HIGH POWER LASER DAMAGE & ANNEALING

Justification for ISO Standard Recommendations

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REASONS FOR LIDT VARIANCE

Values for Laser Induced Damage Thresholds (LIDTs) can vary. Inflated values give a rosy glow to the coater and a redder glow to the end user when their optics damage under seemingly safe conditions. There is much finger pointing within the damage community and there are numerous sources of variance. This situation highlights the importance of following the ISO standards for laser damage testing.

The ISO standards lay out specific requirements for laser damage testing[1]. They also give recommendations. Whether or not these recommendations are strictly adhered to can be sources of large scale variation. For example, they recommend a min spot size of 200 microns. However not all adhere to this lower limit as their test laser may not have sufficient peak power density without reducing the spot size. Many errors result from using smaller spot size. Due to the tight focal plane, small positional errors result in vastly different fluences.

An even larger, more insidious source of variance, is caused by annealing. Optics are annealed by radiation which is the reason behind ISO recommending an inter-site distance of 2 to 3 spot sizes. Contracting this separation results in annealing, which strengthens the optic and results in a raised threshold value. Thus disobeying the observer effect with stark consequences; allowing the measurement itself to alter the value that it is trying to measure. The sample under test has been "improved", but is at odds with the remaining optics from the same coating run which are not annealed and have a lower LIDT value. End users, especially laser manufacturers, see the results of this discrepancy.

Laser annealing occurs when test sites are too close together, resulting in elevated threshold values by up to 60%. Thus, a seemingly unimportant detail on target-site-separation can result in substantially different threshold values.

Damage can lead to systemwide failure. Much of our work is certifying optics for high power laser manufacture. As a company we are regarded as a tough test house. However we refute that and submit this study as evidence of our results being free from annealing effects and a true measure of the coating run capability. We tested a common range of substrates and coated optics. Trying to quantify the annealing effect is problematic, but we observed annealing in each and every case.

ANNEALING

Many glasses are annealed during their formation. Laser glass materials (and toughened glass) can undergo many cycles of annealing during their production. It is century old science/art that amorphous materials can be strengthened by annealing. This is done during production where the temperature of the glass melt is held steady at several annealing points in its cooling process. As relaxation is dependent on time and temperature, holding the melt at a steady temperature for periods of time can effect relaxation. Holding the temperature steady at a relaxation point, allows the glass to very slowly and minutely adjust its morphology. Tiny changes such as frozen-in high energy bond angles and lengths can rearrange (relax) to give stress relieved, lower energy states. Annealing temperatures are well below those required for translational motion i.e. melting.

Post-formation annealing is not so common but can be used and a number of different methods have been explored. Both substrate surfaces and coated optics can be strengthened by annealing. LIDT values are raised in substrates as the surface is pacified. In coated optics both surface and coating interfaces are improved. Sapphire substrate surfaces have been improved by reactive ion bombardment[2]. Coated optics can also be annealed to improve the coating-to-substrate bonding and consequently their laser damage threshold (REO)[3].

Laser annealing is known to be more effective on coated optics than other methods of bulk or particle bombardment. This was first reported in Proceedings of a Damage Symposium 1987, sponsored by NIST[4]. Structural modification of silica glass by laser scanning has also been reported[5]. Many more examples are currently available extolling pulsed and CW laser annealing for both substrate surfaces[6] and coated optics. Radiative methods have better and more controllable annealing qualities being able to penetrate through the optic to the coating interface. Bulk annealing, even irradiating the full structure, is less controllable and can result in delamination and the substrate bubbling through the coating. This has been frequently observed in heterogeneous wafer bonding, where ultra-thin Si layers perforate and/or delaminate from their SiO_2 substrates during annealing[7]. Pulsed laser annealing avoids detrimental material breakdown as heat is localised and dispersion is efficient. By contrast bulk measures always have residual heat dispersion problems which are harder to control.

COMMON ERRORS

We sometimes get requests to have zero distance between test sites to cover the entire optical surface. Here the end-user wants assurance that there are no defects present which a standard ISO test could miss. Reducing the separation to zero causes annealing, creates more inaccuracy and ignores ISO methodology. ISO tests are statistic, analytical measurements where ten sites of the same power level are irradiated, each for several hits. A new ten sites are then targeted at a different (higher) power level and so on until the threshold is achieved and the sample damages. The result is the highest operational value (LIDT). This is the most commonly requested test and is called an S-on-1 test (several hits on each site). The problem with doing a full spot-touching scan is that, as shown in this whitepaper, the results obtained are artificially higher than the true value. Raster scanning does have value but not in threshold determination.

