Scalable production of single 2D van der Waals layers through atomic layer deposition: bilayer silica on metal foils and films

Gregory S Hutchings, Xin Shen, Chao Zhou, Petr Dementyev, Andreas Hütten, Nassar Doudin, Jesse H Hsu, Zachary S Fishman, Udo D Schwarz, Shu Hu and Eric I Altman

1 Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520, United States of America
2 Department of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06520, United States of America
3 Faculty of Physics, Bielefeld University, 33615 Bielefeld, Germany
E-mail: eric.altman@yale.edu
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Abstract
The self-limiting nature of atomic layer deposition (ALD) makes it an appealing option for growing single layers of two-dimensional van der Waals (2D-VDW) materials. In this paper it is demonstrated that a single layer of a 2D-VDW form of SiO$_2$ can be grown by ALD on Au and Pd polycrystalline foils and epitaxial films. The silica was deposited by two cycles of bis(diethylamino) silane and oxygen plasma exposure at 525 K. Initial deposition produced a three-dimensionally disordered silica layer; however, subsequent annealing above 950 K drove a structural rearrangement resulting in 2D-VDW. The annealing could be performed at ambient pressure. Surface spectra recorded after annealing indicated that the two ALD cycles yielded close to the silica coverage obtained for 2D-VDW silica prepared by precision SiO deposition in ultra-high vacuum (UHV). Analysis of ALD-grown 2D-VDW silica on a Pd(111) film revealed the co-existence of amorphous and incommensurate crystalline 2D phases. In contrast, ALD growth on Au(111) films produced predominantly the amorphous phase while SiO deposition in UHV led to only the crystalline phase, suggesting that the choice of Si source can enable phase control.

1. Introduction
Two-dimensional van der Waals (2D-VDW) materials have attracted a great deal of attention over the last decade because of their stability as individual atomic layers, the unique properties that can emerge when they are reduced to their atomic limit, the potential to tease out novel properties by stacking complementary layers, and the ability to fabricate devices by simple mechanical stacking [1–4]. While progress has been made by thinning bulk 2D materials, it was realized early on that practical applications require controllable growth of one to several 2D-VDW layers [5, 6]. Growth also opens the possibility of generating 2D-VDW layers that typically do not exist in bulk layered forms. Thus, a range of growth processes based on chemical vapor deposition, vapor transport, and reaction and surface segregation have been developed [7–12]. Challenges in reproducibly fabricating single 2D-VDW layers with large domains include growth rates that depend strongly on not only the substrate composition but also its crystallographic orientation, defect density, and thickness, which lead to sensitivities to the reaction or deposition time and temperature [6, 13–15]. On the surface, atomic layer deposition (ALD) would appear to be an appealing way to controllably produce any number of 2D-VDW layers on demand. Ideally, the self-limiting nature of each ALD half-cycle would produce a single 2D-VDW layer; in practice, however, the situation is much more complex. Typically, many cycles are required to create a single layer, and given the intrinsic inertness of 2D-VDW basal planes, even more cycles are necessary to produce additional layers [16, 17]. Further complications include disparities in the temperature requirements for the self-limiting reactions and crystallization [18]. In this paper, it will be shown that these challenges can be overcome for 2D-VDW SiO$_2$,
a unique polymorph of silica that can be a structural template for other 2D tetrahedral oxides, and contains the building block of a wide range of 2D silicates [12, 19–31].

2D-VDW SiO$_2$ is constructed of two mirror image planes of rings of corner-sharing SiO$_4$ tetrahedra [19–25]. It can adopt a crystalline form with only six-membered rings and an amorphous form with four- through nine-membered rings [19–25]. Here-tofore 2D-VDW SiO$_2$ has been grown on late transition metal surfaces (Ru, Pd, Pt, and Ni–Pd alloys) by ultra-high vacuum (UHV) molecular beam epitaxy (MBE) of just the right amount of either Si or SiO at mild temperatures (<525 K) followed by annealing above 975 K in low pressure oxygen (~10$^{-6}$ Torr) [23–25, 27, 32]. Two-dimensional SiO$_2$ has also been observed on graphene on Cu but the growth in this case was ill-defined [21]. The substrate, annealing time and temperature, silica coverage, and cooling rate appear to all play roles in the competition between the crystalline and amorphous forms, but thus far selection between the two phases has proven difficult [33, 34].

