A Feasible Mechanism of Molecular Contamination Induced Laser Optic Damage

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Abstract

A mechanism is described for the interaction of vitreous oxide dielectrics in the presence of molecular contamination. The mechanism is based upon well known and documented behaviors of the constituent parts of the laser damage process. It is consistent with nearly all observations of laser optic damage in the presence of molecular contamination. This description is unique in that it describes why damage propagates in some cases and not in others. The descriptive mechanism is very general as would be expected for a description of the interaction of light and matter. The mechanism is consistent with most laser damage reported in the literature within the nanosecond regime, as well as unpublished results and observations the author is aware of.

The incident laser beam interacts with the molecular contaminants, resulting in multiply excited states. These multiply excited states will typically result in homolytic dissociation. The homolytic dissociation forms free radical species. The free radical species collide transferring energy to other species, resulting in the formation of metastable excited states. The metastable excited states are populated and then either form damage precursors or annihilate resulting in no damage. Specific species within an exemplary system of vitreous silica contaminated with toluene, in the presence of environmental species, known to affect damage behavior are addressed.

No attempt has been made to derive a mathematical treatment for the numerous inter-related interactions present in real systems. This has been left up to the reader.

Introduction

The problem is addressing molecular contamination effects on laser induced damage thresholds. Molecular contamination effects are described by a mechanism based upon the chemical and physical interactions of the laser, contaminant and environment. The interactions of the light, material and environmental species are all well documented but not in one particular area of study.

Damage behavior is a function of the formation and annihilation material states that fundamentally change the material. A number of simultaneous mechanistic steps determine the progression or arrest of various damage mechanisms. These involve the formation of energetic precursors and their subsequent decay through manifold routes, some being damage some not.

Background

Molecular contamination is ubiquitous. Contamination in lasers can cause immediate or delayed damage or no damage at all. Because contamination induced laser optic damage in the near infrared is typically a low probability issue in the laboratory few people have addressed it.

Contamination induced laser optic damage has been the subject of a number of recent studies. It is known that there are a number of species and classifications of materials that reduce the laser induced damage threshold (LIDT). No plausible photochemical mechanisms exist for the initiation of the damage in the near infrared region. The proposed mechanisms to date have only dealt with propagation. Thus, all cases of inhibition or lack of damage are anomalous. This is certainly not the case. The propagation rate and final

result of the induced damage are important but not nearly as important as the initiation of the damage process. Without initiation neither propagation nor resultant damage will occur.

In the early to mid 1990's Hovis, et.al.[1], Sharps[2], and Kunz[3] studied the effect of numerous materials including solvents, on the laser damage process. More recently, Scurlock[4], Jager[5], Becker[6], Reide[7], and this author[8,9,10,11,12] have studied the effects of molecular contamination on laser optic damage. Although contamination effects are recognized as a significant risk to laser systems, relatively little work has been carried out until recently.

Toluene has been identified as a bad actor in one-micron laser systems. Hovis, et.al [1] proposed a polymerization-based mechanism for the laser-induced damage resulting from operation of lasers in the presence of toluene vapor. Hovis proposed that toluene formed a trimer that strongly absorbed at one micron. However, the proposition was strictly based upon a third order photon flux relationship. From evaluation of spectroscopic data of polycyclic aromatic hydrocarbons that could reasonably be formed from toluene and evaluation of functional group addition rules, UV-Vis spectral data, and well-documented organic chemistry, this proposed mechanism is inaccurate. In addition, the mechanism predicts damage in all cases, which does not occur.

What is the Proposed Mechanism?

Overview

It is assumed that the formation of a damage precursor is required. Laser optics do not absorb a large amount of light. The optics are inherently stable in the absence of the laser. The optics do not change greatly with limited laser irradiation. In order to change or damage the optical behavior, a change must occur in the optic. It is required that energy above the transition state and reactants be simultaneously present for a sufficiently long time for the damage mechanism to result in damage. With out this required condition, damage cannot occur. In addition, empirical data shows that the behavior follows the limiting case kinetic condition for the formation of a precursor.

It is assumed that laser damage below the intrinsic laser induced optical damage threshold must be precipitated by a change in the optical properties of the optical material. Precursor formation is to be expected. The damage probability increases with increasing laser exposure. Damage does not always occur, therefore, precursors can be expected to be annihilated through one or more routes. Some routes leading to damage and other routes do not lead to damage. Damage occurs as one or more discrete events. One or more things must precipitate the damage event.

It is assumed that materials behave in a canonical manner; their behavior follows certain rules. Laser damage is a laser-induced change in properties of an optic. If damage does not occur under a given set of conditions, then it will not change its behavior without some intrinsic change. There are a number of types of known discrete changes that occur in transparent dielectrics. Discoloration or color center formation occurs in some cases. There are processes that lead to the formation of color centers (strong optical interaction sites.) Other processes lead to the annihilation of color centers. Water is known to affect laser optic damage. Surface roughening is a frequently misunderstood damage mechanism. The loss of surface quality whether it be in a coating or a change in the bulk optic material should be considered damage or decay. Two additional physical effects noticed in laser damage processes are localized heating and luminescence. All of these phenomena should be addressed by the description of the system.

What forms the Precursor?

