Chapter 16 The Atomic Structure of Two-Dimensional Silica

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Abstract Determining the structure of amorphous materials used to be challenging due to the complexity of this material class. Despite many attempts to resolve amorphous materials by various diffraction methods as well as scanning probe methods, no-one has yet been able to carry out atomic imaging and to clearly identify the structure of amorphous materials. Only modern preparation methods in combination with advanced scanning tunneling and atomic force microscopy have succeeded in decrypting the everyday material glass. A bilayer silicate film on a ruthenium single crystal has been developed at the Fritz-Haber Institute. On the atomic level, this film is flat and ideal for using scanning probe microscopy. For the first time a clear image of an amorphous material has been obtained which allowed for the derivation of atomic sites and a detailed analysis from real space coordinates. The text book example of the vitreous silica structure proposed by William Zachariasen in 1932 has thereby finally been verified.

16.1 Introduction

The aim of this work is to explore previously unresolved complex surface structures and to address one of the biggest riddles in solid state physics, namely the structure of amorphous materials. Resolving and characterizing the real surface morphology

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© Springer International Publishing Switzerland 2015 S. Morita et al. (eds.), *Noncontact Atomic Force Microscopy*, NanoScience and Technology, DOI 10.1007/978-3-319-15588-3_16 at the atomic scale is key to answering this fundamental question in surface science. Often the focus in surface science studies is on crystalline, ordered, and well defined surfaces. But the atomic arrangement of oxides, and in particular their surface and defect structures, can range from highly ordered and symmetric to more complex and even completely amorphous networks.

The prototype for amorphous network structures is silicon dioxide. This material is the simplest and most common type of glass. Many elements and compounds can form glasses and some of the oldest man-made objects found are glass materials [1-3].

Glasses are remarkably versatile and important as an engineering material. Glass manufacturers envision the future organization of communication and connectivity involving glass in a variety of forms and functions [4]. Their ideas range from hand-held display glass, electrochromic glass, architectural glass, automotive display and design glass, photovoltaic glass, glass optical fibers to all weather surface glass. Towards this end, glasses should have tunable properties depending on their application. For example, being thin, lightweight, damage resistant, touch sensitive, color sensitive, ultraviolet and visible light filtering, thermally insulating, durable and so on. Glass materials and especially silicates are relevant in various branches of modern technologies, e.g., in semiconductor devices, optical fibers and as a support in industrial catalysis. In order to push this material class forward, we must develop greater understanding of their structures and properties at the atomic scale.

Glasses show unique properties that often depend on the precise process by which they are formed. A common way of making glass is by rapidly cooling from a highly viscous liquid to avoid crystallization. The atomic and molecular processes by which liquids transform into amorphous solids are not fully understood. A review on the current theoretical knowledge of the complex process of glass formation was presented by Debenedetti and Stillinger [5]. A detailed understanding of the glass transition would have widespread implications not only for inorganic glasses, but also for organic polymers, protein dynamics, protein folding and population. To gain a clearer understanding of the complex dynamics involved, the identification of a relationship between different minimum states on the energy landscape is necessary. There is clearly a need for resolving the structure of glass forming materials in their various phases.

Figure 16.1a illustrates how similar crystalline and amorphous samples can be. It shows a crystalline silicate, also called quartz, together with an amorphous silicate, i.e. a glass. The two samples exhibit many similar physical properties [7]. For example, due to very similar optical transparency, it is not possible to distinguish the two states with simply the naked eye. But what is the difference between these two phases? Comparative investigations of crystalline and amorphous silicon dioxide samples were undertaken around a hundred years ago, almost as soon as the Laue method for the diffraction of X-ray or neutron beams on solid bodies had been developed. These methods average over large sample volumes on the macroscopic scale and primarily provide information in reciprocal space. Crystalline samples produce discrete diffraction patterns while glasses do not. The diffraction information obtained from glasses can be compared with theoretical models of possible atomic



Fig. 16.1 Comparison of the structure of crystalline and amorphous materials. Illustration **a** shows a crystalline silicate sample next to an amorphous one. Both samples are optically transparent. Surprisingly, this similarity also holds for most of the mechanical and physical properties for these two phases. W.H. Zachariasen postulated a model for crystalline (**b**) and amorphous (**c**) structures in a two-dimensional representation, depicted here following the example of [6]

arrangements, but do not allow an unequivocal structural assignment. This is one of the greatest problems at the interface between experiment and theory, to get beyond the "averaged" character of diffraction data. For surfaces, at least, the following sections provide a solution beyond this.

16.2 The 2D Glass Model

W.H. Zachariasen postulated the so-called "Random Network Theory" 80 years ago to explain the structure of amorphous materials [6]. At that time, there was a large debate about whether glasses are built up from crystalline material [8]. Zachariasen attempted to rule out the crystallite hypothesis. Due to the comparable mechanical properties of amorphous and crystalline materials he assumed that the bonding forces between the atoms in the two phases should be essentially identical. The lack of periodicity and symmetry are the main features that distinguish a glass from a crystal. Early on it had been suggested that tetrahedral atomic configurations were required to form glasses. Zachariasen used these predictions to sketch an atomic picture of a glass. In his paper he reduced the three-dimensional (3D) picture into a two dimensions (2D) analogy (Fig. 16.1b, c).

For silicon dioxide, the simplest structural unit in the 3D case is a SiO₄ tetrahedron. If the complexity of the system is reduced from 3D to 2D, the simplest structural unit for silicon dioxide changes from the SiO₄ tetrahedron to a SiO₃ triangle. The red triangle in Fig. 16.1b, c marks the SiO₃ building unit. In Fig. 16.1b these SiO₃ triangles are linked to each other as individual building blocks at fixed 180° angles, corresponding to a crystalline material. This creates long-range order and periodicity.

If the angle between these structural units varies, the building blocks can develop an extended network with rings of different sizes. As can be seen in Fig. 16.1c, the uniform structural units are linked to each other at apparently random angles. Zachariasen drew a 2D diagram in which trigonal units are linked together to create the amorphous network. Due to the large variety of Si–O–Si angles which bridge two neighboring building units, the glass structure lacks periodicity and long range order.

