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UV Laser-Surface Interactions Relevant to Analytic Spectroscopy of Wide Bandgap Materials

DOE Contract DE-FG06-92ER14252

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Introduction. Laser ablation has important applications in materials analysis, surface modification, and thin film deposition. We have been examining the details of processes that lead to the emission and formation of particles (atomic/molecular ground state neutrals, excited neutrals, ions, electrons) when wide band gap materials are irradiated with pulsed UV laser light. Our studies bear directly on achieving understanding and control of emission intensities and particle characteristics for use in materials analysis, particularly of wide bandgap materials. These materials are often difficult to transport into the gas phase for analysis and in a number of high technology applications, such as laser etching and deposition, spectroscopic understanding and support of the ablation process is needed. Technologically, wide bandgap materials are of particular interest due to their excellent insulating and optical properties.

Role of Deformation and Fracture. In model wide bandgap materials such as single crystal alkali halides and MgO, nominally transparent materials, exposure to repeated pulses of 248 nm excimer laser radiation of a few J/cm² results in substantial interaction including extensive biaxial deformation and cleavage. Significant surface heating also occurs, consistent with strong free-carrier/laser interactions. We have shown that achieving intense emission of atomic, molecular, and ionic particles actually depends on point defect production by laser-induced deformation and fracture. Defect production via dislocation motion yields orders of magnitude increases in laser vaporization of these wide bandgap materials, including cluster ion formation.

The desorption and ablation of material from nominally transparent, wide bandgap materials by UV excimer radiation can be greatly enhanced by the presence of any lattice defects which allow single-photon excitations to the conduction band.^{1,2} In the previously unexposed solid, absorbing defects may be produced during material processing (e.g., crystal growth, impurities) and sample preparation (e.g., polishing,^{3,4} electron irradiation⁵). The relatively high energy of UV radiation can promote single photon absorption from defects which are much less important at visible wavelengths. While polishing increases the resistance of many materials to laser damage resistance at visible wavelengths (due to the removal of surface scratches etc.), at UV wavelengths mechanically produced defects can actually make polished surfaces more susceptible to laser damage. In MgO ($E_g = 7.9$ eV) and NaCl ($E_g = 8.6$ eV bandgap), these defects can strongly enhance desorption and ablation by 248 nm (5 eV photon energy) UV laser light.³⁻⁶

Cleavage Surfaces. Cleaved MgO surfaces show considerably less sensitivity to single pulse laser irradiation at 248 nm radiation than polished or abraded surfaces.³ We attribute these differences to variations in the density and distribution of point defects produced during the three surface preparations, which involve various degrees of mechanical deformation of the surface. Even on cleaved surfaces, we find very highly localized melting, the formation of holes, and the

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appearance of Mg rich hemispheres. We have shown that these features are most often seen at the etches of cleavage steps where substantial plastic deformation occurs. (See imaging below).

We have demonstrated that many wide bandgap materials show strong incubation effects, in which laser absorption at a given fluence (below that initially required for a strong ablative response) produces an increasing number of absorbing defects which eventually lead to strong, ablative responses. With repeated irradiation at constant fluence, the particle emission accompanying each laser pulse can increase some orders of magnitude. In the alkali halides and fused silica,^{7,8} suitable lattice defects may be produced by the relaxation of excitonic defects created directly by laser absorption (i.e., electron-hole pair production by bandgap excitations can lead to vacancy formation). In MgO, incubation effects were shown to be due to point defects produced by thermally induced deformation and fracture accompanying repeated irradiation. Deformation mechanisms for point defect production were also demonstrated in NaCl, indicating that mechanically produced defects are also important in the alkali halides.