Toluene (in a 1.06um Nd: YAG laser) absorbs approximately 4.7 eV, through a single 4th harmonic photon or multiple photons. This will result in the formation of the benzyl radical (lifetime $\sim 10^{-7}$ sec). (figure 1.) The benzyl radical rapidly collisionally deactivates or quenches (rate constant $\sim 10^{10} sec^{-1}$). The quenching transfers the energy and spin in part or in total to the quenching species. In the case of a metallic surface, where excitonic states have very short lifetimes[13], the energy degrades rapidly either through reaction,

emission or absorption. It is also possible for the formation of excitonic states in surface oxides on metals. In the case of vitreous dielectric materials, excited states of ~4.7 eV are trapped, as predicted by Maxwell[14]. The excited state populations if trapped will redistribute within the material remaining trapped like exciton polaritons. The trapping will occur through photon phonon interactions as described by Knox.[15] These exciton polaritons will move and redistribute through phononic agitation, in the absence of a field. Fields, (thermal, mechanical, compositional, excitational) will attract the more highly polarizable exciton-polaritons as a function of the differential of overall system potential due to the induced polarizability of the exciton-polariton compared to the unexcited material, as predicted by molecular quantum mechanics. The universality of the exciton polariton interactions by different types of fields is because material interactions are primarily electronic. (Dielectrics are attracted to fields below their electronic resonance frequency.[1])

Collision of the benzyl radical with another species will result in the short term formation of an excited state complex. In the case of metals, the lifetime of the excited state will be very short (~10^{-12} sec). This is due to the limited stability of the metal excited state in the bulk phase. In the case of vitreous dielectric materials such as silica, the lifetimes will be extended. The distribution of the energy upon separation of the complex will be dependent upon the lifetimes and stabilities of the excited states of the vitreous dielectric and the benzyl radical. In the case of vitreous silica, the lifetimes can range from microseconds to millenia. This long lifetime is due to the stability of the excited states resulting from the high barrier potentials to the internal degrees of freedom. The limited emissivity of silica within the transmission region is roughly described within the limitations of the applicability of the Einstein relations of absorbtivity and emissivity.[2] Roughly this defines the reemission as being a very low probability event.

The deposition of energy at the surface raises the surface energy of the material. Over time, the energy will be lowered by emission, diffusion of the excited states, adsorption of materials or through energy depleting chemical reactions. In the case of adsorption, the higher surface energy will result in stronger surface adsorption[16].

If the Precursor is Annihilated, How?

In air, the benzyl radical is quenched by both water vapor and oxygen. Quenching is the deactivation of the radical by transfer of the spin state and energy. The quenching of benzyl radical by water vapor forms hydroxyl radical. The quenching of benzyl radical by molecular oxygen forms singlet oxygen. Both hydroxyl radical and singlet oxygen are strong oxidizing agents that will oxidize hydrocarbons to carbon monoxide and/or carbon dioxide. Additionally, hydroxyl radical emission from silica has been noted in the literature Schreiber.[17] Emission of excited hydroxyl radical results in a light blue chemiluminescent emission.

What Precipitates a Damage Event?

The excited states are attracted by field gradients. As phonon transport is required for movement in the trapped state, transport across inhomogeneities (point defects, fractures, scratches) is not possible. In the case of an applied field, such as a laser field, the population of the excited states would be drawn toward the laser beam through electrostriction (Abdeldayem[18].) If the energy density in the optic reaches a critical density, damage will occur, primarily through homolytic cleavage in non-ionic media. With repeated transfer of energy from the quenching of the toluene, eventually the optic will reach a sufficiently high population of excited states that energy transfer would not be favorable, and the excited state toluene lifetime would begin to rise. This will result in the absorption of additional energy from the incident radiation and promotion of the silica to an energy level where the transition to the subsequent states will result in absorbing species and ionization.

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[1] Dielectric materials are by definition attracted to electromagnetic fields. The attraction is based upon the reduction of the field through polarization of the dielectric.

[2] Einstein's relations of absorptivity and emissivity were developed based upon the assumption of an ideal gas in thermal equilibrium.

How is Color Created in Damage?

If the excited state toluene (benzyl radical) is further excited by another 1.165eV photon, and then subsequently transfers the energy to silica, it will leave the silica at 5.8eV. The resultant 5.8eV excited state silica is at an energy at which the activation energy for the formation of color centers is effectively zero Glebov[19]. This will result in efficient formation of color centers within the silica surface. This will result in the formation of discolored zones in the silica. This occurs primarily at the surface. This can result in significant surface absorption and damage.

From vacuum ultraviolet stability studies of vitreous silica, it has been shown that high hydroxyl concentration silica is more resistant to color center formation. The silica is found to eliminate hydroxyls during VUV exposure at levels approaching the color center potential energy. Thus, the elimination of the hydroxyls must be a prerequisite to color center formation.

How is Color Annihilated?

It is common knowledge that color centers can be eliminated from optical materials through either photonic or thermal means. The irradiation of glass possessing high color center populations with white light will result in photo-bleaching of the color centers. Likewise, heating of an optic possessing high color center concentrations can lead to thermal annealing. The same can be said for populations of exciton-polaritons. The radiation-induced defects typically result from a change in the state of the base material, resulting in a population at an energy above that of the Maxwell-Boltzmann described distribution. Providing this additional energy to the system will allow re-emission and relaxation.

What are the Effects of Color?

Color centers strongly absorb light and that has a negative effect upon the optic and the laser system. The absorption of light by a color center can result in either upward promotion in energy, triggering a rapid decay, or localized heating. Each of these can result in damage. Promotion of energy levels toward the ionization energy can cause ionization driven damage. Rapidly stimulated emission can cause intensity driven damage. Localized heating can cause stress driven damage. In combination, high energy levels will result in large non-linear susceptibilities, exacerbated by the local energy differentials and mechanical and stress fields, that will lead to further electrostrictive attraction of excited states.

The increase in the real and imaginary refractive indices of a material will result in increased interaction of the optic with the incident beam. This will increase the perturbation of the beam by the optic and the optic by the beam. It will result in increased absorption, reflection, scattering and non-linear interaction. These behaviors are all manifestations of the laser interaction tensor that includes both linear and non-linear interaction, which define the interaction of the laser and matter.

What are the Effects of Water?

