Quantitative Morphological and Compositional Evaluation of Laboratory Prepared Aluminoborosilicate Glass Surfaces

Yuxuan Gong^{†*}, Anthony W. Wren[†], Nathan P. Mellott[†]

[†]*Kazuo Inamori School of Engineering, Alfred University, Alfred, NY 14803*

*Corresponding Author: Tel.: +1-607-871-2446; fax: +1-607-871-2354. *Email address:*
yg4@alfred.edu (Yuxuan Gong)

Abstract

Surface finishing techniques including polishing, etching and heat treatment can modify the topography and the surface chemical composition of glasses. It is widely acknowledged that atomic force microscopy (AFM) can be used to quantify the morphology of surfaces, providing various parameters including average, peak-to-valley, and apparent root-mean-square roughness. Furthermore advanced power spectral density (PSD) analysis of AFM-derived surface profiles offers quantification of the spatial homogeneity of roughness values along different wavelengths, resulting in parameters including equivalent RMS, Hurst exponent, and fractal dimension. Outermost surface (~8 nm) chemical composition can be quantitatively measured by X-ray photoelectron

spectroscopy. In this paper, we first developed a series of surface finishing methods for an aluminoborosilicate glass system by polishing, etching or heat treatment. The chemical composition and environment of prepared glass surfaces were quantified by XPS and topographical analysis was carried out by fractal and k-correlation model fitting of PSD profiles derived via AFM. The chemical environment of elements, as determined via XPS, present on the prepared surfaces are similar to those within the pristine bulk glass. The compositional evolution of polished and melt surfaces are discussed in context of corrosion phenomena associated with the grinding, polishing, and etching of surfaces and the thermal heat treatment utilized for processing, respectively. Good correlation between surface finishing methods, chemical composition and topographical parameters were observed. More importantly, extensive discussions on topographical parameters including equivalent RMS, Hurst exponent, and fractal dimension are presented as a function of processing method.

Keywords: borosilicate glass; surface finishing; atomic force microscopy; spectral methods; roughness; Hurst exponent

1 Introduction

The surface quality has great impact on the performance properties of many novel and emerging technological applications for glasses including those for displays, biomedical applications, microelectronics and advanced optical lithography systems [1, 2]. In some cases the glass surface morphology and overall roughness has become the threshold for the continued development of novel electronics and portable devices [3, 4]. The surface morphology, chemical composition and homogeneity of glass manufacturing products can influence a wide variety of performance related properties including the mechanical strength and chemical durability [5-8]. Furthermore, smooth, homogeneous and compositionally reproducible glass surfaces are required for mechanistic investigations associated with glass corrosion, chemical tempering, and thin film coating on glasses [9]. For example studies on the dissolution behavior of silicate glasses suggested surface morphology and composition can greatly affect the dissolution or alteration rate of these glasses [10-12].

A variety of processing methods can be utilized to engineer glass surfaces including mechanical force, chemical and mechanical polishing, and thermal treatment [9, 13-14]. Each will affect the glass morphology and composition. For example, the annealing of some glass compositions can deplete or enrich the surface in metallic ions due to evaporation and segregation [15]. In the case of chemo-mechanical polishing, chemical reactions between the glass surface and the polishing media polishing can alter the surface composition relative to the bulk glass composition [16-20]. These changes in surface morphology and chemistry have been shown to effect mechanical, chemical, and aesthetic properties [5-8]. There are a variety of characterization tools available for the

surface compositional and morphological analysis of glass surfaces, each with their own capabilities and limitations. Of particular interest here is X-ray photoelectron spectroscopy (XPS) for quantification of chemical composition and chemical environment and atomic force microscopy (AFM) for surface topographic imaging and quantitative morphological analysis.

XPS is routinely used to determine both the chemical composition and local chemical environment of elements associated with glass surfaces [21, 22]. In particular, under standard operating conditions, as those used in this work, the XPS probes to a depth of approximately 5 to 10 nm and therefore is a useful probe of the uppermost surface composition and chemistry. Through the empirical derivation of relative sensitivity factors and high resolution peak area analysis absolute quantification of the glass surface composition is achievable [23]. Furthermore through analysis of peak position and shape the chemical environment of the glass forming elements can also be analyzed [24, 25].

AFM is one of the more common techniques in the qualitative and quantitative analysis of glass surface morphology, given its flexibility, relatively low cost, high lateral resolution, and high sensitivity to topographic features on the angstrom to micron scale [26, 27]. Quantitative roughness analysis measured by AFM is often represented by simple statistical parameters, such as average roughness, apparent root-mean-squared roughness (RMS), or peak-to-valley roughness. In these cases, 250000 data points (512 X 512 pixels per image for example) are expressed by a single number. However, apparent RMS values are problematic since two drastically different topographies can have the same RMS value [28, 29]. This is due to the fact that apparent RMS values are only sensitive to z-axis (vertical) height deviation, not x, y-axis (horizontal) structures.

Therefore, such measurements are greatly dependent on the homogeneity of the surface scanned and can be quite problematic, in some cases leading to the difficulty in understanding surface roughness and its spatial distribution homogeneity.

Rather than using the simple above mentioned statistical parameters, surfaces can also be represented by power spectral density (PSD) functions over different spatial frequency regions. PSD is advantageous as it allows the comparison of roughness data measured at different spatial frequencies, offering a convenient representation of the spatial distribution and homogeneity of roughness [26]. This is realized through a 2D fast Fourier transformation algorithm allowing correlation of the z-axis height deviation with the x-, y-axis location data in real and reciprocal space. Furthermore, from the PSD profiles a series of spatially sensitive quantitative roughness parameters can be derived including the fractal dimension, Hurst exponent, correlation length, and equivalent RMS roughness [27].

In this paper we provide a systematic method to prepare smooth glass melt and polished surfaces with surface compositions similar to that of the bulk. Glass surface composition and morphology were quantified using complimentary surface sensitive characterization tools including XPS and AFM. In particular, both vertical and spatial distribution of roughness was investigated using advanced PSD analysis and for the first time, we report spatially sensitive roughness parameters of a variety of glass surfaces as a function of processing.