MgO is a highly ionic metal oxide with the rock salt structure. The high binding energy of MgO prevents the production of lattice defects by means of exciton decay, rendering it quite resistant to radiolysis by UV photon and (< 300 keV) electron bombardment. Therefore, MgO is a particularly interesting material for the study of the role of non-photoelectronic induced defects in desorption and ablation. The alkali halides, in contrast, are relatively susceptible to radiolysis due to the ease with which F- and H-centers are produced by exciton decay. However, absorbing point defects can be produced in both MgO and the alkali halides by mechanical deformation. Thus, laser-induced heating [initiated by photon-interactions with existing defects] can produce significant increases in the density of laser-absorbing defects, resulting in the gradual build-up of absorption noted above.³ These effects can have important implications concerning our understanding of UV laser interactions with wide bandgap materials and indicate that the origin and evolution of defects plays a critical role.

Imaging Point Defect Clusters. When semi-brittle inorganic crystals are deformed, i.e. due to thermal cycling under pulsed laser irradiation, stresses result in significant dislocation generation and motion. The field of moving atoms associated with a variety of dislocation structures (e.g., jogs) in turn produce point defects in surprising abundance. We have developed a method using an excimer laser to image the photoluminescence generated by these defects. In MgO, this results in a distinct 400 nm emission band which is due principally to clusters of oxygen vacancies occupied by electrons (F-Centers). This type of luminescence has been previously observed in doped CaO by Chen et al.⁹ Unique patterns of these clusters occur on cleavage surfaces with strong correlation with regions of high densities of dislocation concentrations. These patterns can be observed by the imaging system shown in Fig. 1. Using pulses of unfocused 248 nm (ultraviolet light) from a KrF excimer laser, defects associated with a wide variety of deformation induced dislocations can be viewed and recorded through an optical microscope. All scattered UV is absorbed in the microscope optics. Currently, magnifications up to 250X have been used. With a CCD camera, much higher magnifications could be achieved.

Alignment of clusters of such point defects are observed along cleavage steps. Cleavage steps are generated by cracks running in parallel but on different crystal planes. Swain, Lawn, and Burns¹⁰ have analyzed the process of step formation, finding that adjacent but non-coplanar crack will tend to overlap prior to ultimate failure (see Fig. 2). The overlapped material experiences extreme shear stresses, and in semibrittle materials can be extensively deformed and therefore produce rows of dislocations along the cleavage steps. Often, undercutting occurs which produces highly deformed "platelets" which show up regularly in the luminescent images.

Diamond tip indentations, scratch marks, polishing grooves, and regions involving tribological interactions lead to extensive concentrations of luminescent centers due to the associated plastic deformation, and serve as a means of mapping and monitoring energy dissipative processes occurring during mechanical and fracture phenomena. Real time information (with μ s time resolution) can also be obtained by replacing the imaging system with integrating optics and a fast photomultiplier tube. These measurements allow us to see visually where plastic deformation is occurring during loading and fracture--in transparent, wide bandgap

materials this includes well below the surface. It can also serve as a way of detecting damage on a ceramics surface where flaws are often the cause of failure, as well as coupling laser energy into these defect clusters for the purposes healing microcracks and other flaws by preferential melting and annealing. We have recently made direct measurements of the role of these defects on the mechanically induced decomposition of the surface of ceramics which has importance concerning wear during tribological loading.

As discussed above, these defects also play a critical role in inducing excimer laser ablation in wide bandgap materials. We are currently sorting out additional correlations between different types of plastic deformation and coupling to the laser beam. We have shown previously⁵ in materials that are sensitive to vacancy formation under low energy electron bombardment (e.g., SiO₂ systems, alkali halides) we can lower the threshold for ablation considerably by simply simultaneous bombardment with co-focused electron and laser beams. Since electron beams can be focused to ~50 Å spot sizes, we have proposed that this may serve as a means of analyzing very small regions of the surface in a preferred fashion. As discussed in our research plan for '93, we are pursuing both e⁻ beam and ion beam stimulation of surfaces to induce stronger laser-material interactions.

Publications with cited DOE Sponsorship

R. L. Webb, L. C. Jensen, S. C. Langford, and J. T. Dickinson, "Interactions of wide bandgap single crystals with 248 nm excimer laser radiation: I. MgO", submitted to J. Appl. Phys.

