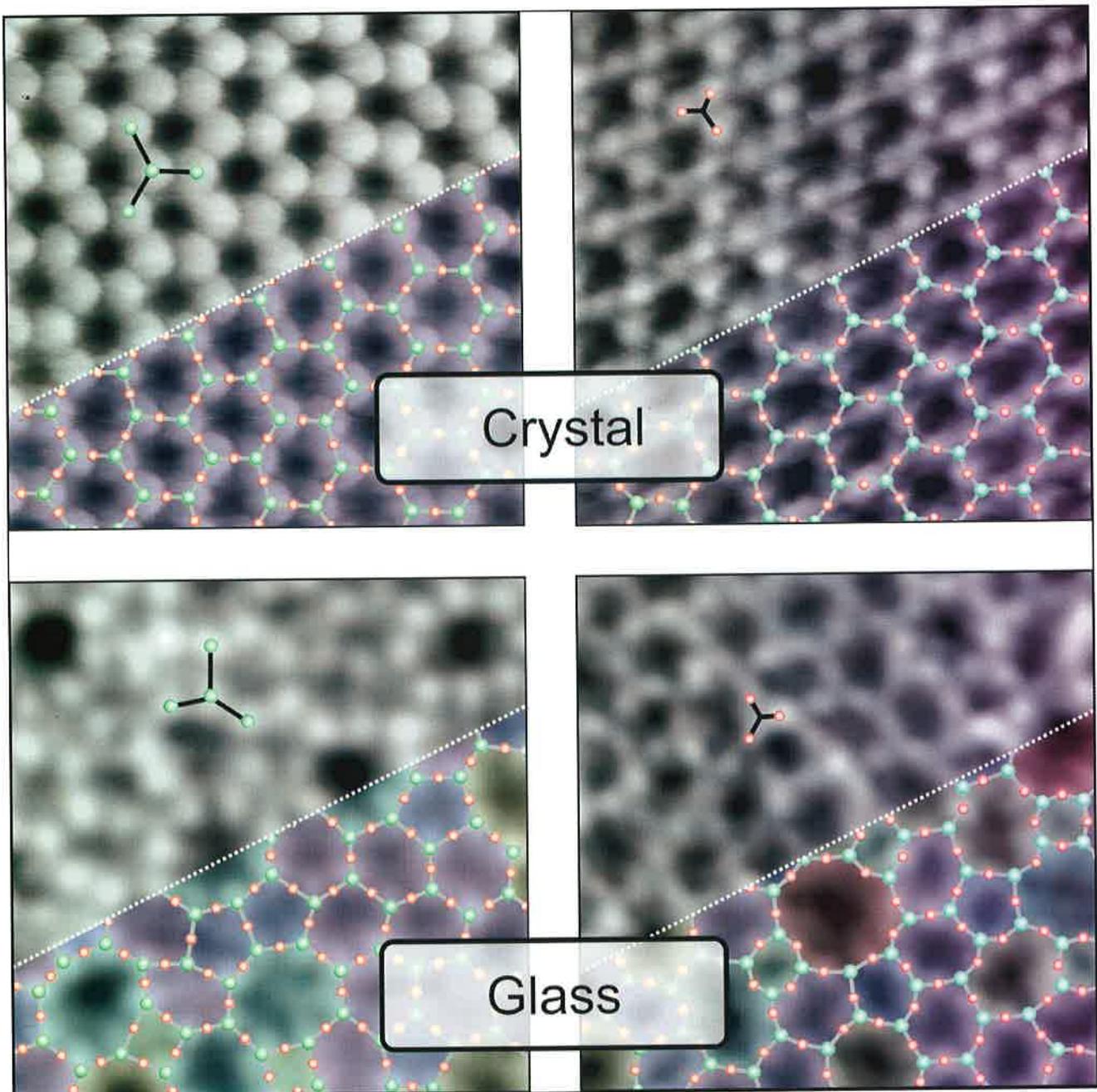


## Silicon Films

# Ultrathin Silica Films: The Atomic Structure of Two-Dimensional Crystals and Glasses

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*Dedicated to Professor Robert Schlögl on the occasion of his 60th birthday*



**Abstract:** For the last 15 years, we have been studying the preparation and characterization of ordered silica films on metal supports. We review the efforts so far, and then discuss the specific case of a silica bilayer, which exists in a crystalline and a vitreous variety, and puts us into a position to investigate, for the first time, the real space structure (AFM/STM) of a two-dimensional glass and its properties. We show that pair correlation functions determined from the images of this two-dimensional glass are similar to those determined by X-ray and neutron scattering from three-dimensional glasses, if the appropriate sensitivity factors are taken