Unlike other 2D-VDW materials, the 2D silica bilayer structure intrinsically includes small molecule-sized (e.g. water) openings making it attractive as an ultimate permeation membrane [35, 36, 53]. When doped with Al it displays similar local chemistry to zeolites, making it of interest in catalysis [28, 37]. As a small molecule-permeable 2D-VDW layer it has potential in the emerging area of catalysis under confinement [38–40]. Other potential applications include dielectric layers in VDW heterostructures. It has recently been shown that GeO$_2$ can form a similar 2D-VDW amorphous phase and a theoretical screening highlighted the potential for AlPO$_4$ and GaPO$_4$ to adopt the crystalline 2D-VDW bilayer structure [26, 33]. Therefore, 2D-VDW SiO$_2$ can be considered a prototype for tetrahedrally-coordinated 2D materials. It has also been shown that 2D-VDW silica can be released from its growth substrate both by delamination and by etching [21, 41]. Thus, a key missing piece in furthering research into and application of 2D-VDW silica and related materials is a simple, precise, reproducible, conformable, and scalable non-UHV growth method. The ALD method introduced here meets these criteria, as the few-cycle ALD process with precursors dispensed in a spatial sequence is compatible with roll-to-roll manufacturing.

2. Results and discussion

The target substrates chosen were polycrystalline Pd, Au, and Cu foils and epitaxial Pd(111) and Au(111) thin films. Palladium was chosen based on prior successful 2D-VDW SiO$_2$ growth on Pd(100) and (111) [24, 42, 43], Au because its inertness enables processing in air, and Cu because of its low cost. The foils were selected for their potential in roll-to-roll processes. Meanwhile, the epitaxial Pd(111) film offered the opportunity for detailed structural characterization by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM), and epitaxial Au(111) access to etching methods that allow characterization by high resolution transmission electron microscopy (HR-TEM).

As shown in previous studies, reflection-absorption infrared spectroscopy (RAIRS) can be used to distinguish 2D phases of silicates on metal surfaces, with the benefits that neither atomic-level flatness nor metal facet control are necessary [23]. In addition, the inertness of 2D-VDW SiO$_2$ allows the measurements to be performed at ambient pressure. These benefits make the technique ideal for primary identification of silicates on metal foils. To provide a benchmark, 2D-VDW SiO$_2$ was grown on a Pd foil using SiO MBE. As shown in figure 1(a), the MBE-grown sample displays a distinct vibration at 1289 cm$^{-1}$, which is consistent with previous reports for 2D-VDW SiO$_2$ on Pd(111) and matches the frequency expected for stretching the 180$^\circ$ Si–O–Si bond that joins the two halves of the bilayer [23, 27]. Notably there are no features near 1000 cm$^{-1}$ that are indicative of Si–O–metal linkages [23, 29]. In a parallel experiment, controlled overdeposition to 2.3 ML (where 1 ML = 8.2 × 10$^{14}$ Si cm$^{-2}$−2, half the amount of Si to form the 2D-VDW bilayer structure) through MBE results in a second RAIRS peak at 1265 cm$^{-1}$ (see supporting information available online at stacks.iop.org/2DM/9/021003/mmedia). Peaks near 1260 cm$^{-1}$ have previously been reported following high temperature annealing of 4 ML SiO$_2$/Ru(0001), and several nm thick silica films grown on Mo and have been assigned to vibrational modes in quartz-like structures [23]. Thus, RAIRS can be used to sensitively distinguish if the target silica coverage is exceeded.

ALD was performed using cycles consisting of exposure to the standard ALD silica precursor bis(diethylamino)silane and an oxygen plasma [44], both with the sample temperature fixed at 525 K. The substrates were pre-exposed to the oxygen plasma prior to the ALD cycles to remove any carbonaceous deposits. Initial experiments were performed on substrates that were ‘pre-cleaned’ by UHV sputter-annealing cycles before transfer through air to the ALD system. Two ALD cycles were tested which follows the required silica coverage based on the 2D-VDW silica bilayer structure. As illustrated in the RAIRS spectrum in figure 1(b), the as-deposited silica exhibits only a broad feature centered around 1220 cm$^{-1}$, which can be attributed to a disordered 3D silica layer. Annealing this layer above 975 K in 2 × 10$^{-6}$ Torr O$_2$ (figure 1(c)) led to a sharp peak at 1286 cm$^{-1}$, consistent with reorganization of the silica into the 2D-VDW structure. Because the ALD system cannot reach the required annealing
temperature, the annealing was performed after sample transfer to a UHV system. Insufficient annealing close to the threshold for bilayer formation resulted in coexistence of this broad feature and the expected bilayer SiO$_2$ mode. The slight difference in the IR peak position for the MBE and ALD grown materials can be due to differences in adsorption at the 2D-VDW metal interface [45]. In particular, water and oxygen have been found to preferentially adsorb at the 2D silica/Pd interface [38, 46]. While no impurities on the Pd sample were detected after re-loading the sample into the UHV system and annealing, Auger electron spectroscopy (AES) cannot distinguish adsorbed oxygen, oxygen in water, and oxygen that is part of the 2D material [38, 39, 45].

