Effect of surface treatments on self-trapped exciton luminescence in single-crystal CaF_2

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We show that near-surface defects produced by mechanical treatments and electron irradiation can significantly enhance the intensity of luminescence due to the decay of self-trapped excitons (STEs) in single-crystal calcium fluoride during 157- and 193-nm irradiation. For example, polishing can double the intensity of the STE luminescence. Defects produced by mechanical indentation can either increase or decrease the luminescence intensity, depending on the indentation force. Electron irradiation also enhances subsequent STE luminescence. When electron-irradiated samples are annealed, additional increases in luminescence intensity are observed. Plausible mechanisms for the observed effects on STE luminescence intensity are discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1904725]

I. INTRODUCTION

The large band gap (11 eV)[1,2] and cubic symmetry of single-crystal calcium fluoride make it an attractive material for vacuum ultraviolet optics. It is currently employed in photolithography at 193 nm and is an important candidate material for use at 157 nm. Although nominally transparent at these wavelengths, defects generated by two-photon absorption[3,4] can potentially degrade optical performance.[3,5,6]

Self-trapped excitons (STEs) play an important role in defect production. In calcium fluoride, STEs are typically formed when a free electron is localized at a self-trapped hole (V_K center). The resulting excitons can decay radiatively, yielding a distinctive luminescence centered near 280 nm, or nonradiatively, yielding lattice displacements.[3,7] Under favorable conditions, these lattice displacements produce halide vacancies and interstitials.[8] In this context, luminescence and defect production are competing processes.

The decay of excitonic defects can be strongly affected by lattice imperfections. Tsujibayashi *et al.* have shown that the STE luminescence intensity and spectrum in calcium fluoride are strongly affected by impurities.[9] In this work, we show that near-surface defects generated by polishing and mechanically indenting cleaved single-crystal samples can significantly increase the luminescence intensity. We also examine the effect of defects produced by electron irradiation, which generates metal colloids in the surface region. Understanding the effect of defects on STE photoluminescence intensities under 157- and 193-nm irradiation may help guide the development of reliable, high-quality optical components for use in this important region of the spectrum.

II. EXPERIMENT

Vacuum-ultraviolet-grade CaF_2 was obtained from Korth Kristalle GmbH and cleaved in air along (111) planes into 0.2-cm-thick, 1-cm-diameter disks. The samples were then mounted on a vacuum-compatible sample positioner and transferred to the vacuum system. Experiments were carried out at pressures below 1×10^{-7} Pa.

A diagram of the experiment is shown in Fig. 1. Luminescence was excited with 157-nm radiation from a Lambda Physik LPF 200 excimer laser (F_2, 20-ns pulses) or with 193-nm radiation from a Lambda Physik Lextra 200 excimer laser (ArF, 30-ns pulses). A portion of the resulting luminescence was directed through a fused silica fiber optic cable into a Model 82-479 Thermo Jarrel Ash Spectrometer with a 300-lines/mm grating blazed at 400 nm. The spectra were imaged with a Roper Scientific PI-Max intensified charge-coupled device (CCD). Spectra acquisition was typically initiated several nanoseconds after the laser pulse and continued for 5 μs. Spectra acquired at a single position on the sample were averaged over 1000 laser pulses. Normally, spectra acquired at ten positions on the sample were again averaged to minimize the small spot-to-spot variations in intensity. After removing the samples from the vacuum system, UV-VIS absorption spectra were acquired with a Perkin Elmer Lambda 900 spectrophotometer.

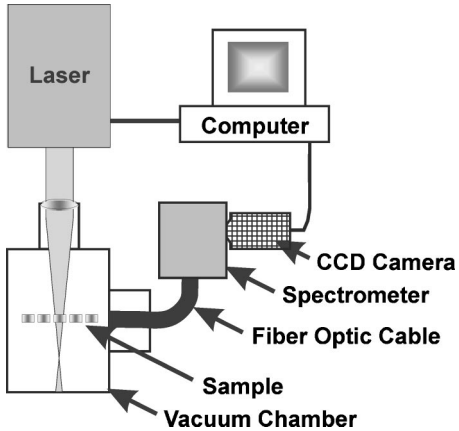

FIG. 1. Diagram of STE luminescence measurements.