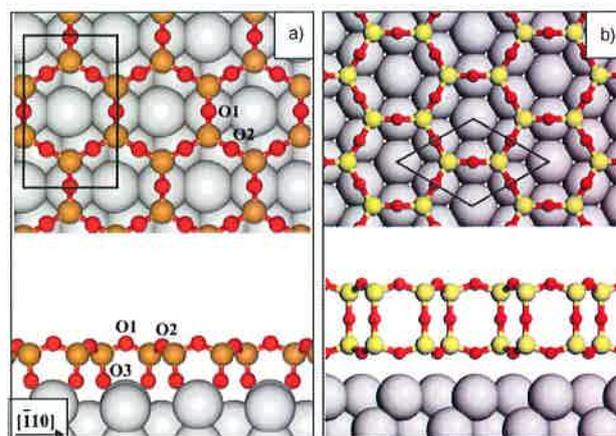
into account. We are in a position, to verify, for the first time, a model of the vitreous silica structure proposed by William Zachariasen in 1932. Beyond this, the possibility to prepare the crystalline and the glassy structure on the same support allows us to study the crystal-glass phase transition in real space. We, finally, discuss possibilities to use silica films to start investigating related systems such as zeolites and clay films. We also mention hydroxylation of the silica films in order to adsorb metal atoms modeling heterogenized homogeneous catalysts.

## Introduction

Silica films form spontaneously, when one exposes a clean, silicon, single-crystal surface to air. This oxide film plays a very important role in the functionality of silicon-based electronic devices and other important topics.<sup>[1]</sup>

The problem is that those oxide films are amorphous. They contain defects, limiting the insulating properties of the oxide films. We have, therefore, and for other reasons connected to the usability of silica as a very important support for dispersed metal catalysts,<sup>[1a]</sup> attempted to prepare well-ordered silica films. In 1998 we started to look into the ways how to prepare ordered silica films,<sup>[2]</sup> and only in 2005 did we report the successful preparation and characterization of an ordered film on Mo(112) (see Figure 1).<sup>[3]</sup>

The proposed structure was heavily debated,<sup>[5]</sup> but finally was independently corroborated.<sup>[6]</sup> Already in 1999, Klaus Heinz and his group published papers<sup>[7]</sup> in which an ordered silica film was prepared and structurally characterized on a SiC surface. This layer was, as was our Mo(112)-supported film, a monolayer of corner sharing SiO<sub>4</sub> tetrahedra forming a hexagonal pattern, in which one oxygen atom is bound to the metal



**Figure 1.** Schematic structures (top and side views) of a) the monolayer silica film on Mo(112)<sup>[3a]</sup> and b) the silica bilayer on Ru(0001).<sup>[4]</sup> The unit cells are indicated.

substrate. The drawback in this case was that the stoichiometry was not SiO<sub>2</sub>, but rather SiO<sub>2.5</sub>, since not all four corners shared another SiO<sub>4</sub> tetrahedron. This problem was finally overcome when we found a way to prepare a bilayer film on Ru(0001).<sup>[4]</sup> This bilayer film consists of two corner-sharing hexagonal SiO<sub>4</sub> networks, connected by the Si–O bond as shown in Figure 1 b. This renders the film stoichiometry as SiO<sub>2</sub>, and produces a completely saturated silica film, which is only bound to the metal substrate by dispersive forces and not by an Si–O metal bond as in the case of a monolayer. As is evident from Figure 1, the mono- and bilayers film look identical from the top, and are thus not easy to differentiate by STM. However, vibrational spectroscopy, in strong conjunction with theory, was essential to clearly differentiate between the two structures.<sup>[3, 4, 8]</sup> This is documented in Figure 2.

Figure 2 shows both the experimental infrared reflection absorption (IRA) spectra as well as the calculated frequencies and intensities. Based on the calculations, the strongest feature in the monolayer (1061 cm<sup>-1</sup>) is due to the Si–O–metal vibration and this band was shifted to higher frequency, when the silicon–oxygen–metal bond was replaced by a silicon–oxygen–silicon bond in the silica bilayer (1296 cm<sup>-1</sup>). While on the Mo(112) substrate we were only able to form a monolayer film,

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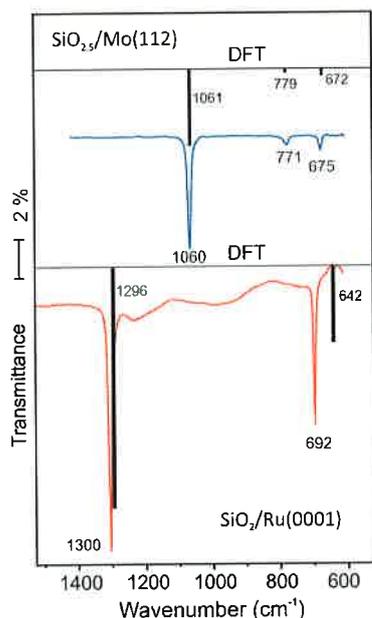
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**Figure 2.** Experimental IR spectra of the silica layers on Mo(112) and Ru(0001) in comparison with calculated frequencies and intensities.<sup>[3a,4]</sup>