R. L. Webb, L. C. Jensen, S. C. Langford, and J. T. Dickinson, "Interactions of wide bandgap single crystals with 248 nm excimer laser radiation: II. NaCl", submitted to J. Appl. Phys.

J. T. Dickinson, L. C. Jensen, R. L. Webb, M. L. Dawes, and S. C. Langford, "The role of cleavage-induced defects in the onset of UV laser ablation of MgO," submitted to J. Appl. Phys.

J. T. Dickinson, L. C. Jensen, R. L. Webb, M. L. Dawes, and S. C. Langford, "Mechanisms of excimer laser ablation of wide band-gap materials: the role of defects in single crystal MgO", submitted to Proceedings, Symposium I, MRS Fall Meeting, Boston, 1992.

R. L. Webb, L. C. Jensen, and J. T. Dickinson, and C. R. Davis, "Sensitization of PMMA to Excimer Laser Ablation at 308 nm Wavelength," in preparation.

Invited Talks

"The Mechanisms of Ablation of Wide Bandgap Materials", American Chemical Soc., San Francisco, April, 1992.

"Fracto-Emission from Ceramics and Glasses," American Ceramics Society, Minneapolis, April, 1992.

"Chaos and Fractals in Fracture", Gorton Conference on Fractals, June, 1992.

"Laser Ablation of Wide Bandgap Materials," Gorton Conference on Particle-Solid Interactions, August, 1992.

"Mechanisms for Ablation of Insulators," DOE Workshop-Lasers in Chemistry, Santa Fe, October, 1992.

"Laser Ablation of Wide Bandgap Materials," MRS Fall Meeting, Boston, December, 1992.

To be presented:

"Laser Ablation of Wide Bandgap Materials", SPIE Annual Meeting, Los Angeles, CA, January, 1993.

"Mechanical Consequences of Laser Bombardment of Insulators", Workshop on Dynamic Response of Materials to Energy Deposition, Los Alamos, January, 1993.

"Laser Ablation of Wide Bandgap Materials", International Workshop on Laser-Materials Interactions, Oak Ridge, April, 1993.

"Fracto-Emission from Polymer Interfaces," ACS, Chicago, August, 1993.

"Dissipative Processes in the Laser Induced Fracture of Crystalline Materials," International Symposium on Fracture and Strength of Glass and Ceramic Materials, PAC-RIM 1993, Honolulu, Nov., 1993.

Contributed Talks:

Scanning Tunneling Microscope Observations of Crack Initiation Zones in Glass and Glassy Polymers," American Vacuum Society, Seattle, Nov., 1991.

"Sub-Microsecond Probes of Mechanical Failure of Polymeric Thin Films and Interfaces," American Vacuum Society, Seattle, Nov., 1991.

"Atomic and Molecular Emission from Fracture of Single Crystals and Silica Glasses," American Vacuum Society, Seattle, Nov., 1991.

"A study of the stick-slip process using fracto-emission," MRS Winter Meeting, Symposium P (Disordered Systems: Fractals, Scaling, and Dynamics), Boston, MA, Nov. 1991.

"Negative Charge Emission Due to Excimer Laser Bombardment of Silicate Glasses," MRS Winter Meeting Symposium B (Photons and Low Energy Particles in Surface Processing), Boston, MA, Nov. 1991.

"Neutral molecule emissions accompanying the fracture of polycarbonate thin films: Evidence for Molecular Bond Breaking," MRS Winter Meeting Symposium D (Thin Films), Boston, MA, Nov. 1991.

"Neutral Molecule-Emission During Deformation and Fracture of Glassy Polymers," American Physical Society, March Meeting, Indianapolis, March, 1992.

"Electrical Transient Measurements During Adhesive Failure," American Physical Society, March Meeting, Indianapolis, March, 1992.

"Excimer Laser Interactions with Wide Bandgap Materials: The Role of Defects," American Physical Society, March Meeting, Indianapolis, March, 1992.

