Atomic Arrangement in Two-Dimensional Silica: From Crystalline to Vitreous Structures

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Supporting Information

ABSTRACT: The atomic structure of vitreous and crystalline regions of a thin silica film on Ru(0001) was investigated using noncontact atomic force microscopy (nc-AFM) and scanning tunneling microscopy (STM). We were able to resolve the atomic arrangement of the Si and the O atoms in the crystalline and the vitreous structures. We discuss characteristic structural properties of the films, such as distances, orientations, and angles, and we compare our results to experiments and simulations of bulk vitreous silica networks. It



was found that order in two-dimensional vitreous networks can extend up to 2 nm.

INTRODUCTION

Exactly one century ago, Max von Laue's discovery of X-ray diffraction (XRD) ushered in a new era in the structure analysis of condensed matter. For the first time, information on the atomic arrangement of materials could be gained. However, XRD measurements were not limited to crystals. Soon, scientists started to investigate glasses using XRD.¹ The absence of sharp diffraction peaks led to the conclusion that glasses are noncrystalline, i.e., amorphous, materials. Nevertheless, a comprehensive picture of the glass structure was absent, until William H. Zachariasen published his postulates on "The Atomic Arrangement in Glass" in 1932.² These ideas were very successful in explaining XRD experiments,³ and his hypothesis is commonly referred to as the "random network theory". A tremendous amount of work has been invested in measuring the exact atomic structure of glasses by diffraction methods.^{4,5} Although these techniques are able to yield very high resolution data, they have several limitations: (a) the structural information is averaged over a large sample volume, depending on the characteristics of the incident beam, (b) they give, in the first place, only information in reciprocal space, and (c) the maximum that can be obtained is a one-dimensional pair correlation function (PCF), which makes it impossible to characterize a three-dimensional (3D) structure in all its details. Therefore, the only way to understand diffraction experiments is by comparing the experimental PCF to PCFs calculated from coordinates of hand-built⁶⁻⁸ or computer-generated⁹⁻¹¹ structural models. However, even a perfect match between model and experiment is not a guarantee that there are no other models that would fit equally well.¹²

The invention of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) opened up another era in materials research. These techniques enabled atomic scale investigations and were successfully applied to a large variety of crystalline surfaces. Most of the surface structures and reconstructions have been known before the rise of scanning probe microscopy (SPM). The strength of SPM lies in the high local resolution in real space, enabling the investigation of single adsorbates, molecules, and defects on the surface. Is it possible to resolve the local atomic structure of an amorphous system? The application of SPM to cleaved glass surfaces^{13–17} and to glassy metals¹⁸ was shown. However, a detailed and unambiguous atomistic assignment of the observed structures was not possible because of rough surfaces and large corrugations. Therefore, to investigate the atomic structure of amorphous materials by SPM, an atomically flat glass is required.

Silica is the prototype glass network former and the basis of many glasses. As it is one of the most abundant materials on earth, it is relevant in various branches of modern technologies, e.g., in semiconductor devices, in optical fibers, and as a support in industrial catalysis.

In a recent publication, we presented an atomically resolved STM image of a bilayer of vitreous silica that was prepared on a Ru(0001) support.¹⁹ The film exhibited a complex ring network with a log-normal ring size distribution.^{20,21} Shortly after, a similar film was observed on graphene by scanning transmission electron microscopy (STEM).²² These findings prove the existence of a new class of materials: two-dimensional (2D) glasses. Furthermore, random molecular ring networks have been reported.^{23,24}

Herein, we present a detailed analysis of the atomic structure of silica films exhibiting crystalline and vitreous phases. The positions of Si and O atoms were resolved on both phases. On the basis of these atomically resolved images, we present a detailed structural analysis including characteristic distances,

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orientations, and angles. Our measurements are compared to experimental and theoretical data from the literature.

