Title

A method for measuring the local gas pressure within a gas-flow stage *in situ* in the transmission electron microscope

Authors

R Colby^{1*}, DH Alsem², A Liyu¹, B Kabius^{1†}

(1) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA

(2) Hummingbird Scientific, Lacey, WA

* Current address: ExxonMobil Research and Engineering Company, Annandale, NJ

† Current address: Materials Research Institute, Penn State University, University Park, PA

Abstract

Environmental transmission electron microscopy (TEM) has enabled *in situ* experiments in a gaseous environment with high resolution imaging and spectroscopy. Addressing scientific challenges in areas such as catalysis, corrosion, and geochemistry can require pressures much higher than the ~20 mbar achievable with a differentially pumped environmental TEM. Gas flow stages, in which the environment is contained between two semi-transparent thin membrane windows, have been demonstrated at pressures of several atmospheres. However, the relationship between the pressure at the sample and the pressure drop across the system is not clear for some geometries. We demonstrate a method for measuring the gas pressure at the sample by measuring the ratio of elastic to inelastic scattering and the defocus of the pair of thin windows. This method requires two energy filtered high-resolution TEM images that can be performed during an ongoing experiment, at the region of interest. The approach is demonstrated to measure greater than atmosphere pressures of N₂ gas using a commercially available gas-flow stage. This technique provides a means to ensure reproducible sample pressures between different experiments, and even between very differently designed gas-flow stages.

1. Introduction

Transmission electron microscopy (TEM) has been an invaluable tool for exploring the structure and chemistry of materials down to atomic resolutions. However, it is often necessary to study materials *in situ* within their operating environment; catalysts, for instance, may evidence very different exposed surfaces in a gas environment than in the high vacuum environment of a typical TEM^{1,2}. Dedicated environmental TEMs (ETEM) can allow high resolution imaging and spectroscopy in a gaseous environment, but are limited to mbar-range pressures³⁻⁶. To simulate

operando conditions for many relevant systems, higher pressures are needed: the decomposition temperature of PdO in O₂, for instance, changes by nearly 300 degrees between 1 mbar and 1 atm⁷⁻⁹. There have been several reports of greater-than-atmospheric pressures using customized stages in which the gas is contained between two semi-transparent windows, typically a pair of amorphous SiN membranes separated by less than 100 μm¹⁰⁻¹⁷. The various commercial and custom-built systems that have been employed share basic operational principles, but vary in the details of design and implementation. Depending upon the geometry and assembly of a particular stage, the pressure at the sample may not have a straightforward relation to the outlet and inlet pressures under flowing conditions. To ensure the reproducibility across various customized gas stage designs, the pressure should ideally be measured at the sample.

Given the limited space within a TEM-compatible gas flow stage, it may be impractical to design a conventional pressure sensor sufficiently near the sample. Several groups have proposed schemes that utilize the bowing of the SiN window membranes, when pressurized by the gas inside the cell, to estimate the gas pressure¹⁷. This requires foreknowledge of the cell materials and geometry and must be compared to simulations for each change in chip or stage design, such as for windows with customized functionality (e.g. for sample heating or biasing). This also neglects any imperfections in the fabrication or assembly of the cell (for instance, dust particles). While this approach is still promising as an approximation, measurement of the bowing requires one to assess the cell thickness at a bare minimum of two positions, which would mean moving away from the region of interest when one wants to know the pressure during an experiment.

The pressure can instead be measured locally within the TEM using the interaction of the electron beam with the gas as detected by electron energy loss spectroscopy (EELS). A logically similar approach has been used to measure the local temperature of H₂ gas by extracting the inelastic scattering from the H K-edge, for the case of a cell with a nominally known pressure¹⁵. Here, we outline a universal approach to measuring gas pressure using the ratio of elastic to inelastic scattering for any area illuminated by the electron beam. The scattering ratio can be related to the density of the gas by measuring the total volume of the illuminated area, and in turn to the gas pressure via the ideal gas law. The spacing between amorphous SiN windows—and thus the volume of the analyzed gas—can be measured locally from a high resolution TEM image through the two SiN layers at slight defocus by comparison of the Fourier transform to the contrast transfer function of the microscope. In conjunction with energy filtered TEM (EFTEM), it is then possible to measure both the ratio of elastic to inelastic scattering and the volume of the imaged gas concurrently, from only two images. These images can be acquired under the operating conditions of an ongoing *in situ* experiment, in a matter of seconds. The result is a straightforward means of measuring the gas pressure at the sample, at any time during an *in situ*

experiment without leaving a region of interest, and requiring no foreknowledge or simulation of the cell geometry.

