104 Experimental Quantization of Surface and Sub-Surface Structure in Float Polished Crystalline Quartz

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Summary

The float polishing process is widely recognized for its ability to produce surfaces to atomic conformance, with extremely high flatness. AT-cut, premium-Q, cultured, crystalline-quartz acoustic resonators were fabricated recently by a float polishing process. The study was conducted to maximize the stress-fracture threshold, by optimizing the fabrication process to eliminate sub-surface damage. Polishing medium and removal were examined as variables. The best results obtained, for quartz resonators polished with colloidal silica, are a surface roughness of less than 0.2-nm rms by AFM, and a near-bulk value of pre-fracture flexural strength of 620 MPa. This indicates that float polishing produces a factor of 10 improvement in the strength and the overall quality of quartz over the conventional CeO2 process.

Key words: Float polishing, crystalline quartz, surface roughness, sub-surface structure, fracture threshold.

1. Introduction

The float polishing process was pioneered in the time frame of the 1970's in Japan by Prof. Y. Namba and his research team, and float polishing processes were studied and developed first in Japan, and subsequently in the US and other locations, for a variety of key industrial components such as laser optics, semiconductor wafers, magnetic materials, and piezoelectric crystals. A considerable amount of literature is in existence, and provides evidence that the float polishing process, used as the final step in surface preparation, is capable of producing surfaces with atomic surface conformity, and unprecedented reference flatness.

The development of float polishing is considered well-advanced in the realm of polishing methods, and chronologically preceded the development of direct topographical measurement techniques such as AFM and STM by several years. It was established for polishing magnetic and optical materials prior to the development of V/ULSI processes for Si-based memory and CPU chips. Two decades ago, microelectronic processing primarily utilized 50-100 mm wafer sizes and had a critical dimension (CD) on the scale of ~1 μm. This situation rapidly evolved under the guidance of Moore's Law, considered ubiquitous within the semiconductor industry, to the current 200/300-mm wafer size and a CD of 0.13 μm. The CD is expected to move to the 0.09-μm level in the very near future, and the full transition to 300-mm wafers is associated with the requirement of nanometer-scale polishing on both the sides and the edge of the wafer. The key requirement for all polishing approaches in the semiconductor industry is the production of substrates with excellent GBIR and SFQR specifications. These results are routinely observed in float polishing, and in this paper we also show the added benefit of extremely low sub-surface damage with deep removal.

In the realm of acoustic resonators the primary piezoelectric material is crystalline quartz. Quartz is beneficial for several reasons, most significant of which are its properties of high thermal stability, wide frequency range (~1-5x10^9 Hz) with high cavity Q (~10^9), high radiation hardness, high shock capacity and low G-sensitivity (~10^-10 G^2), high drive capacity, and low ageing. AT-cut crystalline quartz has an inflection point of 25 °C in the cubic frequency-temperature characteristic. These quartz crystals are thus extremely stable with temperature, and frequently used without any temperature control as frequency standards in commercial mass-market devices such as wristwatches, computer technology, telecom and cell phones, and audio-visual electronics. AT-cut crystals can resonate to frequencies of 10's of MHz and the relation of the fundamental frequency f to the thickness d of the crystal is governed by the empirical formula f = 1.66fd (MHz-mm). Quartz has axial lattice constants on the order of 0.5 nm, is birefringent, and is also widely used in the manufacture of optics, wave plates, prisms, and non-linear optics. Quartz optics are well known for their wide spectral transmission from 180-2800 nm. The global requirement for damage-free crystalline quartz resonators alone exceeds one billion units per year.

We applied the float polishing process to the fabrication of cultured, AT-cut, premium-Q, 103.8-μm thick, crystalline-quartz acoustic resonators. The study was conducted to maximize the surface quality and the stress-fracture threshold by optimizing the fabrication process. The polishing medium and material removal were examined as variables to determine surface and edge fracture parameters. Thicker 500-μm samples were also polished to the removal of 10 μm and 100 μm of material for a comparative study of surface and sub-surface structure. The analysis of the crystals by atomic force microscopy, angle-resolved scatter, scanning scatter, and photo-acoustic spectroscopy shows that there is a significant reduction in the surface roughness with deeper removal. This coincides with virtually non-existent sub-surface structure from pre-processing (sawing, grinding, and lapping) deep within the crystal. The fracture-threshold measurement indicates that float polishing produced a factor of 10 improvement in the flexural strength of the crystals over the conventional process. The best results obtained for quartz resonators, float polished with colloidal silica,
were a surface roughness of 0.2-nm rms, and a stress-fracture threshold of 620 MPa, approximately the bulk value for quartz.