EXPERIMENTAL SECTION

This study was carried out at a custom-built dual mode microscope which combines noncontact AFM (nc-AFM) and STM using a tuning fork sensor. The high resolution measurements were performed at low temperatures (5 K) in ultrahigh vacuum (UHV). Before film preparation, the Ru(0001) substrate was cleaned by repeated cycles of Ar⁺ bombardment at 1 kV and annealing to 1500 K. The substrate was checked for cleanliness by low energy electron diffraction (LEED) and STM. As a first preparation step, a $3O(2 \times 2)$ precover was prepared on Ru(0001). Afterward, Si was evaporated from a Si rod of high purity onto the $3O(2 \times 2)$ precovered Ru(0001) surface at 350 K in an O₂ atmosphere of 2×10^{-7} mbar. Finally, the sample was annealed at 1180 K in 2 \times 10⁻⁶ mbar O₂ yielding an extended and flat silica bilayer. Previous infrared spectroscopy measurements of a similar preparation showed a vibrational band at \sim 1300 cm⁻¹, being a characteristic feature of the silica bilayer structure, which consists of a stack of two tetrahedral layers.^{25,26} Depending on the initial Si load and the cooling rate after the last step we could grow vitreous silica films or films with coexisting crystalline and vitreous regions.²⁶

RESULTS AND DISCUSSION

The capability of the combined nc-AFM/STM setup is demonstrated in Figure 1. Figure 1a shows Zachariasen's



Figure 1. (a) Zachariasen's scheme of a random network (black dots: cations, white circles: anions). (b, c) Both images represent a single atomically resolved constant height measurement, where panel b shows the nc-AFM and panel c the STM channel. Imaging parameters for b: oscillation amplitude = 0.27 nm, gray scale from -1.0 Hz (dark) to +0.6 Hz (bright); for c: $V_S = 100$ mV, gray scale from 50 pA (dark) to 500 pA (bright); for both b and c: scan area = 2.7 nm × 3.9 nm. In panel b the structure of the Si atoms is visible, whereas panel c 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 b and c (green balls: Si atoms, red balls: O atoms).

continuous random network, where the black dots represent the cations (X) and the white circles the anions (Y). In this scheme, well-defined XY₃ units are connected via a varying X– Y–X angle forming a ring network. Figure 1b and 1c represents one single atomically resolved constant height nc-AFM and STM measurement above a vitreous region of the silica film on Ru(0001). Figure 1b is a map of the frequency shift (Δf) and Figure 1c is the simultaneously recorded map of the tunneling current ($I_{\rm T}$). Both images show a ring network with pores of various sizes resembling Zachariasen's scheme. The power of our approach becomes clear if we take a closer look at the atomic structures that were resolved. Whereas the Δf map (Figure 1b) shows the Si positions (green balls), the $I_{\rm T}$ image (Figure 1c) reveals the O positions (red balls) of the topmost silica layer. This can be verified by looking at the nearest neighbor (NN) configurations of the imaged protrusions (see top part of Figure 1b and 1c). In Figure 1c, every three protrusions (red balls) form a three-bladed windmill-shape representing one triangular side of an SiO₄ tetrahedron. Therefore, these positions correspond to O atoms. However, in Figure 1b, four protrusions (green balls) form a three-bladed windmill with one protrusion 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 (see also Table 1). The structural information of both channels can be connected to obtain a complete surface model without any further assumptions (see bottom part of Figure 1b and 1c). Note that the observed chemical sensitivity of nc-AFM and STM strongly depends on the microscopic tip configuration. Previously, we also observed a sensitivity to O atoms with nc-AFM.²

In Figure 2, we present the full analysis of crystalline and vitreous areas by STM. All STM images shown have a size of $3.5 \text{ nm} \times 3.5 \text{ nm}$. Figure 2a and 2b was measured above a crystalline phase and Figure 2c and 2d on vitreous regions of the silica film. We were able to resolve the atomic structure of the topmost Si (Figure 2a and 2c) and O atoms (Figure 2b and 2d). All images are superimposed by an atomic model in the bottom right corner (Si green, O red).