on Ru(0001) it was possible to prepare both mono- and bilayer films. On Pt(111),<sup>[9]</sup> and as recently reported, on Pd(100),<sup>[10]</sup> bilayer films could also be prepared. This suggests that the oxygen affinity of the metal, used as support, plays an important role in determining which structures are allowed. In fact, as pointed out recently,<sup>[9,11]</sup> the heat of oxide formation determined for the various metals directly correlates with the observed trends. Furthermore, there is an additional interesting factor that is important in conjunction with the film formation, which brings us now directly to the specific topic of this paper: depending on preparation conditions, the bilayer film exists in a crystalline and a vitreous or glassy phase on Ru(0001),<sup>[8]</sup> while on Pt(111)<sup>[9]</sup> only the vitreous phase persists. On the other hand, Pd(100)<sup>[10]</sup> has been shown to support a crystalline phase. It is likely, that the formation of the crystalline phase is influenced by its epitaxial relationship to the metal substrate; this would not be the case for the vitreous phase. The silica system on Ru(0001) provides us, as such, with the unique opportunity to study the structure of a vitreous silica phase, as well as the transition between a vitreous and a crystalline phase in real space.<sup>[11,12]</sup>

## Experimental and Theoretical Details

The experiments discussed here have been performed in several custom-built ultrahigh vacuum systems equipped with non-contact AFM/STM, IR spectroscopy, low-energy electron diffraction (LEED), and thermal desorption capabilities within the Fritz Haber Institute. Details of the experimental setups have been published before, and may be looked up in reference [13].

Theoretical work has been carried out in the Chemistry Department of the Humboldt-Universität zu Berlin using density

functional theory with periodic boundary conditions on slab models.<sup>[14]</sup> The Burke–Perdew–Ernzerhof<sup>[15]</sup> functional augmented with a parameterized  $1/r^6$  dispersion term (Grimme-D2)<sup>[16]</sup> was employed. A typical slab model for the Ru(0001) surface would consist of an orthorhombic  $2 \times 2$  supercell ( $5.40 \times 9.35 \text{ \AA}$ ) and five layers of Ru atoms. The atoms of the two bottom layers have been fixed at their optimum bulk positions. The stability of different  $\text{Si}_m\text{O}_n$  surface models was compared using Gibbs free energies of formation per surface area. References to the details may be found in references [3a,4,8,17].

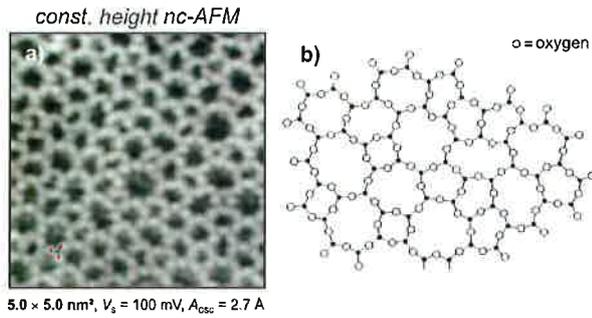
## Results and Discussion

Figure 3 shows an atomically resolved image of the bilayer film on Ru(0001) taken with the custom built NC-AFM/STM set up alluded to in the previous section.<sup>[17a]</sup>

A closer look at the observed contrast indicates that the oxygen atoms of the bilayer film are imaged: the triangular feature in the lower left corner of Figure 3 exhibits distances compatible with a model proposed more than eighty years ago by William Zachariasen,<sup>[18]</sup> who suggested that, based on the X-ray patterns observed and the typical chemistry of silicon and oxygen, an amorphous phase of silica should consist of  $\text{SiO}_4$  tetrahedra, as does quartz, the typical ordered phase of silica. In amorphous silica, however, corner-shared tetrahedra are bound to each other at random angles, allowing for different ring sizes—not only hexagons as in the crystalline form—to occur. Zachariasen depicted this idea within a two-dimensional representation, which is shown in Figure 3b. The experimental image verifies this model almost one to one. Even



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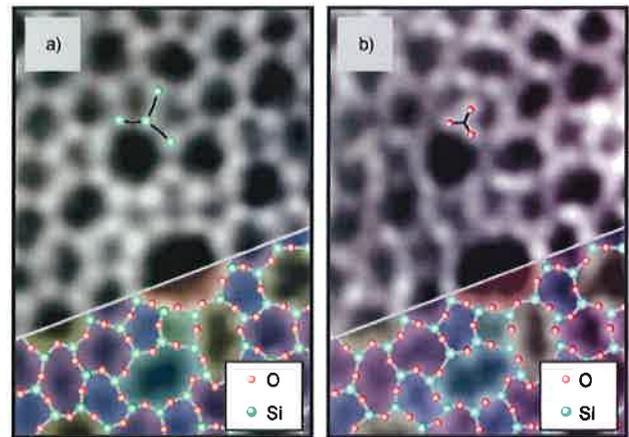