The illustration of the atomic structure in Fig. 16.1c became the most widespread picture for glass. This model was compatible with the existing data from X-ray and neutron diffraction of amorphous materials. Therefore, these postulates were very useful in explaining diffraction experiments on glasses [9].

Although this model has been widely used to explain structures in amorphous materials, it has never been observed in real space before. Can a similar reduction of the 3D structure to a 2D model system also be realized and characterized experimentally?

16.3 The Realization of an Amorphous Model System

The "Chemical Physics" Department of the Fritz Haber Institute is developing and studying model systems in the context of catalytically important processes. Our model systems make it possible to depict part of the complexity of dispersed real catalysts and investigate them by surface science tools. This involves producing thin, well-ordered oxide films on metal single-crystal substrates, which can also be studied under the experimental conditions of surface physics.

The first steps in surface science studies are to determine where the atoms are situated at the surface and to assign the different chemical species. In this context a reduction of complexity is necessary, and thus model systems which allow for a high degree of control over the preparation conditions are required.

In our department thin silicate films had already been specifically prepared back in 2000 [10] in order to be able to study catalytic surface reactions. The first studies investigated silicate films on molybdenum single crystals [10]. More recent work for other metal substrates, including ruthenium [11, 12], has been presented. By using different metal single-crystal substrates it is possible to exert a crucial influence on the growth of these thin silicate films. While on the molybdenum single crystals predominantly crystalline films of monolayer thickness are formed, with ruthenium



Fig. 16.2 *Side view* of the different silicate films with respect to different single-crystal substrate. a Silicate monolayer on a molybdenum single crystal [10], b silicate monolayer on a ruthenium single crystal, c silicate bilayer on a ruthenium single crystal [11, 12]

single crystals it is possible to specifically produce monolayers as well as bilayer silicate films. A detailed description of the sample preparation procedure can be found in [12].

Figure 16.2 shows a side view of models for these film systems. In (a) and (b) the monolayer silicates have an oxygen back bonding to the underlying metal substrate.

In contrast, the bilayer film sketched in (c) is only weakly coupled to the metal support. Surprisingly, the bilayer silicate film on ruthenium single crystals can be produced in crystalline [11] as well as amorphous structure [12]. The film's registry to the underlying crystalline metal substrate can be lost. Thus, the film is structurally decoupled from the metal support. This is evident from measurements with low-energy electron diffraction (LEED).

But can this model film system be used to observe the atomic structure directly and thus corroborate the postulate of amorphous materials?

16.4 The Limits of Scanning Probe Methods

Today, there are promising new surface science tools available. During the last decades the development of scanning probe microscopy (SPM) has had a tremendous impact as an analytical tool to determine structural, spectroscopic as well as dynamical aspects from all kinds of surfaces. Just a few years after its invention by the group of Binnig and Rohrer, the scanning tunneling microscope (STM) [13, 14] turned into one of the most widely used surface analytical methods. In 1986, Quate together with Binnig presented the principle of the atomic force microscope (AFM) [15]. The AFM is an important addition to the STM, because it does not require conducting sample surfaces. However, it should be mentioned that it took almost ten more years to record atomically resolved images by AFM after its invention [16]. Up to today the number of research groups working with advanced AFM

techniques, especially noncontact atomic force microscopy (nc-AFM), is relatively small compared to STM [17, 18].

SPM has been applied to a large variety of problems throughout the natural sciences, ranging from solid state physics to structural biology. Its cheap and relatively simple design, and the large range of applications by SPM methods, make it a valuable tool to study nature. SPM imaging can be done on a wide range of sample types, from atomically flat metal surfaces to living cells [19], and can be performed in vacuum, air, or liquid. This opens up a wide scope for experiments. Special setups were developed for low [20–23], ultralow [24, 25] and variable-temperature studies [26, 27] in ultrahigh vacuum (UHV). Adaptations to perform measurements under high pressure [28], in liquids [29], at high speed [30, 31], time-resolved [32], or in magnetic fields [33] have been conducted as well.

STM and AFM have been used extensively in the field of surface science to characterize surface morphology, structure, physical and chemical properties of bulk and epitaxial samples [34]. The direct observation of molecular film structures [35, 36] as well as the recent achievements in resolving the chemical structure of single molecules supported on flat crystals [37] are promising results. Besides the pure structural analysis, even individual atoms [38] and molecules [39, 40] were manipulated by SPM.

Nevertheless, the atomic resolution of complex surface structures with large unit cells and individual defect network structures still remains a challenge, and only a few examples have been published [41]. The idea of characterizing amorphous surfaces by STM was proposed by Wiesendanger et al. [42] in 1987. Since then, many attempts have been made to atomically resolve amorphous materials, e.g. by SPM [43–48]. However, this goal has never been achieved so far. An early measurements on glass samples made by the research group of Klaus Wandelt and colleagues showed the potential of these methods. However, it has been heavily debated, whether these results provide real atomic coordinates or not.

What is the reason behind this and what are the principle limitations of SPM methods in general? These techniques often suffer from tip convolution effects [49]. Slightly lower lying surface sites are often not imaged due to shielding effects of the neighboring atoms. In the case of corrugated sample surfaces a complicated convolution between tip and sample species takes place. The situation has been sketched in Fig. 16.3 where the number of involved tip atoms is different for corrugated (a) compared to planar (b) sample surfaces.

Furthermore, it is often very demanding to separate electronic from topographic features in STM [44], as well as to distinguish the chemical sensitivity of changing tip apexes towards different surface sites, both in STM and AFM. In a stable imaging mode typically only one type of species is imaged on the sample surface, either the anionic or the cationic site, depending on the actual tip configuration. However, if the probing tip apex is changing then this situation is hard to disentangle.

Clearly, a solution to these challenges is the reduction of dimensionality by using well defined thin film systems grown on metal single crystals while retaining essential aspects of the complexity of real systems. The growth of two-dimensionally flat



Fig. 16.3 *Side view* of a scanning probe tip with respect to a corrugated sample surface in (a) and a 2D flat film system depicted in (b). Although the same tip is assumed in both cases, there is a different number of tip atoms with a similar distance to the underlying sample surface atoms. Depending on the probe position, three or more tip atoms contribute directly to the imaging signal for the corrugated sample surface in (a), while in the case of flat film terraces one atomic tip site is favored in (b)

model systems under carefully controlled preparation conditions allows the use of SPM to gain insight into individual atomic scale surface structures as presented in this book chapter.

