



Contents lists available at ScienceDirect

## Journal of Non-Crystalline Solids

journal homepage: [www.elsevier.com/locate/jnoncrysol](http://www.elsevier.com/locate/jnoncrysol)

# Lateral deformation and defect resistance of compacted silica glass: Quantification of the scratching hardness of brittle glasses

Shigeki Sawamura<sup>a,b</sup>, René Limbach<sup>a</sup>, Harald Behrens<sup>c</sup>, Lothar Wondraczek<sup>a,\*</sup><sup>a</sup> Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Fraunhoferstrasse 6, D-07743 Jena, Germany<sup>b</sup> Asahi Glass Co., Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755, Japan<sup>c</sup> Department of Mineralogy, Leibniz University of Hannover, Calinstrasse 3, D-30167 Hannover, Germany

## ARTICLE INFO

## Keywords:

Glass  
Scratch resistance  
Scratch hardness  
Silica

## ABSTRACT

Human interaction with multimedia devices occurs predominantly over inorganic glass surfaces. Scratch-induced damage is a primary limitation in the suitability of brittle glasses for this purpose. However, neither truly quantitative data nor a topo-chemical understanding of the underlying deformation process which would allow for the development of improved materials is presently available.

Here, we present lateral nano-indentation experiments for determining the work of deformation which is involved in the process of glass scratching. Using a series of hot-compressed vitreous silica with mild degrees of structural densification, we derive relations between quantitative scratch hardness and the underlying glass structure. We show that Young's modulus provides a clear rationale for the observed variations in scratching hardness. In the specific case of silica, the energy needed to generate a certain scratch volume corresponds to roughly one tenth of Young's modulus. This relationship formally indicates that only about one tenth of the bonds which are involved in the deformation process are broken in its course. However, comparison with a more complex glass material with a certain fraction of two dimensional structural units and a strong ability for topological adaption to local stress clearly indicates a deviation from this behavior. This opens a pathway to topo-chemical engineering of scratch-resistant glasses.

## 1. Introduction

Despite the intriguing promise of extremely high intrinsic strength, glasses remain ultimately brittle and usually break in catastrophic ways, even when handled with care [1]. This apparent discrepancy has triggered major efforts in the field of glass chemistry, aiming at the conundrum of plastic deformation and local dissipation of mechanical energy in brittle materials. It is assumed that through tailoring of chemical composition and, thus, network topology of the solid glass (denoted topo-chemistry in the following), the formation and growth of defects which act as stress amplifiers [2] can be avoided on atomic level and, thus, stronger glasses can be derived [3]. Such a tailoring of chemical composition would be a major breakthrough of the field, both in terms of fundamental understanding and application, where glasses have always been enabling materials in societal progress. For example, human interaction with multimedia devices today occurs predominantly over inorganic glass surfaces. This holds for both haptic and visual contact, for example, on smartphones, tablet personal computers and other mobile or non-mobile electronic devices. In those, thin glass sheet is used as a protective cover, barrier and substrate material.

Besides optical and chemical functions, it usually also determines the mechanical performance of the respective interactive display. Most critically, the glass component is to ensure high resistance to scratch damage which compromises optical appearance and, at the same time, presents the major source of strength-reducing surface flaws. Noteworthy, scratch damage may be induced at each stage of the lifecycle: besides actual use of the device, also during sheet production, packaging and transport, display manufacture or, e.g., component assembly. However, in contrast to the subject's fundamental importance, methods of physical quantification and the understanding of the topo-chemical basis of scratch-induced surface deformation are presently not well-developed, presenting a major obstacle in the exploration of glass surfaces with higher scratch resistance.

To date, scratch testing is conducted mostly in phenomenological ways [4–8]. These usually rely on applying a certain experimental protocol to produce a scratch, and examine the thus-created groove by visual inspection. In the archetype experiment a glass surface is scratched with a diamond stylus under monotonically increasing load. The fundamental regimes of plastic deformation, radial cracking, median or lateral cracking and chipping, and microabrasion are typically

\* Corresponding author.