2. Experimental Details

The experiments described here were carried out using a probe-corrected FEI Titan 80-300 equipped with a monochromator and a Gatan QuantumER imaging filter, operating at 300 kV. Energy filtered images were recorded with 5 or 10 eV windows (results shown are for 10 eV). The energy selecting window was centered about 0 eV immediately prior to acquiring images (the total range of the drift was found to be ~ 6 eV over the course of a typical experiment). Energy resolution was ≥ 0.3 eV when monochromated and otherwise ~ 0.8 eV (full-width at half-maximum). A Generation I Hummingbird Scientific gas-flow specimen holder was used with high purity N_2 gas at room temperature. Si chips with 30 nm and 50 nm SiN thicknesses were tested, with the minimum space between windows defined by either photoresist pads or amorphous carbon, patterned on the bottom chip (relative to the microscope geometry). The stage was connected to a gas controller through a series of polyetheretherketone (PEEK) tubes (maximum 0.02" inner diameter, 1/16" outer diameter) and PEEK connectors.

Experiments were performed using the single-channel gas flow controller provided with the stage, and a two-channel system designed in-house. The commercial controller provided inlet pressures up to ~ 1.5 atm (~ 22 PSIA) at flows of less than 1 mL/min. The outlet was connected to a roughly equivalent length of tubing as the inlet (~ 1.5 m) to provide symmetry about the viewing window, with the end open to atmosphere. The two-channel gas controller includes a pair of mass flow controllers (MFCs) rated for 0–10 mL/min attached to the inlet, for seamless gas mixing or switching, and a pressure controller (each from Alicat Scientific, Inc.) rated up to ~ 10 atm (0–150 PSIA) attached to the outlet [Fig. 1a].

3. Approach

The electron inelastic mean free path (λ) can be inferred from the ratio of the elastic (I_0) to total scattering (I) using EELS, where t is the thickness of the volume electrons interact with¹⁸:

$$\frac{t}{\lambda} = \ln \left(\frac{I}{I_0} \right) \quad (1)$$

The pressure (P) of molecules in the gas phases is related to the density of those molecules by the ideal gas law ($PV = nkT$, where T is temperature, n the number of gas molecules, V the volume of the system) and λ is inversely proportional to the density:

$$\lambda \propto \frac{V}{n} \quad (2)$$

$$P \propto \frac{kT}{\lambda} \quad (3)$$

Ignoring (for the moment) the SiN windows, the pressure can then explicitly be described by measurable quantities and a single proportionality constant:

$$P_{gas} = \frac{SkT}{t_{gas}} \left(\frac{t}{\lambda} \right)_{gas} \quad (4)$$

The proportionality constant (S) is inversely related to the scattering cross section of the electrons in the gas. In practice, it is not possible to collect all of the scattered electron due to geometric limitations within the instrument, but the relationship between t/λ and N_2 pressure has been measured at room temperature and for 300 kV electrons in a dedicated ETEM^{6,19}, providing a comparable empirical solution for S acquired under analogous conditions. The lower operating pressures in the ETEM are compensated by the larger volume occupied by the gas; there are a comparable number of gas molecules in an ETEM at 1 mbar and a gas-flow stage at 1 bar. For typical collection angles and the range of gas densities considered here, it is appropriate to treat S as a constant.