2 Materials and Methods

2.1 Glass Melting and Bulk Glass Composition Analysis

The aluminoborosilicate glass used in this study, referred to as international simple glass (ISG), is a reference waste glass composition developed and utilized by a 6-nation collaborative effort in examining nuclear wasted glass corrosion [30]. The ISG glass used in this study was commercially melted by Mo-Sci Corporation, with melting procedures documented in detail elsewhere and briefly described here [31]. The ISG glasses were batched to yield a nominal weight% composition of 56.2 % SiO₂, 17.3 % B₂O₃, 12.2 % Na₂O, 6.1 Al₂O₃, 5.0 % CaO and 2.8 % ZrO₂. Initial batch melting was performed in a platinum-rhodium crucible in an electric furnace at 1300 °C for 4 hours. Following the initial batch melting, resultant water quenched & dried glass cullet were then remelted twice under the same conditions. The melted glass was poured into graphite molds to form ingots. The ingots were annealed at 569 °C for 6 hours and cooled to room temperature at a rate of 50 °C per hour. Bulk glass composition was determined by spectrochemical analyses, based on LiBO₂ fusion techniques followed by analyte quantification using a Perkin-Elmer Optima 5300 inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2 Bulk Glass Thermal Analysis

A 0.5cm x 0.5cm x 2cm bar was cut from a single ISG glass ingot for thermal expansion analysis on a NETZSCH PC 402 Dilatometer. A silicon standard was used for calibration, a heating rate of 4 K/min was used, and data acquisition was automatically stopped after reaching the dilatometric softening point. Glass transition temperature was determined by

a TA Instruments 2960 SDT differential thermal analysis (DTA). Ground ISG glass powder was heated in a Pt crucible from room temperature to 1450 °C with flowing air with at a heating rate of 10 °C/min. High purity alumina powder was used as reference.

2.3 Glass Surface Preparation

An ingot of ISG glass was cut with a 5 inch Buehler diamond saw blade to 1.0 cm x 1.0 cm x 0.2 cm. Samples were then ground with 120, 240, 400 and 600 grit silicon carbide grinding pads for planarization. Polishing of samples were carried out sequentially with 6µm (20 min), 3 µm (10 min), 1 µm (10 min), 0.25 µm (10 min), 0.1 µm (10 min) and 0.05 µm (15 min) oil-based diamond suspension sprays, using a Buehler manual polisher. Two separate polishing pads were used, Buehler Microcloth and Buehler Trident, which resulted in two different sets of polished samples. Between each grit/suspension change, the samples were carefully washed with acetone and dried by nitrogen gas flow. Final-polished samples were the cleaned ultrasonically for 10 min in acetone. Selected samples from each of the two sets were then etched. Etched samples were achieved by soaking the samples in 1 N NH₄OH at 80 °C for 3 min. Followed by rinsing with DI-water, the etched samples were then dried with nitrogen gas flow.

This resulted in 4 different polished surfaces (1) Microcloth polished unetched, (2) Microcloth polished etched, (3) Trident polished unetched, and (4) Trident polished etched. Prior to any surface characterization such as AFM and XPS, the samples were nitrogen blown and ultraviolet ozone cleaned (UVOC) for 10 min for remove of residual hydrocarbons as well as ambient deposits/dust.

In addition to polished surfaces, freshly cut ISG glasses with a size of 1.0 cm x 1.0 cm x 0.2cm were heat treated in a pre-heated oven at 675 °C, 700 °C and 725 °C respectively for 1 hour to create 3 different sets of melt surfaces. Heat treated samples were annealed at 570 °C for 3 hours followed by cooling in the furnace overnight (~12 hrs). Resultant samples were ultrasonically washed in acetone for 10 min and then kept in vacuum desiccator until the time of surface analyses.

2.4 Glass Surface Composition

The glass surface chemical composition (outermost ~8 nm) as well as local chemical environment was analyzed with a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer (XPS). The XPS spectra were collected with Al K α X-rays (non-monochromatic, beam size=100 μ m) at 20 mA anode current, with an electron energy of 1486 eV and a step size of ~0.2 eV. Survey scans were performed with a pass energy of 80 eV to gain qualitative information such as peak identification and position. Peaks identified in all survey scans were used to adjust hi resolution scan binding energy range and dwell time. Pass energy for all hi resolution scans was 20 eV with a beam dwell time of ~2 s to yield a signal-to-noise ratio of >100:1 with exception of B1s peaks, which were adjusted to yield a signal-to-noise ratio of >50:1. The analyzed area was ~2-3 mm in diameter. Standard deviation of peak position and elemental concentration was evaluated by probing five different spots on a 725 °C melt surface.

Quantitative surface chemical compositions were determined for all samples from hi-resolution scans of Si2p, Al2p, B1s, Zr3d, Na1s, Ca2p and O1s peaks. Relative sensitivity factors of all elements ($RSF_{Si}=1$, $RSF_{Al}=0.60$, $RSF_B=0.57$, $RSF_{Zr}=8.62$, $RSF_{Na}=8.33$, $RSF_{Ca}=6.22$ and $RSF_O=2.77$) were derived from hi-resolution XPS scans of fresh air-fractured pristine ISG glass surfaces, assuming that the ISG glass fracture surface was identical to the bulk ISG glass composition. XPS data qualitative and quantitative analyses were performed on PHI MultiPak V8.0 software, peak position was shifted/calibrated using C1s peak with the peak position at 284.60 eV. Area of each hi-resolution scan XPS peaks was fitted by the Shirley-model after automated background subtraction.

