# **Transfer of 2D Silica Films**

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Abbreviations G		Gr	Graphene
2D AES AFM	Two-dimensional Auger electron spectroscopy Atomic force microscopy	LEED ML PMMA STM UHV	Low energy electron diffraction Monolayer Poly(methyl methacrylate)
DFT ESEM	Density functional theory Environmental scanning electron microscopy		Scanning tunneling microscopy Ultra-high vacuum

In the last years, silica bilayers with reproducible preparations and versatile structures have been reported by several groups.<sup>1–5</sup> The films consist of two layers of tetrahedral [SiO<sub>4</sub>] building blocks, connected by bridging oxygen in a mirror plane. All building blocks are coordinatively saturated, and no dangling bonds are present. Furthermore, no covalent bond is formed with the substrate; only weak interactions are assumed. Accordingly, it has been possible to grow SiO<sub>2</sub> bilayers on a range of substrate materials using several growth protocols. Hence, the bilayer structures represent an inherently stable morphology, which can be added to the library of two-dimensional (2D) materials.

Due to the fact that interaction between film and substrate is based on van der Waals forces, silica bilayers exhibit a great structural variety, which can be tuned with choosing appropriate supports and growth conditions. On Ru(0001) single crystals, silica films can be grown as monolayers (MLs), which are covalently bound to the substrate, or as bilayers, where  $[SiO_4]$  tetrahedra arrange in a self-saturated double sheet. Depending on other preparation conditions, the intertetrahedral connection angles can be uniform, yielding a crystalline network, or they can exhibit a range of values, yielding an amorphous network.<sup>6,7</sup> Both variations of the bilayer film are atomically flat, enabling high resolution imaging with scanning probe microscopy techniques. Fig. 1A shows an atomically resolved scanning tunneling microscope (STM) of an amorphous SiO<sub>2</sub> bilayer on Ru(0001). The Si positions are clearly identifiable, and the O positions can be inferred geometrically. The individual building blocks form ring structures which are labeled according to the number of involved Si atoms. Fig. 1B shows a histogram of the ring sizes occurring in Fig. 1A, highlighting that the six-membered ring is the most frequent structural motif. DFT calculations confirm that the six-membered ring is energetically most favorable,<sup>4</sup> and crystalline 2D silica is formed exclusively from six-membered rings.

As indicated by Fig. 1C, the larger scale structure of silica bilayers can exhibit holes, which result from depositing less Si than a full bilayer coverage. The resulting mesopores often go through the whole bilayer and expose the substrate. A fully closed bilayer film is denoted as 2 ML coverage. Some holes with 5–15 nm in diameter are visible in the STM image in Fig. 1D. The preparation shown here has a surface coverage of 1.6 ML and the atomic structure is predominantly amorphous.

Making 2D SiO<sub>2</sub> available for nanoelectronic device building, manufacturing sensors and other applications, requires a certain robustness of the material, methods for handling the thin films and, ultimately, scalable preparation techniques.

The SiO<sub>2</sub> films are chemically inert, as was recently demonstrated in detailed hydroxylation experiments. These studies showed that water vapor or ice layers present on the film surface alone led to no or very little hydroxyl formation.<sup>8</sup> Electron bombardment was employed as activation method to create OH groups in significant surface concentrations.<sup>9</sup> Using a state-of-the-art liquid atomic force microscopy (AFM), it is furthermore possible to image the morphology of 2D silica films under water, which highlights the stability against aqueous environments, even during exposure of several days.<sup>10</sup> It was shown that the mesoscopic hole structure as well as the amorphous arrangement of nanopores is preserved under aqueous environments.

The silica films imaged in liquid AFM were prepared in an ultrahigh vacuum (UHV) chamber; hence the study involved transferring the films from UHV to the liquid cell, including handling them in air for a short time. In a different report, 2D silica was supported on a graphene sheet and exposed to ambient conditions for roughly a year, where no chemical decomposition was observed.<sup>3</sup> Exposure of 2D silica to ethanol and acetone has also been tested, with no significant changes observed in the film characteristics as measured by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES).<sup>11</sup>

The stability of silica bilayers against air, water, and other liquids is promising for incorporating thin  $SiO_2$  films in devices such as nanoelectronic components comprised of 2D materials. This goal requires combining silica bilayer with other nanosheets, in order to achieve the desired functionalities. One option for achieving this combination is layer-by-layer growth, that is depositing