For a gas-flow cell, the effect of the SiN windows must be taken into account. It is a reasonable approximation to assume that the scattering of the gas and windows is additive, as the total t/λ of a gas cell at 1–2 atm, including two 50 nm thick windows, is typically well less than 1¹⁸:

$$\left(\frac{t}{\lambda} \right)_{net} = \left(\frac{t}{\lambda} \right)_{gas} + \left(\frac{t}{\lambda} \right)_{sin} \quad (5)$$

As the effect of the windows should be effectively unchanged over a range of gas pressures, the equation can then be summarized with empirically determinable parameters S and $(t/\lambda)_{SiN}$:

$$P = \frac{SkT}{t_{gas}} \left[\left(\frac{t}{\lambda} \right)_{net} - \left(\frac{t}{\lambda} \right)_{sin} \right] \quad (6)$$

The effect of the windows, $(t/\lambda)_{SiN}$, can be deduced by taking measurements of t/λ for at least one known pressure. The simplest option is to measure $(t/\lambda)_{SiN}$ directly in the absence of the gas by evacuating the cell. However, the Gen. I Hummingbird system used here included plastic components not suited for high vacuum, and it was not possible to ensure that sample was sufficiently evacuated with this setup. A practical alternative was to measure t/λ for a static cell sealed at a known pressure. This latter strategy is convenient, as experiments typically require the cell to be sealed within a nitrogen glove box, operating at a known pressure (e.g., 1 atm). Ideally, one could calibrate the cell sealed at the maximum desired operating pressure for the

desired gas, followed by a second calibration with an evacuated cell to empirically confirm the range of subsequent measurements.

The SiN membranes can have minor variations in thickness; in particular, the windows tend to be slightly (but appreciably) thicker towards the edges of the viewing area. Ideally, one will determine $(t/\lambda)_{\text{SiN}}$ for each region of interest. While these variations are small, they can have a significant influence on the calculation of $(t/\lambda)_{\text{gas}}$, as the windows are much denser than the gas.

As the gas cell is at much higher pressures than the inside of the TEM column, the SiN windows are forced to bow outwards [Fig. 1b]. The minimum spacing between chips can also increase as the pressure difference is increased. This makes it necessary to measure t at the same time and location as t/λ to correctly assess the pressure. The distance between the windows can be calculated locally by measuring the relative defocus of each window. The Fourier transform of a thin amorphous material imaged in the TEM at sufficiently high magnifications contains an expression of the contrast transfer function of the microscope, which depends upon the defocus²⁰.

$$CTF(q) = \sin \left[\frac{\pi}{2} C_3 \lambda^3 q^4 + \pi (\Delta f) \lambda q^2 \right] \quad (7)$$

For simplicity, equation 7 is the one-dimensional reduction of the two-dimensional contrast transfer function approximated to 3rd order, including only centrosymmetric axial aberrations (e.g. no astigmatism), where q is the reciprocal distance, or frequency. For a well-stigmated image, the Fourier transform will contain concentric rings (Thon rings), with their minima corresponding to the zeros in equation 7. The defocus of an image is assessed by fitting the Thon rings in the Fourier transform (FT) to the corresponding minima of the modulus of the contrast transfer function (MacTempas was used here for this purpose).

For a gas cell with two amorphous SiN windows, the defocus of each window can be measured simultaneously by imaging through cell with the upper window at slight defocus, and the lower window at more significant defocus [Fig. 2c]. The difference between these focal planes gives an accurate measure of the spacing between the two windows, plus the thickness of one window [Fig. 2c, inset]. As a typical window spacing is greater than 1 μm , small variations in window thickness on the order of ~ 10 nm are relatively unimportant (unlike for the measurement of t/λ , mentioned above). This approach is more accurate than relying upon calibration of the objective lens strength for measuring the focus at each window individually, which is generally non-linear at larger defoci, particularly in systems with significant lens hysteresis.

EFTEM provides a convenient means to measure both t and t/λ nearly simultaneously for a large field of view. For EFTEM, I_0 is derived from an image recorded through an energy-filtering slit centered about zero energy loss, and I from an unfiltered image of the same location¹⁸. Statistically significant measurements are obtained for ~ 1 s acquisition times under typical high-

resolution imaging conditions [Fig. 2a,b]. The images can include the relevant sample within the field of view—this is additionally helpful for correcting any spatial drift between I and I_0 images—as long as there is a clear area containing only the SiN windows (and the gas). It is convenient to use the filtered image I_0 to measure t , as the Thon rings are much clearer in the absence of the inelastic background. For the case of an evacuated cell, EFTEM imaging can be used at lower magnifications to effectively map $(t/\lambda)_{\text{SiN}}$ for the entire viewable area prior to starting an experiment, with relatively few images.