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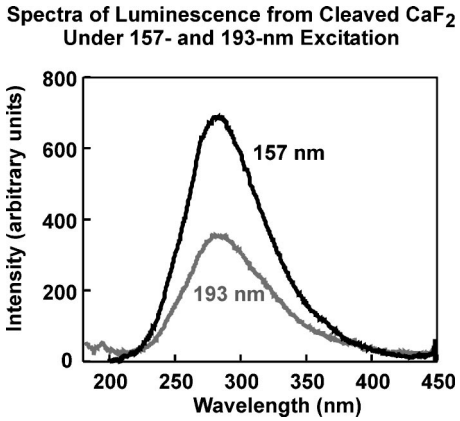

FIG. 2. Spectra of STE luminescence from cleaved CaF_2 generated by exposure to 157- and 193-nm radiations at 120 mJ/cm^2. The spectra have not been corrected for camera and spectrometer responses.

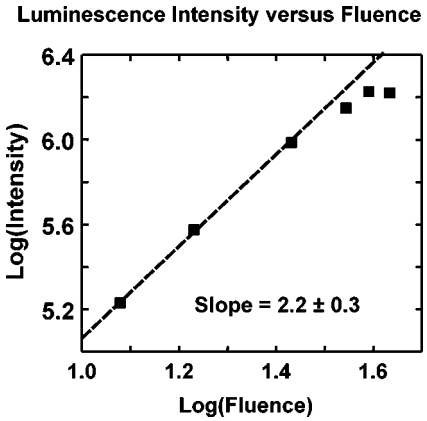

FIG. 3. Log-log plot of STE luminescence intensity vs 157-nm laser fluence.

Mechanical surface treatments were performed prior to mounting in vacuum. Polished samples were cut with a diamond saw or cleaved and polished with aluminum oxide abrasives and finished with 0.1-μm diamond paste. Samples were polished in methanol rather than water to minimize oxide formation. Indentation was performed with a thoroughly cleaned 0.8-mm steel sphere.

Electron irradiation was performed in vacuum with an Auger electron gun operated at an electron energy of 2 keV and beam current of 100 μA. The beam was focused to a roughly 3×5-mm^2 spot on the sample. Sample heating was performed in vacuum with a resistive heater. A chromel-alumel thermocouple was spot welded to the sample holder next to the sample to facilitate temperature control.

III. RESULTS

A. Characterization of STE luminescence

Cleaved samples display relatively low defect densities and thus provide a base line for determining the effect of mechanical treatments and exposure to electron irradiation. Typical luminescence spectra excited by 120 mJ/cm^2 of 157- and 193-nm laser radiation appear in Fig. 2. The broad peaks at 280 nm in both spectra are consistent with STE luminescence spectra reported by others.[9,10] Under 248-nm irradiation (5-eV photons), no measurable STE luminescence was detected at fluences low enough to avoid breakdown.

Exciton formation typically requires band-gap or near-band-gap excitation energies. At 157 nm (7.8-eV photons) and at 193 nm (6.3-eV photons), these excitations require the absorption of two photons. Measurements of STE luminescence versus fluence, shown in Fig. 3 for the case of 157-nm irradiation, confirm this expectation. The slope of the linear, low fluence portion of the log-log plot in Fig. 3 is 2.2 ± 0.3. Similar measurements under 193-nm excitation also yielded a power-law exponent of 2.2 ± 0.3. Both measurements are consistent with two-photon excitations. Under 248-nm excitation (5-eV photons), STE formation would require three-photon absorption; the probability for three-photon absorption at 248 nm in ionic crystals is typically 10^{-5} that of two-photon absorption at fluences of a few J/cm^2 and pulse lengths of a few tens of nanoseconds.[11] This accounts for the lack of detectable STE luminescence at 248 nm at fluences below breakdown.