Gaussian beams are the most stable and are normally used in laser damage testing. The 2-D intensity distribution is shown in Fig.1 [8]

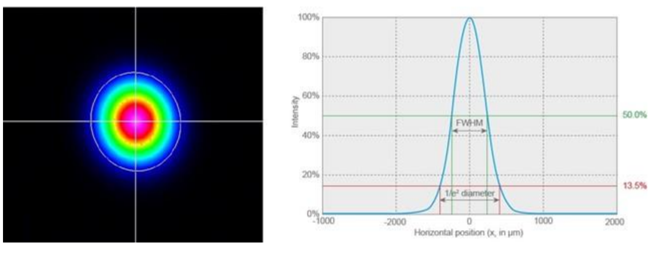


Figure 1

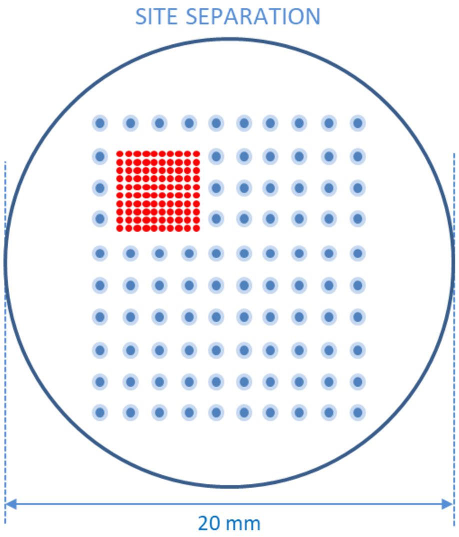
Zero separation enables the tail of intensity beyond the $1/e^2$ spot circumference to overlap with subsequent sites in all adjacent directions. In the nano-second regime this equates to excess heat which is the source of annealing.

Hence recommending an inter site spacing of 2-3 spot sizes prevents any overlap and subsequent annealing.

DISOBEYING ISO STANDARDS

The effort presented has focused on annealing the sample by using **only a single test variable**. And that is reducing the inter site distance. We kept; spot size; number of hits; wavelength; pulse duration; repetition rate and sample, all constant. Annealing is not binary. Increasing the number of hits per site. shortening the site separation, or both, increases the extent of annealing. We are not trying to anneal as much as possible but are interested in showing how seemingly minor deviations to the ISO recommendations can lead to completely erroneous results.

We used a separation of three times our $1/e^2$ spot diameter to attain the ISO threshold and a commonly used one $1/e^2$ spot diameter was set to



illustrate the importance of observing the ISO nuances and recommendations.

Figure 2

The general site pattern is shown in Figure 2. Blue sites are ISO separated sites and red sites are annealed spacings. Thus the common error (above) of requesting a quasi-raster scan has had the opposite effect. In an effort to gain more accuracy and effect a lower, more realistic LIDT, they now have an annealed, inaccurate and higher value, representing the test sample alone and not the coating run resilience. The results shown here can explain some of the inconsistences between different test house results and how very easy it is to deviate from accuracy.

THERMODYNAMICS & KINETICS

Figure 3a[9] illustrates a crystalline structure with corresponding electronic states. Figure 3b[9] gives the amorphous equivalent.