All surfaces that have ever been touched by humans are covered with water. In the absence of water or other adsorbates, surface to surface contact leads to point welding due to surface energy. If the surface is covered with water, benzyl radical from toluene or other substituted methyl benzene, for example, can abstract hydrogen from the water, resulting in the formation of hydroxyl radical. (Hydroxyl radical is a highly reactive oxidizing species responsible for many oxidation processes, including flame propagation.) The abstraction of the hydrogen from water by benzyl radical leaves the resultant toluene near the ground state. Hydroxyl radicals likewise can excite toluene in a similar manner, resulting in oxidation or destabilization through promotion to excessive energy levels. In an excess of water, toluene will be consumed by oxidation by the same process. The water will also effectively screen the energy transfer from the benzyl radical to the silica.

Water Effects, Surface Roughening

The same hydroxyl radical, formed from the homolytic cleavage of R-OH species, will abstract hydrogen from the silanols on the surface of the silica as well, leaving the silica in an excited reactive paramagnetic state. The reactive excited state will be more reactive toward hydrolysis by surface water than the base

silica, and have a larger dielectric response as well. Given an elevated energy, and increased dielectric response, the rate of propagation of micro fractures from the grinding processes will be accelerated. Likewise, the generation of local stresses in the glass will accelerate hydrolysis of the silica at other point inhomogeneities. This behavior will follow the mechanism described by Wiederhorn in 1967.[20]

Populating and Depopulating States

All materials have interactions with incident radiation at all wavelengths. Kramers-Kronig relation relates the extinction or absorption phenomenon to the index of refraction. As the index of refraction is continuous, the absorption must be also. The presence of a finite intrinsic absorption allows radiation to be absorbed. In many cases, the absorption can lead to formation of excitonic states. If the relaxation of the excitonic stated is sufficiently slow (days, months, years, millennia) with relation to the photon arrival rate, the excited state will behave as a virtual ground state. The stable excited state can then be further excited by an independent photon. This eliminates the n-order relationship between an nth level excitation and the photon flux. The limiting factors then become the material's irradiation history and the intrinsic absorption of the material. Thus, it is not necessary to have high photon flux densities to develop high-energy state populations within a material.

Depopulation of excitonic states occurs by a number of well-documented luminescent pathways. Depopulation does not occur significantly by internal decay, through vibrational pathways. As the excitonic states are metastable states, energy is required to overcome the intrinsic barrier energy of the transition. Further, it is necessary for the depopulation transition to provide the requisite energy, momentum, and spin for the emission of a photon. Thus, after forming the excitonic state, the probability of re-emission after an extended duration, is very low.

Depopulation can be driven by chemical, radiation, photonic, phononic, and mechanical and field induced mechanisms. These mechanisms cause changes in the energy and symmetry barriers to transition. Chemical, thermal and white light tend to be the primary routes for the depopulation of the excitonic states. Coherent monochromatic light can only promote a small percentage of the population of excitonic states to a viable emission state. Thermal white light on the other hand has sufficient variability in its quantum statistics to sweep all available states within its spectrum, depopulating them.

Localized Heating

As exciton polaritons are formed from the trapping of a photon by a phonon, the trapping annihilates both a photon and a phonon[15]. In order for the trapping to be long lived, the phonon energy must be well above the ambient energy. This is primarily within the regime of the optical phonons or vibrational regime with optical wavelengths on the order of a few microns. As both the photon and phonon energies are annihilated (as kinetic energy, converted into potential energy) there will be a depletion of kinetic energy during the trapping process, a cooling. This will be a slow cooling based upon the total energy being trapped. In the re-emission of the exciton polariton, it is expected that the release of the trapped photon will release the trapped phonon. The emission will lead to a localized heating in the area due to the creation of phonons from the potential energy, from which the exciton polariton was released. The temperature rise will typically be small.[3]

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[3] It should be noted that there have been reports of anomalously high temperatures present on or within silicaceous substrates during damage events. These reports have largely been based upon measurements using infrared pyrometers. Many if not most of these devices are based upon the assumption of strictly black body emission, and use the ratio of two wavelengths to determine temperature. Bouchut reports in these proceedings infrared emission from silicaceous optical substrates. This violates the operating principles of infrared pyrometers. This resolves the issue of 5000-10,000 Kelvin temperatures reported for silica substrates, which are physically meaningless as silica atomizes and thus does not exist at these temperatures.

Luminescence

Laser induced optical damage has been noted to result in luminescence. Ginther and Claffy[21] studied this effect to some degree in 1971. Glebov[22] and others have since studied this phenomenon. In previous studies of luminescence and color center formation in solid matrices, it is noted that many different types of absorbed radiation result in very similar luminescent behavior. The primary optical and physical effects of radiation in silicaceous dielectrics are primarily a function of the radiation absorbed dose exposure in rads. Emission spectra have been measured both spectrally and temporally for a number of years. Likewise thermal-luminescent and tribo-luminescent behavior of silicaceous materials is likewise a function of radiation absorbed dose. It should be apparent that the primary factor in defining the luminescent properties of a material is the material itself, not necessarily the radiation. That is assuming the radiation does not dramatically change the material composition (elementally or chemically) in a manner inconsistent with the other forms of radiation.