2.5 Glass Surface Morphology

Surface morphology was imaged and quantified using a Digital Instruments Nanoscope Dimension 3100 multimode atomic force microscope (AFM) equipped with Ar/N₂ gas floating table in Tapping Mode ®. Antimony doped silicon probes (Bruker TESP, cantilever length of 125 µm) with nominal tip radius of curvature of 8nm, nominal spring constant of 42 N/m and resonance frequency range of ~230-410 KHz were used for all measurements. Images were taken with a scanning rate of 1.0 Hz and resolution of 512 pixels X 512 pixels. Qualitative tip size and shape calibration was performed periodically during measurements using a commercially available standard (Ted Pella Product No. TCI-BudgetSensor TipCheck). Multiple (10 - 1 µm x 1 µm scans & 2 - 10 µm x 10 µm scans) scans were taken of each sample at different locations on the surface to ensure a large-scale spatial averaging of roughness.

The root-mean-square roughness (RMS) was calculated and averaged from 10 - 1 μm x 1 μm images for each sample using Bruker Nanoscope Analysis software. Standard deviation was determined by dividing the standard deviation of the values by the square root of the number of scans performed on each sample. Line by line flattening and 3rd order plane fitting was performed on each image prior to analysis to remove any artifacts caused by the curvature of piezoelectric material, thermal drift, background vibration noise or lateral forces. Flattening removes vertical offsets between scan lines through calculation of a least-squared polynomial fit for a scan line followed by subtraction of the polynomial fit from the original scan line. Third order plane fitting calculates a third-order polynomial fit to the image in the x - and y -directions and subtracts the polynomial fit from the image, removing tilt and S-shaped bow [12].

Apparent root-mean-square roughness (RMS) is defined as the root-mean-square average of height deviations from the mean elevation plane, calculated from the relative height of each pixel in the captured image.

Surface morphology was also quantified using the power spectral density (PSD) analysis. PSD analysis evaluates surface roughness as the spread of height deviations from a mean plane, and the lateral distribution/distance over which the height variation occurs. The PSD function applied here is given as [32]:

$$S_2(f_x + f_y) = \frac{1}{L^2} * \left[\sum_{m=1}^N \sum_{n=1}^N Z_{mn} e^{-\pi i \Delta L (f_x m + f_y n)} (\Delta L)^2 \right]^2 \quad \text{Eq.1}$$

where S_2 denotes the 2-D isotropic PSD, L is the size of scanned surface, N is the 1-D resolution for one direction (x , or y), Z_{mn} is the profile height at location (m , n), f_x & f_y are the spatial frequency in the x - and y - direction and $\Delta L=L/N$ is the distance between two adjacent sampling points [27].

This function is further translated into polar coordinates through spatial frequency and angular averaging ($\{\varphi\}$) as:

$$S_2(f) = \frac{1}{2\pi} * \int_0^{2\pi} S_2(f, \varphi) d\varphi \quad \text{Eq.2}$$

Therefore, the PSD function depends only on the frequency and can be plotted as a 2-D representation. PSD functions derived from a single AFM image is a function of scan length and sampling distance, and holds the possibility of being effected by spatial inhomogeneity across the glass surface. Any inhomogeneity however, can be factored out by averaging of PSD functions collected across a given samples surface. In this work PSD functions were averaged as;

$$PSD_{combined}(f) = [\sum_{i=1}^M PSD_i(f)]/M \quad \text{Eq.3}$$

where M is the number of scans performed on each sample. In this paper, 10 randomly distributed scanning areas (1 μm X 1 μm size) were chosen for each sample.

This PSD function was then modelled using two different approaches in order to quantify surface fractal dimension (D), Hurst exponent (H), and equivalent RMS roughness (σ_{ABC}). The fractal model was utilized to model the high frequency region (0.02 nm^{-1} to 0.256 nm^{-1}) while the k-correlation model was used to model the low-frequency region (0.001 nm^{-1} to 0.02 nm^{-1}).

The fractal model allows the further translation of power spectral density function high frequency regions into fractal dimension and Hurst exponent, as thoroughly discussed elsewhere [33]. The Hurst exponent is known as the scaling factor or roughness index, and describes the roughness spatial distribution homogeneity at a given wavelength [34, 35]. The fractal model does not allow direct comparison of roughness values at different wavelengths. However, the k-correlation model (or ABC model) can be utilized utilized to quantitatively describe surface topographies by fitting PSD profiles into and equivalent RMS at different wavelengths [36]. Fitting of PSD profiles using k-correlation model upon such approach (derivation of equivalent RMS, correlation length) have been discussed in detail in [36].

3 Results and Discussion

3.1 Bulk Glass Composition

Table 1 shows the bulk ISG glass elemental composition measured from ICP-AES digestion. The atomic concentration of Na, Ca, Zr, Al, B, Si and O in the bulk ISG glass is 8.0 %, 1.6 %, 0.4 %, 2.4 %, 9.4 %, 18.0 % and 60.1 % respectively. Minor deviations, below 0.4 %, compared to the ISG bulk glass composition (Na=7.6 %, Ca=1.7 %, Zr=0.5 %, Al=2.3 %, B=9.6 %, Si=18.0 % and O=60.1 %) as reported by Savannah River National Laboratory [31], were observed.

3.2 Thermal analysis of bulk ISG glass

Figure 1 shows the dilatometry/thermal expansion curve and the DTA curve (inset) of ISG glass. As shown in the DTA trace of Figure 1, a “knee” between 500 °C and 600 °C were fitted by two tangent lines which intersect at 572 °C corresponding to the glass transition temperature (T_g). In addition, two broad exothermic peaks were indicated at 705 °C and 1000 °C, most likely corresponding to crystallization temperatures, as reported elsewhere [37, 38] for glasses of different compositions, but within the borosilicate glass family. The sudden drop observed on the thermal expansion curve at 594 °C denotes the dilatometric softening temperature (T_d) while the glass transition temperature (T_g) is observed at 570 °C. The T_g values as determined by DTA and dilatometry (570 and 572 °C respectively) agree well.

Thermal analyses were utilized to guide our processing of melt surfaces. In particular, the dilatometric softening temperature can denote the transition from geometric

expansion to deformation under surface strain with increasing temperature [15]. Therefore, the processing temperature to yield a smooth melt surfaces was chosen above T_d at 675 °C, 700 °C, and 725 °C. In addition, the annealing temperature of melt surfaces were chosen near T_g (570 °C) to minimize the residual stress caused by heat treatment.