**Figure 3.** a) Atomic resolution NC-AFM Image (conditions and image size are given) of a vitreous silica bilayer on Ru(0001)<sup>[17a]</sup> in comparison with b) the original two-dimensional representation put forward by William Zachariasen.<sup>[18]</sup>

though there have been several attempts to use AFM to image the surface of a cleaved bulk oxidic glass<sup>[19]</sup> (as opposed to metal glasses, for which STM has been used with all the problems connected with the fact that STM images the electronic rather than the atomic structure<sup>[20]</sup>), it has not been possible, before the introduction of the bilayer, to obtain atomic resolution. The reason is the roughness of a cleaved surface of a bulk glass sample. In the present case the bilayer is atomically smooth, so that NC-AFM (NC = non contact) can be applied at its best. This puts us in a position to analyze this structure in some detail and we will attempt to compare the outcome with information from bulk glass samples. We note, that, after our group had published the bilayer glass structure, a second group has detected a similar silica structure on a graphene substrate using transmission electron microscopy.<sup>[21]</sup> Although they referenced our findings in their publication, which was submitted after our results had already been published, they still went on to place their results in the Guinness Book of Records (<http://www.foxnews.com/science/2013/09/13/world-thinnest-glass-shatters-records-accident/?intcmp=features>) as the first observation of the thinnest glass ever studied. In their publication<sup>[21]</sup> they provided an analysis very similar to ours, which we will discuss further below.

Let us use the special properties of our experimental set up to look at the vitreous surface, both with STM and AFM. Figure 4 shows, both, an STM and an AFM image taken simultaneously of the same area of a vitreous sample.<sup>[22]</sup>

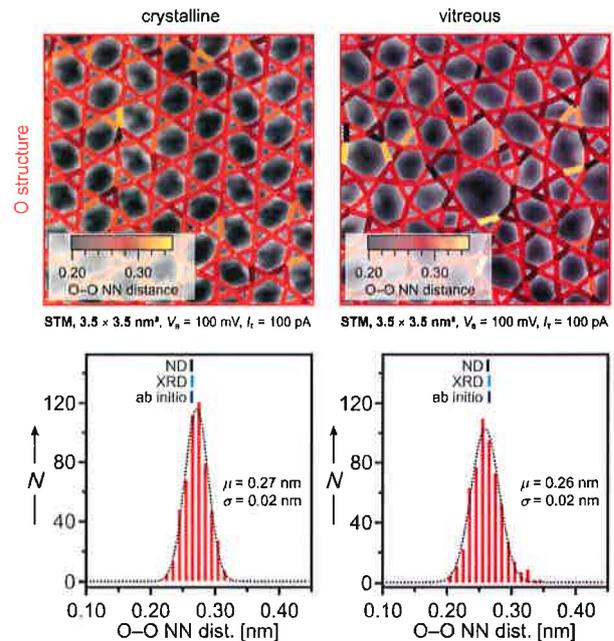
From the ring distribution imaged it is evident that we are looking at exactly the same region in space. The contrast varies between AFM and STM, and the markers, introduced into the images, indicate the positions of silicon (Figure 4a) and oxygen atoms (Figure 4b). Under the given experimental conditions, the AFM produces a Si contrast, while the STM produces an O contrast. This allows us to verify the Zachariasen model<sup>[18]</sup> directly. By changing the various conditions for recording the images (compare for example, Figures 3 and 4a), we were able to show Si and O contrast, both in the crystalline and in the vitreous phase. Let us now look at the properties of the network leading to the vitreous phase, in comparison to the crystalline phase, in more statistical detail. First, we determine, from the images the nearest oxygen–oxygen distances,



**Figure 4.** Two images representing a single atomically resolved constant height measurement. (a) AFM image; (b) STM image. Imaging parameters for a): oscillation amplitude = 0.27 nm, gray scale from  $-1.0$  Hz (dark) to  $+0.6$  Hz (bright); for b):  $V_S = 100$  mV, gray scale from 50 pA (dark) to 500 pA (bright); for both a) and b): scan area =  $2.7 \times 3.9$  nm. In panel a) the structure of the Si atoms is visible, whereas panel b) reveals the arrangement of the O atoms. Details of the measurement may be found in reference [22].

