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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, United States of America

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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.

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 [16–19]. 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

* Corresponding author. Tel.: +1 607 871 2446; fax: +1 607 871 2354.
E-mail address: yg4@alfred.edu (Y. Gong).

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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 [20,21]. In particular, under standard operating conditions, as those used in this work, the XPS probes to a depth of approximately 5–10 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 [22]. Furthermore through analysis of peak position and shape the chemical environment of the glass forming elements can also be analyzed [23,24].

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 [25,26]. 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, 250,000 data points (512×512 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 [27,28]. 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 [25]. 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 [26].

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 [29]. 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 [30]. The ISG glasses were batched to yield a nominal weight% composition of 56.2% SiO_2, 17.3% B_2O_3, 12.2% Na_2O, 6.1 Al_2O_3, 5.0% CaO and 2.8% ZrO_2. 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 h and cooled to room temperature at a rate of 50 °C per hour. Bulk glass composition was determined by spectrochemical analyses, based on $LiBO_2$ 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 0.5 cm × 0.5 cm × 2 cm 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 × 1.0 cm × 0.2 cm. Samples were then ground with 120, 240, 400 and 600 × grit silicon carbide grinding pads for planarization. Polishing of samples was carried out sequentially with 6 μm (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 NH_4OH 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 × 1.0 cm × 0.2 cm were heat treated in a pre-heated oven at 675 °C, 700 °C and 725 °C respectively for 1 h to create 3 different sets of melt surfaces. Heat treated samples were annealed at 570 °C for 3 h followed by cooling in the furnace overnight (~12 h). 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 Kα X-rays (non-monochromatic,