3.3 XPS analysis of ISG glass surfaces

All XPS survey scans (not shown) revealed expected elements on the surface of all samples. All peaks were identified and results consistent with bulk chemical analysis. Minimal contamination, in only trace amounts were observed on some polished samples. Table 1 shows the quantitative composition of melt and polished surfaces as determined by hi-resolution scans and is summarized below.

All melt surfaces showed Na ion concentration depletion of $\leq 1.0\%$ as compared to the bulk pristine ISG glass while Ca ion concentration on the ISG glass melt surfaces were depleted $\leq 0.6\%$ as compared to the bulk glass. Zr showed no measurable difference between the melt surfaces and the bulk composition. Melt surfaces showed a slight enrichment of Al, between 0.4 and 0.8%, and depletion of B, between 4.9 and 6.5%, when compared to the bulk composition. Finally, melt surfaces show a slight enrichment in Si and O on the surface, between 3.1 and 3.8% and 2.9 and 3.3% respectively, as compared to the bulk. However, no clear trends are observed for melt surface composition as a function of heat treatment/processing temperature. The depletion of B and Na is assumed to be associated with the high vapor pressure of both elements as being documented elsewhere [15]. Similar depletion of Ca and Al of a calcium and

aluminum after heat treatment of aluminosilicate glasses has also been previously reported [11].

All polished and polished/etched surfaces showed Na ion concentration depletion of $\leq 4.9\%$ as compared to the bulk pristine ISG glass while Ca ion concentrations were enriched by $\leq 2.9\%$. Zr ion concentration showed no change in concentration with polishing but enrichment of up to 3.2% with polishing and etching as compared to the bulk composition. Polished surfaces showed a slight enrichment of Al while polished/etched surfaces showed a slight depletion in Al as compared to the bulk composition. In all cases, both polished and polished/etched, surfaces were depleted in B (between 4 and 6%) as compared to the bulk composition, with polished/etched surfaces depleted more so than simply the polished surfaces. In all cases, polished and polished/etched surfaces were enriched ($\leq 1.5\%$) in Si with respect to the bulk composition with exception of the Trident cloth polished/etched which was depleted by 0.9%. All polished and polished/etched surfaces were enriched by up to 6.9% in O. There is no clear trend in surface composition as a function of polishing cloth used. However, some general surface composition trends are observed between polished and polished/etched surfaces. In all cases, post-polishing etching of surfaces results in (1) a general increase in a concentration of surface Ca and Zr, (2) a decrease in Al, B, and Si concentration, (3) no observable trend in Na concentration, and (4) no change in O concentration.

Planarization of glass surfaces, which in this work consists of the grinding and polishing, is a chemo-mechanical process. [39, 40]. The chemical processes associated in the grinding and polishing are a complex function of the chemistry and concentration of the water used during grinding and the composition of the oils used during polishing. During these processes, it has been proposed that the surface composition is a function of hydrolysis reactions between the glass surface and the grinding/polishing media; in particular, protons in water replace the modifier ions within the glass surface. Such ion exchange renders a leaching of modifiers, which is consistent with our findings of significant Na depletion after polishing.

Walter [39] and Spierings [40] proposed that the chemical etching of glasses are the result of 2 different mechanisms: 1) leaching of modifier ions (eg. Na, Ca) through ion-exchange reactions with protons and 2) dissolution of network formers (eg. Si, Al, B) with anionic attack. Our XPS results, after etching in a basic solution (NH_4OH), showed observable decrease in the network former Al, B, Si concentration while Na concentration remain relatively unchanged. Such results are consistent with the above mentioned theory; as we would expect anionic attack, in this case OH^- , resulting in network former dissolution and not preferential modifier ion release. The increases in the concentration of Ca and O post etching are consistent with the results reported by Saito [41] in a similar borosilicate glass system.

Si2p peaks for all glass surfaces are located at peak positions of $\sim 102.5 \text{ eV} - 102.7 \text{ eV}$ with a FWHM of $\sim 1.7 \text{ eV} - 1.8 \text{ eV}$; Al2p peaks are located at peak positions of $\sim 74.0 \text{ eV}$

– 74.3 eV with a FWHM of ~1.3 eV – 1.5 eV; B1s peaks are located at the peak positions of ~192.2 eV – 192.5 eV with a FWHM of ~1.4 eV – 1.6 eV; and Zr3d_{3/2} and Zr3d_{5/2} peaks are located at peak positions of ~183.9 eV – 185.2 eV and 181.1 eV – 182.7 eV respectively. All results are within experimental error (peak position standard deviation was measured as 0.08 eV) and no changes in FWHM as well as peak positions with processing of melt, polished, or polished/etched surface of Si, Al, B, or Zr can be concluded from these results.

Si, B, Al and Zr are assumed to be network forming or intermediate ions within the glass structure [10, 42-43]. It is of interest to examine whether the processing methods employed here have an effect on the short range order of the glass surface structure with respect to these elements. It has been shown previously that an elements peak position and FWHM are sensitive to changes in short range order of glasses [24]. Given the lack of such changes observed in XPS analysis, it is thus speculated that chemical environments of the network forming or intermediate ions ISG glass surfaces did not significantly change with processing conditions.

3.4 AFM imaging & statistics of melt/polished ISG glass surfaces

Representative AFM images of all glass surfaces are shown in Figure 2. All images have an x-y scale of 1 micron and a z-scale of 25 nanometers. All polished and polished/etched surfaces show relatively smooth surfaces with linear features/grooves. In addition, these grooves are clearly observed and pronounced on the polished/etched surfaces. It is assumed that these linear features are scratches associated with the

polishing of the surfaces, and have been previously reported throughout the literature [11]. The observation that the scratches are more pronounced after etching suggests that preferential reaction of the etchant and glass surface is occurring along these scratches. Similar results were reported by L. Wong et al. [44] where the authors observed growth of polishing induced scratches after exposure to chemical etchants. It was concluded by L. Wong and others that the growth of polishing scratches after etching is caused by the preferential etching of each individual fracture sites within the polishing scratches [44,46].