An objective aperture was used to restrict the collection semi-angle to match the measurements in the Jinschek, *et al.* used here to derive S for N_2 gas⁶. The aperture is sufficiently large to have no negative impact on high resolution image quality. Measurement of t/λ by EFTEM was calibrated against the standard t/λ measurement from spectra acquired under similar conditions, and compensated accordingly. The resulting value, defined as $(SkT)_{\text{N}_2} \approx 80 (\mu\text{m} \cdot \text{atm})$, is consistent with other reports of t/λ as a function of nitrogen pressure measured by ETEM¹⁹. These values can be used whenever it is sensible to approximate t/λ as linear with P , which should be the case, e.g., for up to at least 5 atm though $\sim 1 \mu\text{m}$ of N_2 gas. In the absence of a convenient ETEM, S could be measured directly as implied above by measuring the desired gas at a known pressure with EFTEM for a given set of microscope conditions, then evacuating the cell *in situ* to calibrate against the effect of the windows.

4. Results

To ensure that the pressure at the sample had reached a steady state before EFTEM measurements, the time required to switch between Ar and N_2 gas was measured. A relatively low rate of 0.5 mL/min, with an outlet pressure slightly greater than 1 atm, was used to provide a very conservative upper limit on the amount of time it could take for small pressure changes at the outlet to stabilize at the sample (e.g., a $\Delta P = 0.2 \text{ atm}$, N_2). N_2 and Ar gases can be differentiated using EELS. The Ar M-edges can be observed at $\sim 12 \text{ eV}$, but the core-loss edges are inconvenient for N_2 gas, as the N K-edge is dominated by scattering from the SiN windows. Many gases have characteristic valence-loss EELS features that can be used to monitor the gas composition²¹. N_2 gas valence features are found at $\sim 13 \text{ eV}$, before the sizable plasmon features contributed by the SiN windows, and specific to the gaseous species. With monochromation (0.3–0.5 eV), it is possible to differentiate N_2 gas from Ar from the low-loss EELS, even through $\sim 100 \text{ nm}$ of SiN. The system was sealed in Ar gas, then connected to N_2 gas while monitoring the spectra over time. The features at 11–13 eV, consistent with Ar gas, disappear within minutes of the system being connected to N_2 , to be replaced by a peak at $\sim 13 \text{ eV}$ that is a good match for N_2 gas [Fig. 3]^{4,21}. Extraneous EELS features are consistent with small amount of air leaking into the stage during the switch, and decrease with time under flowing N_2 . The N_2 feature ceases to

increase within 10 minutes. It is therefore reasonable to expect the sample pressure to stabilize following a system pressure change in under 10 minutes, at flows of ≥ 0.5 mL/min. For a similar test performed a switch from N_2 to CO_2 at the higher flow rate of 5 mL/min (not shown), the spectral features stop changing within 3 minutes.

Using the methods described above, t and t/λ were measured for 5 mL/min of nitrogen with outlet pressures from ~ 1 – 2.2 atm (15–33 PSIA) with a 10-minute interval between pressure changes. The electron beam was blanked between images to minimize exposure. The upper window was coated with a thin discontinuous layer of Au to simulate a sample and aid in alignment of successive images. The stage was sealed in a nitrogen glovebox at 1 atm and regions of interest measured prior to opening the cell to flowing nitrogen. The calculated value of $(t/\lambda)_{SiN}$ was found to be ~ 0.6 through the center of two 50-nm thick windows, consistent with measurements of t/λ through the center of a single window in a vacuum (i.e. differing by a factor of two). The measurements of t/λ and t are recorded in circuits from low to high pressure and back; this ensures reproducibility and accounts for possible changes in the window thickness over time, such as a buildup of contamination under the electron beam (particularly for hydrocarbon gases), or etching of the SiN windows (e.g., with water vapor). The measured pressure, as described in equation 6, is then plotted against both the outlet pressure and an estimated pressure within the stage tip [Fig. 4b]. The estimated pressure is derived assuming that the system is symmetric about the sample, the gas flow laminar, and the gas nominally incompressible at such low flow rates: such that $P_{est} = P_{in} - \Delta P/2$, or the average of the inlet and outlet pressures. While there is variability from one test to the next—attributed to the variability of chips, the loading and alignment of the two windows, and the resulting spacing between the windows—there is always a consistent trend of increasing sample pressures with increasing outlet pressure, for outlet pressures below ~ 2.5 atm.

