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The effect of HF/NH_4F etching on the morphology of surface fractures on fused silica

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ABSTRACT

The effects of HF/NH_4F, wet chemical etching on the morphology of individual surface fractures (indentations, scratches) and of an ensemble of surface fractures (ground surfaces) on fused silica glass has been characterized. For the individual surface fractures, a series of static or dynamic (sliding) Vickers and Brinnell indenters were used to create radial, lateral, Hertzian cone and trailing indentation fractures on a set of polished fused silica substrates which were subsequently etched. After short etch times, the visibility of both surface and subsurface cracks is significantly enhanced when observed by optical microscopy. This is attributed to the increased width of the cracks following etching, allowing for greater optical scatter at the fracture interface. The removal of material during etching was found to be isotropic except in areas where the etchant has difficulty penetrating or in areas that exhibit significant plastic deformation/densification. Isolated fractures continue to etch, but will never be completely removed since the bottom and top of the crack both etch at the same rate. The etching behavior of ensembles of closely spaced cracks, such as those produced during grinding, has also been characterized. This was done using a second set of fused silica samples that were ground using either fixed or loose abrasives. The resulting samples were etched and both the etch rate and the morphology of the surfaces were monitored as a function of time. Etching results in the formation of a series of open cracks or cusps, each corresponding to the individual fractures originally on the surface of the substrate. During extended etching, the individual cusps coalesce with one another, providing a means of reducing the depth of subsurface damage and the peak-to-valley roughness. In addition, the material removal rate of the ground surfaces was found to scale with the surface area of the cracks as a function of etch time. The initial removal rate for the ground surface was typically 3.5× the bulk etch rate. The evolving morphology of ground surfaces during etching was simulated using an isotropic finite difference model. This model illustrates the importance that the initial distributions of fracture sizes and spatial locations have on the evolution of roughness and the rate at which material is removed during the etching process. The etching of ground surfaces can be used during optical fabrication to convert subsurface damage into surface roughness thereby reducing the time required to produce polished surfaces that are free of subsurface damage.

1. Introduction

Fluoride based wet chemical etching can be accomplished by using a variety of reagents including hydrofluoric acid (HF) or, under suitably acidic conditions, fluoride or bifluoride salts. The dissolution of silicate glasses results in the formation of the stable hexafluorosilicate (SiF_6^{2-}) anion [1–11]. When hydrofluoric acid is used, the overall reaction can be summarized as:

$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H_2O + 2H^+. \quad (1)$$

The underlying mechanism of such reactions involves a number of steps and intermediate species. For example, in aqueous solution, HF acid acts as a weak acid where an equilibrium exists between the un-dissociated acid, H^+ ions and the F^- anions:

$$HF \rightarrow H^+ + F^- \quad {}^{25}K_a = 6.7 \times 10^{-4}\ \text{mol/l}, \quad (2)$$

where ${}^{25}K_a$ is the equilibrium constant at 25 °C [12].

In the presence of un-dissociated HF, the fluoride ion reacts to form the bifluoride anion (HF_2^-) which is thought to be a primary species responsible for the attack of the silica matrix [2,11,12]:

$$HF + F^- \rightarrow HF_2^- \quad {}^{25}K = 3.96\ \text{mol/l}. \quad (3)$$

A variety of reagents, so long as they produce both fluoride (F^-) and hydrogen (H^+) ions, can form the bifluoride ions *in situ*, and thus can be expected to etch silicate glasses.

In the present study, solutions of buffered oxide etch (BOE) were used as the etchant. However, qualitatively similar results would be expected using other fluoride based etchants. BOE refers

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to a series of commercially available mixtures of high purity, aqueous-phase hydrofluoric acid (HF) and ammonium fluoride (NH_4F) which were developed for use in the semiconductor industry [1,2,9,10]. In such solutions, NH_4F dissociates completely providing an abundant source of F^- ions which are free to react with the undissociated HF to form HF_2^- ions (Eq. (3)). In addition, the small fraction of dissociated HF (Eq. (2)) provides the H^+ ions which are known to catalyze the overall reaction [13].

Most contemporary studies of fluoride etching on glass surfaces have been performed in the context of the semiconductor industry. Such studies most often concentrate on masking and dielectric film applications, and describe the evolution of masked silica surfaces with etch time [1,2,14,15]. Significantly less work has been reported on the use of fluoride etching during optical fabrication. Preston [3] was among the first to examine how HF etching on ground surfaces of glass changes the surface topology of glass and recognized the utility of acid etching as an inspection aid. Spierings [1] combined the results from the glass science and integrated circuit (IC) fabrication literature in a comprehensive review that describes the etching mechanism, morphological changes of glass surfaces with etching, and the effects of etchant and glass composition [1]. More recently, Zhou et al. [4] and the present authors [5–7], applied HF etching to reveal subsurface cracks.