Images of the melt surfaces are significantly different than the polished surfaces. Melt surfaces processed at 675 and 700 °C show smooth surfaces with randomly distributed positive relief features with a lateral resolution on the order of 10's to 200 nm. The positive relief features were captured in all 10 1 μm X 1 μm scans for 675 °C and 700 °C melt surfaces, and the number of features per scan as well as the height from mean plane is random. However, no positive relief features, but instead a smooth featureless surface is observed on 725 °C melt surfaces. It is speculated that the presence of the positive relief features may be associated with the broad exothermic peak at 705 °C observed in the DTA scan in Figure 1 at 705 °C as previously suggested by others for similar systems [45]. Thus, we assume here the positive relief features are mostly likely to be a result of surface crystallization.

Table 2 shows the apparent RMS roughness (nm) of all melt surfaces. Two different apparent RMS roughnesses are reported for all melt surfaces; one calculated including all positive relief features and one calculated after manual removal of positive relief features.

The removal of positive relief features allows the direct observation of glass surface apparent roughness after heat treatment. After removal of positive relief features apparent RMS does not change, within error of the measurement. In general, the apparent RMS roughness of the 675 and 700 °C melt surfaces, regardless of positive relief feature removal, are less than 1.5 nm while the apparent RMS roughness of the 725 °C melt surface is 0.3 nm. While it is not clear why the removal of the positive relief features do not cause a significant change in the apparent RMS roughness, one trend is clear, that is the apparent RMS roughness of the 725 °C melt surface is significantly less than that of the other temperatures. Such phenomenon was also reported in [47, 48] and it was concluded that the higher heat treatment temperature can lower the viscosity hurdle for glass surface expansion and further smooth the surface. The apparent RMS roughness of the 725 °C melt surface reported here is similar to RMS roughness value reported for other glass melt surfaces [eg. 11].

Table 2 shows the apparent RMS roughness (nm) of all polished and polished/etched surfaces. All apparent RMS values are between ~1.04 and 1.83 nm. The Trident cloth results in a glass surface with lower apparent RMS roughness than the Microcloth. It is assumed the different in apparent RMS roughness is due to the difference in materials of the two polishing cloths; the Microcloth is a long-napped rayon cloth while the trident cloth is a nap-free woven cloth. In addition after etching, the Microcloth surface shows no significant change in apparent RMS roughness, while the Trident cloth shows a marked decrease after etching. While the overall mechanism responsible is not clear, the type of polishing cloth used certainly effects the apparent RMS roughness of the resultant

glass surface. Polished surfaces in our study yield an apparent roughness value close to reported values (~ 0.8 nm to 2.3 nm) in other silicate glass systems [eg. 49].

3.5 Power spectral density (PSD) analysis of ISG glass surfaces

Figure 3 shows the PSD profiles of all processed ISG glass surfaces. Two clear regions are observed for all PSD profiles shown in Figure 3 a “high frequency region”, above 0.02 nm^{-1} and a “low frequency region”, below 0.02 nm^{-1} . It has been proposed that the high frequency region be fit using the fractal model while the low frequency region be fit using the k-correlation model [27]. Figure 4 shows the PSD profile fitting of the 725 °C melt surface using both the Fractal model and ABC (k-correlation) model. In Figure 4 as well as other fittings in this paper, the ABC model is presented by a dashed line; the solid line is the fitted Fractal model, and the raw data is displayed as scattered circles. The fractal model (as shown in Eq.4) was used to fit the PSD profile region beyond the spatial frequency of 0.02 nm^{-1} to derive spatial parameters D & H from the slope of the linear fitted curve.

$$PSD_{fractal}(f; K, s) = \frac{K}{f^s} \quad \text{Eq.4}$$

Fractal dimension is used as a scaling index, which determines the fineness of a geometry/surface with measurement scale variation [50]. In particular, fractal dimension, reported as a value between 2 and 3, can provide information on roughness variation with a given scanning scale; with a value of 2 representing a Euclidean surface and a value of 3 representing an infinitely rough surface [35]. The Hurst exponent is considered as a roughness index & roughness scaling factor [35]. A Hurst value within the range of 0~0.5

indicates a spatial frequency series with continuous alternating features of high and low values while a Hurst exponent value between 0.5 and 1 represents a spatial frequency series with positive autocorrelation, presenting abrupt value changes in a series of spatial frequencies. Thus, a Hurst exponent in the range of 0~0.5 indicates a rough surface with spatial homogenous distribution of roughness while a Hurst exponent between 0.5~1 suggests a non-homogeneous surface is [51-53]. However, while useful to provide spatial homogeneity information of a surface, the fractal model lacks the ability to present a physical roughness parameter that can be comparable to the apparent RMS.

This inherent disadvantage of the fractal model was overcome here by the use of the ABC-model in this study. Below the spatial frequency of 0.02 nm^{-1} , the PSD profile was fitted by the ABC model (as Eq.5) to extract parameter A, B, and C, which can be used to derive the equivalent RMS by Eq.6.

$$PSD_{ABC} = \frac{A}{(1+B^2 f^2)^{\frac{C+1}{2}}} \quad \text{Eq.5}$$

$$\sigma_{ABC}^2 = \frac{2\pi A}{B^2(C-1)} \quad \text{Eq.6}$$

As shown by Fig.5, the ABC model fits the “knee” region of the PSD profile below the spatial frequency of 0.02 nm^{-1} . The position of the “knee” is determined by parameter B and is an equivalent term to the correlation length. Beyond the “knee” region, the ABC model is mathematically equivalent to fractal model since parameter C is the only dominant factor to PSD values. Thus, in this study both models were adopted to complimentary characterize the surface morphology as well as spatial homogeneity. Morphological parameters, including fractal dimension, Hurst exponent, and equivalent

RMS roughness, resulting from the modelling of all individual PSD curves are shown in Table 2.