To find the O coordinates from the measured Si positions in Figure 2a and 2c, we calculated the center between each pair of Si NNs and defined this as the O position. A Si-O height difference $(\Delta z_{s_{i-0}})$ of 0.52 Å was assumed in this case. This number was obtained in density functional theory (DFT) calculations of the crystalline bilayer film.²⁵ In contrast to this procedure, the Si positions were computed self-consistently from the O coordinates in Figure 2b and 2d without assuming a fixed $\Delta z_{\rm Si-O}$. For this purpose, first, a circumscribed circle was calculated for every triangle of O NNs. Afterward, the circle center was defined as the Si position. Finally, for every SiO₄ tetrahedron $\Delta z_{\rm Si-O}$ was set to the radius of its insphere $r_{\rm in}$ = $\overline{r}_{\rm O-O}/(24)^{1/2}$, with $\overline{r}_{\rm O-O}$ being the average O–O NN distance in this particular SiO_4 unit. Via this procedure, an average $\Delta z_{\rm Si-O}$ of 0.55 Å \pm 0.04 Å and 0.53 Å \pm 0.04 Å was obtained for the crystalline (Figure 2b) and the vitreous structure (Figure 2d), respectively. These heights are in good agreement with the DFT value of (Δz_{Si-O}) justifying the use of the latter in the Si case. The coordinates of the atomic models from Figure 2a-d are provided in the Supporting Information.

To visualize rings of different size, the pores were color coded in Figure 2. Clearly, the crystalline phase is built up from only one ring type, namely the six-membered ring (a ring consisting of six Si and six O atoms). On the contrary, the vitreous phase is constructed from differently sized pores ranging from four- to nine-membered rings. A typical ring size distribution histogram of the vitreous silica bilayer on Ru(0001) can be found in ref 19 or the Supporting Information of ref 21. The atomically resolved images from Figure 2 served as a starting point for further evaluation of the silica film's structure.

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crystalline	STM^a	STM^b	\mathbf{XRD}^{c}	ND^d	ab initio ^e	
Si-O [Å]	1.67 ± 0.08	1.66 ± 0.06	1.61	1.61	1.61-1.62	
O-O [Å]	$2.71\pm0.18^*$	2.72 ± 0.11	2.63-2.65	2.63	2.62-2.65	
O-Si-O [°]	109.4 ± 8.1	110.1 ± 5.7	108.8-110.5	108.7-110.5	108.5-110.2	
Si-Si [Å]	3.12 ± 0.08	$3.15\pm0.11^*$	3.06	3.06	3.07	
Si-O-Si [°]	139.9 ± 2.3	143.5 ± 1.2	143.7	143.6	144-148	
Si-Si-Si [°]	120.2 ± 6.3	$119.5\pm6.9^{\ast}$				
vitreous	STM^a	STM^b	XRD ^f	ND^h	ab initio ⁱ	B&D ^j
Si-O [Å]	1.60 ± 0.09	1.61 ± 0.11	1.62	1.61 ± 0.05	1.61-1.63	1.59 ± 0.03
O-O [Å]	$2.59\pm0.21^*$	2.65 ± 0.19	2.65	2.63 ± 0.09	2.63-2.67	2.60 ± 0.08
O-Si-O [°]	109.2 ± 10.9	109.4 ± 12.6	109.8	109.7 ± 4.5	109.3-109.5	109.4 ± 4.9
Si-Si [Å]	3.01 ± 0.12	$3.07\pm0.23^*$	3.12	3.08 ± 0.11	3.03-3.12	3.11 ± 0.07
Si-O-Si [°]	140.5 ± 2.3	142.6 ± 2.7	$144 (152^g)$		143.4-152.2	154.2 ± 9.3
Si-Si-Si [°]	120.2 ± 14.7	$118.8\pm15.3^*$				104.9 ± 17.8
Si-Si-Si [#] [°]	119.9 ± 10.6	$119.9\pm13.2^{\ast}$				

^{*a*}STM results from this study are compared to results from X-ray diffraction (XRD), neutron diffraction (ND), and ab initio simulations on α -quartz and bulk vitreous silica, as well as the handmade model of Bell and Dean for vitreous silica. ^{*b*}STM with O structure, this study (Figure 2b and 2d). Values given are the mean ± standard deviation from a Gaussian fit to the data. ^{*c*}STM with Si structure, this study (Figure 2a and 2c). Values given are the mean ± standard deviation from a Gaussian fit to the data. ^{*c*}STM with Si structure, this study (Figure 2a and 2c). Values given are the mean ± standard deviation from a Gaussian fit to the data. ^{*d*}From refs 28 and 29. ^{*c*}From refs 30 and 31. ^{*f*}From refs 32 and 33. The given ranges represent results from different basis sets. ^{*g*}Directly measured values, this study. ^{*h*}From ref 34. ^{*i*}Reanalysis of the same data; from ref 35. ^{*j*}From ref 36. ^{*k*}From ref 11. The given ranges represent results from different basis sets. ^{*i*}Calculated from the coordinates in ref 8. ^{*m*}Six-membered rings only.