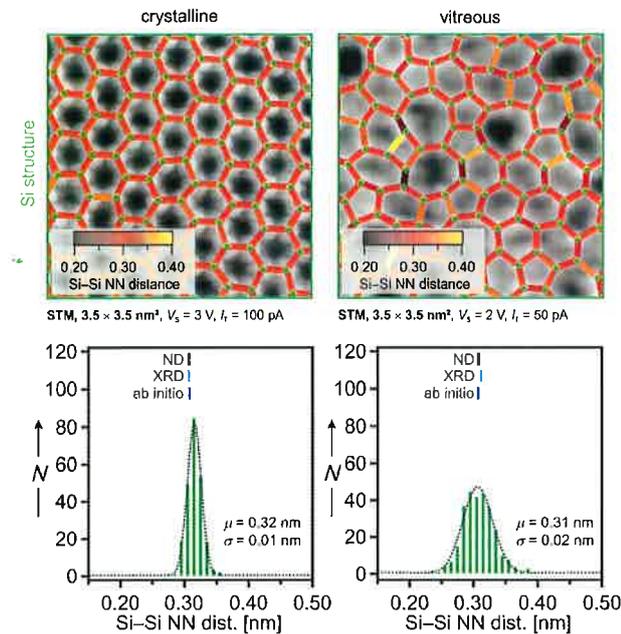
which represent the internal distances within the tetrahedra. Figure 5 shows them as bars in the images of a crystalline and a vitreous area.<sup>[11,17a,22]</sup>

The distributions are also plotted, and the position of the maxima is compared with values derived from X-ray (XRD) and neutron (ND) diffraction as well as ab initio calculations. The



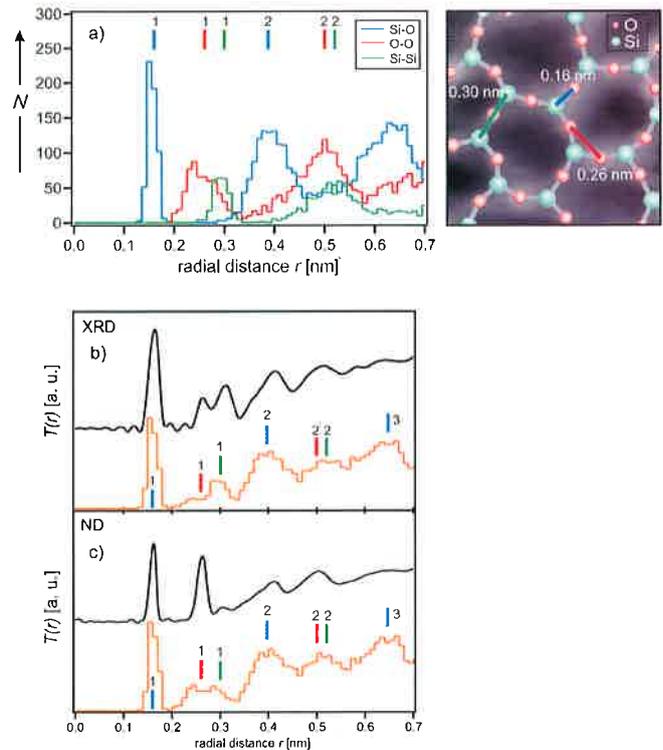
**Figure 5.** Statistical evaluation of experimentally determined O–O distances in a crystalline and vitreous bilayer of SiO<sub>2</sub> on Ru(0001).<sup>[22]</sup> The determined distributions are similar in both cases and agree well in their maximum with values determined from X-ray (XRD) and neutron (ND) diffraction as well as the expectation from ab initio calculations (respective values indicated above histograms).<sup>[23]</sup>

distributions are very similar in both phases, and so is the comparison to the reference data.<sup>[23]</sup> If we now record the Si–Si distances, which are influenced by considerable angle variations across the oxygen linkage as shown in Figure 6, it is evident that there is a clear difference between the crystalline and the vitreous phase, leading to a considerably broader distribution in case of the vitreous system.



**Figure 6.** Statistical evaluation of experimentally determined Si–Si distances in a crystalline and vitreous bilayer.<sup>[22]</sup> The determined distributions are considerably different in width as expected from the strong variations in angles, but agree well in their maximum with values determined from X-ray (XRD) and neutron (ND) diffraction as well as the expectation from ab initio calculations (respective values indicated above histograms).<sup>[23]</sup>