A fluid mechanical model of float polishing is presented with a view to further analysis and numerical modeling of the process. We propose an empirical relationship for the pressure which implies that the local pressure at the crest of a groove exceeds the ambient fluid pressure. In general, the groove profile, the fluid viscosity, the fluid velocity, and the load can be examined as variables. A shallow saw tooth groove with a constant gradient may produce uniform high-speed removal, and may also lead to ultra-smooth surfaces. A proposal for finite element numerical methods to understand the fluid dynamics in three dimensions is presented for further study.

2. Fabrication Procedure for Float Polished Quartz and Fracture Threshold Evaluation

The float polishing apparatus is described in detail in literature, and is shown in Fig. 1.1(2) We started with commercial quartz resonators (see Fig. 2) of ~175-µm thickness with a 3-µm CeO₂ edge and surface finish. Batches of six of these samples were fixed with wax on a steel base. The samples were first lapped on a diamond-turned Cu lap with a 2-% (by weight) TiO₂ : D.L.-H₂O slurry. The rotational rates of the sample and the lap were set at 55 rpm. The average removal rate in this procedure was approximately ~1 µm/hr, as measured by a digital micrometer at 4-hr intervals. The samples were lapped for ~35 hours to remove 35 µm of material off each surface. Thickness was monitored with a Mitutoyo ruby-tipped micrometer.

The TiO₂ slurry was changed every 8-9 hours. As a final lapping and planarization step, the samples were finished with a slurry of the same composition as above on a Sn lap for 4 hr to remove an additional ~1 µm of material. Since Sn is a softer material the removal rate was slower than that measured with Cu. This procedure may also reduce any strain damage introduced by the TiO₂-Cu-lap process.

The samples were then divided into two batches and were final float polished in two separate processes: (1) 2-weight % 7-nm fumed SiO₂-deionized-H₂O slurry on a freshly machined Sn lap, and (2) 10-volume % 1-nm colloidal SiO₂-deionized-H₂O slurry on a Delrin lap. The slurry was circulated through a constant temperature bath, set at 20 °C, to prevent any lap warpage from occurring due to local temperature changes in the polishing process. The rotation rates of the samples and the lap were set at 55 rpm. At this stage we are confident that float polishing does occur for two reasons. First, the operating conditions determine that laminar fluid flow exists between the sample and the lap, and second the SiO₂ particle sizes at 7 and 1 nm are significantly smaller than a ~1 µm-scale fluid layer thickness. Each sample was polished for 4 hr in this procedure. The removal rate in this procedure was extremely slow and not measurable by standard techniques. The substrates were detached and wax residue was removed by soaking the samples in 1,1,1-trichloroethane.

The quartz samples were then evaluated for stress-fracture threshold in a triple knife-edge system. The crystal was supported at the lower surface on two of the edges, and the third edge was placed symmetrically on the upper surface and used to apply a calibrated stress at the upper surface.

Referring to Fig. 2, the knife-edges were aligned parallel to the easy cleavage plane of the crystal, which is oriented at a 55° rotation from the z-axis to the x-axis. In this arrangement the applied flexural stress is maximized perpendicular to the easy cleavage plane. The results are shown in Table 1, and are sorted to distinguish fracture, originating at the edge, from that occurring at the surface. From this table we can make two important observations: the first is that the 1-nm colloidal-SiO₂ provides a much better polish quality and fracture threshold. The second is that a majority of quartz blanks fractured from defects at the edge in all three cases. The end result is a best-case improvement of the fracture threshold by a factor of 3.
A subsequent study was carried out to investigate if the edge condition could be improved to make the crystals even stronger. We followed two approaches: (1) the edges of quartz blanks were polished with a micro-fine CeO$_2$ grit after the traditional 3-µm CeO$_2$ finish. (2) a fractional part of the batch with edge treatment were then soaked in an isotropic HF-based etchant to remove an additional 20-µm material from the edges. Following this edge preparation the crystals were prepared in the same manner (with TiO$_2$ and 1-nm colloidal SiO$_2$ polishing fluids) as in the previous experiment. Figure 3 contains the composite stress-fracture results.

