TESTING QUANTUM DOTS AS A MEANS OF ASSESSING SUBSURFACE DAMAGE IN POLISHED GLASS

Wesley B. Williams¹, Brigid A. Mullany¹, Patrick J. Moyer², Wesley C. Parker², and Mark H. Randles³
¹Department of Mechanical Engineering and Engineering Science, University of North Carolina at Charlotte, Charlotte, NC, USA
²Department of Physics and Optical Science, University of North Carolina at Charlotte, Charlotte, NC, USA
³Northrop Grumman Synoptics, Charlotte, NC, USA

SUMMARY
Fluorescent materials in the form of quantum dots (nanocrystals of cadmium-selenide) were added to the abrasive slurries used in lapping and polishing glass samples in an attempt to tag damage sites as they were created during the material removal processes (Figure 1). Quantum dots that were trapped in these defects were then subject to laser excitation and imaged on a confocal fluorescence microscope. Samples which were lapped in the presence of quantum dots showed numerous significant features, features which were not detected with optical microscopy or white light interferometry, but which were confirmed with follow up etching of the samples that revealed a fractured layer.

BACKGROUND
Subsurface Damage
Subsurface damage (SSD) is a layer of fractures, stressed material, and other defects that can lie beneath a polished glass surface that shows no indication of the underlying damage. SSD is thought to be a result of more aggressive material removal processes in the finishing of glass such as lapping and grinding. SSD is described as a layer of deformed material over the bulk layer is covered by a layer of fractures and defects. These defects are then covered over by a thin layer of smooth material in subsequent polishing operations [1, 2].

FIGURE 2. Illustration of the various SSD layers and their depths [2].

The presence of SSD in a polished component can be detrimental to the performance as it can introduce optical aberrations, reduce the fatigue strength in oscillating components, and reduce the laser induced damage threshold (LIDT), which is a measure of how much laser energy a component can tolerate without risking catastrophic failure. Defects in the subsurface layers may also propagate to the surface under stressed conditions (such as coating operations or deployment in extreme conditions).

As it lies beneath the surface, SSD cannot be detected with interferometry or contact methods, as these methods measure only the topmost polished layer. Traditionally, SSD has been evaluated by etching away the smooth polished
layer to reveal the defect layer beneath or polishing a known shape into the surface (either taper polishing or dimpling) then using geometry and microscope observations to determine the depth of the damaged layer [2, 3]. Papers by Brinksmeir [4], Lucca [5], and Shen [6] have reviewed recent techniques to assess SSD such as X-ray diffraction, laser modulated scattering and Raman spectroscopy.

Quantum Dots
Quantum dots are semiconductor nanocrystals that fluoresce with narrow emission spectra when subject to excitation by a light source. They possess several characteristics that make them more desirable: the fluorescent dyes such as higher fluorescent response, narrow emission spectra, and resistance to photobleaching (the inability to fluoresce after a series of excitations) [7].

EviDots from Evident Technologies were used as the quantum dots in these experiments. They consist of cadmium selenide cores surrounded by zinc sulfide shells (which increase the resilience of the quantum) and a layer of ligands (~2 nm thick) to improve the solubility. The particular EviDots used have a crystal diameter of 3.8 nm and an overall diameter of 7.8 nm as well as an emission peak of 553 ± 10 nm with a 40 nm full width half maximum (FWHM) breadth to the emission peak [7].

EXPERIMENTAL PROCEDURE
Sample Preparation
Glass samples were lapped for twenty minutes by hand on an iron platen with an abrasive slurry containing 20 µm alumina particles to which a mixture of quantum dots in toluene were added. The samples were immersed in a quantum dot solution for one hour, then polished on a Dacron cloth pad for 30 minutes with an abrasive slurry containing 0.45 µm ceria particles as well as quantum dots in solution. Prior to imaging, the samples were wiped clean with isopropyl alcohol soaked tissues, a process shown to remove quantum dots adhered to the glass surface. Details on these finishing and cleaning processes can be found in the author’s earlier report on this work [8].

The glass samples also underwent a 5 minute pitch polishing process on an Acculap™ Standard pitch tool. A 0.45 µm ceria abrasive slurry was used in the pitch polishing, but the slurry did not contain any quantum dots. This step was performed to see if polishing dynamics would remove any quantum dots that were embedded in the surface, but not trapped in the subsurface. AFM measurements had shown spots on the sample surface that occurred with a similar frequency to features present in the confocal fluorescence images [8]. This pitch polishing step was estimated to have removed 250 nm from the surface (based on mass loss) and dramatically reduced the incidence of low intensity fluorescent sites on the surface.

