Plasma
Technology
Solutions

Surface modification on soda lime and alumina silicate glass surfaces by Ion implantation – developments by AGC

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1. Introduction

Ion implantation technologies have been used for many years in electronic industries but never on a large scale for materials surface treatment and especially for flat glass. This technology consists in bombarding in a vacuum chamber the surface of a material with highly energetic ions. The ions penetrate violently into the surface of the material, then stop and lose their energy because of a cascade of collisions. The surface reorganization and the implantation of ions into the surface of the material can modify the physico-chemical properties of various materials from polymers to metals, from glass to crystals. The judicious choice of the implanted ions allows obtaining re-alloying, amorphization or nano-restructuring of the surface, improving the material's properties or adding new functionalities.

2. Ion source

AGC uses the Hard*ion*+ ion gun (Figure 1. left part) developed by its partner Ionics. This ion gun is based on the Electron Cyclotron Resonance (ECR) technology that allows the formation of multi-charged ions (dissociation of the molecule and up to 4 positive charges) thanks to the use of high frequency microwaves (10 GHz) and strong permanent magnets to confine the plasma. Since the ion kinetic energy is the product of its charge and the applied voltage, lower voltages are required to obtain high energy ions (40 kV to have N^{4+} ions with an energy of 160 keV) compared to ion gun generating mono-charged ions. Furthermore, the presence of ions with different charges allows simultaneous ion implantation at different depths (Figure 1. right part).

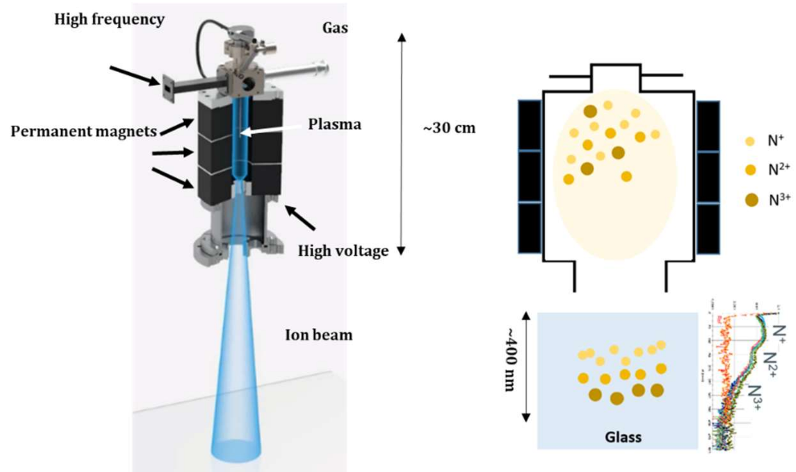

Figure 1. Schematic representation of the ion gun and its components (left), schematic representation of multi-charged ion implantation with SIMS[1] dynamic profile of nitrogen of a representative implanted glass (right).

The ECR technology enables AGC to develop ion implantation on an industrial scale (the standard dimension for a glass producer is 3,21 m by 6 m) thanks to the high ion current (1 to 8 mA) making high dose (up to 10^{17} ions/cm²) on large surface obtainable. The key parameters during ion implantation are the ion current (1 to 8 mA), the voltage (10-40 kV), the dose (10^{14} to 10^{17} ions/cm²) and the type of implanted ion (classically ions of N, O, He and Ar). These key parameters for the ion used gun are presented on Figure 2.

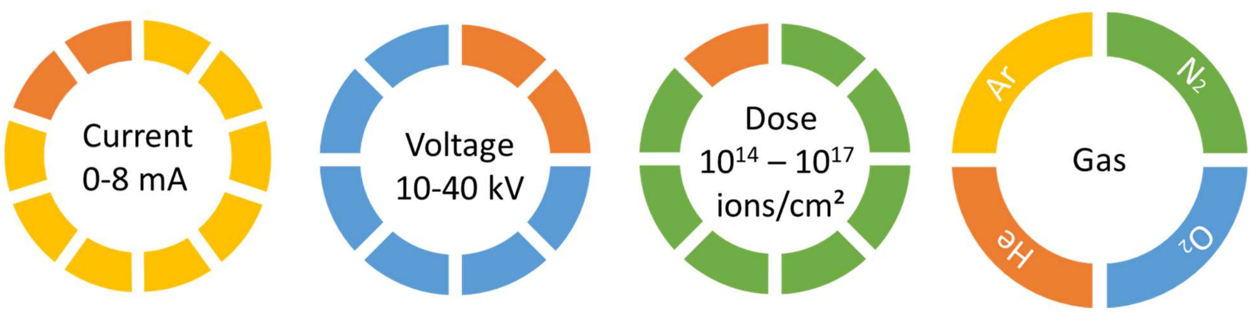

Figure 2. Key parameters of the AGC's ion implanter.