Spontaneous emission and photo-stimulated emission of exciton polaritons have been measured. This can be seen in the luminescence in the Raman spectra (figure 1.) Note that the total Raman scattering (non-linear interaction) has significantly increased with laser exposure. The increase is primarily due to the increase in the excited state hydroxyl (water) content in the silica, as manifested by the large broad Raman scattering peak(s) from 3450 cm^{-1} and below.
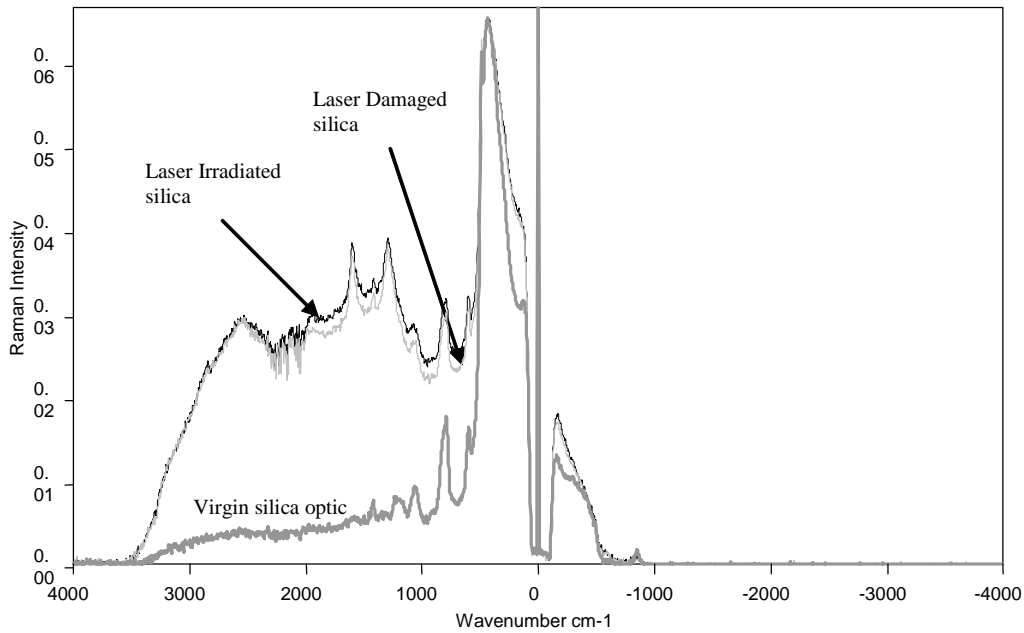

Figure 1, Raman spectrum of as received (broad light gray) , laser exposed (black) and laser damaged artificial fused silica (Narrow light gray)

 In addition, Heraeus publishes a transmission calculator program showing the 950 nm hydroxyl absorption in UV or 1200ppm water content high purity silica[23](figure 2). This absorption will lead to resonant or nearly resonant Raman scattering in silica due to both the bulk OH content and the surface OH content from polishing. Higher surface OH content than the bulk concentration was speculated in 1947. It has since been determined that the grinding and polishing processes hydrolyze the silica at the surface. This is well known.
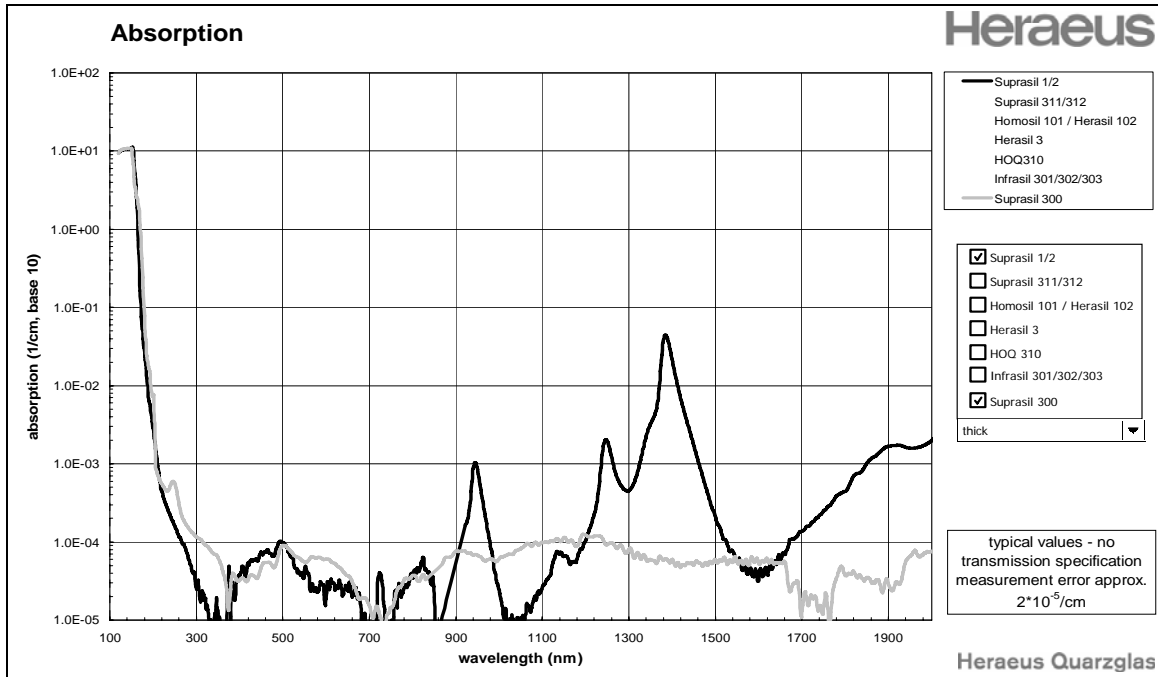
Figure 2 Absorption of UV grade (black) and IR grade (gray) silica, Used with permission of Heraeus Optics, LLC

In addition, in radiation damaged silica, both thermo-luminescence and triboluminescence have been detected, as has tribothermoluminescence. Neither of these behaviors exists in un-irradiated silica. These behaviors are indicative of the storage of energy from the absorbed radiation dose.

Discussion

Known Behaviors in Silica

Below is a list of known behaviors in the induction of contamination related laser induced optical damage.

