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Formation and Evolution of Ultrathin Silica Polymorphs on Ru(0001) Studied with Combined *in Situ*, Real-Time Methods

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ABSTRACT: Silica mono- and bilayer films on Ru(0001) can be physisorbed or chemisorbed, with ordered or vitreous structures, depending on the particular preparation procedures applied. Using the SMART spectro-microscope at BESSY-II with its capabilities for μ -spectroscopy, μ -diffraction, and LEEM imaging with lateral resolution below 5 nm, *in situ* and in real time and applied to identical areas, we have investigated the formation of these layers, defined and characterized their properties and their connected morphology, and followed their evolution. Two distinct chemisorbed monolayers and three bilayers (physisorbed crystalline and vitreous, and chemisorbed zigzag phases), and some transitions between them, have been studied. We found that, apart from the deposited silicon amount, the most important parameter for steering the evolution to a particular well-defined layer is the oxygen content at the



Ru interface. Nucleation and growth of all layers are homogeneous on the scale of our resolution, leading to rather small domains (20-40 nm), mostly of the same phase, separated by defect lines. We discuss these and other basic findings in context and point out open questions. We also offer alternative recipes for the preparation of some phases, to obtain more homogeneous layers on a mesoscopic scale.

1. INTRODUCTION

Silicon dioxide is one of the most abundant materials on earth, with a broad range of applications such as in drug delivery,¹ electronics^{2,3} and catalysis^{4–6} (both as a support and active component in catalysts). Particularly in the area of catalysis, the development of silica-based model systems can provide a deeper understanding of the fundamental properties of the material in a controlled environment. In this sense, this approach opens the possibility of forging new concepts that can be later applied to real systems.^{7,8}

In recent years a multitude of well-defined ultrathin silica films supported on different transition metal substrates have been produced and investigated.^{9–20} On the Ru(0001) support, the existence of various silica polymorphs has been reported. On the one hand, two different types of chemisorbed monolayers (ML) were reported where corner sharing SiO₄ tetrahedra represent the basic construction unit of the film.¹¹ In these cases, the layer is chemically bound to the Ru substrate through Ru–O–Si bonds and their orientation with respect to the underlying Ru atomic layer can be tuned by the preparation conditions.

On the other hand, SiO_2 bilayers (BL) can be produced on Ru(0001) with two kinds of bonding: either chemisorbed (i.e., fixed to the substrate by localized chemical bonds)¹² or physisorbed (i.e., quasi-free-floating, only interacting with the substrate by van der Waals forces).²¹ In the case of the

physisorbed BLs, two different phases exist, namely: crystalline and vitreous bilayers.²² STM experiments have revealed the atomic structure of both types,²² with a specific ring size (*n*) distribution for the vitreous BL in the 4 < n < 9 range.¹⁹

A variety of preparation procedures have been used by different groups characterizing the film with various techniques such as scanning tunneling microscopy (STM),^{8,11,23} transmission electron microscopy (TEM),²⁴ low energy electron diffraction (LEED), X-ray induced photoemission spectroscopy (XPS)^{25,26} and infrared reflection absorption spectroscopy (IRAS).²⁷ On the basis of STM measurements, the coexistence of different phases has often been found, with domain sizes of 10 to 50 nm,^{12–14,19} thus making the comparison with semi-integral methods requiring larger uniform areas difficult. In this regard, little information is available in the literature regarding the morphology of these films on a mesoscopic scale and, more importantly, on its development during sample preparation. It appeared advisable, therefore, to carry out a systematic investigation using spectroscopic, diffractive and imaging techniques which, combined with *in situ* observations on the

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same sample area, will allow the determination of optimal growth conditions for the various layers. The SMART apparatus,^{28,29} a spectro-microscope enabling low energy electron microscopy (LEEM, with its bright field and dark field variants), μ -spot LEED (μ -LEED), μ -spot XPS (μ -XPS), and X-ray induced photoemission electron microscopy (XPEEM, not used here) on the *same* area and in real time during sample preparation is an ideal tool for such a task. With this program we not only aimed at a descriptive catalog but also hoped also to be able to single out the important parameters like oxygen pressure, temperature, and heating rate, which are active in steering the layer development in one or another direction.

In the following we describe the resulting data on three BL and two ML polymorphs. This work has mainly been carried out as a Ph.D. thesis,³⁰ which contains more detail as to the procedures, results, and analyses than can be given here, so further information can be found there. Some results obtained for the physisorbed BL (crystalline and vitreous) with the same apparatus have been published before, in particular pertaining to the morphology of films.³¹ For this reason, we briefly summarize them here in order to give a complete picture of the silica system.

2. EXPERIMENTAL SETUP, METHODS, AND PROCEDURES

The experiments were carried out in the SMART microscope operating at the UE49-PGM beamline of the synchrotron light source BESSY II of the Helmholtz Centre Berlin (HZB). The aberration corrected and energy filtered LEEM/PEEM instrument combines microscopy, diffraction, and spectroscopy techniques for comprehensive characterization. The instrument demonstrated a lateral resolution of 2.6 nm in LEEM and 18 nm in XPEEM and an energy resolution of 180 meV. For a detailed description and discussion of its various functions and capabilities see refs.^{28,29} The base pressure of the system is 10^{-10} mbar. The probed surface area can be selected by introducing a field aperture into an intermediate image plane, and the magnification can be varied, resulting in a selectable area of interest between 10 nm and 20 μ m; in this work usually a sample area of 5 μ m was used, unless stated otherwise. By scanning the surface with this probed area, the homogeneity of an area up to 4×4 mm could be checked and ascertained. The absence of radiation induced changes or damage by the primary beams of electrons or photons was carefully excluded by tests with shifted probe spots and by comparing the observed dynamics under irradiation with the same with beam turned off.

The main capabilities of this apparatus used in the present work were μ -LEED, μ -XPS, LEEM (bright field and dark field, BF and DF), and LEED-IV and LEEM-IV (i.e., reflectivity) curves. In BF-LEEM the specularly reflected beam is used for imaging, whereas in DF-LEEM one of the other LEED spots is selected making this imaging mode sensitive to (variable) superstructures. For LEED-IV and LEEM-IV results the *x*-axes are labeled with "electron energy", which is the kinetic energy of the reflected electrons with an offset added due the difference between the (variable) work function of specimen surface and the fixed work function of the e-gun emitter. The latter also contain, via the recording of the so-called MEM-to-LEEM transition (i.e., the energy at which the incoming electron beam is not reflected any more from the surface), a determination of the sample's work function change, $\Delta \phi$. Also, both types of IV curves contain information on the geometry of the layer and of the density of empty states of the sample. In the present work we will not attempt a quantitative analysis of these data which is possible (see e.g., refs 32 and 33). Instead, we will use the LEEM-IV curves of the (0,0) spot as fingerprints of local layer situations, as it has turned out that they are highly characteristic for them.