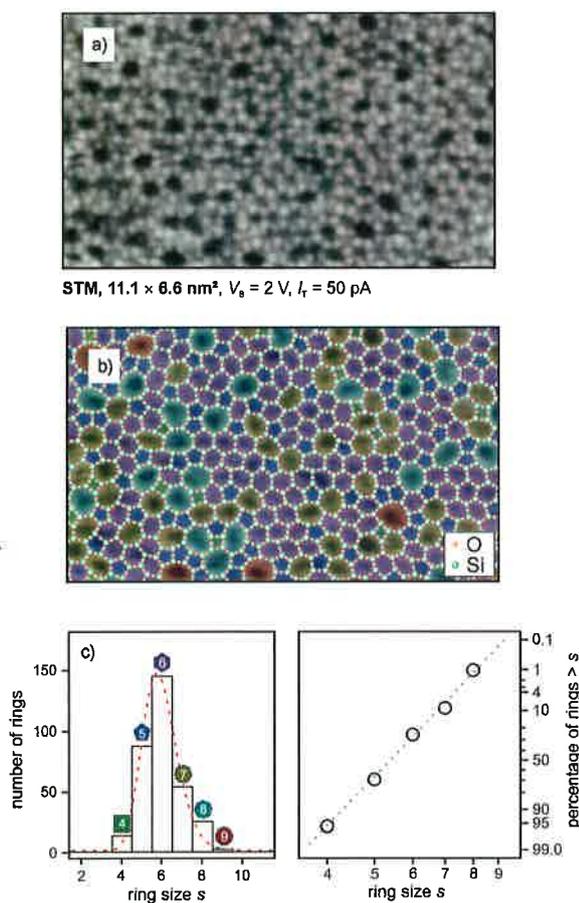
Such analyses may be performed over larger sample areas, so that one may take the Fourier transform of the spatial images, which then leads to the so called pair distribution functions. Pair distribution functions measure the number of atoms within a certain distance from a reference atom. These functions, of course, increase in value for increasing distances, and systems with nearest-neighbor order, but long-distance disorder, will show oscillations. On the basis of the real space images, we are able to determine element specific pair distribution functions, allowing us to multiply them with appropriate sensitivity factors for X-ray and neutron diffraction, sum them up into a total pair distribution function, and compare them with corresponding X-ray and neutron diffraction data from glass bulk samples.<sup>[11,17a]</sup> This is done in Figure 7. We show the element specific distributions together with the sensitivity corrected calculated pair distribution functions for X-ray and neutron diffraction, as determined from our two-dimensional bilayer in comparison with pair correlation functions determined by X-ray and neutron diffraction, respectively, from bulk glass samples. The overall comparison is quite fair: the



**Figure 7.** Pair correlation function. a) The pair distance histograms for Si–O (blue), O–O (red), and Si–Si (green). b) Comparison of the total pair correlation function,  $T_{STM}(r)$  (orange curve), with the PCF obtained from X-ray diffraction measurements on vitreous silica (black curve).<sup>[24]</sup> c) Comparison of  $T_{STM}(r)$  (orange curve) with results from neutron scattering on vitreous silica (black curve).<sup>[25]</sup>

number and the position of peaks are well reproduced, and also the increasing width of peaks with increasing distance is found in all data sets. The relative maximum intensities of the features are less well reproduced, in particular for the second peak in the X-ray diffraction data sets.

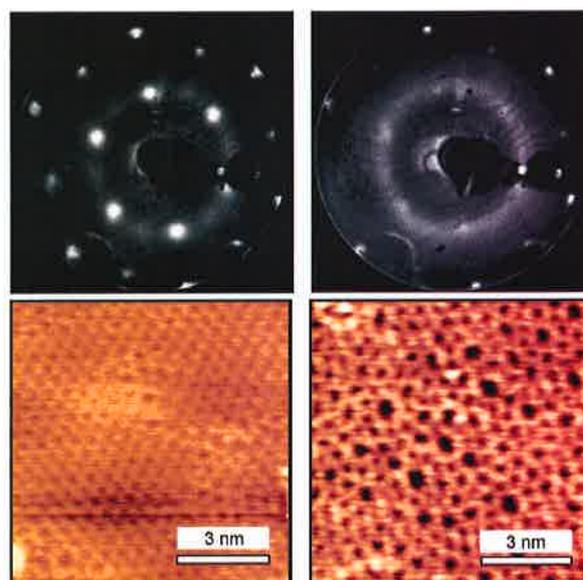
Certainly, the observed differences are connected to the fact, that in bulk glass samples one investigates three-dimensional distributions of corner sharing tetrahedra, while in the present case, the symmetry of the bilayer perpendicular to the surface plane, restricts the distribution. We had noticed this already in the first publication.<sup>[17a]</sup> However, the overall comparison of the data sets allows us to claim that the bilayer film has the intrinsic properties of a vitreous system. We are looking at a two-dimensional glass, indeed! Being able to provide real-space images allows us now to investigate ring statistics, that is, the question of how frequently certain ring sizes do occur in the glass. Figure 8a shows a large-scale image of a vitreous area, and the ring sizes in color code are shown in Figure 8b. The interesting observation is that the distribution is not symmetric (Figure 8c). While the maximum of the distribution is represented by six-membered rings, there are always more five- than seven-membered, and always less four- than eight-membered rings. As already pointed out by Shackelford and Brown,<sup>[26]</sup> the ring distribution is expected to follow a log-normal distribution, which may be tested by plotting the data



**Figure 8.** Evaluation of the ring size distribution in a vitreous bilayer of silica on Ru(0001). a) STM image, b) schematic model based on oxygen and silicon atoms, and c) ring size distribution as a bar diagram (left panel) and as a test for a log-normal distribution (right panel).

accordingly (Figure 8c). If one plots the percentage of rings larger than a certain ring size as a function of the logarithm of the ring size, one expects a linear graph. The fact that the bilayer shows exactly the expected behavior is another indication that we are dealing with a vitreous system.