1. Damage does not occur at a uniform constant probability. Hovis
2. Toluene initiates laser optic damage.
3. Toluene is found in adhesives, residence time of toluene is long due to molecular trapping.
4. Toluene does not interact strongly with 1064nm or 532 nm light, in the first order.
5. Exciton polariton populations are created in the range of 1,3 & 4 eV when exposed to air. Up to 7eV or more in vacuum in combined 532nm & 1064nm laser.
6. Energy is required to create damage. Photoemission is seen with damage events.
7. Degradation of damage thresholds occurs with repeated sub damaging exposure.
8. Green and UV photoemission is seen from damaged glass.
9. Polarization of damaging radiation is maintained in the re-emission of the light from the glass.
10. At least four photoluminescent lifetimes are known for radiation damaged silica. Microsecond, day, week, millennium.
11. Changes in optical glass due to solar exposure, M. Faraday(1825). Determination of exposure band related to color center formation Duzing (1938),
12. Color center generation approaches a near zero activation energy at ~ 210nm. Glebov
13. Toluene and Xylene (benzyl radical) quenching from the first excited state is fast ~ 1 collision, approximately 10^{-10} seconds at one atmosphere. Quenching is transfer of energy in form of an unpaired electron.
14. Toluene in the presence of oxygen and/or water does not readily result in damage.
15. There is an induction period for toluene/contamination induced damage.
16. Toluene fluorescence is highly quenched on surfaces.
17. Benzyl radical formation and quenching provides the formation and transport of 4.66eV quanta at a transition probability at a surface of ~1.

18.   Interaction of 4.66 eV quanta (metastable states) with 1.17eV photons gives 5.83eV which is approximately the minimum for color center formation, and therefore rate maximum.
19.   Organic molecules are highly active in terms of multiple photon absorption.
20.   Aromatic molecules such as toluene and xylene are highly effective in transferring energy from one molecule to another, which is why they are often used in scintillation counting systems.

Addressing behaviors

It has been noted in numerous cases, including by Hovis, et.al. that the probability of laser optic damage in the presence of trace contamination goes through an induction period followed by an onset of damage. This indicates that there is either a damage mitigating mechanism or a requisite latent damage effect in operation. In the absence of either of these cases, the damage probability would be uniform from the first pulse up to some lower tail damage probability number. Scurlock identified this onset as an indication of the presence of an additional limiting step within the damage mechanism. Becker, et.al. determined that in the presence of trace levels of contamination, below their detection limit, that as the number of incident laser shots increased, the LIDT decreased in a nearly proportional manner. Becker et.al. specifically noted a minimum threshold of laser exposure below which no damage was detected.

In any description of contamination induced reduction of LIDT's it is necessary to address not only the steps leading to initiation and propagation behavior but also the steps that do not lead to damage. Any model that does not provide both will be inadequate in describing either.

Workers at Lawrence Livermore National Laboratory noted the mitigation of molecular contamination in the presence of 50 ppm oxygen. Arenberg, and Frink[24] in 1987 noted that exposure of laser optics in the presence of water vapor resulted in a decrease in the probability of laser optic failure in the presence of coexisting molecular contamination, a conditioning effect. This author noted that in the presence of a surge of water and hydrocarbon vapor within a vacuum chamber with a multiple wavelength laser (532nm and 1064nm) operating that the concentration of carbon dioxide and carbon monoxide were found to increase at a rate that was in direct proportion to the rate of hydrocarbon decrease upon continued laser operation. These rates were significantly faster than could be accounted for by the pumping rates of the species in the system. These changes are indicative of multi photon oxidation of the contaminants due to the water vapor present in the system.

Becker et.al[6] saw similar changes in the carbon oxides in their system, directly attributed to the firing of the laser, but attributed the change to release of surface adsorbed carbon dioxide. (It should be noted that carbon dioxide is considered a permanent gas in that it is not adsorbed from vacuum systems even at liquid nitrogen temperatures.) Thus, it is not feasible that carbon dioxide is being photo desorbed from surfaces. Within carefully controlled and monitored high vacuum systems that the incidence of high intensity light results in the oxidation of hydrocarbons and other carbonaceous species to carbon dioxide and/or carbon monoxide (depending upon the partial pressure of water and oxygen).

Photo induced oxidation of organic matter by water is the prime method for the preparation of organic free water. This is primarily accomplished with the use of mercury arc lamps with a peak emission at 254nm. Water photolyzes into hydroxyl radical and molecular hydrogen at a wavelength of 245nm in the gas phase. In the condensed phase, especially at a surface, the energy required to photolyze water should shift toward lower energy, based upon the stabilization of the polarized state in the condensed phase, particularly at a surface. It is well known that hydroxyl radical is one of the most reactive oxidizing species present in the oxidation of organic molecules, as well as other materials. This has been shown experimentally, through the use of empirical calculations and calculations at the ab-initio level as well.[25]

With the storage of energy as exciton-polaritons, it is not necessary to have single photons of adequate energy to drive classically photochemical reactions. Feynman in his classic work on Quantum Electrodynamics shows the transfer of energy in diagrammatic form[26]. This treatment of energy transfer can address virtually all if not all, photonic and electronic energy transfers. The proposed energy transfers are simply described using Feynman's notation, or other energy transfer descriptions. Further, as lattice changes or molecular vibrations result in perturbations of the electronic density of the system, most any change in a system can be described in terms of perturbation of the existing electronic state of the system.

Water

Water is present on virtually all surfaces. Since the advent of mass spectrometry and high to ultra high vacuum systems, water has been known to be the most ubiquitous and persistent surface adsorbed species. Only through the application of temperatures in excess 250 degrees centigrade for durations of weeks or through the extended use of ultraviolet or higher energy radiation is it possible to remove water from a vacuum system. At ambient temperature, in the absence of high-energy radiation, under the most stringent conditions, water can be expected to be retained within a vacuum system for on the order of 1000 years. Under ambient atmospheric conditions water is expected to be present in measurable amounts on virtually all surfaces to a depth of 50-200 molecular layers.

In addressing the behavior of any system in which surface behavior is of significance, it is necessary to address the effects of water on the behaviors of the system. The formation of ad-layers on surfaces decreases the surface energy. The absence of such surface adsorbed layers will result in a surface energy on the order of ten to one hundred times the tensile strength of the material. This level of surface energy will result in the near immediate permanent bonding of any material contacting the surface. (Adhesive strength is the difference of the sum of the two bonding surfaces and the final energy of the bonded area, as the surfaces are no longer present.) Thus, two contacting glass surfaces will adhere with a strength equivalent to the cross sectional area of the contact multiplied by the surface energy, which is effectively the tensile strength of the glass. This value significantly exceeds the common surface energy of a material under ambient conditions. Conversely, removing the ad layers from a materials surface raises its surface energy and makes it more attractive.