We have used the LEED function (LEED patterns, spot intensities during preparation steps) for a qualitative assessment of order or disorder and as the basis for DF-LEEM; the XPS function for a qualitative (from binding energies, BE) and partly quantitative atomic analysis of the layers; the LEEM-IV curves for determination of work function changes and for a fingerprint of the layer situations; and the LEEM function for in situ imaging of the respective surface with a lateral resolution of below 5 nm; with all of these usually combined on the same area. The BF-LEEM gives an overall image of the surface, while DF-LEEM allows distinguishing rotated domains by using distinct LEED spots for imaging. This ability of DF-LEEM is very important for highly symmetric surfaces like ours, where the LEED pattern often looks much more symmetric than the structure in real space because of rotated domains coexisting within the probe area of 5 μ m. Its images give a better picture of the real island morphology and their evolution.

The Ru(0001) single crystal was prepared by cycles of Ar⁺ sputtering at room temperature and annealing in oxygen at 1170 K, with a final heating to 1350 K in ultrahigh vacuum (UHV). Cleaning cycles were repeated until no contamination could be detected by LEEM and XPS, and a bright and sharp (1×1) LEED pattern resulted. LEEM showed roughly parallel 200 to 500 nm wide and very long (many μ m) terraces, separated by single steps or step bunches. Sample temperature was measured either by a W26%Re/W5%Re thermocouple or by a pyrometer (IMPAC IGA 740) with an absolute accuracy of ~10 K. Oxygen (99.999%) was dosed directly into the experimental chamber; Si was sublimated from a 4 mm thick rod (99.999%) using a commercial evaporator (Omicron EFM3) under grazing incidence of 20°. For the preparation of the silica films the necessary amount of Si was deposited onto the Ru (0001) substrate precovered with a 3O (defined below) layer at room temperature and in 2×10^{-7} mbar O₂. In a subsequent step, annealing to variable final temperatures depending on the desired silica polymorph, usually in 5 \times 10⁻⁶ mbar of oxygen, was performed to completely oxidize the deposited Si. Details on the variations of this procedure for the different polymorphs are properly addressed in the corresponding sections of the results.

3. RESULTS AND INTERPRETATION

3.1. O Adlayers on Ru(0001). It has turned out that all preparations of silica thin films on Ru(0001) need a partial O coverage as starting condition, and that the amount of O present on the Ru interface can be an important parameter to determine the dynamics and even partly for the final film formed (see below). We therefore investigated the defined O/Ru(0001) layers with the same arsenal of methods as that used for the silica films (see above), and start with a summary of the main results. We note that these systems are very well-known and have been studied intensely by experiment and theory in the past 40 years.^{32,34–40} In well-annealed layers the O atoms always occupy hcp sites; there are 4 well-defined layers with coverages 1/4, 1/2, 3/4, and 1 relative to Ru surface atoms, which will be termed *n*O layers (*n* = 1 to 4). All layers except

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Figure 1. Characterization of the nO/Ru(0001) phases. Upper row: LEED patterns. Second row: LEEM images. Dark field LEEM (1O to 3O) and bright field LEEM (4O), bottom row: dark field LEEM (color) of the 2O phase, where the different colors, obtained by the use of all rotated spots, indicate the three domains each on two adjacent terraces. All data were taken at room temperature. Electron kinetic energies were selected for good contrast (electron energy = 17.5, 16, 18.5, and 42 eV for 1O to 4O; 42 eV for LEED).



Figure 2. Properties of the *n*O layers on Ru(0001): (a) Reflectivity curves (LEEM-IV) containing the MEM-LEEM transition and (b) O 1s and (c) Ru $3d_{5/2}$ photoemission spectra.

40 (which has a (1×1) pattern) show an apparent (2×2) LEED pattern which are true (2×2) structures for 10 and 3O, and are due to three domains of a (2×1) structure rotated by 120° for 2O. Energies, quantitative geometries, and

electronic states are well-known and well understood.^{39,40} An interesting finding—also used in this work—is a strong adsorbate-induced surface core level shift: the number of O neighbors shifts the XPS binding energy of the Ru 3d core level by up to 1 eV; it has also been successfully modeled theoretically.⁴¹ However, so far no investigation has been done on the morphology of these layers and their evolution with an *in situ* methodology like our present one; so these findings also add to the general knowledge on this much-researched system. In the present context our results form a point of comparison for the silica layers.

The 1O layer has been prepared at room temperature by short oxygen exposure (about 2×10^{-8} mbar for 2 min) such that the intensity of the (2×2) spots reached a first sharp maximum.³⁴ The best procedure to obtain well-developed 2O, 3O, and 4O layers was found to start O₂ exposure with the crystal at 1170 K: for 2O 1 min at 5×10^{-8} mbar, followed by cooling to 470 K in O₂, then closing the O₂ leak valve, and finally cooling to room temperature. 3O and 4O need much higher exposures: for 3O (4O) 10 min at 10^{-6} mbar (10 min at 5×10^{-6} mbar) at 1170 K, cooling to 520 K and then in UHV to room temperature.

Figure 1 summarizes our findings with qualitative LEED and with DF-LEEM for the fully developed nO layers. Upon O adsorption the quite wide and very long terraces separated by single steps are preserved. All the expected contrast inversions for the two rotational terminations of the basic Ru(0001), the rotational domains for 2O, and the antiphase domains for 1O, 2O, and 3O have been found and used for differentiation of the island structure. The island borders appear dark due to destructive interference. The domain sizes for 1O are small (20-50 nm); for 2O and 3O they are up to 10 times larger, presumably due to the high preparation temperature and annealing procedure. For 1O and 2O the evolution during increasing coverage could also be observed; this was not done for 3O and 4O because of their need of very high exposures at high temperature. Many more details were observed (e.g., crossing of steps by antiphase boundaries for 1O, in agreement with previous work,42 and occasionally even for 2O. Island fluctuation and disappearance due to the order-disorder transition for 20⁴³) which are not important in the present context; these and more detail can be found in ref 30.

The 3O is the most important O layer for this work, as it is the starting point for preparation of the silica layers. The domains it forms on the preserved terraces are very large (~100 nm), and again the expected antiphase domains which are the same as for 1O, since the 3O is a 1O-hole structure—have been found. Also, here a reversible order disorder transition was found by the temperature dependence of the (2 × 2) spot intensity, which changes rapidly between 500 and 540 K. DF-LEEM proved that the 3O domains fluctuate strongly down to ~400 K.

Results of the other methods which are important for comparison are shown in Figure 2. They include the MEM-to-LEEM transition and the LEEM-IV curves (containing similarities for the *n*O layers but clear differences compared to other surfaces, making them good fingerprints), the O 1s XPS peaks (BE 529.2 eV not changing with coverage, intensity in agreement with expected coverage), and the Ru 3d XPS peaks. The latter are compatible with the adsorbate induced chemical shifts mentioned above⁴¹ considering our much lower energy resolution and smaller surface sensitivity. Instead of separate peaks we see an asymmetrically broadened peak which

is also characteristic of the O layer concerned. Generally, all of these spectra will be usable to gain information on the state of oxygen chemisorbed directly on Ru (termed O_{Ru} subsequently) under the silica film.