At somewhat higher fluences, the STE luminescence tends to saturate, as seen in Fig. 3. We have recently demonstrated that 157-nm light produces defects which absorb significantly at 157 nm. Although these associated defects have not been identified, V-like centers produced by nonradiative STE decay are a good candidate. This absorption increases with 157-nm laser fluence and would limit the increase in luminescence intensity as the energy/pulse approaches 1 J/cm^2.

The decay of luminescence intensity after the laser pulse was consistent with STE luminescence lifetimes measured previously by others. Figure 4 shows the natural log of the integrated STE luminescence intensity generated by 140-mJ/cm^2, 193-nm laser pulses as a function of time after the laser pulse. The slope of the plot indicates an exponential decay with a time constant of 1.14 ± 0.1 μs, consistent with the measurements by Görling *et al.*[3] Similar measurements under 157-nm excitation yielded a decay time constant of 1.3 ± 0.2 μs.

B. Consequences of mechanical treatment: Polishing

In previous work, we have demonstrated that polishing treatments can significantly enhance laser absorption and lu-

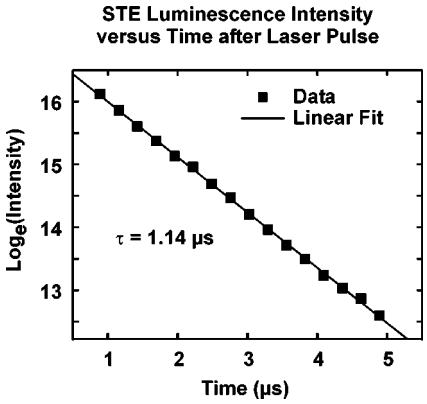

FIG. 4. Natural log of STE luminescence intensity vs time for a cleaved CaF_2 sample under 193-nm irradiation at 140 mJ/cm^2. The slope yields a time constant of 1.14 μs.

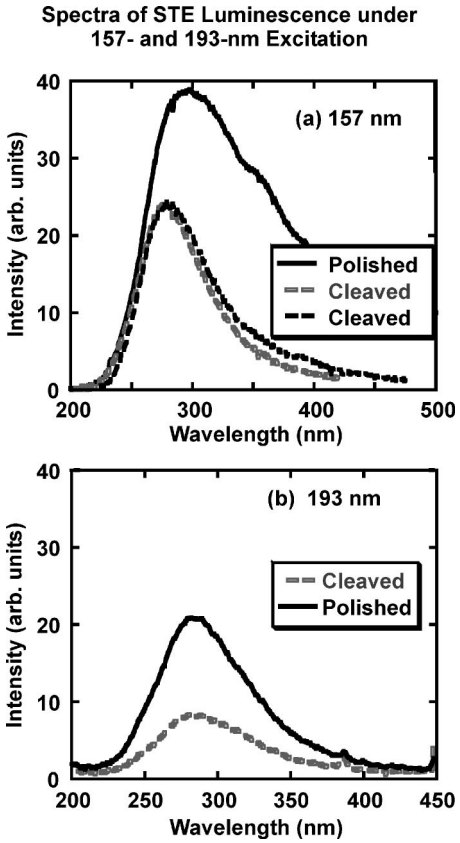

FIG. 5. STE luminescence spectra for cleaved and polished CaF_2 exposed to pulsed (a) 157-nm radiation at 87 mJ/cm^2, and (b) 193-nm radiation at 80 mJ/cm^2. The integrated emission intensity from the polished sample is about twice that from the cleaved samples.

minescence from ionic materials.[12,13] Luminescence spectra acquired during 157-nm excitation of two cleaved CaF_2 surfaces and a heavily polished surface are compared in Fig. 5(a). Small but significant differences are observed in the spectra of different cleaved specimens, especially on the long-wavelength side of the emission band. We expect that variations in the density of cleavage-induced defects are responsible for these differences.