Toluene

Toluene undergoes an n to pi* transition at an energy of approximately 4.67 eV. This transition results in the formation of a benzyl radical. This radical is highly stabilized and in the absence of an efficient quenching mechanism has a lifetime on the order of 10^{-7} seconds. Although free radicals tend to be very unstable, the benzyl radical is responsible for the first UV absorption of toluene in the liquid state. Thus, the formation and population of benzyl radical is sufficient under normal laboratory conditions to result in a strongly absorbing transition.

The polarizability and density of states and thus the transition probabilities and the optical interaction of the excited state increase greatly beyond that of the ground state molecule. Further, the effective oscillator strengths and lifetimes of the allowed and forbidden transitions in the excited states often greatly exceed that of the ground state, due to the wealth of opportunities for energy transfer both intramolecularly and intermolecularly at the higher energy levels. Thus, the effect of the excited states on a number basis greatly exceeds that of the ground state. This can be seen by the requirement of the inclusion transitions between the ground state and the first through the third excited states in order to define the base low energy electronic absorption spectra.

Laser Interaction with Matter

The interaction of light with matter has both particle and wave characteristics. At a rudimentary level the scattering (interaction) of the radiation with matter can be expressed as either corpuscular or wave-like with equal validity. A photon entering a material interacts with the existing poles, driving the poles into oscillation. This oscillation results in absorption of energy into the near field of the atoms or molecules. This can then either be re-emitted as kinetic energy, (photon(s) or phonon(s)), or the energy can result in a change in the potential energy of the system (chemical, electronic or mechanical). The lifetimes, routes and lack of routes define the behavior of the system. If the lifetime of the energy of the in either the near field or the potential energy states of the atoms or molecules is sufficiently long, there can be a second interaction with the energy in the near field, resulting in a change in energy, momentum or spin. This change in electron momentum or spin can and must change the quantum statistical properties of the incident photon and or the material. This results in the combined interactions changing the net energy, momentum, and spin, within the behavioral requirements of the material(s), photon(s) and phonon(s) under

the applied field. This describes at the most basic level the description of all interactions of light and matter, both linear (elastic) and non-linear (inelastic).

Organic molecules have the propensity to undergo multiple photon absorption. The multiple photon behavior is a function of the large density of states: excitational, configurational, connectional, and/or conformational. This provides the opportunity for the formation of high-energy excited states. These excited states result in laser-induced fluorescence at frequencies higher than the base frequency of the laser irradiation. These excited states in many cases will be paramagnetic. Paramagnetic organic molecular states are commonly known within chemistry as free radicals. These free radicals are extremely reactive and transfer energy between species at rates that classically have exceeded the capability of being measured. To chemists the transfer of energy from the species of interest to species not of interest is commonly known as quenching, and is thus disregarded as a parasitic loss mechanism.

Within a q-switched Nd:YAG laser, the photon arrival rate is on the order of or less than the transition lifetimes of non-metals, based upon the cross sectional area of the electronic orbital distributions. As a result, a significant portion of the materials can be assumed to be at the potential of the photon energy of the base laser mode frequency. Thus, in a one micron pulsed Nd:YAG laser a significant fraction of the material can be assumed to be at 1.165 eV, during the pulse.

The presence of the laser pulse results in a defined polarization state field on the material. This changes the selection rules of the transitions within the material during the pulse. Likewise it changes the interactions of the incident photons with the material. If the field changes at a rate comparable to or faster than the rate of relaxation of the material from the photon induced energy state, the re-emission of the photon energy may be forbidden.

The parasitic loss of energy from an excited state toluene radical (commonly known as a benzyl radical) results in the transfer of the excitation energy to the quenching species. In the case of transfer to water the result is the formation of the highly reactive hydroxyl radical.

The excited states are attracted by field gradients. As phonon transport is required for movement in the trapped state, transport across inhomogeneities is not possible. In the case of an applied field, such as a laser field, the population of the excited states would be drawn toward the laser beam. This would induce a stress between two adjacent excited states if a field gradient exists between them. Further, the attraction and thus the population, given adequate time, would be at a maximum not at the peak intensity, but rather at the peak of the intensity gradient.

Silicone degradation

The emission of hydroxyl radicals from the surface of a vitreous dielectric, silicone monolayers will be rapidly oxidized to form silicic acid. This silicic acid is hydroxylated and will emit hydroxyl radicals from its surface. Having a higher hydroxyl radical concentration, higher surface area, higher curvature, higher energy and higher surface potential from the rapidly quenched silica oxidation, the rate of emission of hydroxyl radicals will be significantly higher. This higher emission rate of hydroxyl radical and higher surface energy of the pristine fresh deposit will result in the preferential reaction of depositing silicone on the surface of the deposited material. Additionally, this will be even further accentuated at points of deposits, due to increased potential and accessibility. This will in effect drive the formation of spinels from the vacuum phase deposition of silicone.

It is also within the scope of this model to describe the behavioral differences between pre-existing silicone films as compared to the more damaging vapor phase deposition. The case of pre-existing silicone films will result in the formation of more planar deposits at a reduced rate. Due to the dissolution of the formed silica fume, quenching of the hydroxyl radical energy, and reduction of the surface energy and the availability of other oxidizing materials at the reaction sight. Thus, the apparent damage due to pre-existing films of silicone should be significantly less than that seen with deposition from the gas phase.

Effects of exciton polariton creation

The creation of the exciton polaritons within vitreous dielectrics results in a number of distinct changes in the dielectric. Because of the high energy density both absorption and emission of energy are much more favorable. Emission from one site and absorption at another site is probable. Excited states are much more polarizable than the ground state. This is evidenced by their attraction to fields (figure 3), and the generation of a bathochromic shift of the matrix. (Figure 1) This leads to a stronger interaction of the matrix with incident light. Raising the potential energy in the material effectively decreases the band gap of the material, decreasing the photon energy required for ionization. In the case of ionization, stimulated emission of the trapped exciton polaritons can result in avalanche like release of energy.