3.2. Si Deposition and Absolute Calibration. In order to form silica layers with well-defined Si content, the deposited amount of Si has to be highly reproducible and well calibrated. This task was tackled by (1) deposition on Ag(111) for which the formed silicene structure is well-known, and then (2) using the derived flux to form complete silica bilayers on Ru(0001) using the recipes developed by other groups of our institute,^{11,13} and finally comparing the infrared reflection absorption spectroscopy (IRAS) spectra for these layers *ex situ* to verify the resulting layers. This was successful; for details see ref 30. These experiments did yield another important piece of information: the very first small deposit of Si on nominally clean Ru turned out to be oxidized; then only metallic Si was deposited. This shows that Si on Ru(0001) reacts readily with small amounts of residual O (here present as impurity) even at room temperature.

Some interesting observations have been made during Si deposition onto a 3O-covered Ru(0001) which was carried out at room temperature in 2×10^{-7} mbar oxygen. After starting the Si source, the $p(2 \times 2)$ spots of the 3O structure are weakened and become blurred, and around 0.2 ML Si, a Henzler ring,^{44,45} indicative of the growth of small islands, is formed around the (0,0) spot. At ~0.5 ML Si the ring has its maximum intensity which then decreases strongly; only weak, broad remnants of the (2×2) spots can be discerned. At 1 ML both have nearly disappeared; this remains the case when increasing the coverage to 2 ML. The intensity of the central (0,0) spot exhibits a damped oscillatory behavior with a first maximum at 1 ML, which we used for calibration of the Si evaporator rate.

After deposition of an amount corresponding to a silica monolayer at room temperature, the $p(2 \times 2)$ spots due to 30 are gone, the Si 2p XPS indicates full oxidation, the O 1s XPS shows the formation of Ru-O-Si and Si-O bonds and little O_{Ru} and the Ru 3d XPS is even narrower than for 1O/Ru (see Figure 2c). This proves that even at room temperature all arriving Si up to a silica monolayer is fully oxidized by the O_{Ru}. Since oxidation of bulk Si needs much higher temperatures (700 K at low pressures) or oxygen pressures (1 bar at room temperature),46-48 this means that even at quite low temperatures Si is readily oxidized by adsorbed O atoms on the Ru surface which acts as a catalyst for dissociation of O₂ and transfer of O atoms to Si. LEEM shows no structure, and the LEEM-IV curve is featureless, so the resulting SiO₂ film is fully disordered in all 3 dimensions. Further deposition to achieve a BL does not cause qualitative changes. For LEEM images of these developments, see ref 31.

3.3. Silica Monolayers. As described above, the SiO₂ film formed by deposition and oxidation at moderate temperatures is fully disordered in 3 dimensions and most likely is quite rough. In order to produce an ordered silica ML, annealing is necessary. It can produce two different types of ordered layers, depending on the oxygen pressure: Annealing in 5×10^{-6} mbar oxygen—as used in the *ex situ* investigations so far²⁵—produces a p(2 × 2) structure, while annealing to 1000 K in UHV produces predominantly a (2 × 2)R30° phase. Mixtures of these two structures can result. In the following, these phases and their evolutions are described.

3.3.1. The $p(2 \times 2)$ ML Phase. This phase has been widely described and investigated on Mo and Ru surfaces by various experimental methods and by theoretical calculations.^{17,49-56} The usual procedure on Ru is to anneal the Si (corresponding to a ML and deposited on a 3O/Ru surface at room temperature) in 5 \times 10⁻⁶ mbar oxygen to ~1050 K. During this procedure LEED shows a strong increase of the (0,0) spot intensity. The Henzler ring intensity increases up to 900 K, indicating growth of small islands; above that it decreases, and at 1050 K it disappears. The $p(2 \times 2)$ spots, initially derived from 3O, show a structured increase with temperature (which cannot be due to 3O any more, since this is totally disordered then), followed by a decrease above 900 K; at 1050 K they are weak and blurred. Cooling down to room temperature makes them sharp, and their intensity increases by a factor of 10. Figure 3 shows the well-developed $p(2 \times 2)$ pattern and two



Figure 3. Production of the $p(2 \times 2)$ ML: LEEM and LEED images at room temperature after annealing in oxygen to 1050 K and holding for 10 min. The white arrows in parts a and b mark the same surface spot at different magnification. LEED image (c) shows the $p(2 \times 2)$ unit cell of silica. An electron energy of 42 eV was used for all images.

LEEM images at different magnification. Small grainy features (\sim 30 nm, sometimes fused to \sim 90 nm) are visible in BF-LEEM; they are homogeneously distributed over the field of view, but some areas have less intensity, and some holes are visible, appearing as black areas. The larger FoV (field of view) in Figure 3b shows that these holes are preferentially located at substrate step bunches which appear as bright blurred lines. This preference can be explained by strain caused by the step bunches underneath the silica film, which covers the substrate like a carpet.

Figure 4 compares the LEEM-IV curves of the 3O layer, the film after Si deposition at room temperature, and after annealing the film in oxygen and in UHV (see next subsection). The curve for the amorphous Si deposit (red curve) is characterized by its weak structure; the similarities between the curves of 3O layer and the $p(2 \times 2)$ ML, and the quite different curve of the other ordered ML structure (to be discussed below) are obvious. It is possible to prepare a ML film with only $p(2 \times 2)$ structure.

To study the morphology of the ML film, DF-LEEM images were obtained and compared to BF-LEEM (Figure 5). In BF the grainy domains seen in Figure 3 are found to be distributed over the surface, irrespective of the Ru terraces with different truncation which DF-LEEM allows to distinguish, and the island structure on both types of terraces, imaged by different (2×2) spots, is similar. This ML is characterized by domains of around 30–50 nm in size which are distributed uniformly with no preference to steps. The fact that the superstructure spots are quite distinct, albeit somewhat diffuse, shows that the ML is rather well aligned to the Ru lattice.