E-mail address: [lothar.wondraczek@uni-jena.de](mailto:lothar.wondraczek@uni-jena.de) (L. Wondraczek).

differentiated visually [4,9], and their onset is subsequently related to the normal load which was applied on the scratching device. More fundamental efforts to relate the defect resistance of glasses to their composition and structure, on the other hand, rely on normal indentation testing [3,10–12]. The hardness parameter which can be extracted from such experiments is strongly dependent on the experimental conditions. Its physical meaning and relation to material properties such as fracture toughness, brittleness or elasticity are therefore not readily visible. As an early consensus, it was derived that the indentation response of inorganic glasses results from the interplay of elastic deformation, structural compaction and shear [13–15]. Tailoring between these contributions has been assumed to enable the design of glasses with reduced brittleness and improved defect resistance [16]. More recently, however, it was noted that the structural reactions which underlie damage infliction are significantly more complex [17,18].

In terms of lateral deformation (which includes scratching, but also aspects of friction, wear and abrasion), some phenomenological understanding and correlation to chemical properties has been reached for reactive polishing or grinding processes with the goal to improve on the fabrication of optical-grade surfaces [17,19]. With some minor exceptions [9,20], systematic analysis of the scratching behavior itself remains largely limited to soda lime silicate glasses [6,20–24]. Rather than elucidating the chemical origin of deformation at the onset of scratching, however, these studies focused on the emergence of cracks, crack morphology and the underlying (transient) stress profiles [25]. A first notion of scratching hardness was derived by Yoshida et al. [26], using normal load and vertical contact area. Without entering into details, they suggested that the scratching hardness of glasses is related to the fracture mechanism, not the elastic behavior. Extending this view, fracture ultimately occurs at the limits of plastic deformation. Thus, the scratching hardness reflects the resistance of the considered material to plastic deformation during quasi-static lateral indentation. In the present report, we provide a chemical rationale for this argument, determining initially the work of nanoscale lateral deformation across the plastic regime. Using the example of vitreous silica with different degrees of off-set compaction, we obtain a direct dependence of deformation work on Si–O bond density. This observation will enable the design of glassy materials with specific tribological properties using topo-chemical principles.

## 2. Materials and methods

For the present study, we selected silica as the archetype glass material with the highest degree of structural compressibility among all presently available oxide glasses. Its ability to compact originates from the large free volume and reflects in an exceptionally low Poisson ratio [27]. The structure of silica comprises tetrahedral units of  $[\text{SiO}_4]^{4-}$  which are interconnected over all four edges to form a continuous network of  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  entities. The dominant super-structural units are six- to eight-fold rings of tetrahedra. Bonding is strongly covalent with the Si–O bond cleavage energy of 624 kJ/mol [28]. Fracture is usually assisted by adsorbed water [29], which reduces the energy of bond cleavage to 163 kJ/mol [28]. In order to test the structural dependence of lateral deformation, a set of samples is produced by compacting chemically equivalent glasses within the regime of congruent compression ( $< 1$  GPa, see Fig. 1b) in which no changes occur in ion coordination or topology. This enables us to attribute variations in scratching hardness solely to variations in density.

### 2.1. Compression experiments

Compacted silica glass samples were prepared from commercially available Suprasil 2 fused silica (Heraeus Quarzglas GmbH & Co. KG) by isostatic compression in an internally heated gas pressure vessel, similar to the procedure described in Refs. [30–35], Fig. 1a. For this,