The results of this experiment are quite surprising. The unpolished blanks with the 3-µm CeO$_2$ surface and edge finish were the weakest, fracturing in equal quantities at ~70 and ~150 MPa. The blanks with the micro-fine CeO$_2$ polished edges and float-polished surfaces were significantly better and fractured at an average of 340 MPa, a best-case improvement of 5 times over unpolished blanks. The most significant improvement occurred in blanks with edges that were etched with HF in addition to the micro-fine CeO$_2$ edge polish and then float polished.

We observe that the average fracture strength was improved to 480 MPa, or a best-case improvement of a factor of 7. Some blanks fractured as high as 620 MPa in both of the latter cases, which is approximately the flexural strength of bulk quartz. This indicates that float polishing produced a best-case improvement of approximately 10 in the strength of the quartz wafers.

### 3. Surface properties and Sub-surface Damage

The study of float polished quartz surfaces reveals the damage-free capability of the polishing process. We examined next the quartz surfaces with the techniques of talystep profilometry, atomic force microscopy (AFM), angle resolved scatteringmetry, scanning scatteringmetry, and photoacoustic spectroscopy. These techniques were chosen for analysis and direct quantitative comparisons of sub-surface structure.

A topographic comparison of the crystals in the consecutive stages of preparation was first carried out with a Talystep profilometer. The results are shown in Fig. 4. In these measurements the rms roughness of the CeO$_2$ blanks was estimated at 175 nm with a horizontal measurement scale of 30 µm per division. This is considered typical for any commercially available blank. The probability of fracture is somewhat evenly distributed at this stage between surface and edge defects. At the same horizontal scale the TiO$_2$ lapped blanks with 35-µm removal showed a dramatic improvement in surface finish and registered at a very low 2.8 nm rms. While this is respectable in terms of surface quality, only marginal improvement was seen in the fracture threshold (see Table 1 and Fig. 3).

<table>
<thead>
<tr>
<th>Finish:</th>
<th>Failure Stress (MPa)</th>
<th>Mean</th>
<th>Std. Deviation</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>134</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td>7-nm fumed SiO$_2$</td>
<td>186</td>
<td>47.5</td>
<td></td>
</tr>
<tr>
<td>1-nm coll. SiO$_2$</td>
<td>216</td>
<td>43.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Examination of stress-fracture threshold of edge-prepared quartz crystals
Figure 5: AFM scan comparison of surfaces with 100-μm (upper) and 10-μm (lower) removal.

The measurements in Fig. 5 are organized as 3-D scans placed side-by-side with 1-D line-cut scans. The upper measurement is of the 100-μm surface and the lower one is of the 10-μm surface. The 3-D scan of the 100-μm surface has a contrast range of 1.8 nm, and the corresponding 1-D scan has a vertical scale of 0.5 nm/division. The scan displays atomic-level crystalline structure produced by float polishing together with atomic-scale crystalline dislocations or grain boundaries diagonally superimposed on the surface. The overall rms roughness of the 100-μm surface is < 0.2 nm, and is in agreement with our earlier Talystep measurements.

The AFM measurement of the 10-μm surface is interesting in its own right. The contrast scale in the 3-D image is 10 nm and the 1-D scan has a resolution of 5 nm per division. The 3-D image has uniformly-distributed, coarse spatial harmonic content, which cannot be correlated to atomic crystalline structure but could be attributed to exposed, highly dense, sub-surface structure, which is still present in the material. We note that the rms roughness of the CeO₂ blanks was measured at only 175 nm in the Talystep measurement. 10 μm of material removal, which is approximately 20 times the peak-to-valley roughness of the unpolished blanks, would ordinarily be thought of as sufficient to eliminate any residual structure of the CeO₂—finish. This appears not to be the case from the AFM measurements. Indeed the granular structure seen in the scan is possibly a remnant of CeO₂ lapping. The rms roughness of the 10-μm surface is 1 nm. In both cases we see atomic-layer by atomic-layer removal by the float polishing process.

