
Relationship between subsurface hardness and silicate network connectivity of soda-lime-silica glass surface modified by superheated steam

Barsheek Roy^{*†1}, Andreas Rosin¹, Thorsten Gerdes¹, and Stefan Schafföner²

¹Keylab Glass Technology, University of Bayreuth – Germany

²Chair of Ceramic Materials Engineering, University of Bayreuth – Germany

Abstract

Glass surfaces govern the properties of strength, chemical durability, adhesion and optical quality (1). The surface acts as an interfacial site for a variety of physical and chemical processes to influence the underpinning structural characteristics. The disruption of the local subsurface silicate structure is closely associated with the alteration in silicate network connectivity (2).

This research was aimed at studying the interrelation of surface structural and mechanical properties of soda-lime-silica (SLS) glass. The subsurface hardness was altered by using sub-Tg superheated steam as a medium of interaction with the SLS glass surface. A significant enhancement in hardness up to 30% was evidenced by instrumented indentation up to a depth of about 300 nm below the glass surface. The corresponding relationship with the associated alteration in silicate network connectivity was investigated by X-ray photoelectron spectroscopy (XPS). The O1s spectral line was deconvoluted to extract the respective contributions of bridging oxygens (BOs), non-bridging oxygens (NBOs) and hydrous species (SiOH/H₂O) (3-5). The atomic ratios of the different oxygen speciations to silicon are indicative of the extent of silicate network connectivity. The XPS investigation was performed as a function of depth from the glass surface, accompanied by Ar⁺ sputtering. A comparative study was performed between two SLS surfaces derived from different sources. It was observed that the rearrangement of the silicate network in response to the interaction with superheated steam relied on the initial network connectivity of the pristine surface prior to the treatment. The pristine surface with higher concentration of BOs underwent network repolymerization, indicated by a subsequent increase in BO/Si. On the contrary, the pristine surface with relatively higher concentration of NBOs and lower concentration of BOs underwent network depolymerization, reflected by an increase in NBO/Si after steam treatment. This suggested that a weaker pristine subsurface network favored the creation of NBOs when subjected to the interaction with superheated steam. The diffusion of water molecules into the silicate network was linked to the structural rearrangement during steam treatment, that played an influential role on hardness. The surface with depolymerized silicate network was marked by the availability of micro channelized pathway for the diffusion of water molecules to fill up the interstitial voids. This contributed to a substantial increment in hardness by 30%. The corresponding OH vibrations were detected by attenuated total reflection infrared (ATR-IR) spectroscopy (6). Comparatively, the glass surface that underwent repolymerization of silicate network obstructed the diffusion of water molecules with a marginal increase

^{*}Speaker

[†]Corresponding author: barsheek.roy@uni-bayreuth.de

in hardness by 4%. It is noteworthy to mention the absence of any evidence of ion-exchange between sodium and hydronium ions in the near-surface region by the influence of superheated steam, unlike the hydrothermal treatment of SLS glass surface around 150°C with a decrease in hardness (7).

This study suggests that the effect of stuffing of the interstitial sites within the silicate network plays an essential role in enhancing the subsurface hardness. An increase in the extent of network connectivity (degree of polymerization) does not necessarily increase the subsurface hardness. It serves as a critical input to generalize that the silicate network connectivity together with the availability of free volume in interstitial voids are intimately inter-related to govern the subsurface hardness. The inherent interstitial voids are proposed to be highly detrimental to the propagation of cracks from the surface through the depth of the glass network to decrease the subsurface hardness.

References

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Keywords: Soda lime silica glass, surface, superheated steam, silicate network connectivity, subsurface hardness