Figure 2. Atomically resolved crystalline and vitreous regions of the thin silica film (the scan area of all images is 3.5 nm × 3.5 nm). (a) STM image of a crystalline area showing the positions of Si atoms (V_S = 3.0 V, I_T = 100 pA). (b) STM image of a crystalline patch showing the arrangement of O atoms (V_S = 100 mV, I_T = 100 pA). (c) STM image of a vitreous area revealing the positions of Si atoms (V_S = 2.0 V, I_T = 50 pA). (d) STM image of a vitreous area showing the arrangement of O atoms (V_S = 100 mV, I_T = 100 pA). (a–d) Arrows indicate one crystallographic axis of the Ru(0001) substrate.

In Figure 3, characteristic atomic orientations are evaluated. A quantity that reflects the order of a particular film region is the directed distance orientation (DDO) between two atoms, i.e., the slope of a line segment connecting two atoms with respect to a certain fixed axis (here, we used the image ordinate as a reference). Figure 3a visualizes the O–O NN DDOs using colored bars. The color scale represents the DDO value (see scale bar). Apparently, three different orientations are present in the STM image.

For a better visualization of the DDO distribution, a histogram of the O-O NN DDOs is plotted in Figure 3b. Due to the three-fold symmetry of the crystalline silica bilayer, we observed three peaks in the orientational distribution. The peaks are centered at $+55.2^{\circ}$, -4.3° , and -64.7° and have equal peak heights. Surprisingly, the peaks are quite broad and have an average standard deviation of 8.6°. There are two possible explanations for this experimental result: (a) the determination of the atomic positions is not exact enough and/or (b) the crystalline region is not perfectly ordered. As we show in the Supporting Information, the deviation resulting from effect a was quantified by determining the atomic positions of a perfectly crystalline structure as a benchmark. The DDO error that stems from the manual determination of atomic coordinates should not be larger than 1.7°. Thus, effect a is quite weak. Therefore, we conclude that some regions consisting of hexagonal rings only are not perfectly crystalline. This residual disorder might be induced by a closely situated vitreous area. Furthermore, the network structure might allow additional degrees of freedom and lead to certain distorted structures, which are close in energy. A detailed discussion on the influence of a vitreous region on the crystalline phase and the crystalline-vitreous interface can be found in ref 21.

Finally, Figure 3c displays the histogram of all O–O DDOs, i.e., not only NN DDOs but also DDOs between higher order neighbors. In this distribution we observed six sharp peaks on a large background. The three largest peaks can be identified as the average orientations of O–O NN rows, centered at +55.2°, -3.8° , and -64.2° (compare with Figure 3b). These sharp



Figure 3. Analysis of the O–O directed distance orientations (DDOs). (a) The O–O nearest neighbor (NN) orientations of the STM image in Figure 2b are represented by colored bars (see scale bar; image size = $3.5 \text{ nm} \times 3.5 \text{ nm}$). (b) A histogram of the O–O NN DDOs. These orientations represent the three-fold symmetry of the crystalline phase. (c) A histogram of all O–O DDOs. Additionally to the NN peaks, second NN peaks are present. (d) O–O NN orientations of the STM image from Figure 2d. Colored bars represent the DDO value (see scale bar; image size = $3.5 \text{ nm} \times 3.5 \text{ nm}$). (e) A histogram of the O–O NN DDOs. (f) The histogram of all O–O DDOs exhibiting a completely random distribution of angles. For the evaluation of panels b, c, e, and f, slightly larger surface areas were used ($5 \text{ nm} \times 5 \text{ nm}$). (a, d) Arrows indicate one crystallographic axis of the Ru(0001) substrate.

peaks verify the long-range order of the crystalline phase. Moreover, these three main orientations are parallel to the crystallographic axes of the Ru support. The other three peaks represent the mean O–O second NN directions at +85.5°, +25.7°, and -33.8°. In a perfect crystalline structure, DDO peaks originating from third and higher order NNs are visible (see Supporting Information). However, these peaks are not present in Figure 3c, being another indication for the residual disorder of this crystalline region.