The effect of polishing on the STE luminescence intensities depends strongly on the duration of the polishing treatment. Figure 5(a) shows the STE luminescence generated under 157-nm excitation after an extended polishing treatment that may have introduced impurities into the near-surface region. Not only is STE luminescence from the polished sample particularly intense, but the spectrum also displays a prominent tail to long wavelengths. Tsujibayashi *et al.* reported STE luminescence spectra from impure CaF_2 crystals that showed similar features.[9] By way of comparison, Fig. 5(b) shows the STE luminescence spectra excited by 193-nm radiation from a sample polished just long enough to remove surface steps introduced by cleavage. Although this minimal polishing treatment has doubled the integrated luminescence intensity relative to the cleaved samples, any changes in the shape and position of the luminescence band are small. We propose that impurities introduced by prolonged polishing are the cause of the long tail to the red in the spectrum of STE luminescence in Fig. 5(a).

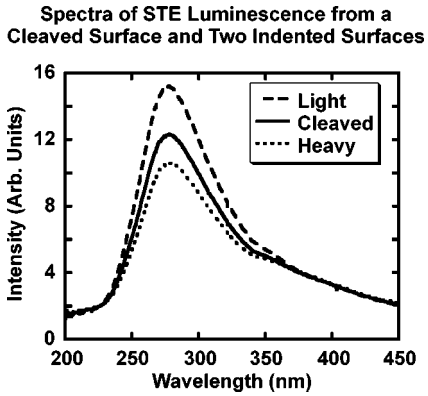

FIG. 6. Spectra of STE luminescence from cleaved and indented samples excited by 157-nm radiation at 290 mJ/cm^2. The solid black line corresponds to emission from the cleaved surface, the dashed-line corresponds to emission from a surface indented with a low contact force, and the dotted line corresponds to emission from a surface indented with a high contact force. Care was taken to avoid fracture.

C. Consequences of mechanical treatment: Indentation

Mechanically indenting a surface also produces defects that can influence the STE luminescence intensities. We indented the surface by applying a downward force on a steel sphere resting on the surface. To minimize the possibility of fracture, a rather large sphere was used (radius ~0.8 mm). The sphere was then moved and the procedure repeated until the irradiated area was populated by a large number of indents. Indented regions showed no evidence of enhanced backscattering, which would reduce the intensity of laser radiation reaching the interior of the sample. Figure 6 compares the STE luminescence spectra acquired from a cleaved surface from a surface with indents formed by applying a low force to the sphere, and from a surface with indents formed by applying a relatively high force to the sphere. Significantly, low-force indents increase the STE luminescence intensity relative to the cleaved surface, while high-force indents decrease the luminescence intensity. A similar effect, where low-force indentations enhance luminescence intensities and high-force indents quench them, has been observed in single-crystal MgO.[14,15]

The effect of defects produced by indentation on the STE luminescence spectra is principally confined to the 250–350-nm region, near the center of the luminescence band. In particular, the luminescence intensity at wavelengths longer than 350 nm is hardly affected by either indentation treatment in Fig. 6. This is further evidence that the enhanced emission from the polished sample in Fig. 5(a) at long wavelengths is due to impurities introduced by extensive polishing, rather than mechanically produced defects.

D. Consequences of exposure to 2-keV electron irradiation

The STE luminescence of the polished samples can be further increased by exposure to energetic electrons. Figure 7 shows the integrated luminescence intensities under 157 -nm excitation at three laser fluences before and after exposing polished CaF_2 to a 500-mC/cm^2 dose of 2-keV elec-