**Fig. 1** Characteristic structure of silica bilayers. (A) STM image with atomic resolution, revealing Si positions. In the lower right half of the image, Si positions are marked with green circles, and subsequently inferred 0 positions with red circles. Scan size 5 nm  $\times$  5 nm,  $V_S = 1$  V,  $I_T = 50$  pA. (B) Histogram plot of ring sizes observed in panel (A). (C) Schematic representation of the 2D film on a Ru(0001) substrate; due to the partial surface coverage some holes in the silica expose the substrate. (D) STM image showing holes in the film. Scan size 40 nm  $\times$  40 nm,  $V_S = 3$  V,  $I_T = 10$  pA. Reproduced with permission from Büchner, C.; Wang, Z.-J.; Burson, K.M.; Willinger, M.-G.; Heyde, M.; Schlögl, R.; Freund, H.-J. A Large-Area Transferable Wide Band Gap 2D Silicon Dioxide Layer. *ACS Nano* **2016**, *10*, 7982–7989, http://dx.doi.org/10.1021/acsnano.6b03929.

each layer on top of the stack. It has been shown, however, that growth substrates for silica bilayers must allow annealing temperatures of several hundred degrees, both for achieving cleanliness prior to growth and for postdeposition annealing of the silica films. This requirement is mostly met by metal substrates, where single crystals, nanoparticles, and thin films have been successfully used for growing 2D silica.<sup>1,2,5,12–14</sup>

More flexibility for device building is provided by the ability to deliberately place 2D SiO<sub>2</sub> layers on other materials, including those that may not be suitable as growth substrates. Fig. 2 shows a schematic representation of a reliable transfer procedure for silica bilayer films grown on Ru(0001).<sup>15</sup> A SiO<sub>2</sub> bilayer supported on a Ru(0001) single crystal (panel A) is spin-coated with a thin layer of poly methyl(methacrylate) (PMMA) (panel B). By mechanically exfoliating or lifting off the polymer layer, the silica film is also delaminated from the metal substrate (panel C). Hence, the silica bilayer is supported on the PMMA film (panel D). This stack can be placed on a new support material (panel E). For this study, a Pt(111) crystal was chosen and the polymer was removed by applying a gentle heating step. Panel f shows the silica bilayer supported on the new substrate.

#### **Experimental Section**

The metal-supported silica layers were grown and investigated in a custom-built UHV chamber, equipped with an LEED/AES unit, and a low-temperature STM with a Pt/Ir tip. Transferred films were imaged using an environmental scanning electron microscope (ESEM), providing morphology information from nanometer to millimeter length scales. This instrument can image samples at elevated temperatures in partial pressures of reactive gases. Scanning electron microscopy commonly suffers from carbon deposits on sample positions that were exposed to the electron beam.<sup>16</sup> In the ESEM, the formation of carbon deposits is prevented by an oxygen partial pressure provided during scanning.

Silica bilayer films are grown on ruthenium supports by a physical vapor deposition procedure with subsequent oxidation. Through varying the deposition time, the final coverage of the film can be tuned precisely. Films that were transferred with the procedure, laid out in Fig. 2, typically had coverage between 1.6 and 1.8 ML. The corresponding film morphology shows flat terraces and holes, where the substrate is exposed.

 $SiO_2/Ru(0001)$  samples are removed from the vacuum chamber and mounted in a spin coater. A 20.7 wt.% solution of PMMA in acetone is used to spin coat a thin layer on the sample. The PMMA used for this study (product name: Polymethylmethacrylat



**Fig. 2** Schematic for transferring 2D silica films. (A) SiO<sub>2</sub> bilayer supported on Ru(0001). (B) Sample spin-coated by PMMA. (C) Mechanical exfoliation of PMMA layer to which SiO<sub>2</sub> adheres. (D) Silica bilayer supported on PMMA. (E) PMMA-silica stack on new Pt(111) substrate, heating step removes the polymer. (F) SiO<sub>2</sub> bilayer supported on Pt(111). Adapted with permission from Büchner, C.; Wang, Z.-J.; Burson, K.M.; Willinger, M.-G.; Heyde, M.; Schlögl, R.; Freund, H.-J. A Large-Area Transferable Wide Band Gap 2D Silicon Dioxide Layer. *ACS Nano* **2016**, *10*, 7982–7989, http://dx.doi.org/10. 1021/acsnano.6b03929.