Figure 4 shows the PSD profile fitting of the 725 °C melt surface and Figure 5a-d shows the fitting of experimental PSD profile of 675 °C melt surface, 675 °C melt surface with positive relief feature removal, 700 °C melt surface, and 700 °C melt surface with positive relief feature removal respectively. The fractal dimension (D), Hurst exponent (H), correlation length (B) and equivalent RMS are 2.75, 0.25, 420.98 nm and 0.34 nm respectively for 675 °C melt surface. After removing the positive relief features, the D, H, B and equivalent RMS were reported as 2.69, 0.31, 169.21 nm and 0.53 nm respectively. For the 700 °C melt surface, the D, H, B and equivalent RMS is 2.84, 0.16, 345.39 nm and 0.27 nm respectively. D, H, B and equivalent RMS of the 700 °C melt surface were reported as 2.81, 0.19, 130.23 nm and 0.48 nm after positive feature removal. In comparison, for the 725 °C melt surface, the D, H, B and equivalent RMS is 2.93, 0.07, 692.04 nm and 0.11 nm respectively. All values are summarized in Table 2. A few trends are observable when comparing these values. In general the fractal dimension decreases upon removal of positive relief features and increases with increasing processing temperature. The Hurst parameter increases with removal of positive relief features and decreases with an increase in processing temperature. The correlation length decreases with removal of positive relief features and no clear trend is observed with processing temperature. Finally, the equivalent RMS increases with the removal of positive relief features and decreases with increasing processing temperature.

After removing the positive relief features on 675 °C and 700 °C melt surfaces and comparing those results to the 725 °C melt surface, it was found that the roughness (both apparent RMS and equivalent RMS) decreases with increasing heat treatment temperature. It is proposed here that the higher heat treatment temperature lowers the viscosity of the glass, and thus smoothing the surface by surface expansion. In addition the spatial distribution of roughness became more homogeneous with increasing heat treatment temperature (increased D values, and decreased H values).

Experimental and fitted PSD profiles of micro cloth polished, micro-cloth polished/etched, trident-cloth polished and trident cloth polished/etched surfaces are shown as Figure 6a-d. The resultant fitted parameters D, H, B and equivalent RMS are listed in Table 2. For the micro-cloth polished surface the D, H, B and equivalent RMS were reported as 2.42, 0.58, 660.74 nm and 1.47 nm respectively. For the micro-cloth polished/etched surface the D, H, B and equivalent RMS were reported as 2.60, 0.40, 702.80 nm and 0.66 nm respectively. For the trident-cloth polished surface the D, H, B and equivalent RMS were reported as 2.18, 0.82, 516.94 nm and 1.59 nm respectively. For the trident-cloth polished/etched surface the D, H, B and equivalent RMS were reported as 2.09, 0.91, 101.38 nm and 0.63 nm respectively.

The fractal dimension, Hurst parameter, and correlation length of polished and polished/etched surfaces vary with type of polishing cloth used, however a trend with respect any changes with the etching of polished surfaces is not observed. However, the equivalent RMS roughness of polished and polished/etched surfaces are observed to be a

function of polishing cloth, and equivalent RMS roughness decreases after etching of polished surfaces. Spierings [40] and L. Wong [44] both concluded that the decrease of RMS roughness post etching is due to the coalescence of intersecting scratches.

One of the purposes of this work was to develop a method to produce both melt and polished glass surfaces which are atomically smooth with good spatial homogeneity and have a similar composition to that of the bulk glass. The results show that 725 °C melt surfaces have the lowest apparent/equivalent RMS roughness value (0.30 ± 0.01 nm/ 0.11 nm), most homogeneous distribution of roughness ($D=2.93$, $H=0.07$) and the longest correlation length ($B=692.04$ nm). In addition these surfaces, show only minor deviations in composition with respect to the bulk, with the exception of boron. The Microcloth polished/etched surface is shown to be the smoothest and most spatially homogenous surface (apparent RMS= 1.04 ± 0.03 nm, equivalent RMS=0.66 nm, $D=2.60$ and $H=0.40$). In addition, it is also shown that this surface is closest to the bulk composition when compared to all other polished and polished/etched surfaces.

Conclusions

In this paper, ISG glass surfaces were prepared through both melting and polishing/etching and the surface composition and morphology were quantified as a function of processing method. In particular, for the first time glass surface morphology as a function of processing method was quantified using PSD analysis, followed by both fractal and ABC model fitting, resulting in a comprehensive description of the spatial distribution of roughness.

All melt surfaces showed a depletion in Na, Ca, and B with respect to the bulk composition. Polished/etched surfaces showed a depletion in Na, B, and Al with respect to the bulk composition. The chemical bonding environments of the surface elements were not affected by either processing method. It was found that increasing heat treatment temperature of melt surfaces lead to a decrease in equivalent roughness and an increased spatial homogeneity of roughness while etching of polished ISG glass surfaces decreases the roughness and spatial distribution homogeneity of roughness. It has also been shown that the roughest and non-homogenous glass surface was found to be the most compositionally altered.

Acknowledgements

Funding for this work was provided by the Department of Energy Nuclear Engineering University Program (DOE-NEUP) program under contract number DE-AC0705-ID14517. The authors would like to thank Vince Bojan of The Pennsylvania State University Materials Characterization Laboratory for XPS analyses. We acknowledge Melanie Saffer of The Pennsylvania State University Laboratory for Isotopes and Metals in the Environment for bulk ICP analysis.