Figure 6 shows the XPS results, also including the rotated ML to be discussed below. The Si 2p peak indicates full



Figure 4. $p(2 \times 2)$ ML: LEEM-IV curves after thermal treatment in oxygen. For comparison, the LEEM-IV curves of the 3O terminated ruthenium surface, the Ru-3O surface after silicon deposition and the (2×2) ML, obtained by thermal treatment in UHV (section 3.3.2) are shown. The intensities are normalized to the maximum intensity of the MEM mode. The $\Delta \phi$ values (relative to clean Ru and derived from the MEM to LEEM transition) are given in the legend. The similarity of the curves for 3O and for the $p(2 \times 2)$ ML and the strong difference to that of the rotated ML are obvious.

oxidation and shows only small changes at various steps of the annealing process, with the fully ordered layer (black line) having a narrow peak width (the other ordered ML structure also has a narrow peak), showing that the layer becomes more homogeneous by ordering; the peak shifts are due to small work function changes as indicated. The work function of the $p(2 \times 2)$ silica ML is very close to that of the 3O layer (see $\Delta \phi$ values in Figure 4) showing that these two layers have about the same overall surface dipole. The O 1s line indicates considerable O_{Ru} and Ru-O-Si contributions, and the Ru 3d line (Figure 6c) of the $p(2 \times 2)$ ML is close to that of the 3O layer. This also agrees with the similarity of the LEEM-IV curves of the $p(2 \times 2)$ ML to that of 3O. In this case, the XPS peak shifts of O 1s of Si-O and Ru-O-Si are due to different chemical environments.

These data are well compatible with the structural model given in ref.¹¹ Its lattice is aligned to and commensurate with the Ru surface with doubled lattice constants, resulting in sharp 2×2 spots and no moiré pattern. It has been calculated to be compressed by 1.9% relative to the freestanding film.¹¹ The O atoms of SiO₄ tetrahedra directed toward the substrate bind to either top or fcc sites on Ru. Per silica unit cell one O atom is found on Ru in an hcp site, so the O_{Ru} coverage corresponds to 10. The lattice can be described as a 10 layer with the O at (0,0) combined with silica tetrahedra at $\binom{1}{4}$, $\binom{1}{4}$ and $\binom{3}{4}$, $^{3}/_{4}$) positions of its unit cell. The DF-LEEM images show that the $p(2 \times 2)$ ML grows homogeneously in relatively small (~30-50 nm) domains. The observed structure of relatively small domains may well be a result of the strain induced by the compression. Interestingly, the 3O like appearance of the Ru 3d XPS indicates that the action of an O neighbor to a Ru surface atom is similar to that of a Ru-O-Si bond. The almost identical overall surface dipole of the $p(2 \times 2)$ ML and the 3O is compatible with this, but there could also be a contribution of an intrinsic dipole of the ML and/or its polarization by the



Figure 5. Structural fingerprints for the $p(2 \times 2)$ ML structure. The upper row shows a series of (I) BF and (II–IV) DF-LEEM images utilizing the LEED spots marked in the lower inset. The plotted DF-LEEM-IV curves are analyzed at different terraces and in the overall field of view by using LEED spot (II). LEEM images were taken at 20 eV.



Figure 6. XPS results for the $p(2 \times 2)$ ML structure and their evolution during preparation, all measured at room temperature after the treatment given. The respective peaks for the rotated ML (see below) are included: (a) Si 2p, (b) O 1s, and (c and d) Ru $3d_{5/2}$. In part c, the respective curve of 3O is included and shows the good agreement with that of the $p(2 \times 2)$ ML; in part d that of 1O is included and demonstrates good agreement with that of the rotated ML. The XPS curves for the surface after Si deposition are also shown.

 O_{Ru} dipoles which could offset a somewhat different behavior of the Ru–O–Ru and the O–Ru dipoles.

Overall a picture consistent with the earlier results is found, with some additional details mainly related to the morphology and its evolution during preparation. 3.3.2. The Rotated (2 × 2) ML Phase. This ordered ML, which shows (2 × 2) spots rotated by 30° and has therefore been called $(2 × 2)R30^{\circ}$ structure despite its incommensurability to the Ru surface, has so far only been investigated by ex situ investigations.⁵⁷ In them a p(2 × 2) ML was prepared first as described above, followed by annealing in UHV, which

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Figure 7. LEED, LEEM and DF-LEEM images of a ML annealed in UHV to 1010 K obtained at room temperature which leads to coexisting islands of the $p(2 \times 2)$ and the $(2 \times 2)R30^{\circ}$ ML. I is the bright field image and II–IV are dark field images from a rotated spot. 1–4 are dark field images from $p(2 \times 2)$ spots, as indicated in the LEED pattern on top. Unit cells of the $(2 \times 2)R30^{\circ}$ (red) and the $p(2 \times 2)$ (blue) structures and respective LEED spots used in DF-LEEM, are indicated. In the latter, $p(2 \times 2)$ areas and atomic steps are highlighted. Electron energies: 52 eV LEED; 20 eV for LEEM.

finally yielded partially a rotated phase. With this procedure, the pure rotated phase cannot be produced; there is always an admixture of the $p(2 \times 2)$ phase as clearly visible in LEED (Figure 7). We found that it can be well produced by annealing the Si monolayer, deposited on 3O at room temperature, to about 1000 K in UHV (the O₂ pressure is below 5×10^{-9} mbar). A complex development during T-increase and anneal is observed, which leads to somewhat different end results depending mainly on the final annealing temperature, but also on heating rate (see ref 30). A typical procedure consists of annealing the deposited Si ML film at 1015 K for 75 s, with rapid heating (\sim 7 K/s) and cooling in UHV. During the heatup the Henzler ring intensity first increases and then decreases, and from 650 K, (2×2) spots rotated by 30° start to appear, followed by $p(2 \times 2)$ spots. During the high temperature anneal, the rotated spots become very strong and develop moiré spots, while those of the $p(2 \times 2)$ are much weaker and distorted and the Henzler ring disappears. The pattern obtained after cool-down to room temperature, shown in Figure 7, exhibits the coexisting " (2×2) R30°" and p (2×2) (weaker and blurred) phases; moiré spots are also visible around the substrate spots. BF- and DF-LEEM images are shown in Figure 7, lower part. BF-LEEM shows domains approximately 25 nm in size and in three different intensities, and some dark lines (along Ru steps); no larger domains are observable. Qualitatively the same is seen by DF-LEEM which allows better distinction: on all superstructure spots of the

rotated phase a conglomerate of domains around 25 nm in size with three different brightnesses appear, which fill the surface except for some lines along step edges. In the DF images of all rotated spots the same domains appear the brightest, indicating the nonexistence of rotational domains. Imaging with one of the $p(2 \times 2)$ spots (lowest row) gives similar results, but more blurred graininess of the same scale, however now the Ru terraces switch in contrast and islands appear and disappear when switching the spot. Dark areas along steps appear as well. The contribution of the rotated phase can be further optimized by using a somewhat higher annealing temperature (1015 K), but this occurs at the expense of complete coverage: holes start to appear as seen by LEEM images (see ref 30).

The LEEM-IV curves for the $p(2 \times 2)$ and the rotated (2×2) MLs are very different (see Figure 4) and can therefore be used very well to distinguish them. On the other hand, the IV curves for different rotated spots are identical, in agreement with the DF-LEEM images.