Formmasse 7N, supplier Röhm GmbH, Darmstadt, today Evonik Industries AG) has a molecular weight of roughly 120 kDa.<sup>17</sup> It is important to prepare the solution by slowly dissolving the polymer, as ultrasound treatment used to accelerate the solution process leads to scission of polymer chains,<sup>18</sup> which affected successful transfer in our study. Spinning the sample at 1650 rpm, 0.5 mL of PMMA solution is dispensed on the sample surface so that a ca. 0.3 mm thick polymer layer covers the sample. After approximately 3 min of drying time, this film can be mechanically exfoliated from the crystal, which is most conveniently achieved by using a piece of tape to slowly pull the polymer film up.

The resulting stack of a silica bilayer supported on PMMA is then placed, silica side facing down, on a Pt(111) crystal, which has been cleaned previously in UHV. Platinum was chosen for this proof of concept, because it has previously been demonstrated that silica bilayers supported on Pt(111) are stable.<sup>14</sup> By placing the PMMA/SiO<sub>2</sub>/Pt(111) stack on a conventional hot plate, the sample was heated to just under 300°C for 3 h, resulting in evaporation of the polymer layer. The silica film and metal substrate are not affected by this temperature. The SiO<sub>2</sub>/Pt(111) sample was transferred into the UHV chamber and subjected to a heating step (860°C for 5 min under  $2 \times 10^{-6}$  mbar O<sub>2</sub>) to remove any adsorbates and enable surface analysis.

## Results

The transfer procedure described in the Experimental Section was conducted under ambient conditions. Surface science methods in a UHV environment were used to characterize the sample at several steps. Fig. 3 provides LEED and STM data of the different transfer stages.

The schematics a-d represent the as-grown film on Ru(0001), the plain ruthenium crystal after the silica film is exfoliated, the platinum crystal before the SiO<sub>2</sub> transfer, and the SiO<sub>2</sub> bilayer supported on Pt(111), respectively. Below each graphic, the corresponding LEED pattern and a representative STM image are shown.

The silica bilayer on Ru(0001) is comprised of corner-connected [SiO<sub>4</sub>] tetrahedra that form complex network structures. Depending on the preparation conditions, these structures are predominantly ordered honeycombs, amorphous networks, or a mixture of both. The LEED pattern shown in Fig. 3E exhibits a characteristic ring feature, which indicates a predominantly amorphous silica film. The hexagonal reflexes that are also visible represent the highly ordered substrate material. Fig. 3I shows an STM image of a 1.6 ML silica film on Ru(0001). The flat film covers the substrate, mimicking the atomic steps of the ruthenium. Round holes result from the subbilayer deposition of silicon prior to the film annealing. The holes in this sample extend through the whole film and expose the underlying metal. After the PMMA-assisted exfoliation, the remaining Ru(0001) crystal can be transferred back into the UHV chamber to verify the removal of the silica bilayer. The LEED pattern shown in Fig. 3F does not show any signature corresponding to a silica film anymore. The only features are the substrate reflexes. In STM (Fig. 3J), flat terraces typical for clean metals are observed. The round-hole morphology that is typical for 2D SiO<sub>2</sub> is not found after the exfoliation step. Both the LEED and the STM measurements can be taken on different areas of the sample, yielding equal results. This step verifies the complete removal of the silica film through the mechanical exfoliation step.



**Fig. 3** LEED and STM data of transferring a 2D silica film. (A–D) Schematic of silica bilayer on Ru(0001), of plain Ru(0001) crystal, of plain Pt(111) crystal and of silica bilayer on Pt(111) (E–H) LEED pattern of silica bilayer on Ru(0001), of plain Ru(0001) crystal, of plain Pt(111) crystal and of silica bilayer on Pt(111). (i-I) STM image of silica bilayer on Ru(0001), of plain Ru(0001) crystal, of plain Pt(111) crystal and of silica bilayer on Pt(111). (i-I) STM image of silica bilayer on Ru(0001), of plain Ru(0001) crystal, of plain Pt(111) crystal and of silica bilayer on Pt(111). (i-I) STM image of silica bilayer on Ru(0001), of plain Ru(0001) crystal, of plain Pt(111) crystal and of silica bilayer on Pt(111). All scans 50 nm × 50 nm, (I)  $V_S = 1$  V,  $I_T = 50$  pA; (J)  $V_S = 2$  V,  $I_T = 50$  pA; (K)  $V_S = 0.5$  V,  $I_T = 50$  pA; (L)  $V_S = 1$  V,  $I_T = 100$  pA. Adapted with permission from Büchner, C.; Wang, Z.-J.; Burson, K.M.; Willinger, M.-G.; Heyde, M.; Schlögl, R.; Freund, H.-J. A Large-Area Transferable Wide Band Gap 2D Silicon Dioxide Layer. *ACS Nano* **2016**, *10*, 7982–7989, http://dx.doi.org/10.1021/acsnano.6b03929.