16.5 Assignment of Atomic Positions

Here, we present the atomic arrangement of a thin vitreous silica bilayer film grown on Ru(0001) [12]. Details on the experimental setup can by found in the text book series "Noncontact Atomic Force Microscopy Volume 2" in Chap. 7 [18] as well as in the following [50–53]. An atomically resolved constant height nc-AFM image of the vitreous silica film is shown in Fig. 16.4a (scan size = $5.0 \text{ nm} \times 3.8 \text{ nm}$). It is useful to look again at the postulates made by Zachariasen in 1932 [6], sketched for comparison in the lower part of Fig. 16.4a. The complex atomic arrangement of this 2D network film shows a striking similarity.

The observed protrusions at atomic separations are arranged in triangles. By comparing to Zachariasen's model and based on this triangular symmetry the protrusions can be assigned to one face of a tetrahedral SiO_4 building block. Consequently, the protrusions correspond to O atoms (red balls in Fig. 16.4b). Such a triangular unit has been marked by a red triangle in Fig. 16.4.

Here, an O sensitive contrast is observed and the position of the Si atoms has been calculated based on the O coordinates. The Si coordinates are determined using a circumscribed circle around every O triangle. The position determined by this



Fig. 16.4 Assignment of atomic positions [54]. **a** Constant height nc-AFM image with atomic resolution ($V_S = 100 \text{ mV}$, $A_{OSC} = 2.7 \text{ Å}$, scan range = 5.0 nm × 3.8 nm), Zachariasen's picture of the atomic arrangement in a glass is shown for comparison [6]. **b** Image from (**a**), partly overlayed with O model (*red balls*). **c** Image from (**b**), overlayed with the complete model of the topmost Si (green balls) and O atoms

method has the same distance to all the triangle's corners. By placing a green ball in the center of each resulting circle the Si atom is marked. In this way the 2D model of the topmost O and Si atoms has been completed.

Such a structural model completely covers the nc-AFM image presented in Fig. 16.4c. The film consists of rings with different sizes. No crystalline order is observed in this film structure. All of these atoms as viewed from the top plane of the bilayer are arranged in SiO₃ triangles. No under- or over-coordinated species were observed.

This structure corresponds to a network of corner-sharing SiO₄ tetrahedra. The film is highly ordered in the *z*-direction, while it is vitreous in the *xy*-plane (image plane). The SiO₄ tetrahedra of the first layer are linked via bridging O atoms to the SiO₄ units of the second layer with a Si–O–Si angle of 180°. The linking O atoms represent a mirror plane. The character of this 2D flat film is a result of these particular structural elements. Looking from the side, the film structure as shown in Fig. 16.2c consists of four-membered rings standing upright and connected randomly, forming the 2D ring network. A height difference between the topmost Si and O atoms from the density functional theory (DFT) model for the crystalline silica bilayer (52 pm) [11] has been used to compensate for the lack of information in the third dimension for the later evaluations of the atomic coordinates. This assumption has been proven valid in [55].

Let us look again at the observable image contrast in nc-AFM and STM images [55]. Both techniques provide a contrast that allows for identification of individual atomic sites. The observed chemical sensitivity of nc-AFM and STM strongly depends on the microscopic tip configuration. A modified tip termination can make the Si instead of the O positions visible [55]. A sensitivity to the Si positions results in a different local arrangement and distance between the resolved atomic sites.



Fig. 16.5 a Sketch of the used tuning fork sensor device for nc-AFM/STM [52]. The STM tip is electrically connected by a thin Pt/Rh wire with a diameter of 50 μ m. Both the tip and Pt/Rh wire are insulated from the tuning fork and its electrodes. This is necessary to prevent a cross coupling between the nc-AFM and the STM signal. **b**, **c** Both images represent a single atomically resolved constant height measurement, where (**b**) shows the nc-AFM and (**c**) the STM channel. Imaging parameters **b** oscillation amplitude = 0.27 nm, gray scale from -1.0 (dark) to +0.6 Hz (bright); **c** $V_S = 100 \text{ mV}$, gray scale from 50 (dark) to 500 pA (bright); **b**, **c** scan area = 2.7 nm × 3.9 nm. In (**b**) the structure of the Si atoms is visible, whereas (**c**) reveals the arrangement of the O atoms. Also here an atomic model of the topmost layer of the silica film is superimposed onto the lower right corner of the images in (**b**) and (**c**) (green balls Si atoms, red balls O atoms)

Our sensor device has the capability to directly combine nc-AFM and STM. This device is sketched in Fig. 16.5a. When the tip is probing the sample surface, we can detect the interaction force and the tunneling current independently. Here, we can simultaneously and at the same atomic site gather data about interaction forces and electronic structure without cross-talk. Essentially we develop a more complete understanding of the surface by employing the full benefits of AFM and the full benefits of STM in parallel. These provide distinct, but complementary information about the surface.

This unique setup is capable of resolving clearly separated features from the surface in these two detection channels. Figure 16.5b, c represent one single atomically resolved constant height nc-AFM and STM measurement above a vitreous region of the silica film. Figure 16.5b is a map of the frequency shift (Δf), while Fig. 16.5c is the simultaneously recorded map of the tunneling current (I_T). Both images show a ring network with pores of various sizes. The power of this approach becomes clear if we take a closer look at the atomic structures that were resolved. While the Δf -map in Fig. 16.5b shows the Si positions (green balls), the I_T -image in Fig. 16.5c reveals the O positions (red balls) of the topmost silica layer.