"Excimer Laser-induced Fracture of Wide Bandgap Materials," American Ceramics Society, Minneapolis, April, 1992.

"Excimer Laser Interactions with Wide Bandgap Materials: The Role of Defects," Pacific Northwest Section of American Vacuum Society, Richland, WA, Sept., 1992.

Calcite Decomposition by Mechanical Stimulation, Pacific Northwest Section of American Vacuum Society, Richland, WA, Sept., 1992.

"Decomposition of Single Crystal Calcium Carbonate via Mechanical Stimulation," American Vacuum Society Annual Meeting, Chicago, IL, Nov. 1992.

"Mechanisms of Excimer Laser Ablation of Wide Bandgap Materials: The Role of Defects," American Vacuum Society Annual Meeting, Chicago, IL, Nov. 1992.

"Time Resolved Measurements of Mass-Selected Neutral Molecule Emission During Deformation and Fracture of Glassy Polymers," American Vacuum Society Annual Meeting, Chicago, IL, Nov. 1992.

"Unambiguous Measurements of Soft X-Ray Production in a Bayard-Albert Gauge," American Vacuum Society Annual Meeting, Chicago, IL, Nov. 1992.

"Random Walk Description of Fracto-Emission from Polymers and Interfaces," MRS Winter Meeting, Symposium, Boston, Nov. 1992.

1993 Research Plan

There are a number of discoveries we have made that are quite exciting to us and trigger our immediate research plans. We briefly describe them.

1. **Carbon Containing Species from MgO.** When we expose high purity, arc fused, single crystal MgO to a single, 20 ns pulse of 248 nm radiation from an excimer laser, intense emission of several neutral atomic and molecular species is observed. In the fluence range of 1-3 J/cm², we have found that the oxygen containing species were very small [e.g, emissions at 16 amu (O) and 32 amu (O₂)] compared to Mg and Mg⁺ emissions. Careful examination of the emitted species with a quadrupole mass spectrometer has shown that surprisingly intense emissions were found at masses 28 (CO) and 44 (CO₂), over an order of magnitude more intense than O and O₂. *Thus, the great majority of the oxygen leaving the surface is associated with carbon.* Spheroidal, Mg-rich particles are observed in the irradiated region, consistent with the reduction of MgO associated with these emissions. Subsequent pulses on the same area yield decreasing amounts of carbon containing molecules. The crystals we are using have C impurity concentrations on the order of 30-300 atomic ppm. We feel that the mechanism for simultaneous removal of C and O are due to segregation of C to the near surface region (possibly aided by O vacancies) with subsequent reactions of C and O leading to volatile CO and CO₂ production. A number of experiments to elucidate the mechanisms are underway.
2. **Ablation plumes formed during pulsed laser irradiation.** We have seen a number of interesting phenomena concerning the $\pm$ charges that are emitted from insulator surfaces at reasonably low laser fluences. Irradiation of most materials yields copious electron emission. As the emission of positive ions is typically orders of magnitude less efficient, the surface develops a positive surface charge which hinders the escape of the great

majority of emitted electrons. During the laser pulse, a dense electron cloud forms above the irradiated surface formed by those emitted electrons which cannot escape, but which have not yet returned to the surface. Positive ions are emitted in much smaller quantities. Unlike the electrons, their escape is favored by the positive surface charge. Their emission will also favor the escape of a certain number of electrons due to their mutual electrostatic attraction. The number of electrons which escape with the positive ions should be roughly that required to make the net surface charge equal to the net positive charge in the ablation plume. In the limiting case of a planar geometry, this ensures that the region between the charged sheets defined by the charged surface and the escaping ions is at a constant potential. Any deviations from a constant potential would drive the rapid movement of electrons to remove the deviations. The equality of plume charge and surface charge is a measurable prediction of this model.