We may now turn to the area of crystalline to glass transitions.<sup>[8,27]</sup> This is a very challenging area, but the system discussed here opens up opportunities to tackle this problem both in reciprocal and in real space. Figure 9 shows two STM images of a crystalline and a vitreous area, and the corresponding low-energy electron diffraction (LEED) patterns.<sup>[8]</sup> The characteristic Laue diffraction spots indicate the presence of a crystalline phase, and the diffuse ring pattern, which is much more intense in the pattern taken from a mainly vitreous area, is characteristic of an amorphous structure. Since the crystalline and the vitreous areas co-exist on the surface of the Ru(0001) metal single crystal, both domains occur at exactly the same temperature. By changing the temperature and monitoring the intensities of the features characteristic for the crystalline and the vitreous domains, we should, in particular if we use a low-energy electron microscope (LEEM), be able to record the changes as a function of temperature, and relate



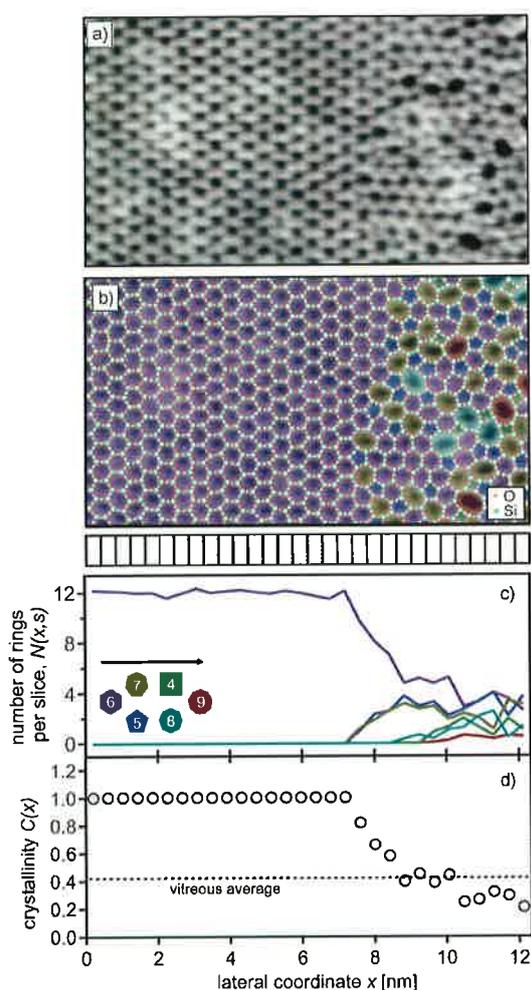
**Figure 9.** LEED patterns (at 60 eV; top) and STM images (bottom) of the bilayer silica films prepared by slow (on the left) and fast (on the right) cooling after the high-temperature oxidation step in the film preparation (tunneling parameters: 2 V, 0.1 nA (left); 3.3 V, 0.1 nA (right)).

those to the properties of the phase transition. Investigations in this direction are under way.<sup>[28]</sup>

Performing similar measurements in real space is considerably more challenging, but will also be undertaken in future. A brief look at the properties determining the interface between a crystalline and a vitreous domain, however, has already been taken. Figure 10a shows a scanning probe image of an interfacial area.<sup>[27]</sup> If one replaces this image by the corresponding model based on the measured Si and O positions one is led to Figure 10b. This plot may now be partitioned into slices, which are indicated below the plot and one may count the number of rings of a certain size within the segment (Figure 10c).

If we plot the number of six-membered rings divided by the total number of rings of any size in a slice, we obtain a crystallinity factor. This is 1.0 in the crystalline phase, because the six-fold ring is the only ring size occurring in this region, and drops as one enters the vitreous phase. The crystallinity of a large vitreous area of the bilayer film was determined to 0.4 and this value is plotted as a reference in Figure 10d.

Figure 10d contains the plot of the crystallinity factor, which indicates that the width of the interfacial region, before the vitreous average is reached, is of the order of 2–2.5 nm. With this it is possible to also plot the occurrence of the various ring sizes in the interfacial region. This is shown in Figure 10c by the color-coded number of rings per slice. The various ring sizes do not occur at the same position in the interfacial region. In fact, certain ring sizes occur simultaneously, and some combinations occur closer to the crystal domain than others, as the interfacial region is entered from the crystalline domain. Based on calculations of how much energy is necessary to change an arrangement of four six-membered rings into two five- and two seven-membered rings versus two four- and



**Figure 10.** Evaluation of the crystal–vitreous interface. a) STM image ( $V_s = 2$  V,  $I_t = 100$  pA, scan area =  $12.3 \times 7.0$  nm), b) atomic model of the layer based on a) as well as the position of 30 vertical, 0.41 nm wide and 6.95 nm high slices. c) The number of rings per slice for every ring size plotted versus lateral coordinate. d) Crystallinity of every slice plotted versus lateral coordinate.<sup>[27]</sup>

two eight-membered rings,<sup>[17a]</sup> it turns out that the former costs less energy than the latter. This is consistent with the general knowledge that the Stone–Wales defect (a combination of a five- and a seven-membered rings) is the lowest energy defect in a hexagonal network.<sup>[29]</sup> Similar conclusions have also been reached for graphene.<sup>[30]</sup> Recently, a group has studied the formation of such defects in the transmission electron microscope and observed the transformation under the electron beam directly.<sup>[31]</sup> One of us has summarized the knowledge in this area within a perspective, published concomitantly to those results.<sup>[32]</sup>

## Summary and Outlook

Thin oxide film systems are well suited for studying a number of phenomena and problems in physical chemistry joining efforts in experimental and theoretical research.