In the top part of Fig. 16.5b, c this can be verified by looking at the nearest neighbor (NN) configurations of the imaged protrusions. In Fig. 16.5c the contrast in the STM signal is similar to nc-AFM image in Fig. 16.4. Every three protrusions (red balls) form a triangle representing one triangular side of an SiO₄ tetrahedron. Therefore, these positions correspond to O atoms. However, in Fig. 16.5b, four protrusions (green balls) form a three-bladed windmill with one protrusions sitting in

its center. These positions represent the centers of four different tetrahedra and therefore correspond to the Si atoms. Furthermore, the NN distances are characteristic for a certain atom type and are significantly larger for Si than for O. The structural information of both channels can be combined in this case to obtain a complete surface model without any further assumptions as plotted in the bottom part of Fig. 16.5b, c.

Please note, that also combinations of nc-AFM and STM images have been observed in which the same surface species have been detected.

In the following analysis the atomically resolved nc-AFM image and the derived model of the topmost layer from Fig. 16.4 has been used as a starting point for further evaluation of the thin film's structure.

16.6 Atomic Force Microscopy Challenges X-Ray Diffraction

In the following section, the atomic structure of the vitreous silica bilayer is discussed and compared to the structural data available from diffraction methods. Since the invention of X-ray diffraction by von Laue, crystalline and amorphous materials have been analyzed over the last century. Figure 16.6a provides the diffraction pattern



Fig. 16.6 Silica X-ray diffraction data. **a** X-ray diffraction pattern from a powder sample of α -quartz (**a**) and vitreous silica (**b**) [58]. **c** X-ray PCF of bulk vitreous silica taken from [59]. Within this plot the ranges of order as proposed by Wright have been indicated for range I, II, III, and IV [56]

of a powder sample from α -quartz. Herein, the randomly oriented crystalline grains in the powder produce a sharp ring pattern. The diffraction pattern of vitreous silica given in (b) only exhibits diffuse halos. Figure 16.6c shows a typical pair correlation function derived from X-ray diffraction data from vitreous silica. A classification introduced by Wright, who divided the order in network solids in four ranges, is used. The following section is divided accordingly into the ranges: I structural unit, II interconnection of adjacent structural units, III network topology, and IV longer range density fluctuations [56, 57].

In range I, the basic structural unit (SiO₄ tetrahedron) is addressed and parameters from the X-ray PCF can be extracted by using peak fitting techniques. However, in ranges II and III, simple extraction of structural parameters is not possible and models are required for interpretations. In range II the interconnection and relative orientation of two corner-sharing SiO₄ units is involved. Here, the variable parameters of the Si-O-Si bond angle and torsion angles can be defined. In this range the first example of disorder in comparison to crystalline modification can be observed. Range III describes the network topology of amorphous network solids. In this range a description of the first neighbors and shortest path statistics has always been desired, but has never been observed in real space before. In the literature a controversial discussion can be found, where theoretical models have been tested by comparison to PCFs from XRD or ND. In range IV the long range density fluctuations are addressed. However, the density differences between more and less ordered regions are likely to be relative small. While there is quantitative knowledge about ranges I and II, ranges III and IV are still much less understood and hence leave opportunities for new developments.

The different orders are visualized by snapshots of atomic structures in Fig. 16.7. This classification turned out to be extremely useful to discuss and interpret the structural information in diffraction experiments.

16.6.1 Structural Unit—Range I

This range deals with the tetrahedron unit schematically drawn in the inset of Fig. 16.8e. A tetrahedron is primarily defined by the side length and the tetrahedral angle. The distance from the center to one corner is another characteristic parameter. With this respect the Si–O, the O–O distance, and the O–Si–O angle have been analyzed.

Figure 16.8a shows the model from Fig. 16.4a with colored bars connecting all Si–O nearest neighbors (NNs). A color coded scale bar represents the Si–O bond length.

Figure 16.8b displays the corresponding histogram of the Si–O distances. A Gaussian distribution was fit to the data and yielded an Si–O mean distance of 0.16 nm with a standard deviation of 0.01 nm. This is in excellent agreement to XRD [59] and ND [60] data obtained on bulk vitreous silica, which are indicated by black arrows in Fig. 16.8b.



Fig. 16.7 Ranges of order in network solids. A 3D arrangement of silica structures for different length scales has been plotted (Si *green*, O *red*). **a** The structural unit of the SiO₄ tetrahedron is assigned as range I. **b** is range II where adjacent units are interconnected. **c** Range III is the network topology while **d** is range IV in which longer range density fluctuations can be analyzed



Fig. 16.8 Characterization of the structural unit in range I [54]. **a** Constant height nc-AFM image $(V_S = 100 \text{ mV}, A_{OSC} = 2.7 \text{ Å}, \text{scan range} = 5.0 \text{ mm} \times 5.0 \text{ nm})$, colored bars representing the Si–O nearest neighbor (NN) distance (see *scale bar*). A cut-out of this image is also given in Fig. 16.4a. **b** Histogram of the Si–O NN distances. Average values from diffraction experiments on bulk vitreous silica are indicated by *black arrows* [59, 60]. **c** Same nc-AFM image from (**a**), superimposed by colored bars representing the O–O NN distance (see *scale bar*). **d** O–O NN distances given in a histogram. Results from diffraction experiments on bulk vitreous silica are indicated by *black arrows* [59, 60]. **e** O–Si–O angles in a histogram plot. The *black arrow* indicates the angle of 109.47°, corresponding to a regular tetrahedron

In Fig. 16.8c the O–O NN distances are visualized. The O–O distances exhibit similar lengths throughout the whole image. The O–O NN distance histogram is shown in Fig. 16.8d. By fitting the data with a Gaussian distribution one can obtain a mean O–O NN distance of 0.26 ± 0.03 nm. As the black arrows indicate, this experimental value agrees well with XRD and ND measurements on bulk vitreous silica [59, 60].

Furthermore, all O–Si–O angles in the atomic model have been computed in the histogram of Fig. 16.8e. A symmetric distribution with an average of 107° and a standard deviation of 17° of the intratetrahedral angle is shown. Once again, this value agrees well with the 109.47° angle in a regular tetrahedron and the 109.8° angle deduced from XRD experiments on bulk vitreous silica [59].