3. Scratch resistant and anti-reflective glasses

Numerous, properties can be brought to a surface by ion implantation. In this chapter, we will focus on scratch resistant (AS) and anti-reflective (AR) glasses. Indeed, both properties are patented and result from our implantation of nitrogen ions. The main difference is the dose, a low dose for the AS property and a high dose for AR property.

[1] Secondary Ion Mass Spectrometry

3.1. Scratch resistant glasses [1]

An AS glass is obtained during the early stages of our ion implantation. At low dose the implanted nitrogen fills the interstitial spaces of glass increasing slightly its density and so its hardness. Surprisingly, this phenomena is not the main factor explaining the improvement of scratch resistant, it is rather a change in the surface composition leading to a more densely cross - linked and stiffer silica network at the top surface of the glass which is at the origin of this improvement (Figure 3).

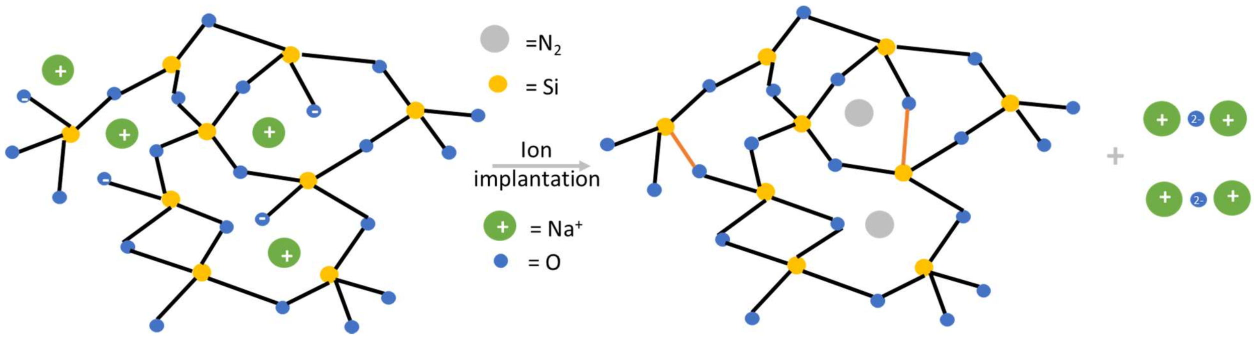

Figure 3. Schematic representation of a glass silica network (left) and the impact of ion implantation on this network.

Indeed, our ion implantation induces a decrease of the network modifier concentration (for example Na) which induces a polymerization of the non-bonding oxygen (NBO) (Figure 3) and so an increases of the hardness (Figure 4).

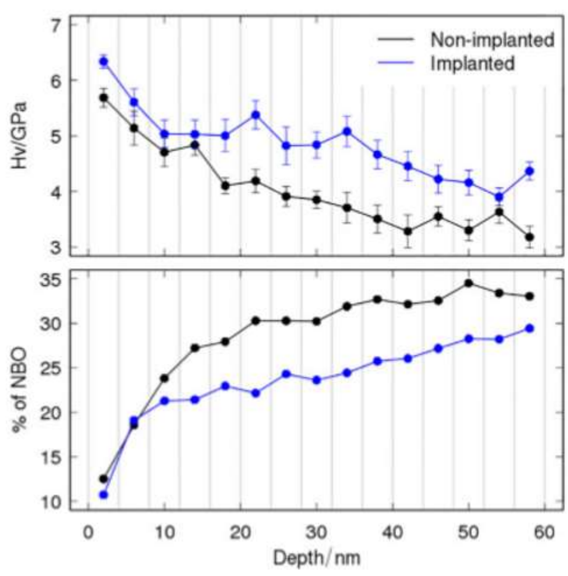

Figure 4. Simulation of the evolution with the surface composition of the Vickers hardness (Hv) (top) and percentage of non-bridging oxygens (bottom) in the non - implanted (black) and implanted (blue) soda–lime glasses [1].