The one line of experiments and theoretical studies described in this Minireview indicates that, even though, in the first place the problem was examined in order to study model systems in heterogeneous catalysis, by the ability to investigate those systems at the atomic scale, we may also learn more about fundamental aspects in physical chemistry and chemical physics. Certainly, the investigation of crystalline and vitreous silica phases co-existing on a Ru(0001) metal surface will allow us to tackle one of the unsolved problems in physical chemistry, that is, the real-space observation of the crystal–glass phase transition. This also poses challenges to theory. We have started to compare the results for the present system with other materials systems, such as two-dimensional Cu oxides and even bubble rafts, in order to generalize on the topological investigations of amorphous systems.<sup>[33]</sup>

Based on the ability to prepare and characterize silica films at an atomic level, we may start to contribute to a number of further interesting areas, such as zeolites,<sup>[34]</sup> clays,<sup>[17b]</sup> and heterogenized homogeneous catalysts.<sup>[35]</sup>

It had been a dream, for example, for a long time to be able to contribute to understanding zeolite chemistry using surface science tools. This is evidently difficult, as zeolite chemistry happens within the solid in micro- and meso-sized pores. However, by replacing some of the silicon atoms in the bilayer silica films, we have been able to create an aluminosilica film that exhibits characteristic features of a zeolite. In particular, we are able to demonstrate the formation of very acidic OH groups on the film. We are now well positioned to investigate with NC-AFM how the doping of a silica film with aluminum atoms in specific positions influences the formation of particular ring sizes and ring assemblies. We may look at such flat zeolite films as representing systems with an infinite cavity.<sup>[34]</sup>

We have recently shown through a combination of theory and experiment that one may also prepare clay structures in thin films, that is, iron-silicate structures.<sup>[17b]</sup> The structure identified consists of an iron-oxide layer bound on one side to a silica layer and on the other side to a Ru(0001) conserving the bilayer structure. This structure is similar to the structure of the clay mineral nontronite, which opens another new area of oxide film research.

By depositing metal atoms by physical vapor deposition and further engineering of their ligand sphere, we should be able to create systems exhibiting characteristics of silica-bound complexes. A series of studies on monolayer films has already been conducted.<sup>[35,36]</sup> However, the bilayer offers the advantage that the surface is less strongly influenced by the presence of the metal underneath due to the weak bonding. One important step towards this is the ability to specifically hydroxylate the silica film.<sup>[37]</sup> We could then even use prefabricated complexes to bind them to those OH groups. Again, studies on the monolayer films have started and are successful. Those results need to be transferred to the bilayer system.

There is more to come, and we may even try to go to thicker, well-ordered silica films, and beyond.

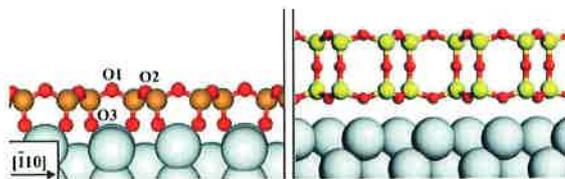
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**Keywords:** bilayers · silicon · surface chemistry · thin films

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## MINIREVIEW



**Polishing up the crystal glasses:** An overview of the preparation and characterization of ordered silica films on metal supports is reported. In particular the specific case of a silica bilayer, which exists in a crystalline and a vitreous variety is discussed and a model of

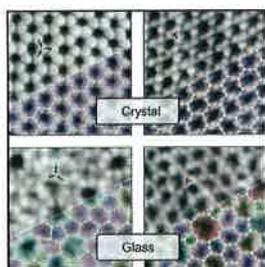
the vitreous silica structure proposed by William Zachariasen in 1932 is verified. Beyond this, the possibility to prepare the crystalline and the glassy structure on the same support leads to the study of the crystal-glass phase transition in real space (see figure).

### ■ Silicon Films

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■■ - ■■

**Ultrathin Silica Films: The Atomic Structure of Two-Dimensional Crystals and Glasses**



### Ultrathin Silica Films

In their Minireview on page ■■ ff., H.-J. Freund et al. describe how the investigation of crystalline and vitreous silica phases co-existing on a Ru(0001) metal surface allowed them to tackle one of the unsolved problems in physical chemistry, that is, the real-space observation of the crystal-glass phase transition.