The 100-μm and 10-μm surfaces were compared next in plane-of-incidence angle-resolved scatter measurements. The results are shown in Fig 6. The angular scanning range was approximately 120° from specular. The measurements are shown first with compressed nitrogen cleaning, and then a spectral-ethanol drag wipe. The float-polished surfaces are considered to be ergodic and no preferred orientation was imposed in the experiment. We see a quiescent lambertian-scatter distribution beyond the specular Snell component at an intensity level of approximately 10⁻⁶ for the 10-μm surface. Since the surface is ergodic, the polarization is irrelevant, and both p and s results are shown for completeness. The 100-μm surface in comparison is significantly smoother and we see an order of magnitude drop to 10⁻⁵ in the quiescent non-

The key result from Table 1, however, is that fracture originated primarily at edge defects. 35-μm material removal by TiO₂ lapping thus produced a dramatic reduction in micro cracks on the surface. The preponderance of the final float polishing process with colloidal SiO₂ was the remarkable result of a 0.17-nm rms roughness on a horizontal scale of 3 μm per horizontal division.

Sub-surface structure was examined next by preparing sets of 500-μm blanks in batches with approximately 10-μm removal and 100-μm removal for comparison. The surfaces of individual blanks in each of the two batches were scanned in a 1.6-μm² area by a supertip-equipped AFM, calibrated to the crystalline lattice of boronated graphite.
specular scatter. Here recall that the AFM results were also different by an order of magnitude for the two different removals.

These results are also significant for the fabrication of optics for high-power lasers specifically for shorter-UV wavelengths. First and foremost, the laser damage threshold of an optic has been shown to be dependent on the level of residual sub-surface structure. This structure is significantly smaller than a wavelength and essentially forms a 2-D array of Rayleigh scatterers distributed at the surface. The interstitial scatter power varies as $\lambda^{-4}$, which becomes quite rapidly significant with diminishing $\lambda$. When radiation is trapped in the index microstructure at the surface, radiative processes may damage by generating a local plasma, while non-radiative processes may produce ablation. Since the scatter power of the 100-µm surface is a decade lower it implies that this surface is highly resilient to laser damage. If we assume a damage threshold benchmark of 1 GW/cm$^2$, the quiescent scatter from this surface is at the relatively low level of 10 kW/cm$^2$.

Parallel results are seen in scanning-scatter measurements of the two surfaces. The scanning images are shown in Fig. 7. The scans are 50 x 50 µm$^2$ with a bi-axial pixel resolution of 100 nm and measured on the Nano InSPECEdge and surface imaging system. This system is a composite piezo-scanning-stage scatter-sensitive nanoscope for imaging defect scatter in the spatial frequency domain. The z-accuracy of this system with the imposition of a high degree of temperature control can readily approach the sub-nanometer level. The advantage of scanning scatter is that it is a non-contact direct observation of the power spectral density variation of the surface. This property is advantageous in that data, which is not normally available in AFM or conventional topographical scans, is readily observed here.

![Figure 7: Scanning scatter images of the 100-µm and 10-µm quartz surfaces.](image)

In our quartz surface measurements we first observe that the peak-to-valley scale increases by an order of magnitude from the 100-µm surface to the 10-µm surface. The radiation refracts into the material and any backscatter is correlated directly to the degree of surface roughness, and underlying sub-surface structure. If we imagine that all sub-surface structure can be modeled as arrays of Rayleigh scatterers then the backscatter is a direct measure of the distribution of sub-surface damage.

The 100-µm surface is extremely flat in this scan. There is marginal roughness in one direction of high-spatial frequency (~ 200 nm) and orthogonal to this is superimposed comparable structure of much lower spatial frequency (~ 7 µm). The peak-to-valley variation is on the sub-nanometer scale. In contrast the 10-µm surface as we know has significant structure and defects. There is no particular orientation to the roughness and it appears to be entirely ergodic. The defect structure is on the order of a few 100 nm, and could conceivably be similar to crystal-originated-particles, which are frequently seen in Si wafers. The bidirectional spatial frequency content is distributed across high (250 nm) to low (50 µm) scales as seen in the figure. To conclude this discussion we see absolutely no correlation between surface structure to groove structure on the lap. This enforces our notion of the occurrence of float polishing in sample preparation.