A similar evaluation of pair orientations for a vitreous area of the silica film is presented in Figure 3d to f. The O-O NN DDOs are displayed in Figure 3d as colored bars (see scale bar). The DDO values of the vitreous state assume a large variety of values. This can be more clearly seen in Figure 3e showing the O-O NN DDO histogram for the vitreous structure. The orientations are distributed over the whole range of -90° to $+90^{\circ}$, and separated peaks are absent. Several faint bumps seem to be present in the distribution. However, after a careful analysis of several other images showing a completely random distribution of NN orientations (see Supporting Information), we ascribe the wavy structure in Figure 3e to the small size of the statistical probe in that case. The evaluation of DDOs between all atoms in the model reveals the true vitreous state of this region (see Figure 3f). In the histogram, peaks are absent, demonstrating the lack of longrange orientational order.

One important aspect in this context is the interaction with the substrate. In the crystalline regions, the regular arrangement of silica pores follows the crystallographic orientations of the Ru substrate (see Figure 2a and 2b). However, the vitreous structures lack symmetry and periodicity and are therefore structurally decoupled from these axes. The weak coupling to the substrate might be one of the driving forces for the formation of vitreous patches. Huang et al. also observed crystalline and vitreous silica bilayer patches on one and the same, crystalline substrate (graphene).²² Defects at the interface might be another influence on the film structure. It is important to note, that in our nc-AFM and STM measurements, we observe only the top part of the bilayer, i.e., information on the interface is not attainable.

As introduced by A. C. Wright, the structural order in a network solid, like vitreous silica, can be divided into four ranges:^{4,12} I, the structural building blocks (i.e., the SiO₄ unit); II, the interconnection of neighboring SiO₄ tetrahedra; III, the network structure; IV, longer range density fluctuations. In this paper, we focus on ranges I–III.

Table 1 shows an overview of distances and angles characterizing ranges I-III in the topmost Si and O atoms of the crystalline and vitreous silica films. As a measure of range I, Table 1 includes the Si-O NN distance, the O-O NN distance, and the O-Si-O mean angle. Further, the Si-Si NN distance and the mean Si-O-Si angle are given, as they determine order of range II. Finally, Table 1 specifies one range III parameter, namely the Si-Si-Si angle, which defines the ring structure inside a network. We fitted our data with a Gaussian, and the values in Table 1 represent the mean \pm standard deviation. Note that only values followed by an asterisk were directly measured in this study. In addition, in Table 1, the STM results are compared to distances and angles from the literature. The data of the crystalline film is confronted with (a) XRD of α -quartz,^{28,29} (b) neutron diffraction (ND) of α -quartz,^{30,31} and (c) ab initio simulations of α -quartz.³² Moreover, we compare values from the 2D vitreous film to (a) XRD of 3D bulk vitreous silica,³⁴ (b) ND of 3D vitreous silica,³⁶ (c) the Bell and Dean handmade model of 3D vitreous silica,⁸ and (d) ab initio calculations of 3D vitreous silica.¹¹

The characteristic range I distances (Si–O and O–O) of the crystalline silica film agree well within the standard deviation with XRD, ND, and ab initio results of α -quartz. The same is true for the intratetrahedral angle (O–Si–O). Further, we observed good agreement of the intertetrahedral angle (Si–O–Si) and the Si–Si distance. The Si–O–Si angle obtained from STM images with an O and Si structures are slightly different (139.9° ± 2.3° vs 143.5° ± 1.2°). This is connected with the different way of calculating the height difference between Si and O in both cases, which was mentioned above.