**Fig. 4** Imaging a transferred SiO<sub>2</sub> film at different length scales. (A) STM image, 50 nm  $\times$  50 nm,  $V_S = 0.5$  V,  $I_T = 100$  pA, showing holes of up to 30 nm in diameter. (B) ESEM image (contrast inverted) 500 nm  $\times$  500 nm,  $H_A = 12.5$  kV, showing holes of 30 nm in diameter and larger. (C) ESEM image (contrast inverted) 500  $\mu$ m  $\times$  500  $\mu$ m,  $H_A = 7.5$  kV, showing holes of various sizes. Reproduced with permission from Büchner, C.; Wang, Z.-J.; Burson, K.M.; Willinger, M.-G.; Heyde, M.; Schlögl, R.; Freund, H.-J. A Large-Area Transferable Wide Band Gap 2D Silicon Dioxide Layer. *ACS Nano* **2016**, *10*, 7982–7989, http://dx.doi.org/10.1021/acsnano.6b03929.

A clean Pt(111) substrate was cleaned in UHV to be used as new support for the silica bilayer. In LEED (Fig. 3G), it exhibits hexagonal reflexes and in STM (Fig. 3K), clean terraces with monatomic step heights. This crystal is transferred out of the UHV chamber and placed on a laboratory heating plate in ambient atmosphere. The silica film on PMMA is placed on the Pt(111) crystal, silica side facing down. Through gentle heating for an extended amount of time, the polymer is evaporated. After transferring the  $SiO_2/Pt(111)$  sample into UHV, it can be studied with surface science methods. The LEED pattern is shown in Fig. 3H, exhibiting a weakly defined ring feature. This feature clearly indicates the presence of an amorphous structure on the platinum substrate. Fig. 3I shows a representative STM image of the silica film on Pt(111), with a flat film structure and characteristic round hole features. The area covered by holes is analyzed to determine the coverage, yielding 1.6 ML, the same amount as before the transfer.

In order to study the outcome of the sample transfer at a larger scale, the  $SiO_2/Pt(111)$  was investigated in ESEM. Fig. 4 compares an STM image (Fig. 4A) of 50 nm × 50 nm scan size with an ESEM image (Fig. 4B) that is ten times larger. While the STM alone can resolve hole features that are a few nanometers in diameter, the largest holes visible in STM are found as well in the ESEM image. In both images, one such feature is indicated with a white arrow. This similarity between the two different images allows us

to correlate the structures on both length scales, indicating that the morphology does not suffer significantly from the transfer procedure. Fig. 4C shows an ESEM image of 500 µm scan size, exhibiting a uniform smooth film and round hole features. We observe that most of the Pt(111) crystal is covered by this film, with the only visible defects being craters and scratches on the micrometer scale that originate from the metal crystal. Hence, we conclude that the film was transferred as an intact sheet, effectively on a cm scale.

#### Discussion

This demonstration of the transferability of silica bilayers is promising for future incorporation of 2D silica in nanodevices. However, the parameter space that is known for growing silica bilayers is relatively large and still expanding. Different choices of substrate, deposition method, surface coverage, temperature ramps, and dopants can yield slightly different silica bilayer outcomes. The films used in this proof of concept represent only a small part of this parameter space. Our growth was typically carried out on Ru(0001) substrates, allowing us to refine our preparation and achieve optimal throughput. On this support, silica bilayers can grow in commensurate honeycomb sheets, or in amorphous topologies.<sup>4-6</sup> Previous studies reported that fully closed films are predominantly crystalline with a honeycomb lattice, while coverages between 1.5 and 1.8 ML are predominantly amorphous.<sup>19,20</sup> The subbilayer films with amorphous topologies could be transferred with the procedure laid out in Fig. 2. Closed silica bilayers with predominantly crystalline order appear to have stronger substrate adhesion, and they were still found on the Ru(0001) after spin coating with PMMA and exfoliation of the polymer. Whether this stronger adhesion is due to the higher surface coverage or the optimized lattice registry or whether the holes in the subbilayer coverage locally weaken the adhesion is not yet understood. However, there is no evidence to suggest that closed, crystalline films are bound to the substrate in a fundamentally different way, but that the adhesive force provided by the PMMA exfoliation is simply not large enough to overcome the substrate adhesion.

