

## Understanding Effects Responsible for Pinhole Development and Coating Adhesion for Atomic Layer Deposited Coatings on Glass

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Glass degradation, referred to broadly as glass disease in cultural heritage contexts, presents a particularly significant challenge for art and museum conservation. Caused by contact between a glass surface and water, or other acidic species in the environment, there are few methods available to museum professionals to slow or stop its progression [1]. This problem also extends beyond the walls of the museum and into other areas of research, such as the stability of vitrified nuclear waste [2]. Recent work in our group has focused on the application of atomic layer deposited (ALD) coatings on glass as a potential method to prevent, or mitigate glass disease.

ALD coatings can be applied to glass surfaces forming a thin, conformal, amorphous film of a metal oxide that can serve as a diffusion barrier between a glass surface and the corrosive agents present in the environment. Initial results from the analysis of glass samples that have been artificially aged, with and without ALD coatings, have shown that the coating significantly reduces the susceptibility to the formation of glass disease.

However, the rate at which glass disease is slowed is limited by the quality of the coating applied. Originally intended for use on silicon based microelectronic devices, ALD coatings are theoretically applied evenly, layer-by-layer over the entire surface of the sample. When applied to more non-ideal surfaces, such as glass, coatings have the potential to be deposited with defects that can range from incomplete adhesion of the coatings, to pinholes in the coating surface. Importantly, pinholes reduce the diffusion path length for corrosive gaseous species from the atmosphere, through the ALD coating to the glass substrate. Artificial aging process of the glass samples involves submerging the coated glass samples in water for several days. This procedure exacerbates the degradation process, as the aged glass swells and expands these cracks, or pinholes, resulting in further failure of the coatings.

The formation of pinholes and other defects in ALD coatings are known and discussed in the literature [4]. Often, simply increasing the coating thickness allows the ALD to coalesce into a more complete coating. Increasing coating thickness on our samples improved, but did not eliminate, the effect of pinholes on successfully protecting the glass. In circumstances where the coating thickness cannot be increased, or remains insufficient, there are several potential methods used to clean and better prepare a surface for coating. These methods range from an ozone pulse prior to coatings in the ALD chamber, to chemical etching and surface functionalization. The results of these different preparation methods on the effectiveness of preventing aging in glass will be explored.

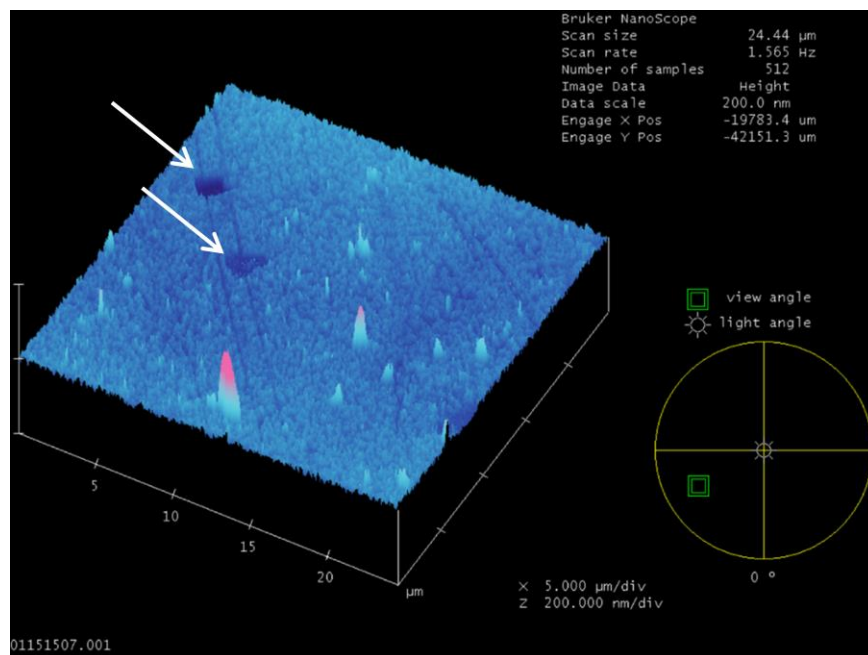
### References:

- [1] R. Hellmann *et al*, *Nature Materials* **14** (2015) p. 307-311.
- [2] J. Weaver *et al*, *American Ceramic Society Bulletin*, **95** (2016), p. 18-23.

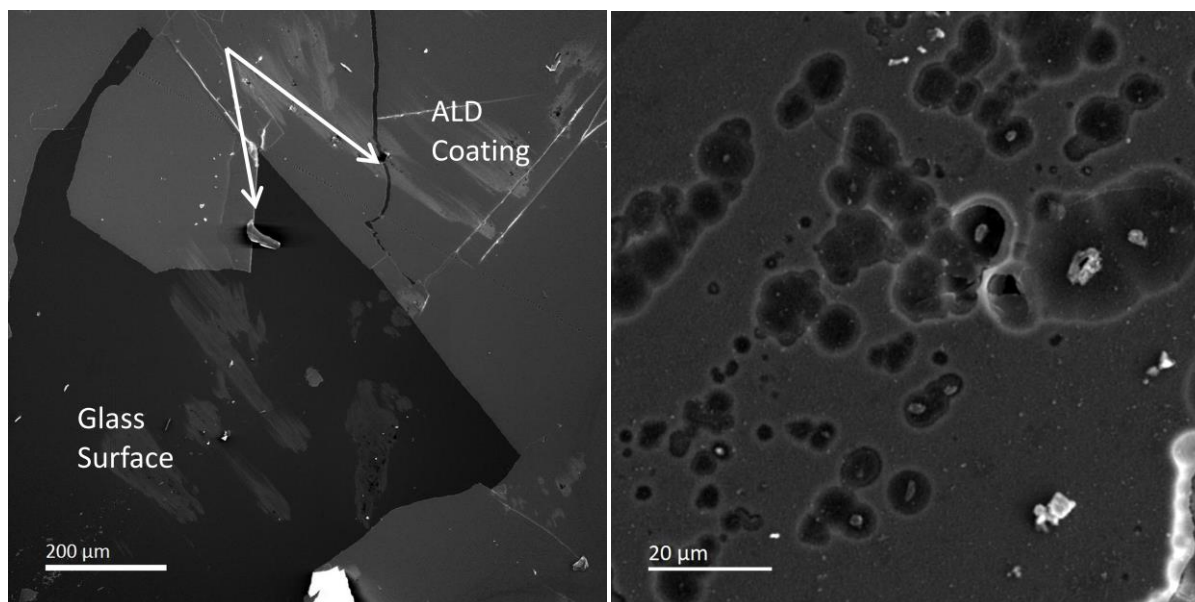
[3] B.C. Bunker *et al*, *Journal of Non-Crystalline Solids* **179** (1994), p. 300-308.

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**Figure 1.** Atomic force microscope image of two pinholes in the surface of glass sample coated with ~25nm of TiO<sub>2</sub> ALD.



**Figure 2.** Secondary electron scanning electron microscopy image of ALD coatings after aging, showing cracking of the coating (left) and pinhole expansion (right).