The data described above were for Pd foils pre-cleaned by sputter/anneal cycles in a UHV system and returned to the same UHV system for the final annealing step. To test whether these two demanding UHV processing steps were needed, two additional samples were prepared by ALD: (a) no UHV pre-clean followed by low pressure oxygen anneal in the UHV system; and (b) UHV pre-clean followed by annealing in a furnace in flowing N$_2$ after ALD. Nitrogen was used rather than air to keep the oxygen partial pressure low enough to avoid Pd oxide formation. At atmospheric pressure O$_2$ are required to avoid SiO$_2$ decomposition, an O$_2$ partial pressure of $4 \times 10^{-8}$ Torr that corresponds to less than 0.1 ppb [27]. The RAIRS spectra for both samples showed peaks at the same 1286 cm$^{-1}$ as the sample that was pre- and post-deposition processed in UHV; this is shown in figure 1(d) for the ambient pressure N$_2$-annealed sample. Thus, neither UHV processing step is necessary. While N$_2$ is mostly inert, x-ray photoelectron spectroscopy (XPS) indicated a faint trace of residual N. The N is not due to the N in the precursor; N was below the XPS detection level for layers annealed in the UHV system (see supporting information). The N incorporation can be avoided by annealing in Ar instead of N$_2$.

To further evaluate the structure of ALD-deposited 2D-VDW SiO$_2$, ALD was used to deposit silica onto an epitaxial Pd(111) thin film. This silica layer was grown using two ALD cycles followed by annealing in low pressure O$_2$ in the UHV system; the RAIRS spectrum showed a peak near 1290 cm$^{-1}$. The LEED pattern for this sample, figure 2(a), exposes a ring of continuous intensity with 12 broad spots superimposed. Analysis of the spot positions in LEED patterns collected at different energies (see supporting information) reproduce prior work on the formation of incommensurate crystalline 2D-VDW SiO$_2$ on Pd(111) in UHV by SiO deposition [42]. Meanwhile, the continuous faint ring is typically assigned to amorphous 2D-VDW SiO$_2$ [23, 41, 43, 47], which has also been reported on Pd(111) [43]. The STM images in figures 2(b) and (c) bear out these assignments. The image in figure 2(b) reveals the hexagonal structure of a crystalline domain while the image in figure 2(c) displays a mostly amorphous region with pockets of crystalline order extending a few unit cells. The coexistence of the amorphous and incommensurate crystalline phases in the ALD grown material is distinct from the prior work, which indicated the
formation of the amorphous phase when elemental Si deposition was the starting point and the crystalline phase when the growth started with SiO deposition [42, 43].

To test whether the ALD process for 2D-VDW SiO$_2$ could be extended to other metal substrates, the same set of experiments was run for polycrystalline Au foils. Gold was chosen for these experiments because its inertness limits the need for pre-processing and allows the annealing step to be carried out in ambient pressure air. RAIRS spectra for two ALD-grown silica layers on Au are provided in figure 3. The spectrum in figure 3(a) is for two ALD cycles followed by annealing at 975 K in 2 $\times$ 10$^{-6}$ Torr O$_2$ while the spectrum in figure 3(b) was obtained following two ALD cycles and annealing in atmospheric pressure flowing air. Both spectra show the characteristic Si–O–Si stretch, in this case at 1284 and 1285 cm$^{-1}$, respectively. AES and XPS of these samples show only Si, O, and Au.