It is expected that closed films can be exfoliated from the Ru(0001) either through a different transfer medium with stronger adhesion force, or by first decreasing the substrate interaction, by means like intercalating small molecules that adsorb between substrate and silica film.<sup>21</sup> Furthermore, 2D silica prepared on other substrates very likely allow transfer of fully closed films. Possible choices include Pt(111) which yields predominantly amorphous films independently of the surface coverage<sup>14</sup>, http://dx. doi.org/10.1063/1.3703609 or Pd(111), which yields incommensurate (and hence less strongly coupled) crystalline films<sup>13</sup>, http://dx.doi.org/10.1039/C7CP02382K. These studies would also help explain the enhanced adhesion of closed films on Ru(0001) substrates.

The transferable 2D silica films represent a promising addition to the library of 2D materials. Although manual transfer methods can generally not be scaled up for industrial production scale, this demonstration enables the creation of van der Waals stacks of 2D SiO<sub>2</sub>, graphene, and other nanosheets for fundamental research. Particularly as a 2D insulator, silica bilayers are expected to serve as a helpful alternative. In order to place 2D layers on a support material, typically oxidized wafer surfaces or hexagonal boron nitride nanosheets are used. The former exhibit an inherent surface roughness however, which especially affects the charge carrier properties of graphene sheets, which conform to the substrate roughness.<sup>22,23</sup> h-BN layers are typically exfoliated from multilayer materials, which limits control over the layer thickness.

Silica bilayers exhibit a band gap of 6.5 eV, as measured with scanning tunneling spectroscopy.<sup>24</sup> A density functional theory study determined band gaps of up to 7.3 eV, depending on the network topology of the respective silica bilayer.<sup>25</sup> This is the largest band gap of any 2D material currently known, making SiO<sub>2</sub> a suitable insulating layer. Table 1 presents the experimentally verified band gaps of several well-known 2D materials with the respective references.

Besides their very wide band gaps, silica bilayers have other useful properties for combining them with other 2D materials. Graphene layers supported on the atomically flat silica films would not show strong deformations and hence presumably maintain their extraordinary properties. Hence, 2D silica can provide sufficiently flat supports for graphene or 2D semiconductors, improving field-effect transistors built from ultrathin films. In contrast to typical few-layer h-BN substrates, silica bilayers have an atomically defined thickness, as shown in the side view in Fig. 5. By stacking several silica bilayers, thicker insulators could be obtained, while maintaining precise control over the thickness.

Fig. 5 also highlights the difference in pore diameters of graphene versus 2D SiO<sub>2</sub>. Several reports show that the pores can be penetrated by small atomic or molecular species, while others are prevented from migrating through the silica films.<sup>21,31,32</sup> This property of 2D silica can potentially be utilized in membranes and gas separators, which allow desirable species to pass through. The exclusion of larger species can be utilized for passivating coating layers, preventing corrosion or biofouling of surfaces.

2D material	Band gap (eV)	Measured by	

Experimentally measured direct band gaps for different 2D materials

Table 1

2D material	Band gap (eV)	Measured by	Reference
Graphene	0	Electronic transport	26
Black phosphorous	2	STS	27
MoS <sub>2</sub>	1.9	Optical spectroscopy	28
MoSe <sub>2</sub>	1.55	Optical spectroscopy	29
h-BN	5.56	UV-vis absorption	30
2D SiO <sub>2</sub>	6.5	STS	24



**Fig. 5** Comparison of characteristic length scales in graphene, hexagonal boron nitride, and silica bilayer. Reproduced with permission from Büchner, C.; Wang, Z.-J.; Burson, K.M.; Willinger, M.-G.; Heyde, M.; Schlögl, R.; Freund, H.-J. A Large-Area Transferable Wide Band Gap 2D Silicon Dioxide Layer. *ACS Nano* **2016**, *10*, 7982–7989, http://dx.doi.org/10.1021/acsnano.6b03929.

Furthermore, an amorphous silica bilayer sheet is isotropic in the xy-plane, hence the relative orientation with other layers in a van der Waals stack may be less crucial than when crystalline nanosheets are combined.

In conclusion, an atomically flat  $SiO_2$  sheet with well-defined thickness can be transferred via a mechanical exfoliation procedure. The bilayer films are exceptionally stable due to their fully saturated atomic structure, and show an unchanged sample morphology after the transfer to a new substrate. This proof of concept makes 2D  $SiO_2$  accessible for incorporation into nanodevices, possibly as a well-defined substrate for graphene layers or 2D semiconductors.

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### **Further Reading**

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