

Controlling Silica in Its Crystalline and Amorphous States: A Problem in Surface Science

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ABSTRACT: Understanding the glass-crystal transition in real space using scanning probe microscopy, thus solving a long-standing problem posed during the first half of the 20th century, is the goal of this research.



 ${\displaystyle S}$ ilica is one of the most abundant materials in the earth's crust. It is the basis for rocks and mountains, it is used to prepare the basic material of our electronics industries, it is used as window glass, and it is used as the materials basis for important catalytic materials such as zeolites and support for heterogeneous catalysts, just to name a few. A detailed knowledge of the structure of silica is therefore of utmost importance. While the structure of crystalline silica is wellknown down to the precise position of the atoms thanks to Xray crystallography, the structure of amorphous silica, that is, silica glass, is only poorly understood in comparison. In 1932, W. R. Zachariasen proposed a model for glassy or vitreous silica,¹ which has since then been the basis for discussion of the structure of vitreous silica in the glass industries and beyond. This model has only recently (2012), 80 years after its proposal, been experimentally verified,² but the direct observation of the transition from the crystalline phase into the vitreous phase, as temperature is changed, still remains one of the big experimental challenges in physical chemistry today. We may actually call it a holy grail! Understanding this transition in detail may have considerable consequences for understanding transformations of silica-based and silica-derived materials. This Account aims at pointing out a strategy of how to tackle this important challenge. Techniques from the tool box of surface science, such as scanning probe microscopies, play a central part in this strategy as they allow imaging arbitrary structures in real space. Another important mosaic piece in the strategy is the preparation of the system to be studied. We propose here to use the preparation of a thin silica film on a metallic substrate that might be eventually peeled off to produce a freestanding silica film. This seemingly minor aspect with respect to preparation turns out to play a major role as it guarantees the flatness of the sample at the atomic scale, which is

important with respect to the applicability of the methodological approach using scanning probes.

A silica film with a crystalline structure, schematically shown in Figure 1a, has been prepared on a Ru(0001) single crystal surface and characterized with respect to structure (scanning probe and electron scattering (Figure 1b), electronic properties (photoelectron spectroscopy), and vibrational properties (infrared reflection absorption spectroscopy (Figure 1c), including its computational modeling at density functional level. It has been prepared by physical vapor deposition, depositing silicon in an oxygen atmosphere setting the chemical potential at a given temperature, within an ultrahigh vacuum setup, providing contamination free settings. Each atom is coordinated to four oxygen atoms in a tetrahedral fashion, and those tetrahedrons are connected into a hexagonal ring system, which repeats in the top and the bottom layer. We call this a bilayer. Parallel to the bilayer, a monolayer forms (if the Si coverage is not perfect), where only one layer of silica is bound chemically by the fourth Si-O bond to the metal while the other three are involved in the hexagonal network. It is important to note that vibrational spectroscopy allows you to directly differentiate the two different layers (see Figure 1c). The Si-O-Ru bond shows up at 1134 cm⁻¹. In the following, we will concentrate on the bilayer system.

Depending on the preparation conditions, such a film may also exhibit a vitreous structure. This is shown in Figure 2a,b. Two scanning probe images are shown, one taken with scanning tunneling microscopy (STM) and the other one with noncontact atomic force microscopy (nc-AFM). Both are taken

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Figure 1. (a) Top and side view of the silica film on Ru(0001). The (2×2) unit cell observed in the LEED pattern (panel b) is indicated. (b) LEED (top panels) and STM (lower panels) of the crystalline (left) and vitreous (right) film. (c) Infrared spectra of the bilayer silica film (blue trace, 2 ML) in comparison to a silica film consisting of only one layer (1 ML).



A_{osc} = 0.27 nm, const. height

 $V_{\rm s}$ = 0.1 V, const. height

Figure 2. (a, b) Both images of the bilayer film represent a single, atomically resolved constant height measurement, where panel a shows the nc-AFM and panel b the STM channel. Imaging parameters for panel a: oscillation amplitude = 0.27 nm, gray scale from -1.0 Hz (dark) to +0.6 Hz (bright). Imaging parameters for panel b: $V_s = 100$ mV, gray scale from 50 pA (dark) to 500 pA (bright). For both panels a and b, scan area = 2.7 nm × 3.9 nm. In panel a, the connectivity of the Si atoms is visible, whereas panel b reveals the arrangement of the O atoms. An atomic model of the topmost layer of the silica film is superimposed onto the lower right corner of the images in panels a and b (green balls, Si atoms; red balls, O atoms). Panel c shows Zachariasen's scheme of a random network (black dots, cations; white circles, anions).

at exactly the same position as may be seen by comparing the features imaged. However, the two techniques show different sensitivity. While STM is sensitive to oxygen, nc-AFM images the Si atoms. By superimposing the two images, we reveal the full structure of this vitreous silica layer. The structure of this overlayer may now be compared with the proposal forwarded in 1932 by Zachariasen, shown in Figure 2c. Here, similar to the crystalline structure, the local coordination (represented by the open circles) of the Si atoms by four oxygen atoms as a tetrahedron is the same (represented by only three black circles within this two-dimensional scheme), but the connectivity is different, leading to an irregular arrangement of ring structures of different sizes. Basically, one has to state that the Zachariasen representation is a perfect model for the experimentally observed structure, noting that the two layers of the film are arranged in an identical fashion. The structure has been

analyzed in detail with respect to the ring size distributions, and large scale images have been Fourier transformed in order to compare resulting pair correlation functions with those observed over many decades using neutron and X-ray scattering data from the dimensional glass.³