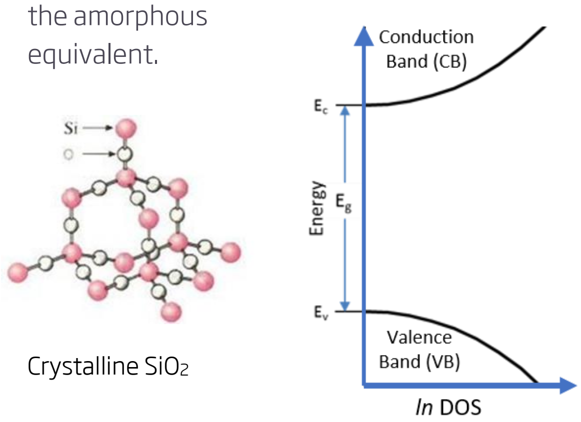


Figure 3a

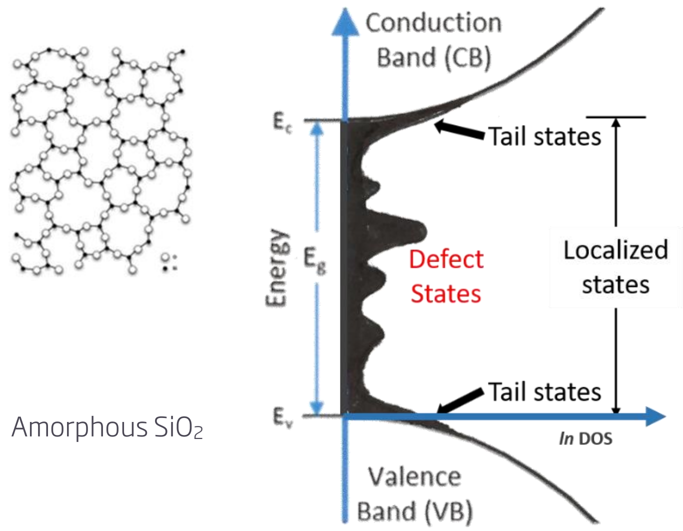


Figure 3b

The tail states always remain and define the glassy state. The localised electronic defect states can be due to surface states, dangling bonds or non-stoichiometric substrate/coating interface bonds. Each defect gives an additional discrete localized energy state. The defect states can be removed but that art remains in the hard-won skill set of good coating houses. Cooling glass from the melt is a kinetic time/temperature continuum. If cooled very slowly SiO_2 becomes a crystal, all its bond angles and lengths are at their lowest strain spatial positions. This is mirrored by the composition having its lowest energy states. If cooled quickly (quenched) to produce a glass, the bond angles and lengths are "frozen in", having no opportunity to adjust to a more comfortable (relaxed) morphology. The all-important rate of cooling and holding at annealing temperatures for extended periods allows the structure to gain a lower average energy morphology. These annealed melts have relaxed their stressed (high energy) bonds and are now strengthened. Any high energy states have had the chance to relax and lower their internal Gibbs energy. The sample now requires higher energy/power to fracture bonds and thus its laser damage threshold value increases. Different morphologies can have several different annealing points allowing different scales of atomic movement within the glass. In the field of condensed matter physics, glass is termed a super cooled liquid. But both amorphous (glass) and crystalline optics exhibit the same abrupt change in bonding and morphology at the surface. Thus all substrates surfaces can be annealed. When testing polished substrates we are determining the surface threshold, not the bulk. Substrate thresholds depend not only on composition but the degree of polishing finish. All silicate materials have higher bulk thresholds than surface thresholds. The surface boundary imposes an abrupt disruption to bonding and creates many "defect states". These take the form of dangling bonds, double bonds and inclusion of the available ambient species.

Morphology always dictates band structure and can be altered even after quenching. Reheating to an annealing point and holding there to get the kinetically determined stress relaxation results in a stronger material. Additional energy states arise from stressed structural factors. Figure 4a[9] gives ideal values for fully relaxed silicate material and illustrates the physical reality of localized inter-band states. "Freezing-in" non-equilibrium bond angles or bond lengths give rise to states of higher energy bonding electrons and lower energy free electron states. Thus these bonds (states) require less energy to break and threshold values are reduced. The vibrational frequency of these states is also critical. Hence impurities such as -OH bonds are a no no for two micron use, but do not adversely affect coatings at 1064nm. Figure 4b illustrates resonance frequency bond length (r_0) and how energy is affected if these bonds are stretched or compressed.

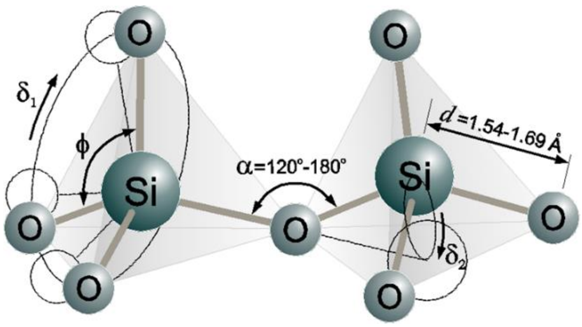


Figure 4a

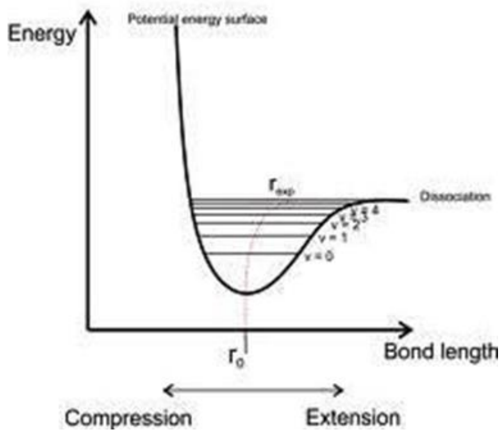


Figure 4b

FTIR spectra give the main guide to where these absorptions occur and thus if they will interfere with the desired operating wavelength.