To determine how the deposition method affects the phase of the 2D material, 2D silica was prepared by both SiO MBE and ALD on epitaxial Au(111) films on mica, which facilitated 2D silica transfer to TEM grids. Both the ALD and MBE-deposited layers were annealed in flowing air at 950 K. As visible from figure 4(a), the layer grown by SiO MBE is highly crystalline. Meanwhile, predominantly amorphous structures could be found on the layer grown by ALD as shown in figure 4(b). These results are characteristic of many images recorded over a wide area on several samples. The implication is that the Si source can play an important role in guiding the phase of the final layer. This contradicts prior reports that the strength of the substrate–oxygen interaction governed whether the crystalline or amorphous phase was favored [33]. Regardless, the ability to produce the amorphous phase is desirable for 2D dielectric applications because it eliminates grain boundaries that create discontinuities in the dielectric constants and trap states within the bandgap [48, 49]. The flexibility of the amorphous structure can also be beneficial in fully covering nanostructured surfaces without gross defects, e.g. grain boundaries.

To determine the number of ALD cycles required to cover the surface with a silica bilayer, a set of silica samples was prepared by exposing UHV-cleaned Au(111)/mica to 2–5 ALD cycles at 525 K followed by annealing in flowing air at 925 K. The samples were then analyzed by RAIRS and AES. As shown in figure 5(a), after two cycles the characteristic bilayer stretch is seen at 1280 cm$^{-1}$, although with a higher background between 1000 and 1100 cm$^{-1}$ than the other samples. Notably, by three cycles the peak in the bilayer region shifts downward toward the range seen for ordered quartz-like structures and peaks emerge
between 1100 and 1200 cm\(^{-1}\) that are consistent with bulk silica phases \([23, 50]\). For four and five cycles the features between 1100 and 1200 cm\(^{-1}\) continue to dominate. The AES data in figure 5(b) paint a similar picture. The ratio of the integral of the major Au peak at 64 eV to the O peak at 503 eV for two ALD cycles is comparable to that for 2 ML SiO\(_2\)/Au(111) single crystal deposited by SiO MBE and annealed in 2 \(\times 10^{-6}\) Torr O\(_2\), and the Au peak rapidly decays as the number of cycles increased (see supplemental information for full AES spectra and further details). These data indicate that for Au at 525 K, two ALD cycles is sufficient to closely reproduce the silica coverage obtained through silica bilayer preparation by SiO MBE and UHV annealing.

The same growth procedure was also attempted on Cu foils as an inexpensive substrate. Unfortunately, AES spectra recorded after deposition revealed substantial Cu oxidation, presumably due to the harsh oxygen plasma environment. This oxidation could not be reversed by annealing in vacuum and in the end there was no evidence of 2D silica formation. Given prior reports of 2D silica forming on Cu \([21]\), ALD growth with a weaker oxidant may still be feasible.

3. Conclusions

With the successful ALD growth of 2D SiO\(_2\) on Pd and Au polycrystalline foils and epitaxial films, we have demonstrated a scalable method to produce bilayer SiO\(_2\) that does not require expensive and time-consuming UHV equipment and processes. ALD is sufficient to deposit the SiO\(_2\) precursor at the appropriate thickness, while annealing at 1 atm in either an inert or even open-air environment can produce the 2D material. Moreover, we show that ALD at elevated temperature allows for efficient deposition with only the two ALD cycles anticipated from the 2D silica bilayer structure needed to closely reproduce the coverage obtained by precision MBE. We also demonstrate the potential to control the 2D phase that forms through the Si deposition method with ALD strongly favoring the amorphous phase on Au and SiO MBE producing the crystalline phase. The ALD method unlocks the promise of roll-to-roll production to more easily integrate bilayer SiO\(_2\) into VDW heterostructures, and also provides a roadmap to forming single layer 2D material coatings on rough and nanostructured surfaces including catalytic nanoparticles where the confined space between the 2D layer and the catalyst offers exciting opportunities to control catalytic reactions \([38–40, 51]\).

4. Methods

4.1. Silica growth

Metal foils were purchased from VWR International (Pd: >99.9% metals basis, 0.1 mm thickness; Au: 99.95% metals basis, 0.05 mm thickness). X-ray diffraction of the Pd foil samples revealed predominant (200), (311), and (220) reflections; the intensity of the (111) reflection was smaller by an order of magnitude, which is the only facet with a near match to bilayer SiO\(_2\) (0.275 nm hexagonal surface lattice constant vs. 0.265 nm for half the repeat distance of freestanding crystalline bilayer SiO\(_2\)). To facilitate RAIRS measurements, the foils were mechanically polished to a mirror finish with a progressive sequence of alumina polishing powders. Pd foils were further cleaned with Ar\(^+\) sputtering and annealing in UHV and checked with AES to confirm the absence of residual impurities.