References

- [1] P.L Bocko, P.M Fenn, L.R Morse, F. Okamoto, *SID 91 Dig.*, 675(1991)
- [2] S.K Tang, V.Y Vassiliev, S. Mridha, L.H Chan, *Thin Solid Films* **77**, 352 (1999).
- [3] M. Depas, M.M. Heynes, T. Nigam, K. Kenis, H. Sprey, R. Wilhelm, A. Crossley, C.J. Sofield, and D. Graf, *Electrochem. Soc. PV-96-1*, 352 (1996).
- [4] M. Kimura, J. Mitsuhashi, and H. Koyama, *J. Appl. Phys.* **77**, 1569 (1995).
- [5] S. Dériano, T. Rouxel, S. Malherbe, J. Rocherullé, G. Duisit, G. Jézéquel, *J. Euro. Cer. Sci* **24-9**, 2803-2812 (2004).
- [6] A.O. Olofinjana, N.Y. Voo, *Appl. Surf. Sci.* **295**, 86-93(2014)
- [7] V. Cannillo, F. Pierli, I. Ronchetti, C. Siligardi, D. Zaffe, *Cer. Intl.* **35-7**, 2853-2869 (2009)
- [8] J. Massera, K. Bourhis, L. Petit, M. Couzi, L. Hupa, M. Hupa, J.J. Videau, T. Cardinal, *J. Phys. and Chem. of Solids* **74-1**, 121-127 (2013)
- [9] N.P. Mellott, S.L Brantley, J.P. Hamilton and C.G. Pantano, *Surf. Interface Anal.* **31**, 362-368 (2001)
- [10] C. Cailleteau, F. Angeli, F. Devreux, S. Gin, J. Jestin, P. Jollivet and O. Spall, *Nature Materials* **7**, 978-983(2008)
- [11] N.P. Mellott, S.L. Brantley, and C.G. Pantano, In: *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar*, edited by R. Hellmann and S.A. Wood **7**, 83-95(2002).
- [12] N.P. Mellott, C.G. Pantano, *Intl. J. Appl. Gls. Sci.* **4-3**, 274-279 (2013)

- [13] Y. Namba, M. Abe, A. Kobayashi CIRP, *Annals - Manufacturing Technology* **42**-1, 417-420 (1993)
- [14] R. Haj Mohammad Jafar, M. Papini, J.K. Spelt, J Mater. *Proc. Tech.* **213**-12, 2254-2261 (2013)
- [15] S. Deriano, T. Rouxel, S. Malherbe, J. Rocherulle, G. Duisit, and G. Jezequel, *J. Euro. Cer. Soc* **24**-9, 2803-2812 (2005)
- [16] L.M. Cook, *J. Non-cryst. Solids* **120**, 152 (1990)
- [17] L.M. Cook, K.H. Mader, *Glastech. Ber.* **10**, 333 (1987)
- [18] L.M Cook, A.J. Maker, K.H. Mader, H. Muller, *Glastech. Ber.* **9**, 302 (1987)
- [19] L.M Cook, K.H. Mader, *Glastech. Ber.* **10**, 333 (1987)
- [20] H. Dunken, *J. Non-Cryst. Solids* **129**, 64 (1991)
- [21] E.C. Onyiriuka, *J. Non-Cryst. Solids* **163**-3, 268-273 (1993)
- [22] D. Sprenger, H. Bach, W. Meisel, P. Gutlich, *J. Non-Cryst. Solids* **126**, 111-129 (1990)
- [23] C.D Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg (eds), *Handbook of X-ray Photoelectron Spectroscopy*, PHI Electronics, 21 (1978)
- [24] R.K Brow, *J. Non-Cryst. Solids* **194**-3, 267-273 (1996)
- [25] R. Bruckner, H.U. Chun, H. Goretzki and M. Sammet, *J. Non-Cryst. Solids* **42**, 49-60 (1980)
- [26] S.J. Fang, S. Haplepete, W. Chen, C.R. Helms and Hal Edwards, *J. Appl. Phys.* **82**, 5891 (1997)
- [27] M. Senthilkumar, N.K. Sahoo, S. Thakur, R.B. Tokas, *Appl. Surf. Sci.* **252**-5, 1608-1619 (2005)

- [28] S.D. Halplepete, H.C. Lin, S.J. Fang, and C.R. Helms, *Mater. Res. Soc. Symp. Proc.* **386**, 383 (1995)
- [29] S.J. Fang, W. Chen, T. Yamanaka, and C.R. Helms, *Appl. Phys. Lett.* **68**, 2837 (1996).
- [30] Y. Inagaki, T. Kikunaga, K. Idemitsu, and T. Arima, *Intl. Appl. Gl. Sci.* **4-4**, 317-327 (2013)
- [31] M4FT-12SR0307084, *FCT Quality Assurance Program Document*, Savannah River National Laboratory (2012)
- [32] J. Ferre-Borrull, A. Duparre, E. Quesnel, *Appl. Opt.* **40**, 2190 (2001)
- [33] E.L. Church, *Appl. Opt.* **22**, 1518 (1988)
- [34] J. Russ, *Fractal Surfaces*, Plenum Press, New York, (1994)
- [35] P.H. Dumas, B. Bouffakhreddine, C. Amra, O. Vatel et al., *Euro-phys. Lett.* **22**, 717 (1993)
- [36] E.L. Church, P.Z Tackacs, T.A. Leonard, *Proc. SPIE* **1165**, 136 (1989)
- [37] H.W. Guo, Y.X. Gong, S.Y. Gao, *Mater. Lett.* **64-8**, 997-999 (2010)
- [38] P.K. Ojha, T.K. Chongdar, N.M. Gokhale, A.R. Kulkarni, *Intl. J. Hydrogen Ener.* **36-22**, 14996-15001 (2011)
- [39] Y. Saito et al., *Appl. Surf. Sci.* **225**, 2290-2294 (2008)
- [40] S.H.V. Waltter, P.B. Adams, *Appl. Opt.* **7**, 845 (1968)
- [41] G.A.C.M. Spierings, *J. Mater. Sci.* **26**, 3329 (1991)
- [42] L.S. Du, J.F. Stebbins, *J. Non-Cryst. Solids* **351**, 3508-3520 (2005)
- [43] K.A. Murphy, N.M. Washton, J.V. Ryan, C.G. Pantano, K.T. Muller, *J. Non-Cryst. Solids* **369**, 44-54 (2013)