The XPS results for the rotated ML are included in Figure 6. The Si 2p XPS clearly shows that all Si is fully oxidized. Compared to the layer before annealing (3D-amorphous SiO₂ ML produced at room temperature) the O 1s XPS shows increases of O_{Ru} and Ru-O-Si, while compared to the $p(2 \times 2)$ ML the O-Ru contribution is strongly decreased; the Ru-O-Si is roughly unchanged. Together these results suggest that—as expected from the UHV preparation—the O_{Ru} is decreased and the number of Ru-O-Si anchors is about the



Figure 8. Characterization of the crystalline silica bilayer: (a-c) XPS spectra, (d) LEEM-IV curves of the deposited Si and of the final BL, and (e) LEED pattern and DF-images taken at the identified spots. The LEED pattern and DF-LEEM images were recorded with electron energies of 42 and 17 eV, respectively. White boxes and arrows in DF-LEEM images highlight the same areas on the sample.

same for the $p(2 \times 2)$ and $(2 \times 2)R30^{\circ}$ structures. However, the Ru 3d XPS peak is much narrower than that of the $p(2 \times$ 2) ML (see Figure 6.c) and close to that of the 10 layer (Figure 6d). Also, the work function change is much smaller (by ~0.7 eV) than for the $p(2 \times 2)$ ML and close to that of the 10 layer. So, in this phase O_{Ru} and Ru-O-Si bonds do not influence the Ru 3d spectra similarly, contrary to the situation for the $p(2 \times 2)$ ML described above. In view of the fact that the Ru 3d core level shift has been shown to depend on the number of O neighbors of a certain Ru atom,⁴² this suggests that in this phase the Ru-O-Si bonds are directed to different Ru sites than in the $p(2 \times 2)$ ML phase. Qualitatively this agrees with the structure proposals that have been made. ^{11,30,56} However, it contradicts the conclusions drawn at the end of the previous chapter: here, O–Ru and Ru–O–Si appear not to be equivalent in their action on the Ru surface core level shift; and the intrinsic dipole of the silica ML may be appreciable. A possible explanation is that the Ru-O-Si polarity is different for the $p(2 \times 2)$ and the rotated ML.

Up to temperatures of ~650 K the $p(2 \times 2)$ phase is favored, while at higher annealing temperatures the rotated phase is preferred if the annealing is carried out in UHV. It is obvious that the steering to either phase is done by the O_{Ru} coverage: if it is low (i.e., in UHV), the forming SiO₄ tetrahedra are free to optimize their bonding to Ru (presumably on hcp and fcc sites³⁰), while high O_{Ru} coverage hinders this and forces the $p(2 \times 2)$ structure. While kinetic contributions to this selection cannot be excluded, the simplest explanation is energetics, i.e. the selection of the rotated (2 × 2) ML by UHV annealing comes from the energy gain by the maximization of occupied adsorption sites on Ru by Si–O–. It is counterbalanced by the energy necessary to strain the local chemical bonds in length and angle in the silica layer and/or from it to the Ru, to produce defects. The two phases accommodate the misfit to the Ru periodicity^{10,56} differently. The rotated ML phase shows a moiré pattern, i.e. the misfit is taken up by the incommensurate periodicity, while the $p(2 \times$ 2) ML phase adjusts to the Ru periodicity and incorporates the misfit inside the silica ML. This difference may be caused by the incommensurability of the rotated phase.

We note that the reversible interconversion of the two ML structures⁵⁷ has been observed here as well (925 K, 5×10^{-6} mbar oxygen).³⁰

3.4. Silica Bilayers. 3.4.1. Physisorbed Crystalline Bilayer. The preparation of the crystalline SiO₂ bilayer is well established.⁵⁸ While it is possible to carry out a one-step procedure (Si evaporation in oxygen at elevated temperature; see ref 31 for details on the growth modes under these conditions), the standard procedure is to use a three-step procedure which produces a continuous film.³¹ In this, the Si

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amount corresponding to a BL is first deposited on a 3O/Ru(0001) surface in 2×10^{-7} mbar O₂ at room temperature. The XPS measurements presented in Figure 8 show that the deposited Si is partially oxidized by the preexisting 3O-layer on Ru but not completely oxidized by the O₂ in the chamber (see Si 2p components). Regarding long-range order, LEED after deposition shows nothing but a blurry background, with the corresponding decrease in intensity of the (2 × 2) spots of the 3O layer during deposition; the LEEM-IV curve is also without structures (Figure 8d). This indicates the formation of a completely (i.e., 3-dimensionally) amorphous SiO_x film which, in contrast to the vitreous bilayer, completely lacks order in the surface plane as well as perpendicular to it.

An additional heating step to ~1050 K with a heating rate of 1 K s⁻¹ in 5 \times 10⁻⁶ O₂ for 10 min completes the oxidation of the film and produces order. The formation of the crystalline bilayer was always followed in LEED, and the appearance of the (2×2) spots in LEED at elevated temperature was used as indication for the onset of structure formation. This is an important detail, because its appearance at high temperatures allows the distinction of the crystalline bilayer phase from the 30 phase which possesses the same superstructure in LEED but would be totally disordered above 700 K (see section 3.1). At the end of the sample preparation, the LEED pattern at room temperature is identical to that shown in Figure 1 for the 30 layer. The Si 2p XPS indicates complete oxidation of Si (Figure 8), as evidenced from the corresponding single peak at 102.5 eV. The O 1s XPS for the freshly prepared sample exhibits two major components, the dominant peak at 531.1 eV due to the O atoms in the silica bilayer, and the smaller peak at 529.2 eV of O_{Ru}. Curve resolution indicates that there is essentially no intensity at 529.7 eV indicative of O in Ru– O–Si bonds.^{11,25} The position of the O_{Ru} component agrees quite well with that measured for the bare 3O/Ru(0001) surface without any silica on top (Figure 2). The amount of O_{Ru} underneath the silica film is not easy to assess from the O 1s line because of the overwhelming intensity of the silica bilayer above it. Information can be drawn from the Ru 3d line which has a very similar line shape in the cases of the silica BL and 3O/Ru(0001), thus suggesting an O coverage of around 0.75 ML under the silica film (slight differences cannot be excluded). The work function change from the MEM-LEEM transition (1.08 eV relative to clean Ru) differs somewhat from that expected for the 3O phase (1.24 eV), but the silica bilayer may well add an induced dipole that counteracts that of the 30-Ru layer. As for film morphology, DF-LEEM images (Figure 8e)) show that the two terraces of Ru(0001)—seen as dark and bright-persist, that the silica film adds a grainy appearance (grain size about 30 nm) but no distinct larger scale structure, and that using different superstructure spots does not change the grainy structure but only their intensity. These findings will be discussed below in context with the morphology of the other films.