5. Discussion

As observed in figure 4, the pressure measured at the sample does not necessarily follow a simple Poiseuille-law argument for the setup used here. In experiments including inlet flow control and outlet pressure regulation, the differential pressure increases dramatically with flow rate: as high as ~ 2 atm for N_2 at 5 mL/min. Sample pressures an order of magnitude lower than expected have been measured for lower pressures and flows and with smaller window spacings; e.g., for 1.1 atm N_2 at 0.5 mL/min, with $t = 240$ nm at the edge of the windows.

The observed differences are greater than the error of the measurement. The error bars Fig. 4b are estimated as plus/minus one standard deviation of t/λ as measured across the field of view in the acquired EFTEM images, avoiding regions of the image occupied by the sample (Au particles here), translated to P through equation 6 assuming Gaussian statistics. By comparison

to the error in t/λ as measured by EFTEM, other sources of error are found to be negligible (e.g. on the order of 1% for CTF fitting). The normal range of intensities in an HRTEM image of an amorphous film at defocus is the largest source of uncertainty, and limits the precision of using a simple EFTEM approach to measure pressure. The natural intensity variations in the filtered and unfiltered images do not entirely cancel each other out, even with good spatial alignment of the two images. The calculated pressure does not appear show a significant dependence upon the specific value of defocus. While the measurement is sufficiently accurate for the purposes considered here, the focus-independence of t/λ measured by EFTEM suggests that further improvements in precision can be achieved by averaging measurements at multiple defoci; for instance, one could take advantage of a focal series to improve both P precision and image interpretability (by exit wave reconstruction). Fortuitously, the precision also improves for an increased ratio of scattering from the gas relative to the windows, as is the case for larger windows spacings (t), higher gas pressures, and thinner windows.

There are no observable leaks on the outside of the system, but the pressure within the microscope column (as well as an *ex situ* pumping station used for testing purposes) reacts to increases in the gas flow stage's internal pressure, or flow rate. This suggests a finite rate between the windows and the stage, the outside of which must be held at better than 10^{-7} Torr in the TEM. At outlet pressures above 2 atm (well past the stage manufacture's recommended limits) the measured sample pressures have been observed to decrease with increasing outlet pressure, eventually compromising TEM column pressure. Measurements of t and t/λ for a sealed system (1 atm N₂) indicates negligible changes in cell pressure after 1 hour within the TEM, suggesting that the leak rate is not significant in the absence of flow. Measurements of t and t/λ after (1) loading a cell into the TEM and measuring, (2) unloading, and (3) reloading and remeasuring suggest that loading procedure itself does not cause a significant drop in the internal pressure. Under flowing gas, a leak near the sample should lead to a lower outlet pressure as well. As the system described above is controlled using the outlet pressure, a leak at the sample is not sufficient to explain the results shown in figure 4b. In future designs it would be sensible to add higher precision mass flow gauges on both the inlet and outlet of the system to allow a more precise realtime assessment of potential leak rates, but leaks alone cannot explain the difference between the expected pressure at the tip, and the measured pressure near the sample.