- [44] L. Wong, T. Suratwala, M.D. Feit, P.E. Miller, R. Steele, *J. Non-Cryst. Solids* **355**, 797-810 (2009)
- [45] A.M. Hu, K.M. Liang, M. Li, D.L. Mao, *Mater. Chem. Phys.* **98**, 430-433 (2006)s
- [46] N. Khan, D. Dollimore, K. Alexander, F.W. Wilburn, *Thermochimica Acta* **367-368**, 321-333 (2001)
- [47] S.B. Shim, D.S. Kim, S. Hwang, H. Kim, *Thermochimica* **496**, 93 (2009)
- [48] P.K. Gupta, D. Inniss, C.R. Kurkjian, Q. Zhong, *J. Non-Cryst. Solids* **262**, 200 (2000)
- [49] E. Radelein, G.H. Frischat, *J. Non-Cryst. Solids* **222**, 69 (1997)
- [50] K. Falconer, *Fractal Geometry: Mathematical Foundations and Applications*, Wiley, New York, (2014)
- [51] J.B. Bassingthwaighe, G.M Raymond, *Annals of Biomedical Engineering* **22**, 432 (1994)
- [52] Y. Zhang, S. Sundararajan, *Appl. Phys. Lett.* **88**, 141903 (2006)
- [53] A.V. Novak, *Technical Phys. Lett.* **39**, 858 (2013)

Table Caption

Table 1 Composition of melt and polished ISG glass surfaces

Table 2 Fitting coefficients of PSD spectra of melt and polished ISG glass surfaces

Figure Caption

Figure 1 Thermal expansion curve and differential thermal analysis curve for ISG glass.

Figure 2 3-D surface topography of ISG glasses; (a) micro cloth polished, (b) micro cloth polished & etched, (c) trident cloth polished, (d) trident cloth polished & etched, (e) 675 °C melt process, (f) 700 °C melt process and (g) 725 °C melt process. Scan area of all images are 1 μ mX1 μ m with a 25nm z-scale.

Figure 3 The experimental PSD profiles of all ISG glass surfaces.

Figure 4 Fitting of experimental PSD profile of 725 °C melt processed ISG glass surfaces using both the Fractal model and ABC (k-correlation) model.

Figure 5 Fitting of the experimental PSD profiles of (a) 675 °C melt surface, (b) 675 °C melt surface with feature removal, (c) 700 °C melt surface and (d) 700 °C melt surface with feature removal using the Fractal model and ABC (k-correlation) model.

Figure 6 Fitting of the experimental PSD profiles of (a) micro cloth polished, (b) micro cloth polished & etched, (c) trident cloth polished and (d) trident cloth polished & etched ISG glass surfaces using the Fractal model and ABC (k-correlation) model.

Table 1 Composition of melt and polished ISG glass surfaces.

Elemens (atm%)	Bulk Composition	Melt Surface at 675 °C	Melt Surface at 700 °C	Melt Surface at 725 °C	Micro Cloth Polished	Micro Cloth Polished & Etched	Trident Cloth Polished	Trident Cloth Polished & Etched	Standard Deviation of Conc. (atm%)
Na	8.0	7.2	7.0	7.0	3.1	3.9	3.5	3.2	±0.3
Ca	1.7	1.2	1.2	1.0	1.8	2.8	2.6	4.5	±0.4
Zr	0.4	0.5	0.5	0.5	0.5	1.3	0.5	3.6	±0.0
Al	2.4	3.2	2.8	2.8	2.9	1.8	2.7	1.8	±0.1
B	9.4	2.9	4.5	4.2	5.3	4.4	5.4	3.4	±0.1
Si	17.9	21.7	21.0	21.1	19.4	18.8	18.8	17.0	±0.6
O	60.2	63.3	63.0	63.4	67.0	67.0	66.5	66.5	±0.4

Table 2 Fitting coefficients of PSD spectra of melt and polished ISG glass surfaces.

Sample Description	Fractal		k-Correlation				Apparent RMS (nm)
	D	H	A (10 ⁵ nm)	B (nm)	C	Equivalent RMS (nm)	
Melt Surface at 675 °C	2.75	0.25	6.59	420.98	2.97	0.34	1.21±0.09
Melt Surface at 675 °C with Feature Removal	2.69	0.31	5.45	169.21	5.33	0.53	1.18±0.07
Melt Surface at 700 °C	2.84	0.16	4.17	345.39	3.96	0.27	1.02±0.08
Melt Surface at 700 °C with Feature Removal	2.81	0.19	6.73	130.23	11.76	0.48	0.97±0.06
Melt Surface at 725 °C	2.93	0.07	0.38	692.04	1.38	0.11	0.30±0.01
Micro Cloth Polished	2.42	0.58	364	660.74	3.43	1.47	1.10±0.07
Micro Cloth Polished & Etched	2.60	0.40	49.1	702.80	2.43	0.66	1.04±0.03
Trident Cloth Polished	2.18	0.82	274	516.94	3.54	1.59	1.83±0.08
Trident Cloth Polished & Etched	2.09	0.91	4.94	101.38	8.69	0.63	1.49±0.03

Figure 1
[Click here to download high resolution image](#)

Figure 2a
[Click here to download high resolution image](#)

a

Figure 2b
[Click here to download high resolution image](#)

b

Figure 2c
[Click here to download high resolution image](#)

c

Figure 2d
[Click here to download high resolution image](#)

d

Figure 2e

[Click here to download high resolution image](#)

e

Figure 2f
[Click here to download high resolution image](#)

f

Figure 2g
[Click here to download high resolution image](#)

Figure 3
[Click here to download high resolution image](#)

Figure 4
[Click here to download high resolution image](#)

Figure 5a

[Click here to download high resolution image](#)

Figure 5b

[Click here to download high resolution image](#)

Figure 5c
[Click here to download high resolution image](#)

Figure 5d

[Click here to download high resolution image](#)

Figure 6a

[Click here to download high resolution image](#)

Figure 6b
[Click here to download high resolution image](#)

Figure 6c

[Click here to download high resolution image](#)

Figure 6d

[Click here to download high resolution image](#)