individual bars of  $5 \times 5 \times 25 \text{ mm}^3$  in size were directly loaded into the vessel and argon gas was employed as the compression medium. The glasses were heated at constant pressure up to a temperature of 1523 K, well above the glass transition temperature of  $T_g = 1393 \text{ K}$ , and equilibrated for 12 min to allow for complete relaxation to the respective pressure. After equilibration above  $T_g$ , the glasses were cooled under pressure at a rate of 10 K/min down to room temperature. Using this method, silica glasses with frozen-in pressures of 100, 300 and 500 MPa were produced. For reference, also an uncompressed sample was made at 0.1 MPa, using the same time-temperature profile. Changes in the density  $\rho$  were evaluated using Archimedes' principle with dry ethanol as the immersion liquid. In order to minimize the influence of argon, which is expected to diffuse into the glass surface during the high-pressure treatments [32], the compacted glasses were subsequently grinded with silicon carbide paper and polished to optical finish using a water-based CeO suspension. The removed layer ( $\sim 200 \mu\text{m}$ ) was much thicker than the expected argon in-diffusion zone [36]. Following the approach of Davis et al. [37], infrared spectroscopic analysis revealed a total water content of around  $490 \pm 13 \text{ ppm}$  in all glasses, independent of the applied compression conditions.

### 2.2. Nano-indentation under normal load

Indentation experiments were conducted through instrumented nano-indentation (G200, Agilent Inc.), using a Berkovich diamond tip (Synton-MDP Inc.) and operating in the continuous stiffness measurement (CSM) mode. The instrument's frame compliance and tip area function were calibrated prior to the experiments on a fused silica reference glass sample (Corning 7980, Corning Inc.) with known elastic properties (Young's modulus  $E = 72 \text{ GPa}$  and Poisson ratio  $\nu = 0.18$ ), using the method proposed by Oliver and Pharr [38]. On each glass specimen, five indentations with a depth limit of  $2 \mu\text{m}$  were created at a constant strain-rate of  $0.05 \text{ s}^{-1}$ . The hardness  $H$ , defined as the load divided by the projected contact area of the indenter tip  $F_N/A_c$ , as well as Young's modulus  $E$  were continuously recorded as a function of the indentation depth  $d$  by applying a weak oscillation to the indenter tip ( $\Delta d = 2 \text{ nm}$ ,  $f = 45 \text{ Hz}$ ) [12]. The value of  $E$  was deduced from the reduced elastic modulus  $E_r$ , according to Ref. [39]:

$$E = (1 - \nu^2) \left[ \frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i} \right]^{-1}, \quad (1)$$

with  $E_i = 1141 \text{ GPa}$  and  $\nu_i = 0.07$  of the diamond tip, respectively. Poisson ratios of the compacted silica glasses were calculated from the longitudinal  $\nu_L$  and transversal  $\nu_T$  sound wave velocities, which were determined by means of an echometer 1077 (Karl Deutsch GmbH & Co. KG), equipped with 8–12 MHz piezoelectric transducers:

$$\nu = \frac{v_L^2 - 2v_T^2}{2(v_L^2 - v_T^2)} \quad (2)$$

All nanoindentation experiments were conducted in laboratory air at ambient temperature of around  $298 \pm 3 \text{ K}$ .

### 2.3. Lateral nano-indentation and scratch testing

Lateral deformation and defect initiation were initially characterized in a ramp-load scratch test using the same nano-indentation set-up as described above. This test comprises an indenter tip moving across the glass surface under monotonically increasing load. Meanwhile, both the indentation depth and the lateral force  $F_L$  were continuously recorded [9]. On every glass specimen, 16 ramp-load scratch tests were conducted across a length of  $L_s = 600 \mu\text{m}$  at a scratch speed of  $50 \mu\text{m/s}$  using a Berkovich diamond indenter tip in edge-forward orientation. The peak load at the end of the scratch was set to 300 mN, resulting in a constant loading rate of 25 mN/s. Prior to each test, the pristine glass surface was pre-scanned with the Berkovich tip under a load of 50  $\mu\text{N}$ .

Download English Version:

<https://daneshyari.com/en/article/7900509>

Download Persian Version:

<https://daneshyari.com/article/7900509>

[Daneshyari.com](https://daneshyari.com)