Variations of this procedure have been tried, as described in refs 30 and 31. They have not yielded other preferable paths. This stresses that under rather widely prescribed conditions the crystalline bilayer phase is a stable layer. However, it is amenable to disorder as will be discussed in the next subsection. Also, at slightly higher temperature the evaporation of SiO_2 starts, leading to dewetting as shown by hole formation. These effects have been described in ref 31. In short summary, heating to temperatures above 1100 K leads to evaporation of SiO_2 , first from step bunches and steps of the

substrate, and then also from continuous terraces. It has been shown that holes in the BL containing ML coverages, as well as holes down to the Ru surface, covered with 3O, are formed. At the borders of the latter holes ML regions can be imaged.^{30,31}

3.4.2. Physisorbed Vitreous Bilayer. If the high temperature annealing during the bilayer preparation is continued under 5×10^{-6} mbar O₂, the disordered (usually called vitreous) bilayer phase¹³ can be obtained, indicated by the transformation of the (2 × 2) superstructure into a ring in LEED and characterized in real space by a range of variable Si ring sizes with a definite size distribution.^{10,20} Thus, this phase is characterized by a very special, two-dimensional disorder in which the correlation between the two Si–O networks of the BL is fully maintained and the BL becomes disordered only *in* the plane. Since in this way a realization of the disorder in bulk silica glass, suggested more than 80 years ago by Zachariasen,⁵⁹ can be obtained, this is a very interesting process which can be used as a model for disordered silica.²²

The two important parameters governing this transition have been found to be temperature and time, with a certain parameter space in which the transformation proceeds; when changing the temperature, the rate of change becomes important as well. Within this range, the lower the temperature the longer one must wait for the complete transformation, and fast temperature ramps are less effective than slow ones, both as expected for an activated process. On the other hand, the system is not far from destruction which occurs by evaporation of SiO₂ and consequent formation of holes in the layer (see ref 31). As expected, evaporation is the process becoming dominant at higher temperatures, as the process requiring more energy. While increasing temperature (1120-1180 K) leads to faster disordering, evaporation increases even more, resulting in more holes in the final layer. This was seen before, 30,31 and attempts were made to avoid it, possibly sometimes arriving at disordered bilayers with holes (with 30 layers at the bottom causing $p(2 \times 2)$ LEED spots to become visible below the 3O disorder temperature of ~500 K, with complete disorder >700 K³⁰) rather than mixed crystalline and vitreous bilayers. With our methods, we can clearly separate these processes on a mesoscopic scale, making sure that we are only concerned with the phase transition from crystalline to vitreous BL. Alternatively, we can preferentially study hole formation and their structure, as described in ref.³¹ Here, the transformation of the crystalline into the vitreous bilayer was followed in LEED and LEEM at different temperatures above the 3O disordering temperature, chosen such that hole formation was minimized, so the $p(2 \times 2)$ intensity must be due to the crystalline silica BL. Since the $p(2 \times 2)$ intensity is superimposed on the developing disorder ring, it is not a good parameter for studying the disorder kinetics; however, it was found that the electron reflectivity of the (00) beam at 42 eV strongly differed for the crystalline and the vitreous phase (being very small for the former and large for the latter for this particular energy) so that it could be used to follow the disordering process in situ for varied temperature. From the temperature dependence of these changes, the activation energy for the transformation was determined in UHV as well as in O2 atmosphere. This analysis is the subject of a detailed paper on the order-disorder phase transition which has been submitted elsewhere,⁶⁰ so only these main facts need to be listed here.

Following the phase transformation in LEEM, as presented in Figure 9, does not reveal any special behavior other than an



Figure 9. Results for the crystalline to vitreous transformation under oxygen pressure: real time recording by (a) LEEM (at 14.5 eV) and (b) LEED (at 42 eV) and comparing the initial and final states in (c) LEEM-IV.

increase in the intensity indicating the higher reflectivity of the disordered film at the energy used. Again, all images show a grainy structure (grain size 20 to 30 nm), as for the crystalline surface, with no major changes. Similar patches of the vitreous layer have been seen with STM, where the boundaries were found to be caused by accumulation of defects (5-5-8) antiphase domain and 5-7 rotational domain boundaries⁶¹). Most importantly, no distinct changes such as new domain structures and/or moving reaction (here disorder) fronts (refs 62-64) have been found. This shows that on the scale of our spatial resolution, the crystalline to vitreous conversion happens homogeneously all over the surface, not by formation of rare nuclei and their coordinated growth, and that the domains indicated by the grainy structure are roughly the same for ordered and disordered silica BLs.

In XPS, the O 1s and Si 2p lines (not shown) show the same behavior as for the crystalline case with two components under the O 1s line due to Si-O-Si and O-Ru bonds. This is not surprising, since apart from the order parallel to the film there are no changes. The work function change derived from the MEM to LEEM transition (Table 1) shows that the vitreous bilayer (1.17 eV relative to clean Ru(0001)) has a slightly stronger O-Ru dipole (higher interfacial O-Ru concentration) or smaller film polarization than the crystalline one Article

(1.08 eV). In principle, the former possibility fits with the shape of the Ru 3d line (not shown) for the vitreous bilayer prepared in O_2 atmosphere, as this is very similar to the one collected for the bare 4O/Ru surface without any silica on top. As expected, a much lower O–Ru content was produced by UHV preparation (see below).

One significant change occurs in the number of oscillations in the reflectivity curves, with the more prominent features surprisingly arising for the vitreous films. As we do not enter into the quantitative discussion of these curves here, we just note that for distinguishing the crystalline from the vitreous phase these curves are excellent fingerprints, as proved by Figure 9c.

The disorder reaction can also be carried out in UHV (p_{O_2} < 5×10^{-9} mbar). The necessary temperatures change somewhat as mentioned above, but no significant differences result. The main difference is that $\Delta \phi$ as well as Ru 3d and O 1s XPS indicate lower $O_{Ru}.$ In fact the O_{Ru} can be varied from 10 to 40 by proper treatment without noticeably influencing the kinetics of the disordering process.⁶⁰ Because the onset for the thermal desorption of O_2 is roughly 900 K, the relatively high temperature required makes it rather difficult to produce Opoor samples without compromising the integrity of the film in some places³¹ (see above). As a result, holes are found in the final silica films with low O_{Ru} , often at step bunches. However, the LEED patterns taken at different stages of the treatment showed that the vitreous structure is predominantly preserved; also, XPS does not show any drastic change (there is a small binding energy shift due to the dipoles of the removed O, see Table 1). The LEEM-IV curves (Figure 10) show that the



Figure 10. Thermal stability of the vitreous BL: Dewetting occurs predominantly at step bunches and steps. The energy axis of the LEEM-IV curves is referred to the MEM-LEEM transition energies, which are given in the legend.

main features of the curves remain unchanged (i.e., the reflectivity modulations are almost identical), with only a small shift of the curves, again consistent with the changed work function by removal of O-Ru.