We wish to use Langmuir probe analysis as well as charged particle and fluorescence detectors to measure pulse by pulse the surface charge, plume motion, plume particle densities and structure, and temperatures in these lower fluence regions to develop a predictive model of the formation and behavior of the plume. In addition, we have seen responses of these low density plumes to externally applied E fields which we wish to explain and again predict. These types of studies have considerable importance to the use of laser desorption and laser ablation for mass spectroscopic analysis. Also, we would like to develop more definitive mechanisms for the production of the plume fluorescence in conjunction with the charged particle measurements.

3. **Delayed Bursts from Brittle Materials.** Normally one examines the desorption and ablation products accompanying pulsed laser irradiation on a time scale commensurate with the time-of-flight of particles produced essentially during the laser pulse. Thus, for flight paths of a few tens of cm, this corresponds to time scales of 10-500 μ s. We have recently examined the emissions that follow the laser pulse by 5-25 ms at higher fluences from a number of samples and found there to be considerable emission of electrons, ions, and neutrals in this time frame. These include atomic and molecular species from NaCl, LiF, and MgO and occur as bursts that gradually disappear after each pulse. For example, from LiF we observe neutral Li, F, LiF, and Li₂F. There is a strong link between these delayed emissions and previous work involving dislocations and point defects. We have examined delayed emissions following the fracture of NaCl and LiF which also yielded atomic and molecular emissions of a similar nature.¹¹ We wish to work out the mechanism and connection of these emissions with fracture, dislocation production and motion, and point defects possibly emerging onto the crystal surface.
4. **Photo-luminescence Imaging.** As reported above, we have been able to begin imaging a number of point defect structures in MgO induced by mechanical processes by means of photoluminescence; a number of these defects are generated by laser irradiation. We would like to use this method to examine portions of a crystal surface prior to laser irradiation, then on the same region attempt to produce laser melting, evaporation, ablation, and possible laser damage (e.g., fracture) and draw connections between the density of defects, resulting material damage and/or removal, and influence on the species removed. Furthermore, we wish to examine the same types of defects in alkali halides where photoelectronic processes as well as fracture can produce halide vacancies.
5. **Simultaneous Ion or Electron Beam Irradiation with Laser Irradiation.** We would like to explore in more detail the influence of energetic particle bombardment on laser desorption and ablation, similar to the results previously reported.⁵ The use of ions in a material such as MgO would be extremely interesting. Connecting part 4 with these studies, where photoluminescence could be used in a quantitative fashion to see the build up of defects prior to laser irradiation would also be done.

6. **Cluster Formation Mechanisms.** There is clearly a number of studies needed to firmly establish the mechanisms of ionic cluster formation from materials such as alkali halides, MgO, and other materials. This is important technologically, because of the beneficial role of clusters in thin film deposition. We have shown that in MgO there does not appear to be a direct ejection of cluster ions from the surface, whereas in the alkali halides, small clusters appear to be ejected. In the presence of a buffer gas, clusters many times larger in mass have been seen (and attributed to direct emission from the surface). We wish to explore this in more detail and resolve the issue of gas phase agglomeration vs direct ejection.
7. **Back Side Plume on MgO at 308 nm.** In some preliminary studies of the interaction of 308 nm laser light on MgO, we found that plume formation was often occurring preferentially on the *back side* of the crystal. At 248 nm, plumes always formed on the front surface. The crystal is much more transparent at 308 nm. Also, there is an E field enhancement at an internal reflection (i.e., right at the back surface), but we do not feel this is the dominating effect due to SEM evidence of substantial melting occurring. Our goal is to determine why this effect is occurring and what is the nature of the emissions from this back side. One question concerns the ejecta: does macroscopic particle ejection happen on the back side?

1992 Funds Remaining

As of November 30, a total of \$6500 remains unspent.

I am currently faced with paying off a \$20,000 repair bill on our Excimer Laser and at the same time purchase a second laser (for driving a dye laser to do resonance ionization of product molecules and other laser fluorescence experiments). By combining with funds provided by the State of Washington, I will try to cover these expenses.

System for Imaging F-Center Cluster Luminescence

Plastic Deformation of MgO Produces Vacancies.
One mechanism is glide of jogged screw dislocations.

Fig. 1

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