The range I and II distance values for the vitreous silica film show also good agreement with XRD and ND diffraction, as well as with the handmade model and ab initio simulations. The O-Si-O angle exhibits in all six vitreous cases nearly the same magnitude and approaches the mathematical tetrahedral angle of 109.47°. However, there is a discrepancy in the Si-O-Si angle, which is important for the connectivity of the network structure. This angle has been largely debated in literature.^{4,37} The original XRD measurements from Mozzi and Warren yielded a most probable Si-O-Si value of 144°.³⁴ Some years later, the data were reanalyzed by Da Silva et al.³⁵ They found 152° to be the most probable value for the Si-O-Si angle. Furthermore, Bell and Dean obtained a similar value for their hand-built model of bulk vitreous silica.⁸ When these authors attempted to build a structure with a mean Si–O–Si value of 144°, they observed poor agreement with experiment. Ab initio simulations yielded mean Si–O–Si angles ranging from 143.4° to 152.2° depending on the potential, basis set, and the structural optimization scheme applied.¹¹ A detailed analysis of the literature on measured and simulated Si–O–Si angles can be found in ref 37. These authors estimate the most probable Si–O–Si angle to be situated near 147° with a full width at half maximum of 23° to 30° (corresponding to a standard deviation of 10° to 13°). If we compare all these Si–O–Si values to the angles calculated from distances of the 2D silica network in this study, we find a difference of about 3° to 14°.

The smaller Si–O–Si angles are an intrinsic feature of 2D vitreous networks. Figure 4 illustrates the different intercon-



Figure 4. Comparison of Si–O–Si angles in 2D and 3D vitreous networks (Si green, O red). (a) A side view on the building block of the 2D vitreous silica bilayer. Here, the Si–O–Si angle is constrained by the flat structure. (b) Four SiO₄ tetrahedra connected in 3D space. The Si–O–Si angles can assume a wider spectrum of values due to more degrees of freedom.

nections of tetrahedral units in 2D and 3D vitreous silica. In 2D, the connection of the building blocks is constrained by the flat structure of the film (see Figure 4a for a side view). There is a maximal Si-O-Si angle, which cannot be surpassed, because the Si atoms of a certain layer all lie in one plane. This effect is expressed in a characteristic sharp edge in the Si-O-Si distribution of a 2D vitreous network.¹⁹ However, in 3D, the Si-O-Si angles can assume a larger range of values, as there are more degrees of freedom. A sharp boundary in the distribution is absent.³⁷

By comparing the values of crystalline and vitreous silica films, we note that range I and II distances are slightly larger in the crystalline case. However, this effect is only about 3% and is negligible within the standard deviation. Furthermore, in a recent evaluation of the distances on both sides of a crystalline-vitreous interface in the thin silica film we did not observe any significant difference of the atomic distances.²¹ If we concentrate on the directly measured distances with STM (O-O and Si-Si), we see that the standard deviation of the O-O NN distance distribution is nearly equal in the crystalline and the vitreous case (0.18 Å vs 0.21 Å). This result is in line with the identical tetrahedral shape of crystalline and vitreous building blocks. In contrast, the standard deviation of the Si-Si NN distance distribution is larger for the vitreous structures than for the crystalline ones (0.23 Å vs 0.11 Å). This effect might be connected with the larger distribution of possible intertetrahedral angles (Si-O-Si) in the vitreous film enabling a larger variety of Si-Si NN distances.

It is in range III, where considerable differences between crystalline and vitreous structures are found. One range III parameter is the Si–Si–Si angle, which can be directly measured from STM images resolving the Si positions (Figure 2a and 2c). In the imaged crystalline phase, the Si-Si-Si angle has a mean value of 119.5°. As the crystalline structure consists of 6-fold rings only, this angle agrees well with the 120° angle in a regular hexagon. In the vitreous phase we observed ring sizes ranging from four to nine. For regular polyhedra with four to nine edges, angles ranging from 90° to 140° are allowed. Correspondingly, we measured Si-Si-Si angles ranging from 80° to 170° . The most common ring type in the vitreous phase is the six-membered ring. This fact explains that the vitreous structure yields a mean Si-Si-Si angle of 118.8°. The difference can be found in the width of the Si-Si-Si angle distribution. The standard deviation of the vitreous phase is larger than for the crystalline case by a factor of 2. Further, it is interesting to note that even the 6-fold rings in the vitreous phase have a broader Si-Si-Si angle distribution than the crystalline film. We conclude that the 6-fold rings exhibit a larger deformation in the vitreous regions than in the crystalline ones. In 3D, rings and loops are not limited to a planar shape, and therefore a different Si-Si-Si angle distribution is predicted $(106^{\circ} \pm 20^{\circ}).^{38}$