The increase of the hardness results in an increase of the critical load required to observe lateral cracks in the glass (Figure 5 top) and so of the glass scratch resistance. This improvement is observed for all glasses (soda-lime or aluminum silicate glasses), chemically tempered (CT) or not (Figure 5 bottom).

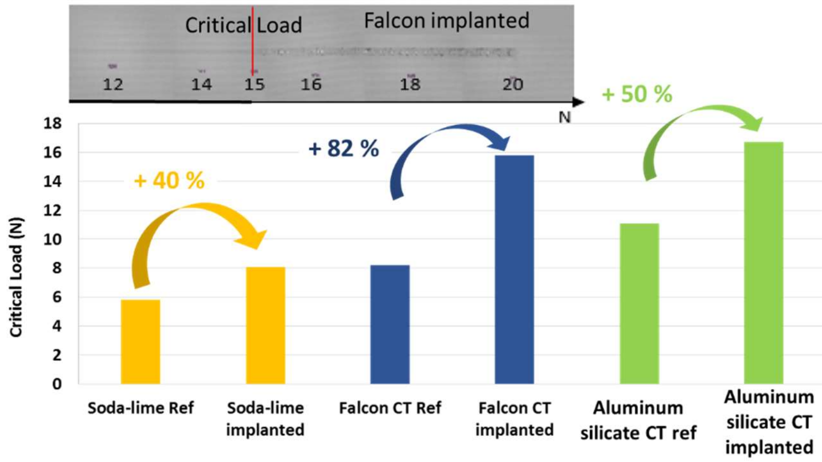

Figure 5. Example of critical load measurements (top) and critical load values for reference and implanted glasses of various composition, chemically tempered or not (bottom).

3.2. Anti-Reflective glasses

An AR glass is obtained for high implanted doses of nitrogen ions. Indeed, the accumulation of nitrogen will generate bubbles; increasing in number and size (Figure 6). The refractive index gradient caused by these bubbles leads to increasing anti-reflective properties (cf. 6 supporting information).

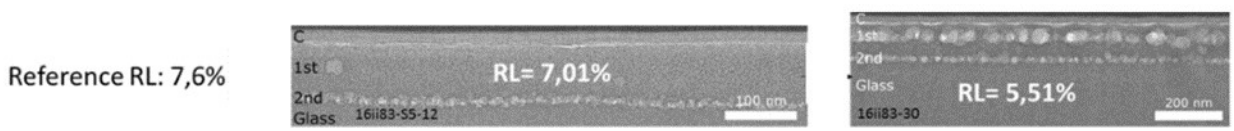

Figure 6. TEM pictures of two implanted glass substrates, their respective light reflection (RL).

The decrease of light reflectance (RL) is up to 3% and can be selected by the dose (Figure 7).

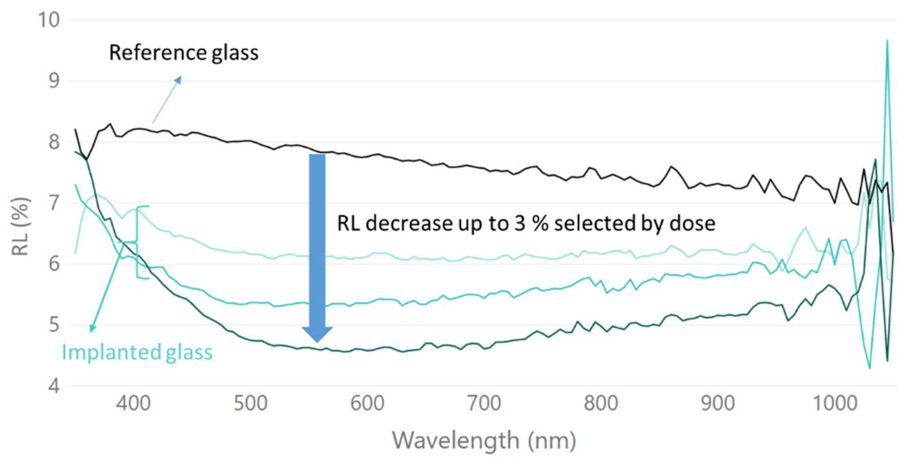

Figure 7. Reflectance spectra for a reference glass and implanted glasses at different doses.

The RL spectra are flat in a wide range of wavelengths (Figure 7 and Figure 8) contrary to classical coatings. However, the wavelength with the minimum RL can be selected by the applied voltage (Figure 8).