Epitaxial Pd(111)/Cr\(_2\)O\(_3\)(0001)/\(\alpha\)-Al\(_2\)O\(_3\)(0001) films with a Pd thickness of 30 nm were prepared as described previously \([52]\). Epitaxial Au on mica substrates were obtained from either Phasis Särl or Georg Albert PVD. Results for the two sources of epitaxial Au substrates were indistinguishable. Prior to silica deposition the Au on mica samples were annealed in flowing air at 875 K; for the MBE growth the thin film surfaces were also cleaned by sputter/anneal cycles prior to SiO deposition.

ALD deposition was performed using a Veeco Fiji G2 Plasma Enhanced ALD system. To avoid impurities during growth, a two-step pre-conditioning procedure was carried out prior to deposition. The reactor chamber was first baked at 575 K, with the addition of 40 water pulse (0.2 s per pulse) to neutralize possible residuals in the reactor. Then the chamber was cooled to 525 K, and 40 SiO\(_2\) ‘dummy cycles’ were performed to set the desired SiO\(_2\) growth environment. After the preconditioning steps, the sample was loaded and then treated by the oxygen plasma at 300 watts plasma power for 2 min to remove residual C accumulated during atmospheric exposure. Finally, the formal ALD growth of SiO\(_2\) was achieved. Each ALD cycle started with a 0.06 s pulse of the silane precursor, followed by a 15 s pause. Then the O\(_2\) flow rate
was raised to 50 sccm (standard cubic cm per minute), followed by a 20 s O₂ plasma pulse (300 watts), and ended with another 10 s pause. The sample temperature was fixed at 525 K while the reactor pressure was kept near 4 × 10⁻⁴ Torr.

MBE growth was performed by depositing SiO with the sample held at room temperature in 2 × 10⁻⁶ Torr O₂. A high temperature effusion cell (DCA Instruments) was used to sublime SiO. The deposition was monitored with a quartz crystal microbalance to achieve a silicon coverage commensurate with the density of crystalline 2D VDW silica, i.e. 1.64 × 10¹⁵ Si atoms cm⁻².

Final annealing of the samples in UHV was conducted under 2 × 10⁻⁶ Torr O₂ with the temperature measured by an external pyrometer. Ambient pressure annealing was performed under either pure N₂ or air in a tube furnace.

4.2. Characterization

All polarization modulation RAIRS experiments were recorded on a ThermoFisher Nicolet iS50 FTIR spectrometer at a grazing angle of 82°. Baseline correction was applied consistently across samples to minimize introduction of artifacts. Samples were kept in air prior to measurement.

STM images and LEED patterns were recorded in a UHV chamber with a base pressure of 1 × 10⁻¹⁰ Torr, as described previously [24]. Cut-and-pulled PtIr alloy tips biased were used for imaging the SiO₂ bilayer on Pd/CrO₃/α-Al₂O₃. The tunneling current setpoint for the constant current images was set between 0.1 and 1.0 nA; over this range the images were not sensitive to the tunneling current. AES data were collected in the same system using a double-pass cylindrical mirror analyzer at a primary beam energy of 3 keV; the data were collected as N(E) vs. energy and then numerically differentiated to obtain standard dN(E)/dE vs. energy spectra. XPS measurements were performed using a separate PHI VersaProbe II system.

HRTEM images were recorded in a field emission transmission electron microscope JEOL JEM 2200FS operating at 200 keV with the CMOS camera `OneView` from Gatan. The Au/mica substrates carrying 2D silica were first coated with poly(methyl methacrylate) (PMMA) and then etched with I₂/KI in water. Following the rinse with ultrapure water, 2D silica was transferred onto Quantifoil Multi A TEM grids (Quantifoil Micro Tools GmbH), and the PMMA layers were dissolved in acetone. The contrast between the 2D silica and the TEM grid was obvious (see supplemental information).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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ORCID iDs

Gregory S Hutchings @ https://orcid.org/0000-0002-0819-9654
Petr Dementyev @ https://orcid.org/0000-0002-9957-2070
Daniil Naberezhnyi @ https://orcid.org/0000-0002-6848-9434
Udo D Schwarz @ https://orcid.org/0000-0002-5361-0342
Shu Hu @ https://orcid.org/0000-0002-5041-0169
Eric I Altman @ https://orcid.org/0000-0003-4032-271X

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