Increases in the potential energy result in the increase of the surface interactions of ad layers, increasing both adhesion and perturbation. Re-emitted energy will have different quantum statistics than the incident light leading to higher efficiency interactions of light with the matter as predicted by the Quantum Statistics of non-linear interactions. The differences in the quantum statistical properties can be measured and quantified to resolve the base interactions mechanisms.
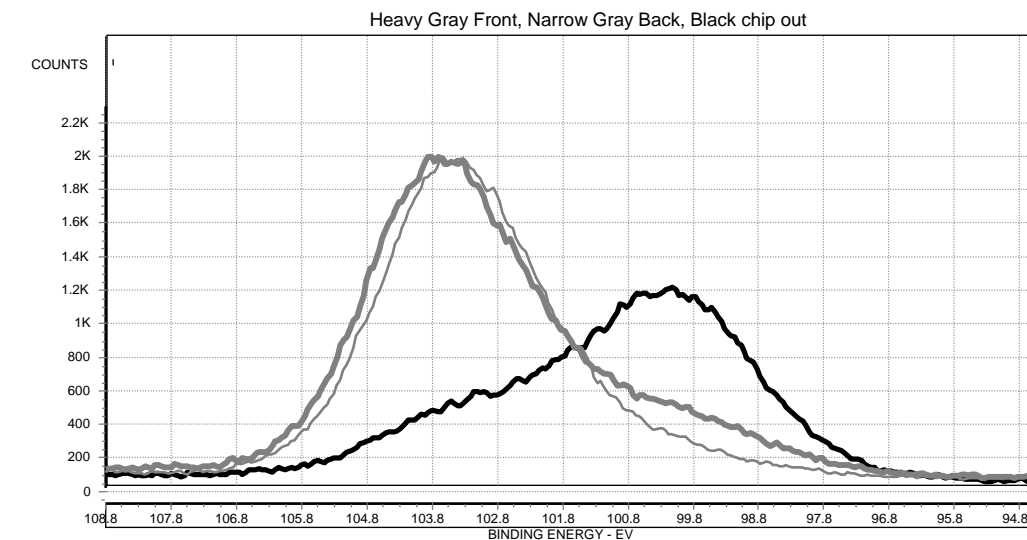

Figure 3 ESCA spectrum of silicon 2p electrons of laser exposed silica. The back window was dropped impacting a tile floor, the result being the excitons were attracted by the stress field and trapped when the fracture occurred. This depleted the exciton population in the rear window, concentrating the exciton population in the chip.

Based upon the mobility of the exciton polaritons and the retention of the polarization of the incident light to the emitted light over a number of days, it can be expected that the population density of the exciton polaritons is well in excess of the proposed limit of 0.03%. At 0.03% the exciton polaritons will largely be isolated within a nearly anisotropic matrix and are not be expected to retain polarization through mutual interactions. At higher concentrations, the interaction of the exciton polariton wave functions will be feasible and would be expected to result in additional barriers to loss of polarization. The mere retention of polarization within an irradiated optic immediately redefines an anisotropic medium into an isotropic medium because of the directionality and thus birefringence induced by the polarization.

As optical non-linearity can be defined as a change in the quantum statistics of an incident photon upon interaction with a material, the presence of the excitons polaritons and their propensity to interact with incident radiation releasing both the photon and the phonon, the non-linear behavior of a material is required to change. This is predicted from molecular quantum mechanics and other descriptive spectroscopic behavioral models.

The low quantum efficiency of these mechanisms makes them a low probability event in terms of single photons. Because of the low re-emission probability, the formation of the excitonic states will become linear based upon the simple absorption /emission kinetics. More critical is the fact that the time constants are sufficiently long to allow the absorption to become integrated to the total dose seen by the optic. It appears that the extreme stability of these states provides a significant step in explaining why the behavior of glass is dependent upon its entire history, in spite of annealing and extended relaxation times.

Beam Diameter and Damage Morphology

Classical nonlinear electrodynamics is limited to infinite constant uniform materials. These materials must be free from defects and the field must be uniform in x, y and z. The mode must be of an infinite plane wave of single uniform phase as well. While this might be of value in laser design, it is not useful in laser damage diagnostics. The very act of damaging an optic violates a base assumption of the model. Further, the model specifically exempts inhomogeneities, where damage most often occurs. The models are not relevant in this case. The model is incapable of functioning in more than one dimension.

Exciton polaritons and dielectrics are attracted to fields. The attraction of the exciton polariton or the dielectric is due to the polarizability of the material being larger than that of the medium surrounding the species. Thus, the movement of the species into the field will lower the field into which it is attracted, decreasing the total energy. This attraction is a function, neither of the total potential nor photon flux, but of the curvature of the field. At a given intensity, the gradient will increase with decreasing mode size. Therefore, a small mode will have a greater attractive force than a large mode.

In the measurement of laser optic damage threshold, it has been noted that there exists proportionality between laser beam diameter and laser damage threshold between beams of similar modal structure and pulse length. As the beam diameter decreases, the damage threshold decreases. This is outside of the scope of existing models. Existing models do not address fields orthogonal to the laser propagation.

The same electrostrictive force in effect upon the dielectric contaminants in reference 5, will apply to both the exciton polaritons and the molecular contamination in the system. Thus, the exciton-polaritons and contaminants will be accelerated toward the point of greatest field gradient. This can be imagined to be a cylinder aligned with the z direction of the beam.

The emission of the hydroxyl ions will be at a maximum at or near the highest intensity, and will result in an emission gradient of hydroxyl radical approximating the laser intensity profile, if the emission is not kinetically controlled by the migration of the hydroxyls through the vitreous medium.(figure 4) If it is, there may be a plateau due to the limiting conductance of the hydroxyls to the center of the beam location. For low energy pulses in the presence of atmospheric humidity, there should be no limit to the hydroxyl source provided by the atmospheric water. Under more limiting water conditions and higher total energy flux, the concentration is expected to plateau.