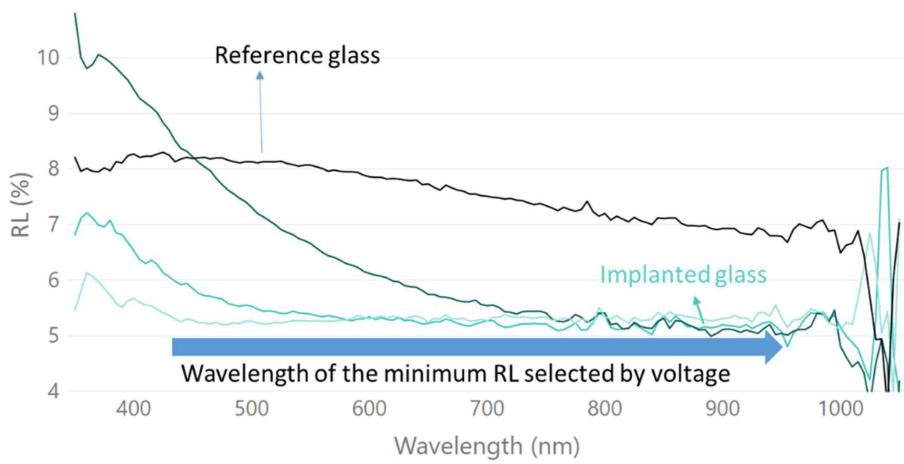

Figure 8. Reflectance spectra for a reference glass and implanted glasses at different voltage.

Finally, AR glasses obtained by our ion implantation have a good angular stability compared to a glass with a typical AR coating (Figure 9).

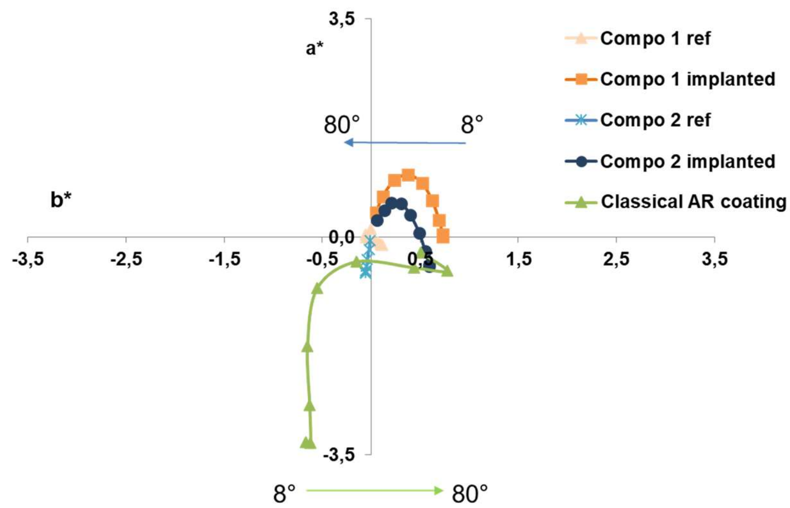

Figure 9. Color box (a and b*) variation for angle from 8 to 80 ° of implanted glass and their reference compared to a classical AR coating.*

4. Conclusions

ECR technology-based ion implantation of nitrogen has been used to bring scratch resistant or anti-reflective properties to glass. The two different mechanisms, filling of interstitial spaces with polymerization for AS property and nitrogen accumulation resulting in bubble formation for AR property, have been described. The versatility of ion implantation to fine tune the properties and the resilience of the process to the glass composition have been demonstrated.

5. Bibliography

[1] J. Idé *et al.*, "Glass Hardness Modification by Means of Ion Implantation: Electronic Doping versus Surface Composition Effect," *Adv. Theory Simulations*, vol. 2, no. 7, p. 1900039, 2019.

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6. Supporting information

It is known that a change of refraction index gives some reflection. The light reflection is given by (Eq. 1) :

$$RL = \left(\frac{n_0 - n_s}{n_0 + n_s}\right)^2 \qquad \textit{(Eq. 1)}$$

Where,

RL is the light reflection

n_0 is the refractive index of the first media

n_s is the refractive index of the second media

If the difference between the two refractive index is important, the RL will be important. However, with successive layers which have close refractive index between them and allow to fill the gap between n_0 and n_s the RL will dramatically decrease.