The overall agreement is remarkable although small differences are observed, which is not surprising given that the scattering data have been taken on three-dimensional materials while the present structure is two-dimensional. Therefore, those observations indicate that the present system may be a good model system to allow a more detailed investigation of the conversion of a vitreous silica phase into a crystalline phase. We expect, based on the experience with three-dimensional materials, this transition to occur around 1000 $^{\circ}$ C. Therefore, an instrument needs to be built that may take scanning probe microscopy images as a function of

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temperature while maintaining atomic resolution. This is work in progress. There is some expectation as to what we might see: Joachim Sauer and his group² had calculated the energy necessary to form two five- and two seven-membered rings from four six-membered rings, which would lead to the socalled Stone–Wales defect. Some experimental observations using a TEM studying^{4,5} a supposedly similar SiO₂-system on graphite used the electron beam to induce such changes, leading to observations consistent with such defect formation. However, the temperature driven transformation has not yet been observed, and real space imaging is essential. One may extrapolate toward some more expectations from looking at the crystal–vitreous interface in a sample where the two phases coexist. Figure 3 shows such an interface (Figure 3a) together



Figure 3. Analysis of the rings at the crystalline–vitreous interface of the silica film. (a) STM image of the interface. (b) Visualization of the different ring sizes. Polygon areas range from 0.1 to 0.5 nm^2 and ring sizes from four to nine Si atoms per ring (see the scale bar). (c) Designation of slices for data plotted in panel d. (d) The number of rings per slice for every ring size plotted vs the lateral coordinate.

with a statistical analysis of the ring sizes (color-coded in Figure 3b) as they occur in going from the crystalline into the vitreous phase.⁶ It is noteworthy that pairs of ring combinations occur simultaneously as one moves from the crystalline into the amorphous phase across the interface, as indicated by the color-coding in the plot of the number of rings of a given size after slicing the picture according to Figure 3c and defined in Figure 3d. The pair of five- and seven-membered rings (the Stone– Wales defect) occurs first and only deeper into the interface do

four- and eight-membered rings appear. At last, nine-membered rings are observed. In a way, this is consistent with the above suggestion but still must be considered as circumstantial evidence. Structures of this kind have also been observed in graphene layers,⁷ water layers on metal surfaces,⁸ and thin Cuoxide films.⁹ One may also think of forming the same structure for germania (GeO₂) prepared for silica. This has, in fact, already been done!

Knowing the structure of the thin silica film as described above stimulates many more interesting questions, which are not only connected with the glass-crystal transition but also with a number of other research areas. One of them is catalysis. Here, as mentioned earlier, zeolites, that is, alumino-silicates, play a very important role. In zeolites, the presence of aluminum substituting for silicon leads to specific ring combinations, which then build up the three-dimensional alumino-silica structure. We think it is an interesting question to ask whether this also occurs in the investigated twodimensional materials and what may be learned toward the understanding of alumino-silica formation. We have undertaken such studies¹⁰ and find that the incorporation of alumina has a strong influence on the ring size distributions within the alumino-silica layer, favoring ring sizes of four and eight. If one compares such a finding with three-dimensional zeolites, one indeed realizes that, for example, in chabasite, eight and four membered rings dominate. Whether such findings are relevant needs to be discovered, but again, the silica layer may be a platform for such investigations. Substitution of silicon in silica is, of course, not the only option. One may look into boron or germanium. Both could have interesting effects on the ring size distribution, which, in turn, would influence the chemistry of those so-called glass forms. Another thought: the chemistry of silica is widely determined by hydroxyl (silanol) groups present in the material at vacancy defects. If one wants to use these materials as models to react species from the gas phase or solution with the silica surface, it needs to contain those silanol groups. It turns out, that the silica film as prepared, both in the crystalline and in the vitreous form, is extremely stable against thermal hydroxylation. One may put the film on its substrate into water, image it with an appropriate AFM,¹¹ take it out, and bring it back into ultrahigh vacuum. However, under electron radiation, the film will hydroxylate more easily, which puts us in the position to prepare model catalysts on crystalline and vitreous supports with specific ring arrangements around a reactive center, for example, a bound metal atom carrying appropriate ligands. One should be able to image the environment of the reactive center, in spite of the fact that it is vitreous, and thus get new insight into what is called heterogenized homogeneous catalyst systems. One prominent system of this kind is the Philips catalyst based on Cr, which polymerizes ethane to polyethylene. The following questions may be posed: Is it possible to watch a polymer chain growing on the surface? Are its length and tacticity of the polymer chain correlated with the active center?

Another area, which would open up the future use of silica, would be based on the ability to peel off the silica film from the metal substrate and use it without the metal support it was grown on. Since it has been shown that the film is transferable,¹² perhaps this scenario is no longer pure science fiction. Such a development might open up avenues for new catalytic but also electronic materials, as the silica film exhibits a band gap of approximately 7 eV, and one might imagine

combinations with other two-dimensional materials in applications.

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