![Figure 8: Comparison of photo acoustic scatter of the 100-µm and 10-µm quartz surfaces.](image)

A final comparison between the two surfaces was made with the technique of photoacoustic spectroscopy. Here a laser grating pattern at $\lambda=532$ nm, with 10-ns pulse duration, and 10-Hz repetition rate is imaged on the surface. The non-radiative absorption in the material manifests as acoustic waves, which propagate in a major longitudinal Rayleigh-Lamb mode through the bulk of the sample, and a minor transverse surface acoustic Love mode. The transverse surface wave is primarily acoustic scatter from sub-surface structure and is periodic over several cycles.

We measured this signal and compared it for the two surfaces. The results are shown in Fig. 8. We note that the noise-floor calibration signal is $\pm 3$ mV peak-to-peak and was obtained by placing the beam on a reference target directly on the transducer. The signal produced in the 100-µm surface is approximately

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\( \pm 5 \text{ mV peak-to-peak} \) and is very near the instrument noise floor. It is possible that a part of this signal could arise from non-uniform coupling between the sample and the transducer rather than from the sample itself. The appropriate conclusion here is that the sub-surface structure is virtually non-existent in this sample.

The 10-\( \mu \text{m} \) surface in contrast has an order-of-magnitude higher surface structure, and significantly higher sub-surface damage, as we have seen in earlier complementary measurements. The surface acoustic scatter signal is on the order of \( \pm 20 \text{ mV peak-to-peak} \). We speculate that a significant amount of this structure originates from lapping with \( \text{CeO}_2 \). The AFM results in Fig 5 and scanning scatter measurements in Fig. 7 seem to corroborate this observation.

4. The Fluid Mechanics of Float Polishing

The pressure \( p \) produced in float polishing for arbitrary groove function \( g_s(x) \) may be generalized as:

\[
p = p_0 + \sum_{k=1}^{n} (-1)^{k} \phi_k \frac{\partial g_s(x)}{\partial x} \bigg|_{x=0}
\]

for just the \( 1^{st} \) order approximation, where \( x < 0 \), and \( p_0 \) is the ambient pressure. \( \phi_k \) is a constant for each independent order \( n \), which includes proportionality to the fluid viscosity, relative velocity, and the shape of the groove. Using this argument, it appears that a uniform pressure distribution across a polishing surface may be possible for a simple, shallow, short-period saw tooth groove profile. Given Eq. [1], we also see that the maximum pressure which may be developed at a polishing surface is for a groove with a rectangular cross section, where the partial derivative is proportional to a Dirac-delta function at the rising edge of the groove. This empirical equation suggests finite-element numerical techniques for understanding the laminar flow and the pressure pattern, which exists in float polishing. A complete solution to the float polishing process would involve a complex, numerical, three-dimensional analysis of laminar and vortical flows across superimposed groove patterns with non-trivial boundary conditions.\(^{(7)}\) The pressure gradients could be calculated and investigated along all three coordinate axes to understand the complexities of fluid motion in the process. The relative motion of the sample and the lap, and the load could also be investigated to optimize the removal rate, and to effect uniform removal for the best possible surface finish.

5. Conclusions

In conclusion we have developed a damage-free float polishing process for commonly used AT-cut quartz crystals. This process is based on the combined processes of 100-\( \mu \text{m} \) deep removal, and a final colloidal-SiO\(_2\) based float polishing process. Our 105-\( \mu \text{m} \) thick 16-MHz quartz crystals had a peak fracture threshold of 620 MPa, which is approximately the bulk value for quartz, and is a factor of 10 improvement over conventionally prepared crystals. The best float polished surfaces had rms roughness of \( < 0.2 \text{ nm} \) measured by AFM. The examination of the crystals by optical scatterometry and photoacoustic spectroscopy showed that sub-surface damage structure was virtually eliminated by deep removal. We also proposed a model for the pressure profile for an arbitrary groove, and numerical analysis of the polishing process for further study.

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