Initially, there will be a region of high oxidation potential at the center of the laser beam. Surrounding this center at somewhere near the beam waist, assuming it is not flooded with contamination, there will be a transition to an equivalence point between the attracted contaminants and the emitted hydroxyl concentrations. Just beyond this region, from about the beam waist to the outer beam footprint, there will be a region of reducing composition. There will be emission of some hydroxyl radicals in this region, activating the contaminants, but there will be insufficient hydroxyl radical concentration to complete the oxidation. These conditions result in the deposition of soot. This is analogous to a candle flame. Near the center of the flame, there is a high concentration of hydroxyl radicals. A glass surface exposed to this region does not blacken. Moving the glass surface out from the center to a region with limited hydroxyl radical concentration result is lamp black deposition.
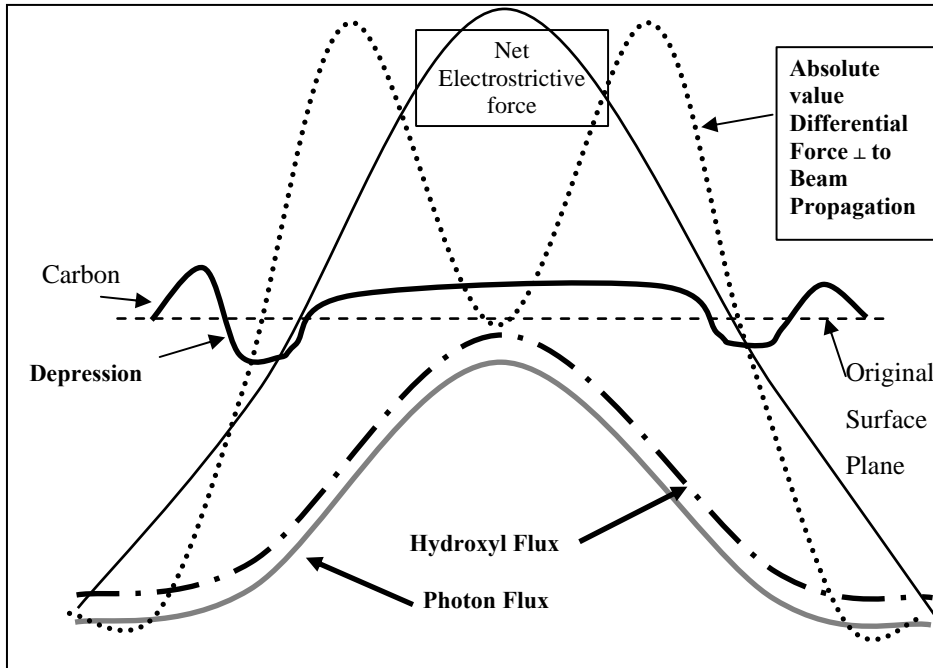
Figure 4, a graphical representation of the interacting forces and fields and the resultant damage morphology of a silica optic damaged by a 1064nm q-switched Nd:YAG laser in the presence of toluene.

Sufficient depletion of the hydroxyl population within the silica will result in the formation of color centers. It is expected that the hydroxyl concentration on the surface of the optic will be more mobile than that within the bulk as surface movement requires less movement of the bulk. The hydroxyls on the surface of the optic surrounding the beam can be expected to be attracted to the laser beam. In combination with the simpler transport along the surface, the emission from the optic will also be simpler due to the lower restriction to movement. Surface diffusion is more favorable, and simpler due to the lack of bulk diffusion. Thus, it is expected that the silica surrounding the beam, and the silica within the region of the attraction of the excited state contaminants, that color center formation will be more significant.

Conclusions

The proposed mechanism above is unique in that it describes virtually all of the behavior measured to date in contamination induced laser optic damage observations in the presence of toluene or other aromatic hydrocarbons and many of their derivatives as well as silicones. In addition, many of the degradation pathways of laser optics below the intrinsic laser damage threshold are likewise within the scope of this mechanism. The mechanism should be capable of describing both damage initiation, and mitigation. It should be noted that the various known mechanisms for depopulating excitonic states without material damage have not been listed above. The relaxation of these states will result in significant increases in laser lifetime in the presence of contamination providing this mechanism is correct.

Ginther and Claffy in 1971 proposed using thermoluminescence as a technique for the identification and measurement of laser damage. In the application of a one micron laser they found that the doping of laser glass with neodymium that there was virtually no thermoluminescence. Ginther and Claffy failed to realize that the lack of thermoluminescence that they found was in fact evidence of the depletion of energy from the glasses by spontaneous emission. Chromium III has been used to prevent radiation damage to Nd:YAG laser slabs. The addition of neodymium and chromium to laser glass will result in the elimination of energy of the radiation absorbed dose of laser radiation.

Irradiation of glass by radiation from sources such as UV, x-ray, gamma, electron and laser irradiation affects glass in relation to the radiation absorbed dose (RAD). This dose will result in changes in the physical and chemical properties of the glass. Including the softening, darkening and densification of the glass. Population of elevated energy states occurs through the population of metastable states in the glass.

Edwards, et.al. 1969[27], showed that the Raman spectroscopy was at the time the most sensitive method for the detection of laser induced optical damage and pre damage sites. The reason for this is that the Raman scattering is a sub function of the laser/material interaction tensor, and not separate from any of the other linear or non-linear interaction tensors. Thus, any change in the inelastic interaction of the laser light with the optical material will be reflected in the Raman scattering, either by the frequency or the scattering efficiency. Due to the complexity of the Raman interaction tensor, it is feasible to determine compositional, energetic, and numerous other properties of the optic resolved both spatially and temporally[28].

Acknowledgements

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