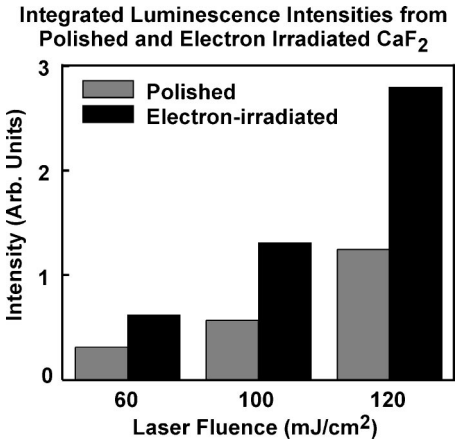

FIG. 7. Average STE luminescence intensities from polished and electron-irradiated surfaces excited by 157-nm radiation at three fluences.

trons. The nonlinear increase with laser fluence both before and after electron bombardment is consistent with a two-photon excitation. Electron irradiation is known to produce defect aggregates that include metallic calcium nanoparticles.[16–18] At this dose, the sample is visibly colored by nanoparticles with average diameters of about 20 nm.[19,20] We have recently shown that significant nanoparticle absorption at 157 nm is predicted by Mie theory.[21] Although this absorption would compete with STE production for 157-nm photons, the net effect of electron irradiation is to increase the STE luminescence intensity. Significantly, electron irradiation has little effect on the shape of the STE luminescence spectrum; it simply enhances the probability of generating STE luminescence.

The size and density of the nanoparticles in CaF_2 can be increased by annealing treatments at modest temperatures.[16] Normally, annealing also reduces the density of mobile point defects. Figure 8 compares the average luminescence intensities observed immediately after exposing a polished sample to 1200 mC/cm^2 of 2-keV electrons, and after subsequent 30-min anneals at 50 and 180 °C. Significantly, both annealing treatments increase the STE luminescence intensities,

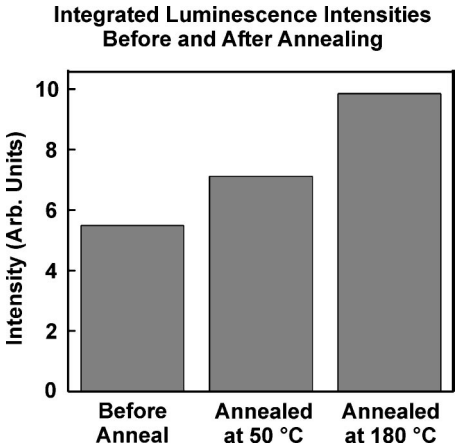

FIG. 8. Average STE luminescence intensities from an electron-irradiated sample before and after two 30-min annealing treatments in vacuum. The first anneal was at 50 °C and the second at 180 °C. Luminescence intensities were measured in vacuum at room temperature under 157-nm excitation at 300 mJ/cm^2.

with the higher-temperature anneal producing the greatest increase. This increase suggests that annealing has either removed point defects that quench STE luminescence or that the nanoparticles themselves play a role in STE luminescence.

IV. DISCUSSION

The luminescence of self-trapped excitons in CaF_2 at excimer laser wavelengths has been previously studied.[3,4,22] Görling *et al.* verified that STE formation requires two-photon excitations at both 193 and 157 nm and estimated the two-photon absorption cross sections.[3] The wavelength, lifetime, and fluence dependence of the luminescence described above are consistent with these previous observations.

Any defect capable of electronic excitation by reactions with free electrons or holes is a potential competitor for the excitation energy required for luminescence. The formation of STEs in calcium fluoride and the alkali halides is believed to involve initial hole localization, followed by electron recombination.[23] Hole localization near preexisting defects is often favored, and the perturbation of the trapped hole by nearby defects is likely to alter the efficiency of radiative decay. In the case of impurities, Tsujibayashi and Toyoda have found a strong effect on the wavelength of emission as well.[4]

In some materials, mechanically produced defects can be excited to produce intense luminescence.[24–28] In previous work, we exploited the luminescence of deformation-induced defects in single-crystal MgO to provide a probe of deformation and surface damage.[12] Dislocation motion in ionic materials can generate high densities of point defects by a jog dragging mechanism.[29,30] Both polishing and indentation involve extensive deformation and generate high defect densities in the near-surface region. In the case of polishing and indentation with low contact forces, these defects appear to increase the overall STE luminescence. This increase is especially remarkable in the case of polished surfaces, where the depth of the deformed region is small, on the order of a micron. Gogoll *et al.* found that polished CaF_2 surfaces were often less resistant to laser-induced damage under pulsed 248-nm radiation than cleaved samples, presumably due to absorption at 248 nm by polishing-induced defects.[31]