In the order of range I the thin vitreous silica film reproduces the structural parameters derived from diffraction measurements on bulk vitreous silica. Nevertheless, range I order is not determining the characteristic features of the vitreous state. This range consists of well-defined building blocks (SiO₄ tetrahedra) and is defined by the chemical Si–O bond characteristics. Characteristic features of the vitreous structure can be found in the longer ranges.

16.6.2 Interconnection of Silica Units—Range II

This range is characterized by the interconnection of neighboring tetrahedral building blocks. By looking at the distance between the tetrahedral centers and the connection angle, this linkage can be evaluated. In this section, the Si–Si NN distance and the Si–O–Si angle are analyzed. A schematic is plotted in Fig. 16.9c marked by arrows.

The real space distribution of Si–Si NN distances is shown in Fig. 16.9a. The colored bars represent the distance between two neighboring Si atoms. The corresponding length is given in nm in the scale bar. In Fig. 16.9b the corresponding histogram for the Si–Si NN distances is plotted for the image in (a). A mean Si–Si NN distance of 0.30 ± 0.02 nm has been derived from a Gaussian fit to the data. The derived measurements are compared to XRD and ND results on bulk vitreous silica, indicated by black arrows. The small offset can be explained by a larger variety of Si–O–Si angles in 3D bulk silica compared to the 2D film structure.

Therefore, a histogram of the Si–O–Si angles is shown in Fig. 16.9d. In the Si–O–Si angle distribution a characteristic asymmetric shape is visible. A mean Si–O–Si angle of 139° with a standard deviation of 3° is obtained by fitting the data with a Gaussian function.

In the literature this Si–O–Si angle has been largely debated within the glass community [57, 63]. It is a very important angle for vitreous networks, describing the interconnection of two tetrahedral building blocks. A Si–O–Si value of 144° has been determined by XRD measurements on bulk vitreous silica [59]. Later, the data were re-analyzed by another group yielding a Si–O–Si angle of 152° [64].

A similar value has been obtained from a hand-built model of bulk vitreous silica by Bell and Dean [62]. Poor agreement between experiment and model was observed,



Fig. 16.9 Features of the interconnection in range II for the vitreous silica film [54]. **a** Image from Fig. 16.4a, overlayed with *colored bars* representing the Si–Si NN distance (see *scale bar*). **b** Histogram of the Si–Si NN distances. *Black arrows* indicate the average values from diffraction experiments on bulk vitreous silica [59, 60]. **c** Histogram of the Si–O–Si angles. For a comparison, *black arrows* indicate the values from ab initio calculations [61], XRD [59] and molecular model from Bell and Dean [62]. **d** Two SiO₄ tetrahedral units connected via the bridging O atom. *Black arrows* indicate the Si–Si distance and the Si–O–Si angle. **e**, **f** Comparison of Si–O–Si angles in 2D and 3D vitreous networks (Si *green*, O *red*) [55]. **e** *Side view* on the building block of the 2D vitreous silica bilayer. Here, the Si–O–Si angle is restricted by the flat film structure of the bilayer. **f** Four SiO₄ tetrahedra connected in 3D space. Due to more degrees of freedom in the Si–O–Si angles a wider spectrum of values can be assumed

when the authors attempted to build a structure with a mean Si–O–Si value of 144°. Later on, ab initio simulations of bulk vitreous silica yielded mean Si–O–Si angles ranging from 143.4° to 152.2°. The angles depended on the potential, basis set and the applied structural optimization scheme [61]. An overview of the literature on measured and simulated Si–O–Si angles can be found in [63]. Here, the most probable Si–O–Si angle of bulk vitreous silica has been estimated to be near 147° with a standard deviation of 10°–13°. A sharp boundary in the distribution is absent [63]. The Si–O–Si-angles terminated from our real space data deviate from the values found in the literature by 4°–13°.

It is clear that the smaller Si–O–Si angle is an intrinsic feature of 2D vitreous networks. The different interconnections of tetrahedral units in 2D and 3D vitreous silica are illustrated in Fig. 16.9e, f. In the side view of the film structure in Fig. 16.9e, building blocks made out of 4 tetrahedra become visible. These building blocks introduce the flatness of the 2D film structure. The Si atoms of the bottom and top layer lie all in one plane, respectively. Therefore, the bonding arrangement in the z-direction is predetermined. The angles in which the three remaining bonds per Si atoms can arrange is limited. A certain Si–O–Si angle can not be exceeded in this structural arrangement. The characteristic sharp edge in the Si–O–Si angle

distribution of a 2D vitreous network visible in Fig. 16.9c can be assigned to this effect. In the 3D case, structures with a larger degree of freedom (f) are allowed (sketched in Fig. 16.9), resulting in a larger range of values for the Si–O–Si angles. In this range II, small but distinct differences due to the increased symmetry of the vitreous silica film structure have been observed in comparison to bulk silica. This increased symmetry causes the film to be atomically flat, which allows us to tackle the even more important range of the network topology, described in the following section.

16.6.3 Network Topology—Range III

This range of order is the most discussed and least understood topic in the glass community. In this range the differences between crystals, with periodicity and order, and glass, with no periodicity and no order is most striking. In both phases the initial buildings block are the same. The difference between a crystalline and a glass phase is in the relative orientation of these building blocks. A detailed comparison of crystalline and vitreous regions of the thin silica film is given in [55]. Characterization of the larger radial distances, ring statistics, and Si–Si–Si angles have been evaluated for the thin silica film.

In direct comparison to diffraction data a PCF helps to characterize the atomic order in a material. The computed long range distances for the silica film structure can be compared to literature values. Radial pair distances for Si–O (blue), O–O (red), and Si–Si (green) measured from the nc-AFM model are indicated in Fig. 16.10a. A histogram of distances between all atoms in the model is plotted versus the radial distance (r) in the so called pair distance histograms (PDHs) in (b). Vertical colored bars mark significant peak positions.

The first peaks in all three distributions correspond to the first respective NN distances. The origin of these positions has been presented in Sects. 16.6.1 and 16.6.2. Second peaks of each curve represent the next NN distances.

The second peaks exhibit a larger background compared to the first peaks. They are broader and more diffuse, which is an intrinsic feature of the vitreous nature of the film. The first peaks represent order of ranges I and II introduced by the chemical bonding of the building blocks. The following peaks are broader and characterize range III.