After producing the disordered BL in UHV, the amount of interfacial oxygen under the bilayer, $O_{Ru\nu}$ can be tuned by exposure to O_2 (1 to 5×10^{-6} mbar) at high temperature (typically 1170 K) for extended time periods (20 min or more), up to a coverage of 4O as shown above and indicated

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Figure 11. Characterization of the ZZ structure (the chemisorbed BL): (a to c) XPS, (d) LEEM-IV, and (e) LEED (42 eV) and DF-LEEM (15 eV).

by the Ru 3d XPS (not shown³⁰). The same procedure applied to a crystalline BL does not change the O_{Ru} appreciably which shows that the oxygen intercalation must mainly proceed through the larger meshes of the disordered BL, not by adsorption in mesoscopic holes of the overlayer and subsequent diffusion of O under the BL. It has also been found that small molecules like CO^{65} and $H_2^{26,64}$ can be intercalated, showing that both intercalation and removal of material, with bonding to Ru under the BL, essentially preserves the film structure. This made it possible to study a reaction under cover (water production from $O_{ad} + H_2$ and removal) with surprising results as reported in ref.⁶⁴

3.4.3. Chemisorbed Bilayer (Zigzag Phase). In the course of this work, a bilayer structure was observed which was clearly distinct from the physisorbed bilayers and observationally was characterized by a highly symmetrical, complex LEED pattern (Figure 11). The appearance of this LEED pattern is due to the superposition of three rotational phases. The geometry of each of these domains is characterized by a rectangular unit cell with a glide mirror plane (observable by a missing LEED spot). DFT calculations arrived at essential agreement with the structure derived from the STM images.¹² The proposed structure shows that this layer is chemisorbed, because there are Ru-O-Si bonds tying down the layer to the substrate. It appeared very interesting, therefore, to investigate the conditions under which this polymorph (subsequently termed the ZZ phase) is produced, and its evolution during formation. Of particular interest was to find out what steers the evolution of a Si deposit suitable for a silica bilayer to become either a

physisorbed or a chemisorbed layer. We therefore used our arsenal of methods to investigate the formation of the ZZ phase on two different paths: (1) annealing slowly in UHV³⁰ or (2) annealing rapidly in O_2 .¹²

Both recipes start with the deposition of the amount of Si corresponding to a silica bilayer in 2×10^{-7} mbar O₂ (like for the two physisorbed bilayers). In recipe 1, the Si deposit is then completely oxidized in an intermediate step in 5×10^{-6} mbar O₂ at ~590 K, again demonstrating the catalytic effect of the Ru interface to oxidize Si. After this step, the O₂ is pumped out of the chamber and the film is slowly heated up at 1 K s⁻¹ in UHV (p_{O2} < 2 × 10⁻⁹ mbar) to 1080 K. Because the structure formation is continuously observed with μ -LEED all the way to the final temperature, it is possible to follow the development of the spots in LEED to the point where the rich pattern of the ZZ structure is obtained (about 1080 K).

Recipe 2, reported in ref 12, follows the normal procedure for the preparation of the physisorbed bilayers (oxidation in 5 \times 10⁻⁶ mbar O₂) but then the sample is flashed to 1080 K with high heating rate (>10 K/s). Using this procedure, we also followed the entire process by in situ μ -LEED, and the same structure formation was seen to evolve.

The most important result is that both recipes give the same type of sample in terms of structure; only some minor differences in the LEEM-IV curves are visible (Figure 11). The work function changes from the MEM-LEEM transitions (see legend in Figure 11d) show that the sample produced in UHV has a somewhat lower work function (by 0.26 eV). This is

	ML		BL				
structure	(2×2)R30°	p(2×2)	ZZ structure		p(2×2)	vitreous	
po2 (mbar)	< 5×10 ⁻⁹	5×10-6	< 5×10 ⁻ 9	5×10- 6	5×10 ⁻⁶	< 5×10 ⁻⁹	5×10-6
Tanneal (K)	1075	1045	1080	1080	1050	>1025	>1075
Heating rate (K/s)	7	1	1	7.5	1	1	1
Holding time (min)	1.25	10	5	2	10	$\sim \exp(-\frac{E}{kT})$	$\sim \exp(-\frac{E}{kT})$
LEED, 42 eV at RT			۲		۲	0	
Δφ referred to Ru(0001) (eV)	0.58	1.28	0.57	0.83	1.08	0.19	1.17
XPS peak shape of Ru 3d _{5/2}	10	30	10	10	30	10	40
E _B Si 2p Si-O (eV)	102.8	102.3	102.8	102.6	102.5	102.9	102.4
E _B O 1s O-Si (eV)	531.7	531.2	531.7	531.4	531.0	532.0	530.9

Table 1. Overview about Structures and Preparation Parameters:

likely caused by a smaller O_{Ru} concentration, compatible with the O-deprived atmosphere during formation.

The XPS data (Figure 11) do not show any clear differences between the two types of samples created following the two recipes. In the O 1s region, both Ru–O–Si and O_{Ru} are weak for both recipes, and the Ru 3d peak is quite narrow and corresponds to a coverage between 1O and 2O. However, there are differences compared with the physisorbed silica bilayers (crystalline and vitreous), the clearest one being in the O 1s line where the component corresponding to the O_{Ru} species is weaker or lacking for the ZZ phases.

The dark field LEEM images in Figure 11, taken by using the marked LEED spots, show that, by choosing different LEED beams, the three rotational domains can be distinguished. As for the physisorbed BL, no major structures can be discerned apart from step bunches which appear dark (in BF-LEEM they appear bright), and the grainy domains seen for the other bilayers; here, their scale is around 15-20 nm. The LEEM-IV curves are identical for all domains and distinctly different from the physisorbed BL; in the fully developed layer, they are found over the entire surface. In their evolution, no structural changes happen during the heat-up during which the layer stays amorphous; the LEED structure develops at 1080 K uniformly over the entire surface. The LEED pattern contains the 3-fold rotational and 2-fold mirror symmetries. The size of the rectangular unit cell is 9.4 Å \times 7.6 Å, with the short axis being incommensurate to Ru(0001) (see ref 12). As mentioned above, the main aspects could be modeled by DFT calculations, and agreement with the STM results was reached, except for the inaccessible incommensurate axis.

Examining the optimized structure,¹² we note that they agree quite well with our results. The unexpectedly weak O 1s signal component indicating Ru–O–Si bonds may be explainable by partial shielding of the exiting photoelectrons by close Si atoms. The fact that the Ru 3d signal indicates more O_{Ru} than expected suggests again that the surface core level shift of Ru atoms not only responds to chemisorbed O atoms on Ru, but partly also to Ru–O–Si bonds (as seen for the $p(2 \times 2)$ ML phase, see above); this would again indicate a strong polarity of that bond.

The described procedure leads to a rather pure ZZ layer. With slight changes of the procedures one can also produce inhomogeneous layers, in which there is coexistence of two or even all three BL phases. They can be clearly seen by superimposed LEED patterns. Some have been described in ref 30. In the STM study, where such coexistence makes it possible to observe more than one phase on the same surface, this was achieved by very fast heating to lower maximum temperatures (1135 K).