ANNEALED SUBSTRATES

We report results in terms of Δ LIDT % giving the difference between ISO (non-annealed) and annealed results as a percentage of the ISO value. Results for substrate witness pieces are given in Table 1. A spot size of 0.8mm was used.

Table 1: SUBSTRATES

#	SAMPLE	Δ LIDT %
1	N-BK7	4
2	N-BK7 high polish	56
3	SF11	4
3*	SF11 Sep 0.1mm	11
4	Fused Silica	26
5	Crystal Quartz	34
6	Infrasil	31

The results show improvement in the threshold of all common substrate materials polished to varying degrees. Comparison between different materials was difficult as each has a different LIDT. Surface quality is also important; highly polished surfaces give high LIDTs which decline with lowering polish grade.

We noted that lower glass thresholds present a problem here as the sample damages before enough power density is delivered to effect annealing. Hence it is not possible to present a trend in substrate annealing. SF11 gave the lowest ISO LIDT and annealing effects were also very low (~4% which is our total test bed error). We annealed further by overlaying the existing annealed area with another, closing the separation further to 0.1 mm . The result (3*) gave an LIDT gain of 11%. In order to check our reasoning on power requirement, we looked at the next lowest LIDT. It was an industry standard surface NBK7. Also, in an effort to raise the power density, a highly polished sample was acquired. The ISO test gave 4.6 GW/cm^2 and closing the separation gap gave 7.01 GW/cm^2, a massive 56% increase obtained simply by using 1 x spot size inter site separation. The power density used was high enough to facilitate annealing and the quality surface did not damage at these high power densities, showing NBK7 is just as prone to annealing as any other silicate.

We conclude that the entire range of common optical substrate surfaces were annealed by reducing the inter site distance. One trend that we did observe was that the higher the power density allowed, i.e. the higher the LIDT value, the better the annealing effect.

WHAT HAPPENS TO THE SURFACE

We discuss annealing and threshold improvement interchangeably, but what actually happens to the substrate surface to make it stronger? All silicate surfaces under standard temperature and pressure (STP) have at least three layers of water adhering to the surface. These layers align themselves in an ordered configuration, dictated by the hydrogen-bonding present. Figure 5[9] illustrates in 2-D the surface of a common soda-lime-silicate glass at STP.

Silicon atoms at the surface have either mono sites with a single (-OH) or gem sites which have two (-OH) groups attached to a single silicon.

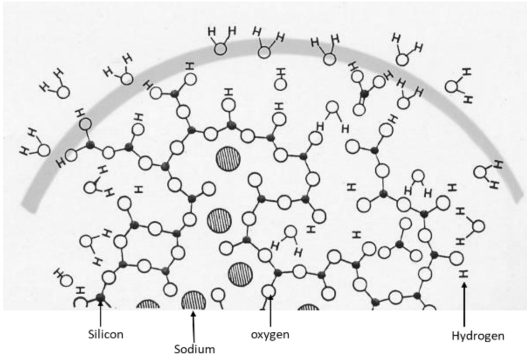


Figure 5

At elevated temperatures these are lost in favour of mono -OH sites and double bonds as shown in Figure 6[9]. This new surface does not easily hydrate and further annealing can remove even the remaining mono sites to give double bonds.

$$\equiv \text{Si- O H + H O-Si} \equiv \xrightarrow{\text{Elevated Temp}} \equiv \text{Si-O-Si} \equiv \ +H_2O$$

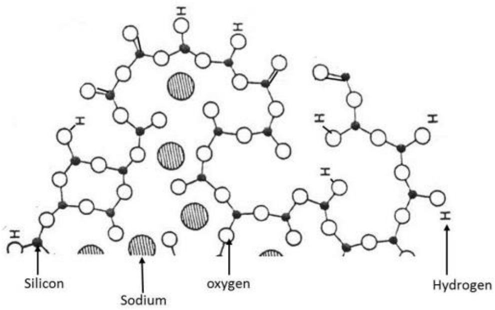


Figure 6

The resultant inert surface has changed character, it is now free from dangling bonds and is incapable of hydration. These surfaces appear highly polished to the naked eye and exhibit roughly twice the LIDT value of the best polished equivalent.