In the present work, we report on the effect that fluoride etching has on the morphology and observability of three classes of fractures: static indentation fractures (digs), sliding indentation fractures (scratches), and ensembles of fractures typical of ground fused silica surfaces. The present work suggests the use of etching both as an aid in the inspection process and as a means of removing subsurface fractures/damage (SSD) introduced during the fabrication and finishing of silicate based glasses or ceramics, particularly in those applications where SSD must be minimized in the final product. Examples include the finishing of SSD free optics for use in high-peak-power laser systems [16] and applications where material strength is of paramount importance, such as for windows or barriers used in aerospace or deep-sea applications.

2. Experimental procedures

2.1. Etching of isolated fractures (static and sliding indentations)

A series of static and sliding indentations were created, under ambient conditions, on the surface of polished fused silica (Corning 7980) substrates and the morphology of these cracks was monitored as a function of BOE etch time. Static Hertzian (blunt) fractures were created on a polished, fused silica substrate (Corning 7980; $7 \times 7 \times 0.7\ cm^3$) using a 1 mm diameter stainless steel Brinnell indenter using a Zwick microhardness tester (Model 3212) using loads of 39 and 49 N. A loading rate of 0.3 mm/s and a dwell time of 60 s were used in each case. Static Vickers (sharp) indentations were also created on the same substrate using a standard Vickers diamond indenter at loads of 1, 2, 59, 78 and 98 N. The 1 and 2 N loads were applied using a Shimadzu microhardness tester (Model HMV2) while the 59, 78 and 98 N loads were applied using the Zwick microhardness tester. In all cases, the loading rate was nominally 0.2 mm/s and the dwell time was 60 s. Finally, a series of sliding blunt indentations [5,17]) were created by sliding an 11 mm diameter stainless steel ball across the substrate surface at ~1 cm/s with a nominal load of ~90 N.

All etching was performed by affixing the substrate to a Teflon® kinematic mount. The entire assembly was then immersed in 20:1 BOE (Air Products, Allentown, PA) for various etch times and subsequently removed from the etchant for characterization. The kinematic mount provided a means of reproducibly mounting the sample during subsequent characterization and metrology cycles so that the same location of the substrate could be measured and characterized. This characterization included weighing of the sample to the nearest 1 mg, recording the surface morphology, in both reflection and transmission using optical microscopy (Nikon Optiphot 300), and recording the surface topology using a stylus profilometer (KLA Tencor P-10) which has a vertical resolution of 1 Å and horizontal resolution of 1 μm. Based on the scale resolution, the uncertainty in the measured mass is ±1.4 mg. All measurements from the photomicrographs were made using Image J software (National Institutes of Health) and the uncertainty calculated for each length measurement is ±0.42 μm. For the roughness measurements, the peak heights (and valleys) are 3–4 orders of magnitude greater than the instrument resolution and thus, no formal error analysis was performed. The accuracy of the profilometer is dominated by the ability of the needle to penetrate into the narrow and deep cracks. This is discussed in detail in Section 4.1. For clarity, the error bars are not shown on the figures in the results section.

2.2. Etching of ground surfaces

One of the faces of each round fused silica samples (Corning 7980; 10 cm diameter × 1.0 cm thick; polished on all surfaces) was ground using either fixed or loose abrasive processes. The first sample was ground using a Model II Blanchard (S/N 7769) equipped with a 150 grit (100 μm) diamond in a metal matrix tool (downward feed rate = 230 μm/min, rotation rate = 41 rpm, time = 20 s). The second sample was loose-abrasive ground on an 8" borosilicate glass lap (load = 0.3 psi, rotation rate = 15 rpm, time = 1 h) using a 30 μm Al_2O_3 abrasive particle slurry (Micrograt WCA30T). The SSD distributions of the two ground surfaces (150 grit, fine Blanchard and 30 μm, loose abrasive) were determined by: (1) creating a shallow (~40–50 μm) wedge/taper on the surface by magneto-rheological finishing (MRF); (2) exposing the SSD by acid etching; and (3) performing image analysis of the observed cracks from optical micrographs taken along the surface taper. Details of this characterization technique are provided elsewhere, including the error analysis associated with the obscuration measurement [5–7]. A second set of the ground samples described above were etched for various times in 20:1 BOE and characterized in the same manner as described in Section 2.1. Based on the scale resolution and time measured to the nearest minute, the uncertainty in the measured mass removal rate and the thickness removal rate are ±0.012 g/h and ±0.2 μm/h, respectively. Again, for clarity, the error bars are not shown on the figures.

3. Results

3.1. Etching of static and sliding indentations

Fig. 1 shows optical micrographs and the surface profilometry of the static Brinnell and Vickers indentations before etching and as each indentation fracture evolved during a total of 18 h of etching. The morphology of the surface before etching was typical of those expected following Brinnell (Hertizan cone cracks) and Vickers (radial and lateral cracks) indentation (see Fig. 2 and top of Fig. 1). In the absence of etching, the surface ring crack at 39 N is barely visible (Fig. 1(a)). At a higher applied load of 49 N, the ring crack is more discernible although the extent of the surface fracture in either case is not readily apparent (Fig. 1(b)). After even a short etch time (30 min), corresponding to the removal of ~500 nm of material, both the surface cracks and the overall depth and extent of the subsurface fractures resulting from each indenta-