The possibility to convert the phases into each other has also been checked. It was found that it is possible to convert the ZZ phase into the crystalline and vitreous BLs.

4. DISCUSSION

Our data and their interpretation have shown many characteristics of the three bilayer and the two monolayer silica phases, their optimal production including variants, and their dynamics of evolution and conversion (where applicable). The most likely interpretations have been given following the data presentation. Where overlap exists, the result has been in very

good agreement with previous work in most cases. Some open questions require the combination of the different data sets to be addressed. Table 1 gives a compilation of all phases and their main characteristics, and Figure 12 compiles the connections between them.



Figure 12. Preparation pathways for (a) MLs and (b) BLs depending on oxygen pressure and sample temperature. Point A indicates the Si deposition at room temperature in 2×10^{-7} mbar oxygen for both films. The solid points of different color indicate the obtained phases as listed in the figures. The annealing pathways including conversions are indicated by solid lines with arrows. Dashed lines indicate only changes of oxygen pressure. Conversion pathways (D for ML, and E and H for BL) are depicted by horizontal lines with arrows.

The two most interesting aspects of our results which deserve discussion concern the steering of the same starting condition into different phases, and the observation by our microscopies that all the phases grow and convert (where possible) homogeneously over the surface. For the first aspect, the compilation of pathways in Figure 12 emphasizes the branching, from the same initial ML or BL deposits, into one of two ML phases or into either physisorbed or chemisorbed silica BL phases. The strong influence of the oxygen pressure is obvious from it. It has been discussed before for the MLs;⁵ our results confirm these findings and extend them to the dynamics of the processes. For the BLs, work on the O_{Ru} influence on the electronic states of the BL has been published (refs 25 and 26), but its steering effect on the selected phase is new. In addition, annealing temperature and heating rate are important: starting with BL deposits, fast heating to the required ordering temperature produces the chemisorbed ZZ structure while slow heating leads to the physisorbed (crystalline or vitreous, depending on anneal temperature) BL. We explain this by the following scenario: in order to make the decoupled, self-contained physisorbed bilayer possible, the formation of Ru-O-Si bonds has to be suppressed. This is done by chemisorbed O on Ru; the BL can be anchored by Ru-O-Si bonds only where the Ru surface is not blocked by them. If there is not sufficient O_{Ru} present, a physisorbed phase will be formed. In order to maintain sufficient O_{Ru}, O atoms have to diffuse on Ru below the (still 3D-amorphous) silica during annealing. If the heating rate is higher than the O diffusion rate under the deposited layer, the ZZ phase will form; otherwise one of the physisorbed BL results. So the local O concentration under the layer steers the reaction; but that concentration under reaction conditions depends on the heating rate which becomes the external determining parameter. The physisorbed bilayers can be produced without

admixture of the chemisorbed one; optimizing for the ZZ phase needs higher temperature, where competition with SiO_2 desorption and hole formation sets in. The crystalline BL is converted to the disordered one irreversibly. The ZZ phase can be converted into the physisorbed ones, but the necessary high temperature (1125 K under 5×10^{-6} mbar oxygen) leads to partial disordering of the formed crystalline BL, so that surfaces with coexistence of all three BLs can be prepared in this way.

As for the two ML phases, they must be close in energetics. The $p(2 \times 2)$ phase likely is the preferred one (energetically or kinetically) since it can be produced pure while the rotated phase always contains a certain preparation-dependent amount of coexisting $p(2 \times 2)$, albeit in smaller domains as judged from the diffuse LEED spots. The formation of the rotated phase is activated. As already observed for the bilayers, the O_{Ru} concentration directs the growth of one or the other phase: heating in oxygen only develops the $p(2 \times 2)$ phase while by heating in UHV the rotated structure is also formed. This may be due to the fact that in the $p(2 \times 2)$ structure the site on Ru of the connecting silica tetrahedral is always the same, while in the rotated (2×2) , which is incommensurate to Ru, connection to different Ru sites occurs. A lower O_{Ru} concentration will allow this site flexibility. Again, optimizing for the rotated phase runs into the problem with desorption and hole formation. The two ML phases can be interconverted reversibly, as reported before.

For the second aspect, we emphasize that, as shown by the DF-LEEM images, all these reactions occur homogeneously all over the surface, on the scale of our resolution (5-10 nm). For all phases we find domains (indicated by a grainy structure best seen in DF-LEEM) which are uniform over distances of the order of 15-40 nm. They are separated by domain boundaries which most likely consist of defect accumulation, possibly by the type that has been seen in STM.¹² This is most easily understandable for the ZZ phase which is incommensurate with Ru in one direction but tied down to it, since this will accumulate misfit. For the better matched physisorbed layers which furthermore are not tied down by chemical bonds, this is more difficult to understand. But also for those layers there is a misfit: according to calculations mentioned above the free bilayer would have a lattice constant larger than Ru(0001) by 1.9%.⁵⁶ And there is coupling too, as shown by the alignment of the BL to the Ru surface. As this cannot be mediated by chemical bonds, it must be mediated by the corrugation of the potential above the surface: Any of the O/Ru terminations produces a corrugated potential plane parallel to the surface that will couple to the BL; if then a $p(2 \times 2)$ fit develops this will lead to strain in the BL. Again, after a number of cells a misfit will accumulate that will relax by defect lines. For the MLs there are also misfits between the free and the tied-down layer⁵⁶ which in the $p(2 \times 2)$ case is taken up by strain in the layer, while for the rotated phase a moiré structure develops, so the misfit manifests itself by strain between the layers. Coupling to the Ru lattice is easy here since both MLs are anchored to the latter by chemical bonds.

Another explanation (both not necessarily mutually exclusive) for the small domains could be that for any forming phase the nucleation is homogeneously distributed over the layer, so that small islands with different orientations and shifts start to expand and collide with each other when they meet. The size of the "grains" which we see in LEEM could then be a measure of the mean distance of nucleation centers for the respective phase. Unfortunately, our spatial resolution is not

good enough to resolve these processes; and STM presently lacks the real-time, *in situ* capabilities. One might consider model calculations to simulate these processes.

5. SUMMARY AND CONCLUSIONS

This work has addressed the details of the characteristics and the formation and evolution of two monolayer and three bilayer silica films on Ru(0001). Table 1 summarizes the various data comprehensively. Figure 12 gives an overview of the various paths for the preparations. As for morphology, we have shown that the nucleation and growth of all phases occurs homogeneously and results in domains of the various phases of sizes between 15 and 40 nm; the distances between nucleation centers are correspondingly small. The importance of interfacial oxygen for determining the selection of phases has been corroborated and its understanding amplified, and mechanisms for this steering effect have been demonstrated. The variations of preparation procedures used and the ability to find conditions for optimization of the various phases or for coexistence will be helpful for future work with homogeneous samples exceeding the nanometer scale.

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Notes

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