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Relaxation of scratch-induced surface deformation in silicate glasses: Role of densification and shear flow in lateral indentation experiments

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ABSTRACT

Similar to normal indentation studies, structural compaction and shear flow occur also in the lateral deformation of glass surfaces through scratching. Here, we apply instrumented indentation with tangential displacement in order to study the elastic-plastic regime of scratch-deformation on silica, borosilicate and soda lime silicate glasses. We adopt the protocol of volume recovery analysis by high-temperature annealing to determine variations in geometry and volume of the scratch groove before and after the release of scratch-induced densification. While very similar relative recovery behavior is found for both normal indentation and scratch testing, inherent differences occur in the absolute presence of deformation modes across all three types of glass. In particular, caused by shear deformation at the apex of the employed Berkovich scratch tip, pronounced material pile-up occurs in scratching for normal loads which are about one order of magnitude below reference experiments of normal indentation. This leads to an increase in the effective friction coefficient and a non-trivial correlation between the scratch hardness and the normal hardness of glasses.

1. Introduction

When exposed to local mechanical contact glass surfaces undergo permanent microscopic deformation reactions [1]. The type and extent of these reactions is strongly composition-dependent. Using normal indentation experiments, a general distinction has been made between "normal" and "anomalous" glasses according to the presence of shear flow and structural compaction, respectively [2–4]. It was found that the degree of possible structural compaction correlates with the atomic packing density and the Poisson ratio of any given glass composition, providing parameters and a guideline for dedicated chemical tailoring [5]. Based on this understanding, less brittle glasses have been discovered [6] which offer increased defect resistance. A large number of studies have been following this route [7].

The contributions of shear flow and structural compaction to the overall of permanent deformation can be quantified through classical relaxation experiments [8]: using a normal indentation test, volume and topography of the residual imprint are compared to those of the same imprint after exposure to a temperature around T_g for prolonged time [9,10]. Assuming full recovery of structural compaction as a result of thermal relaxation, the degree of compaction is then obtained from the volume difference while the residual is related to shear flow. Studies of this type have been conducted on a variety of glass types, e.g., Refs. [9-13].

On the other hand, normal indentation studies produce a quasi-isostatic pressure field, whereas more complex stress fields are expected in other contact situations, most prominently, scratching [14]. In addition, normal indentation experiments on brittle materials usually ignore contributions of friction [15] or stick-slip reactions [16]. This leads to fundamental differences in material behavior during normal hardness testing or in lateral contact situations [17].

In the present communication, we report on relaxation experiments following scratch deformation of glass surfaces. Using lateral nano-indentation within the plastic regimes of silica, borosilicate and soda lime silicate glasses [18–20], we adopt Yoshida's protocol of deformation volume analysis [9,10] before and after thermal treatment in order to reveal the roles of compaction and shear flow in comparison to normal indentation.

2. Experimental

2.1. Glass samples

Commercial-grade vitreous silica (Suprasil 1, Heraeus), a borosilicate glass (Borofloat BF33, Schott), and a standard soda lime silicate glass (Optiwhite, Marienfeld) were chosen for the present study.

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Table 1
Glass transition temperature T_g, density ρ, Young's modulus E, shear modulus G, bulk modulus K, atomic packing density C_g and Poission ratio ν of the studied glasses.

sample name	Composition	T_g (°C)	ρ (g/cm³)	E (GPa)	G (GPa)	K (GPa)	C_g	ν
silica	SiO_2 (Suprasil 1)	1120	2.203	72.0	31.2	34.6	0.457	0.153
SLG	$72.6SiO_2$. $13.9Na_2O$. 8.8CaO. 4.3MgO. $0.6Al_2O_3$. $0.4K_2O$. $0.2SO_3$. $0.02Fe_2O_3$	545	2.569	71.0	28.8	44.5	0.514	0.234
BF 33	$81SiO_2$. $13B_2O_3$. $4Na_2O/K_2O$. $2Al_2O_3$	525	2.215	62.3	26.1	33.7	0.475	0.192

Compositions of these glasses are provided in Table 1. The silica samples were polished stepwisely on dry silicon carbide powder with grain sizes of 70 μm, 40 μm and 9 μm. In the final polishing step, a suspension of diamond power with a grain size of 1 μm was used. The other two glass types were used as received. Specimens of about 30 mm in diameter and 2 mm (silica and soda lime silicate) or 1.1 mm (borosilicate) in height were cut from the glasses and stored in vacuum between experiments. Directly before indentation studies, the samples were rinsed with acetone and dried in flowing nitrogen.

2.2. General characterization

Physical properties of the three glass types are provided in Table 1. They were obtained for this study by instrumented indentation using a nanoindenter platform (Agilent G200) and ultrasonic resonance, respectively [21]. All indentation and subsequent scratching experiments were performed in air at 25 °C. Normal indentation was done at constant strain-rate in the continuous stiffness measurement (CSM) mode, allowing for continuous measurement of stiffness by superimposing a small oscillation on the primary loading signal and analyzing the resulting response of the system.