ANNEALED COATED SAMPLES

Good quality coatings pacify surfaces and have a similar effect on thresholds to that of high quality polishing. Most laser damage occurs first at the substrate/coating interface. However optics that effect more complex functions other than AR or HR can have many layers and have more opportunities to damage. Defects can exist at any interface and these types of coatings have the opportunity to damage before enough power can be delivered to effect annealing. Hence it is not possible to present a coherent trend in coated samples.

A range of results are given in Table 2. We used coated witness samples of the same substrate material as used above in the substrates section. All samples exhibited some improvement and again the lowest threshold samples showed the least improvement.

Table 2: AR COATED		
#	**SAMPLE**	**Δ LIDT %**
1	N-BK7 witness piece	4
1*	Above sample Sep 0.1mm	27
2	SF11 witness piece	16
3***	Crystal Quartz Optic	61
4**	Fused Silica witness piece	11
5	Infrasil witness piece	25

The situation was further complicated by the polished reverse side of coated witness pieces damaging, in particular fused silica (4**). Here the power density values are increased by coating and annealing increased them to such a degree that the rear (polished) side of the sample ablated. As a result, the front surface prematurely damaged and again hampered quantification. The latter effect was even more pronounced with crystalline quartz witness pieces (3mm thick). We were however able to verify that samples with higher threshold values anneal to a greater extent. We tested a large crystalline quartz optic, coated both sides, and were able attain 60% elevation in threshold value, again emphasising the extent of possible error.

LITHIUM NIOBATE

Bucking all the trends are Lithium Niobate Q-Switches (don't they always). Lithium Niobate is an electro-optic crystalline material with a very low bulk threshold. We were unable to get uncoated samples and so present only the coated threshold elevations.

Despite the low threshold values, these optics are easily annealed and present with high delta values as shown in Table 3. It would be informative to see the band gap but endless attempts in both academia and industry to measure it have drawn a range of varying results. As the optics are easily annealed we can say that defect states at crystal unit cell edges are so low in energy that they respond to significantly smaller power density than amorphous, silicate based optics.

Table 3: AR COATED		
#	**SAMPLE**	**Δ LIDT %**
1	Lithium Niobate	50

These optics tend to be small and often test personnel try to cram as many test sites as possible on to the tiny surface. The elevated (annealed) results have given endless annoyance to laser manufacturers as they overestimate (50%) the true threshold value.

TEST HOUSE ETHOS

BRL give more information than just a number. And more than just attention to detail, which we do as a matter of course - the devil's in the detail. Our forte lies in our range of high level in-house expertise and intelligent testing. We make each test follow appropriate procedures and relay all additional information we have to give you a cost effective experience. Our diverse team are highly approachable and interface with coaters and laser physicists alike.

BRL are not unfair to coaters, giving them lower threshold values, we are true to the ISO test standards. Standards which have been devised and modified over time to give the most accurate results. Optics which BRL have tested have had zero failures in the field.

[1] ISO Standards: 21254-1, 21254-2, 21254-3, and 21254-4
[2] Concetto R. Giuliano "Laser-induced damage in transparent dielectrics: ion beam polishing as a means of increasing surface damage thresholds", APL 21:1, 39-41 (1972).
[3] Dale C. Ness and Alan D. Streater R.E.O. "A laser preconditioning process for improving the laser damage threshold, and the search for subtle laser damage from long-duration laser exposure for IBS thin films", Proc. SPIE 6720, Laser-Induced Damage in Optical Materials: 2007, 67200R (2007)
[4] A. Stewart, A. Guenther, and F. Domann, "The Properties of Laser Annealed Dielectric Films," in *Laser Induced Damage in Optical Materials: 1987*, 369-387.
[5] J. Zhao and J. Sullivan "Structural modification of silica glass by laser scanning" JAP 95, 5475 (2004);
[6] Rona E Belford et al., "Strained silicon via plasma enhanced dCTE bonding", Int. Symposium on Semiconductor Wafer Bonding, Mexico, Oct/ Nov 2006. Rona E Belford et al., "Surface Activation Using Remote Plasma", 209th Electrochemical Society Meeting Denver, May 2006.
[7] Rona E Belford and Sumant Sood, "Surface activation using remote plasma for silicon to quartz wafer bonding", Microsystem Technologies: Vol. 15(3), 407 (2009).
[8] Figure obtained from Gentec-eo Beam profilers.
[9] Rona E. Belford PhD thesis "Principles and Practice of hybrid sensors. The University of Edinburgh 1986.