carriers are produced by this absorption.[13] Recent measurements of laser-induced Ba ion emission from vacuum-cleaved BaF_2 show sharp resonances arising from surface states,[4,5,6] so such levels deep in the bandgap exist for ionic materials as well.

Despite its rather innocuous appearance, the electronic desorption discussed in the preceding paragraph may play a central role in optical damage. For example, the energy transferred to the surface, either by the primary excitation process or by subsequent excitation of the free carriers released by the absorption, is a possible source of the heating that can cause cracking or cleaving, thus releasing many HE neutrals and ions. The carriers might also precipitate avalanche ionization. These consequences will be most likely if the absorbing defects are clustered in small regions, perhaps in the vicinity of cracks, grain boundaries, dislocations or foreign particles. If the emission alters the composition of the surface, a catastrophic, positive feedback into the density of absorbing defects could result. For this reason the possibility of delayed or unequal emission of Zn or S from ZnS is very significant. This could produce S vacancies, and possibly F-centers, at the surface. Obviously, this surface ablation could also reduce the damage threshold for multiple-pulse excitation. Laser annealing studies on GaAs show that the emission yield of As becomes larger than that of Ga as the surface temperature increases,[14] so surface composition changes due to laser ablation may be a common phenomenon.

Conclusions

Laser-induced neutral emission appears to be a common precursor to observable optical surface damage. Not only is it a signature of the interaction of the light with the surface, but it may be a cause of optical damage. In order to further evaluate its significance, it is important to investigate the spatial dependence of the emission and obtain quantitative information on the relative yields of various surface constituents. The wavelength dependence of the emission yield is also an important piece of evidence to use in identifying the absorbing centers.

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In fitting the temperature to the emission how can you be sure, particularly in cases where there is a very high temperature, that you are not observing a laser plasma electron ion neutral coupling so the temperature observed is not at all indicative of the surface temperature? The speaker replied that the suggestion is probably correct for ZnS when you don't get temperatures of 10,000 K without plasma. On the other hand, when measuring neutral emission characterized by temperatures of 300 K to 1000 K it is definitely not true since you cannot have a hot plasma at 1000 K.