By summing up the different PDHs using X-ray and neutron scattering factors of Si and O according to the formula in [62, 65], total pair correlation functions of the experimentally derived structural model, $(T_{nc-AFM}(r))$, have been obtained. Due to the 2D structure of the thin film, $T_{nc-AFM}(r)$ was normalized by r^{-1} . The PCF obtained in an XRD experiment and ND measurements on bulk vitreous silica in Fig. 16.10c, d have been plotted together with the respective curves $T_{nc-AFM}(r)$ calculated for the silica film structure. Reasonable agreement with the XRD and ND PCFs with $T_{nc-AFM}(r)$ was achieved for the major peak positions, their relative magnitudes and peak shapes. But as already indicated in the discussion of range II,



Fig. 16.10 Analysis of pair distance histograms and pair correlation functions of the silica film in comparison to diffraction data [54]. **a** Cutout of a vitreous silica image with a superimposed atomic model. *Colored bars* indicate the types of distances that are evaluated in (**b**). **b** Pair distance histograms (PDHs) derived from the nc-AFM image given in Fig. 16.4. Radial distances for Si–O (*blue curve*), O–O (*red curve*), and Si–Si (*green curve*) are plotted. Peaks are indicated by *vertical colored bars* for first and second NN. **c** Comparison of the total PCF, $T_{nc-AFM}(r)$ (*orange curve*), with the PCF obtained from X-ray diffraction measurements on bulk vitreous silica (*black curve* has been retraced from [59]). **d** Comparison of $T_{nc-AFM}(r)$ (*orange curve*) to results from ND on bulk vitreous silica (*black curve* has been retraced from [60]). The PDH peak positions are in line with the respective colored bars from (**b**)

small deviations induced by the different dimensionality of the two systems are visible. While the silica glass studied in diffraction experiments is 3D, the silica bilayer on Ru(0001) is 2D. Nevertheless, a good agreement between the PCFs obtained in diffraction studies of bulk vitreous silica and the vitreous silica film is achieved.

Looking at the ring size distribution of the thin vitreous silica film is another way to characterize the network topology. From diffraction measurements and other averaging techniques such ring size distribution are not directly attainable. This quantity can only be obtained from real space data and represents the biggest advantage this model system has to offer. The ring size s is defined as the number of Si atoms per ring. These rings are quite large objects and therefore a large statistical sample is required. For this analysis the atomically resolved STM image in Fig. 16.11a has been used. This particular STM image shows a sensitivity to the Si atoms in contrast to the nc-AFM image from Fig. 16.4, where O atoms are visualized. The sensitivity of the scanning probe is mainly dominated by the microscopic tip termination. An overview of different tip contrasts for this film system has been presented in [55]. The lower right part of Fig. 16.11a is superimposed with the atomic model of the topmost Si and O atoms. A complex ring network is revealed similar to Fig. 16.4c.



Fig. 16.11 The 2D vitreous silica ring size distribution [55]. **a** Large scale STM image of the vitreous silica film with a sensitivity to Si sites ($V_S = 2$ V, $I_T = 50$ pA, scan range = 11.2 nm × 6.6 nm). Half of this image is superimposed by the atomic model of the topmost Si and O atoms. **b** Visualization of the ring size distribution in real space. The different rings are indicated by *colored polygons*. **c** Histogram of the ring size distribution from the STM image in (**b**). A log-normal fit to the data is given by a *red dashed curve*. **d** A log-normal plot of the ring size distribution guided by a *dashed line*

Figure 16.11b presents the real space visualization of the ring size distribution. The polygonal area spanned by the Si atoms has been color coded for every ring. The environment of a ring apears to depend on its size. Rings with more than six Si atoms tend to be surrounded by smaller rings. The possible angles inside an SiO_4 tetrahedron govern the ring arrangement.

In Fig. 16.11c a histogram of the ring sizes from the STM image is depicted. The distribution of rings ranges from four Si atoms to nine Si atoms. The most common ring has six Si atoms. The distribution is asymmetric regarding the maximum. A log-normal behavior characterizes the ring size distribution of the vitreous film. Such analysis was first presented by James F. Shackelford and Brian D. Brown for an extended Zachariasen network [66]. Therein, they have also used a log-normal ring size distribution to characterize the 2D random network. The connectivity requirements of 2D random network seem to be the origin for the behavior of the ring size distribution [66]. The silica/Ru(0001) ring size distribution can be fitted by a log-normal function or a line in the log-normal plot (dashed lines in Fig. 16.11c, d) with good agreement.

Surprisingly, the ring size distribution over several sample preparations, even within a certain range of preparation conditions, have provided very similar distributions for vitreous silica film regions. The properties of bulk glasses strongly depend on their preparation conditions and it is believed that these are presumably influenced through their ring size statistics. Thereby an important parameter seems to be the fictive temperature from which the glass was quenched from the liquid state. It is expected that the ring statistics would also depend on preparation parameters for the silica film. However, our current preparation procedures seem to always yield an ideal 2D glass configuration. Currently, we are only able to change the ratio between crystalline and vitreous regions in our sample systems by controlling the bilayer coverage.

From Fig. 16.11b Si–Si–Si angles can be computed. The internal structure of the ring is guided by the Si–Si–Si angle. For four- to nine-membered rings histogram plots of the internal Si–Si–Si angles are shown in Fig. 16.12a–f. The corresponding edge angle of the regular polyhedron is marked by a black arrow for every ring size. Since the rings in the vitreous silica film can have a flexible shape, a broadening of the Si–Si–Si angle is observed. The mean value of each distribution, however, is in good agreement with the ideal polyhedral angle. The sum of all ring contributions is plotted in Fig. 16.13. The Si–Si–Si angle shows a broad distribution, having a



Fig. 16.12 Histograms of Si–Si–Si angles [55]. **a–f** Histograms of Si–Si–Si angles in four- to nine-membered rings are plotted separately. Internal angles of regular polyhedra are indicated by *arrows* and *numbers* at the *top*



Fig. 16.13 Total Si–Si–Si angle distribution [55]. Comparison of the Si–Si–Si angle distribution for different ring sizes. The ring sizes are *colored* correspondingly



Fig. 16.14 2D mass density analysis of the silica film [54]. The *green* wireframe corresponds to the model from Fig. 16.11b. The *white dashed box* displays a bilayer slab used to calculate the 2D mass density. *Colored boxes* represent the lateral variation of the 2D mass density (see *scale bar*)

maximum at 120° corresponding to the average edge angle inside the most frequent, i.e., sixfold, ring. The broadness of the distribution further shows how flexible this 2D amorphous structure can be.