The samples were examined with a Mitutoyo Finescpe at magnifications of 50×, 100×, and 200× with very low incidence of scratches or pits. The sample roughness was measured with a Zygo NewView White Light Interferometer to be 1 nm Rₚ over a 80 µm × 110 µm scan.

Confocal Fluorescence Imaging
The glass sample is mounted on a cover slip and placed in a custom inverted confocal microscope as described in detail by the author in an earlier publication [9]. A confocal microscope differs from a conventional microscope in that the scan area is illuminated and imaged point by point instead of all at once. This allows the confocal microscope to reject fluorescence from out of focus planes and adjacent points.

The sample is moved during the 40 µm × 40 µm scan while the optics remain stationary. The stage is then translated in the Z-axis and a new 40 µm × 40 µm scan is taken at a new focal plane. Excitation is provided by a 470 nm diode laser, while the fluorescence is measured by a single photon avalanche diode, which is filtered by a 538 nm long pass filter (to reject any reflected light from the laser). The fluorescence counts are collected by the Nanoscope software controlling the stage. The data is then exported for analysis in MATLAB, where the fluorescent signals are normalized with a relative fluorescence of one being equal to the maximum fluorescence observed on a sample without any quantum dots. Thus a relative fluorescence much greater than one corresponds to a significant number of quantum dots within the excitation volume of the confocal microscope at that position.

Etching to Reveal SSD
The glass sample was suspended in a dilute (2%) solution of hydrofluoric acid for varying
durations. The samples were examined with an optical microscope for any signs of fractures and defects. Sample masses before and after each etching step were used to estimate the depth of material removed.

RESULTS
Confocal Fluorescence Results
Significant fluorescence was detected on the samples which had been lapped and polished with quantum dots, then pitch polished for 5 minutes without quantum dots. While the vast majority of the scan area registered fluorescence values within the background (relative fluorescence <= 1), there were features with relative fluorescence more than an order of magnitude greater than the background (Figure 3 and 4).

While the fluorescent images at the surface look similar between the locations shown in Figure 3 and Figure 4, the fluorescent response as the focal plane moved deeper into the sample were quite different. The intense fluorescent feature in the bottom right corner of Figure 3, quickly diminished in fluorescence as the focal plane went deeper into the sample (Figure 5). This drop off in fluorescence is similar to that seen in slides with quantum dots dried on the surface, where the maximum fluorescence drops by 40%-60% when the focal plane is 10 µm below the surface.

The large fluorescent feature in Figure 4 had a relative fluorescence at the sample surface comparable to the feature discussed in Figure 3. The fluorescence in this feature however did not diminish as the depth of the focal plane beneath the surface reached 10 µm (Figure 6).
Etching Results
Examination of the etched samples with the Mitutoyo Finescope showed a definite fractured layer beneath the polished surface. Many of the defects observed were comparable in size and occurrence to the fluorescent features observed in the confocal scan. These fractures remained distinct to a depth conservatively estimate to be 3 µm to 7 µm.

CONCLUSIONS AND ONGOING WORK
Adding quantum dots to the abrasive slurries used in lapping and polishing the glass samples did tag features in the subsurface that were not detectable by optical microscopy or white light interferometry. The fluorescent responses observed show indications of different distributions of quantum dots in defects. The first distribution with its rapid falloff of fluorescence as focal depth increased matches previous observations of quantum dots trapped on the surface or in the immediate vicinity of the surface. The second distribution with the persistent fluorescence as focal depth increases, suggests that quantum dots are still in focus, which would only be possible if they were trapped in a defect that extended that deep.

In ongoing work, the fluorescence profiles of additional samples are being review to gauge the prevalence of the two types of features. Additional samples are undergoing etching and fracturing to obtain a better estimate of the depth of SSD to see how this correlates with the observed fluorescent responses.

ACKNOWLEDGEMENTS
Bryan Stanley, Kevin Stevens and Adam Dittli at Northrop Grumman Synoptics made many contributions. Dr. Gloria Elliot and Jimmie Miller at UNC Charlotte were also valuable resources. Thanks also to the American Society for Precision Engineering, which provided a student travel grant to the author in 2008 which facilitated fruitful discussions that advanced this work. This material is based upon the work supported by the Nation Science Foundation under Grant No. 0620783. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

REFERENCES