The densities ρ were determined with the Archimedes method at 25 °C in ethanol. From this, the packing density C_g was estimated, [22].

$$C_g = \rho \frac{\sum f_i V_i}{\sum f_i M_i}, \tag{1}$$

where $V_i = 4/3\pi N\,(x r_A^3 + y r_B^3)$ is the theoretical molar volume of the ions of a generic compound A_xB_y, M_i denotes the molar mass of the ith component present in the molar fraction f_i, N is the Avogadro number, and r_A and r_B are Shannon's ionic radii of the involved ion species (using $r_O = 135$ pm) [23].

2.3. Scratching and indentation tests

Since literature data on indentation volume recovery by thermal relaxation exhibit notoriously high scatter [9,10], we initially conducted original reference experiments by normal indentation. For comparability with the subsequent lateral tests, these were done with a 3-sided Berkovich tip (instead of a Vickers tip which is used in most of the literature studies). Lateral testing was subsequently performed in accordance with other reports [18–20]. If not stated otherwise, we used the tip in edge-forward configuration with constant normal loads of 30, 23, and 17 mN on silica, SLG and BF33, respectively, and two different loading rates for each sample (10 and 50 μm/s). The loads were chosen so as to avoid the occurrence of chipping or microabrasion. In each scratching experiment, a pre-scan was conducted at a low loading force of 50 μN. After that, the desired load was applied rapidly (limited only by the indenter response rate) and kept constant on lines of 35 μm (BF33 and SLG) and 70 μm (silica), respectively. A post-scanning phase with the same load value as the pre-scan concluded each scratching measurement. All experiments were carried-out at ambient humidity, using the same tips and shortest possible delay times (< 12 h) between each experiment.

2.4. AFM imaging and subsequent heat treatment

After normal and lateral indentation, the residual indent and the scratch groove were imaged by atomic force microscopy (AFM, Nano Wizard 4, JPK instruments) in tapping mode. Prior to that, the samples were again cleaned in an ultrasonic bath of ethanol for 5 min at room temperature, flushed with acetone and dried properly. Silicon probes (PPP-NChauD, Nanosensors TM) with a nominal force constant of 42 N/m and a nominal resonance frequency of 330 kHz were used for mapping.

Thermal annealing was conducted in dedicated furnaces with high temperature stability. For SLG and BF33, we used a dilatometer furnace (Netzsch) with fine temperature control and a flat profile over a length of > 5 mm. The silica sample was relaxed in a bottom lift furnace (Nabertherm P 310) with an additional thermocouple positioned directly on the sample for manual control of the local temperature. For all samples, annealing was done at 0.95 T_g, i.e., 511 ± 2 °C for SLG, 498 ± 2 °C for BF33, and 1060 ± 5 °C for silica (the T_g values were extracted from the data sheets of the glasses; they are provided in Table 1). For SLG and BF33, annealing was done for 1 h. For silica, two separate experiments were conducted at 1 h and at 2 h, respectively.

AFM images were taken before and after annealing. The time between images was limited only by the cooling rate of the annealing furnace; it was < 3 h for SLG and BF33, and < 6 h for silica. Through this rapid data acquisition, secondary relaxation reactions were excluded as far as possible.

2.5. Data analysis

The AFM images were first flattened using the WsxM software [24] to exclude the slope of the untreated substrate from the analysis. The same software was used to measure the indentation volumes and to extract the scratch groove cross-section profiles. An exemplary image of a typical scratch groove (BF33, after relaxation) is provided in Fig. 1. For each scratch, the average of 10 cross-sections spaced about 2 μm from each other perpendicular to the scratch direction was used in the further analysis. The pile-up and sink-in areas were estimated from the integrals of the projected cross-section and multiplied by the length of the considered scratch section to obtain the corresponding groove volumes. In the following, V^+ and V^- will denote the pile-up volume (above the flat surface) and the sink-in volume (below the flat surface), respectively. Parameters obtained before and after annealing have the additional subscript "i" (initial) and "a" (after), respectively.

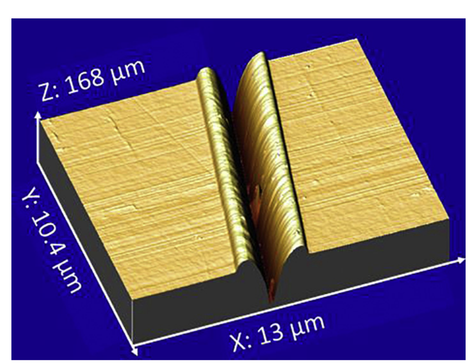

Fig. 1. Typical AFM micrograph of a scratch groove as used for volume analysis (here: sample BF33, scratching at normal load F_N = 23 mN, 50 μm/s, after annealing for 1 h at 498 ± 2 °C).