16.6.4 Density Fluctuations—Range IV

The data in Fig. 16.11b for this silica film allows us to address even range IV, where the long range mass density is evaluated. In Fig. 16.14 the 2D mass density has been visualized. The green wireframe was used as a model for the density determination. Under the wireframe, small colored boxes depict the local mass density in mg/m². The boxes have dimensions of 0.34 nm \times 0.30 nm. For each box the local mass

density from a 2 nm × 2 nm slab around it was calculated. One slab has been indicated by a white dashed square. Its dimensions have been chosen to be larger than a typical ring size. The 2D mass density varies from 1.46 to 1.83 mg/m² and has been color coded in the small boxes for each slab. In the calculated 2D mass densities the complete bilayer structure has been considered. Both the topmost SiO₄ tetrahedra and the lower ones have been taken into account.

A total 2D mass density of 1.65 mg/m^2 has been calculated for the silica film. A pure crystalline phase of the silica bilayer has a slightly higher 2D mass density of 1.68 mg/m^2 . Small local fluctuations of the 2D mass density are observed for the vitreous film. This might be induced by the local ring environment. Larger rings have a lower density than areas consisting of smaller rings. The center of the image is dominated by smaller rings (four to sevenfold) indicated by the higher mass density, while in the lower left corner larger rings with a lower density are observed. This evaluation is just a starting point for the range IV order. Further insights might be gained by a detailed analysis of the ring size environments.

16.7 Crystalline-Vitreous Interface in 2D Silica

Interface structures between crystalline and amorphous phases are of great interest. In the glass community, there has always been a controversy about how crystalline and vitreous phases are connected to one another. From the experimental point of view, a real-time observation at the atomic scale of an active front during a glass transition process is not currently feasible. But a static image of such an interface region can be gained.

In this silica film a transition between crystalline and amorphous regions has been imaged and characterized [67], as shown in Fig. 16.15. The image of this boundary layer makes a direct contribution to understanding the topological glass transition at the atomic level. Figure 16.15a shows an atomically resolved STM image of an interfacial area [67]. This image has been superimposed with Si and O positions in Fig. 16.15b. A smooth interface without under- or overcoordinated atomic sites has been found. No new building blocks were observed. A detailed analysis of atomic distances and angular distributions has been performed [67]. In the crystalline, the vitreous, and the interfacial region the Si–Si distances appeared to remain constant. However, the orientation of the Si–Si directed distances showed a clear change at the interface. Three discrete peaks in the angular distribution representing the crystalline axes are observed in the crystalline area. In the vitreous part these orientations are randomly distributed in all directions.

For a further analysis the image in Fig. 16.15b has then been partitioned into slices, which are indicated below. Thereafter, the number of rings of a certain size within the segment has been counted (Fig. 16.15c).

With this approach it is also possible to plot the occurrence of the various ring sizes in the interface region. This is shown in Fig. 16.15c by the color-coded number of



rings per slice. The various ring sizes do not occur at the same position in the interface region. In fact, certain ring sizes occur simultaneously, and some combinations occur closer to the crystal domain than others, as the interface 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 two eight-membered rings, 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 five- and seven-membered rings) is the lowest energy defect in a hexagonal network [68].

Wooten and Weaire generated an early calculation of a crystalline-amorphous interface for silicon [69]. In crystalline silicon the shortest-path rings of atoms are all six-membered. By repeating random rearrangements of bonds, different ring sizes were generated that lead to an amorphous phase. In the interface region between the crystalline and amorphous phases, incorporation of five and sevenfold rings occurs.

This structural evolution is very similar to the one observed in our silica film.

Huang et al. reported recently on the observation of structural rearrangements in this amorphous silica bilayer film [70]. The authors used a probing electron beam of a transmission electron microscope (TEM) to deliberately cause rearrangements. Remarkable images and videos show the movements of structural building blocks at the atomic scale. The opening and closing of ring structures and the subsequent rearrangements can be directly observed. The results confirm our early models and DFT calculations [12] and open new ground for future modeling of dynamics in glasses. By providing the opportunity to study vitreous materials at the atomic level, this unique model system is likely to have great impact on the general understanding of dynamic processes in amorphous bulk materials. Future work might allow a direct assessment of atomic structures at the transition temperatures, where the liquid solidifies to either the crystalline or the amorphous state.

16.8 Topological Analyzes of Two-Dimensional Network Structures

The presented advances in structural research allow one to search for a means of new classification for amorphous solids. Different concepts of classification and comparisons encompassing a number of non-ordered natural and theoretical systems were described in a milestone publication by Weaire and Rivier [71].

In a recent paper [72], the silica film structures in its crystalline and vitreous state were compared to structural elements and configurations of other network structures, e.g., Si(111) 7×7 reconstruction [73], triangle rafts [66], amorphous graphene [74], copper oxide [75], molecular network structures [76], and bubble rafts [77, 78].

For all these networks, we can analyze real space structure data to determine characteristic properties and define descriptors of amorphous structures. The different network systems range from highly-ordered to completely unordered, include experiments and theoretical models, and span length scales from Ångströms to millimeters in bond length equivalents (Fig. 16.16).

All networks consist of rings that are defined by the number of comprised connection points (structural equivalents to Si atoms in the silica film). For each system, a ring size distribution with six-membered rings as the most abundant species can be determined. By calculating the second and third central moment of each ring size probability distribution, the variance and the skewness of a distribution can be captured in one number and allow for quick comparison.