To quantify the structural order of range III, Figure 5 presents the O-O and Si–Si pair distance histograms (PDH)



Figure 5. Pair distance histograms (PDHs) of crystalline and vitreous phases of the silica film. (a) Si–Si PDH of a crystalline patch. The black lines represent Si–Si distances from the density functional theory (DFT) silica bilayer model.²⁵ The blue dotted curve shows the artificially broadened DFT PDH. (b) O–O PDH of a crystalline region. As in panel a, the black lines and the blue dotted curve represent the DFT values. (c) Si–Si PDH of the vitreous phase. (d) O–O PDH of a vitreous area of the film. For panels a–d, 5 nm × 5 nm images were evaluated. Images at the right show local coordination of atoms (green balls: Si, red balls: O; image size: 1.3 nm × 1.3 nm).

of crystalline and vitreous areas of the silica film. The onedimensional PDHs from Figure 5a–d were extracted from atomically resolved STM images with equal size (scan ranges: 5 nm \times 5 nm; cutouts shown in Figure 2a–d). Radial distances (*r*) up to 1.6 nm were evaluated. At the right side of Figure 5, model cutouts show the local order and coordination of the corresponding atom type for every PDH curve (green balls: Si, red balls: O; image size: 1.3 nm \times 1.3 nm). For a better peak

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interpretation of the crystalline PDHs, we plotted the PDH of the DFT model for the crystalline silica bilayer (black bars in Figure 5a and 5b).²⁵ Evidently, the experimental curves are much broader than the DFT PDH, but they agree well with the artificially broadened DFT peaks (blue dotted curves in Figure 5a and 5b). Similar to the discussion of Figure 3, the reason for this broadening might be two-fold: (a) experimental uncertainty and/or (b) minor disorder of the crystalline phase. As we show in the Supporting Information, effect a should be in the range of ± 0.08 Å for the first crystalline peak in the O–O distribution. However, the standard deviation of the first O–O peak in Figure 5c is 0.18 Å, which means that only half of the broadening can be explained by reason a. Thus, Figure 5a and 5c gives another indication for the residual disorder of the crystalline region.

Although the experimental crystalline distance distributions exhibit broadening, the PDHs of the crystalline (Figure 5a and 5b) and the vitreous regions (Figure 5c and 5d) clearly show several differences: (a) the vitreous peaks are in general broader and have a lower intensity than the crystalline ones, (b) the vitreous peaks get broader and diffuser with increasing r, and (c) the background of the curves is more pronounced in the vitreous case. It is noteworthy that in the vitreous PDHs peaks can be identified up to about 2 nm, which is in good agreement with the estimated distance up to which order can extend in bulk vitreous silica.^{39,40} The PDH of an extended Zachariasen scheme^{20,41} also shows peaks up to radial distances of at least 2 nm (see Supporting Information). 2D vitreous networks might have an even longer correlation length than bulk glasses, as the 3D structure has more degrees of freedom and there are more possibilities to lose order.⁴

CONCLUSION

Herein, we investigated the atomic structure of crystalline and vitreous regions in the silica bilayer film on Ru(0001). The atomic arrangement of Si and O atoms could be resolved for both cases. Some crystalline regions exhibit minor effects of disorder, which can be attributed to the flexible network structure. The evaluation of characteristic distances and angles showed good overall agreement with diffraction data and simulated networks. Even the extension of order is similar for the 2D and 3D vitreous structures. The results prove that the vitreous silica bilayer film is a convenient model system to study and understand various properties of bulk glasses.

ASSOCIATED CONTENT

Supporting Information

Coordinates and further analysis of crystalline and vitreous silica films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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