The difference between the effect of high-force indentation and low-force indentation is mirrored in the studies of deformation-related cathodoluminescence in single-crystal MgO.[14,15,25,26] At low contact forces, indented regions are marked by high luminescence intensities. However, at high contact forces, the central part of individual indents is visibly dark under electron irradiation. The centers of indents formed at high contact forces display especially high defect densities that apparently quench luminescence. Although the quenching mechanism is not clear, nonradiative deexcitation may be enhanced when defects are so close together that their excited-state electron densities overlap. At high densities, defects which normally enhance the radiative decay of nearby excitations could provide an efficient path for nonradiative decay, thereby *reducing* luminescence intensities.

The effect of annealing on STE luminescence from

electron-irradiated material suggests that the corresponding enhancement is not due to isolated point defects. Annealing treatments, which increase the STE luminescence intensities, typically reduce point defect densities and enhance nanoparticle growth in CaF_2.[16,32–34] Even prior to annealing, our absorption measurements on electron-irradiated material[21] show that the F-center concentrations are relatively low, in agreement with other studies by Bennewitz *et al.*[19,33] Instead, the UV-VIS absorption spectra are dominated by the nanoparticle Mie absorption peak. Calculations further show that the nanoparticles absorb significantly at 157 nm (Ref. 21) due to a plasmon excitation in metallic calcium.[21,35] Plasmon resonances are also responsible for surface-enhanced second-harmonic generation along silver thin films, where the resonance strengthens the electric field near the surface.[36] We propose that similar electric-field enhancements near calcium nanoparticles are responsible for the observed increase in STE luminescence intensities from electron-irradiated CaF_2. Annealing samples electron-irradiated at room temperature alters the nanoparticle size and distribution and would account for the additional increase in luminescence intensity.[16]

As in the case of polished material, surface modification in electron-irradiated material is confined to a thin region near the surface. Etching experiments show that the damaged layer is less than 600 nm deep. Given the small volume of the affected material, the effect of the associated defects on the local STE luminescence must be large to account for the observed, factor of 2 increase in STE luminescence produced by electron irradiation.

The strong correlation between STE luminescence intensities and the density of preexisting defects suggests that STE luminescence could be exploited to locate patches of damaged material on CaF_2 optical materials. In previous work, we have imaged defect-related luminescence in MgO to reveal damaged portions of the surface.[12] The effect of polishing and indentation on STE luminescence intensities in CaF_2 is comparable to the changes in defect-related luminescence produced by these same treatments in MgO.[28] Therefore, we expect that STE luminescence provides sufficient contrast to distinguish defective and nondefective regions on CaF_2 surfaces. The identification of optical surfaces damaged by mishandling, for instance, can otherwise be difficult in the absence of fracture.

If luminescence competes with F–H pair production as a STE decay mechanism, as in the case of many alkali and alkaline-earth halides,[37,38] one can imagine scenarios where the introduction of carefully chosen defects could prolong the lifetime of vacuum ultraviolet optics by reducing the rate at which detrimental defects accumulate in the material.

V. CONCLUSION

We have shown that defects produced by several surface treatments, including electron irradiation, polishing, and indentation, can significantly increase the STE luminescence intensity from single-crystal CaF_2 during 157- and 193-nm laser irradiation. At the high defect densities associated with high contact-force indents (without fracture), the effect of defects becomes more complex. These defects are likely to limit the lifetime of vacuum ultraviolet optical components. Luminescence imaging under 157-nm excitation can potentially reveal surface and near-surface damage in vacuum ultraviolet optical components.

ACKNOWLEDGMENTS

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