The ring size probability can also be plotted versus the ring size on a logarithmic axis. This lognormal probability plot was suggested by Shackelford and Brown [66]. They postulated that a lognormal ring size distribution is inherent to all amorphous networks. We find that this is true except for the network formed by the bubble raft.



Fig. 16.16 Comparison of different network structures. Connection points in the center of the occurring ring structures are marked with small green circles. Different sized rings are indicated with respective colors and partially superimposed onto the images. a Model of a Si(111) surface in the 7×7 reconstruction [73]. A rhombus shape indicates the unit cell. Si positions are marked with small green circles, different ring sizes are marked in different colors on part of the model. Five-, six- and eight-membered rings, occur in this complex crystalline surface. The unit cell also contains one 12-membered ring. **b** STM image of a crystalline SiO_2 sheet (taken from [55]). The contrast reveals the Si positions of the SiO₂ film, which are partly marked with *small green circles*. Sixmembered rings (marked with large green circles on part of the image) are the only ring size in this highly ordered system. c nc-AFM image reveals the atomic structure of an amorphous SiO₂ bilayer [72]. Four- to nine-membered rings occur, six-membered rings exhibit the highest occurrence. \mathbf{d} A computational model for a sheet of amorphous graphene [74]. On part of the image, C positions are indicated with small green circles and different ring sizes are shown with colored circles. In addition to the five- to nine-membered rings also two 12-membered rings occur. e STM image of a defect-rich Cu₂O(111) surface is shown [75]. It is partly superimposed with *small green spheres* at the O positions and colored circles indicating polygon size. In the Cu₂O, only five-, six- and sevenmembered rings are observed. f STM image of an amorphous film of polymerized TBPB-Molecules on a Au(111) substrate [76]. The molecule centers constitute the connection points of the resulting amorphous network, marked with small green circles. Rings from four to eight connection points are observed. g The image shows a triangle raft suggested by J. Shackelford as a model for amorphous SiO₂ networks [66]. The algorithm for creating the triangle raft limits possible ring sizes from four to eight. h Photo of a macroscopic bubble raft. Soap bubbles form a space-filling arrangement that exhibits different sized polygons (shown with colored circles) and lacks long-range order. Ring sizes from four to eight are observed

This deviation is attributed to the larger variation in connection point distances, since the formation is not governed by chemical bond length or angle limitations.

Diffraction techniques yield total pair correlation functions including all atomic positions. An advantage of real space information is the possibility to discern between different species. Atomic position data were used to create partial pair correlation functions of the connection points. They allow conclusions regarding characteristic building unit distances and degree of order in the system. All systems exhibit similar characteristic bond distances far beyond the primary tetrahedral building block.

An additional benefit of real space information is the information regarding network topology over a larger scale. Several preferred arrangements of ring sizes have been identified as characteristic larger building units. They all consist of four rings in a cluster of the sequence A-B-B-A with two rings of size B sharing two Si-atoms and a ring of size A on either side, sharing one of those Si atoms, respectively. The occurrence of the 5-7-7-5, 7-5-5-7, the 5-8-8-5 and the 8-5-5-8 clusters have been analyzed and their occurrence probability is in line with a qualitative model of ring strain.

These different approaches at structure analysis can serve as a starting point for discussing and comparing unordered network structures in the future.

16.9 Summary

This vitreous silica model system, which can be investigated by well-established surface science tools, provides the unique possibility to study an amorphous model system with atomic resolution in real space.

The structure of this atomically flat and extended vitreous silica film on Ru(0001) has been presented. nc-AFM/STM revealed the thin film's atomic arrangement consisting of corner-sharing SiO₄ units. These silica building blocks form a complex network which lacks long-range order and registry to the substrate. This model system corroborates Zachariasen's predictions of a random network theory for glass structures. An atomic model of the topmost Si and O atoms has been directly derived from nc-AFM/STM images. The atomic structure has been discussed in the following ranges: the SiO₄ tetrahedral unit, interconnection of adjacent structural units, network topology, and longer range density fluctuations. Distances, angles, PCFs and histograms of ring sizes were given. A comparison between the PCF derived from our experimental model and the PCF obtained in diffraction experiments on bulk vitreous silica was drawn and showed satisfying agreement.

The behavior of the ring size distribution at a crystalline-vitreous interface was investigated. A gradual and smooth transition at the interface was found, where five and sevenfold rings occur closer to the crystalline region than four-, eight-, and nine-membered rings.

Certainly, such structural studies are a step forward in developing of a comprehensive framework for understanding amorphous networks. In future experiments, the aim is to directly follow glass-formation phenomena. A possible route to do so is the application of the spectro-microscope SMART (spectro-microscope with aberration correction for many relevant techniques) [79] that was installed at the BESSY II (Berliner Elektronen-Speicherring-Gesellschaft für Synchrotronstrahlung) electron storage ring. This instrument enables for real-time observation of layer growth, structure formation, diffusion and reaction fronts as well as phase transitions. Future work might allow for a direct assessment of atomic structures at transition temperatures, where the liquid solidifies to either the crystalline or the amorphous state. In current experiments, the preparation of this unique silica film is adapted to the SMART setup. But also certain designs of SPMs presented in the literature have been shown to be, in principle, capable of following atomic motions at elevated temperature. Results from such machines may open new room for modeling the dynamics in glasses [80]. Studying vitreous materials at this scale will have a great impact on the general understanding of dynamic processes in amorphous bulk materials [3].

The silica film might also be used in the context of Cr-doped porous silica glass as a model material to describe Phillips catalyst properties [81]. Doping [82], additional growth [83], adsorption, and chemical reactivity [84] studies on this silica based film system are still the focus of ongoing experiments.

It should be mentioned that these silica films can be grown on various substrates [12, 85–87], which leaves room for the possibility of a completely new materials class of its own. Band structure measurements or other materials properties of this silica film might reveal unexpected features similar to those of graphene. This film may even find applications as a new gate material in the semiconductor industry. However, this strongly depends on the final stability and properties of this film system.

To conclude, by this work our understanding of oxide surface structures and complex materials, e.g., amorphous solids, was significantly enhanced owing to the use of high-resolution imaging and spectroscopy by SPM. The presented work can be referenced as a stepping-stone for future studies.

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