For an idealized single-channel geometry, in which all of the gas flowing through the system passes across the sample, conservation of energy dictates that the pressure across the narrow constriction defined by the chips should be reduced with respect to the inlet and outlet pressures for a fixed flow rate of gas (assuming laminar flow, and that flow rates are small enough that the gas is nominally uncompressed). Under these assumptions, for example, 1 atm N₂ entering a constriction with a 10^4 reduction in area with respect to the inlet tubing would experience a local pressure drop of >20%. This calculation is very sensitive the flow rate and constriction area for a

channel this small, and the precise magnitude of this effect during an experiment would depend on the internal geometry of a gas-flow stage and the channel defined by the chips—which can vary significantly for each set of chips and every time the cell is loaded together. It is not clear how the entire internal geometry could be accurately measured after a cell, such as was used here, is sealed. A larger main channel for the gas should minimize the possible effects hypothesized above, and can be implemented by fabricating cells with a thicker spacer between windows. In practice, cells with larger window spacings did function more intuitively relative to system pressure (up to $\sim 14\text{ }\mu\text{m}$ has been tested). As mentioned above, a thicker gas volume also improves the precision t/λ measurements. Beyond a certain thickness the scattering from the gas could degrade image quality and the relationship between P and t/λ should become non-linear. For e.g. $t \approx 14\text{ }\mu\text{m}$ with an outlet pressure of $\sim 1\text{ atm}$ (N_2) and 50nm thick SiN windows, t/λ was still less than 1 at 300 kV. As the scattering is still dominated by the contribution of the windows ($t/\lambda \approx 0.6$), thinner membranes would relax the cell thickness requirements even further.

For the setup used in this study, gas can also pass around the chips creating a secondary, or “bypass” channel. This design choice allows for fairly straightforward cell assembly and is intended to make the system more robust against sudden pressure changes. However, the volume of this bypass channel is more than an order of magnitude larger than the main channel (which is only microns tall), and thus should host a higher gas flow rate for a given pressure, or vice versa. If the majority of the gas were bypassing the main channel there could, for instance, be a relatively large pressure drop across the sample, but not reflected in a pressure drop across the system. One could further speculate that if the flow rate through the bypass channels is proportionally higher than the main channel, it could create a negative pressure on the main channel.

While the method described here has been demonstrated at room temperature, it should apply to higher temperature gases as long as T is well known, and t/λ remains well less than ~ 1 . It would be important to calibrate $(t/\lambda)_{\text{SiN}}$ at the desired temperature owing to the temperature-dependent low-loss response of SiN (insufficient to measure T_{SiN} independently, but not negligible). One can measure either P_{gas} or T_{gas} *in situ* using the methods outlined here, but not both simultaneously. A more practical approach is *ex situ* temperature calibration—e.g. using the typical infrared imaging techniques to estimate the local temperature under the desired gas flow conditions—followed by *in situ* pressure assessment.

Finally, while the requirement of an imaging filter/spectrometer is not particularly onerous given the increasing ubiquity of EELS on modern TEMs, it may also be possible produce a similar pressure measurement scheme even in the absence of a spectrometer. The full expression of the CTF includes an envelope damping function (not included above, for simplicity) related to the attenuation of higher frequencies due to effects such as chromatic aberration²⁴. In practice, there is a visible decrease in Thon ring contrast with increasing pressure (readily observed

between 1–3 atm), as well as a decrease in the information limit. In theory, fitting of the unfiltered FTs to the full transfer function including a damping envelope model could provide an additional measure of the extent of inelastic scattering, which could be again calibrated against a series of known cell pressures, as was done for EFTEM. As with EELS, the changes to the damping envelope should be more obvious for larger window spacings or higher gas pressures (i.e. more gas), and for thinner windows.

6. Conclusions

A simple, rapid method for measuring the pressure *in situ*, regardless of the particulars of the gas flow stage design and setup, has been developed and demonstrated. This protocol requires only basic electron optics and an imaging filter/spectrometer, and could be achieved on most common modern TEMs. The necessary calibration factors, S and $(t/\lambda)_{\text{SiN}}$, can be solved empirically at the outset of an experiment, and for several common gases S can be approximated using analogous ETEM measurements already in the literature. The technique should be compatible with any process gas, and does not rely upon the accessibility of specific core-loss energies. The local pressure can then be measured without interrupting an experiment or leaving the region of interest. The precision of this approach would improve for thicker cells and thinner membrane windows, both of which would be desirable for *in situ* experiments and are expected options in future gas-flow stage designs. While it was shown that greater-than-atmosphere pressures can be achieved for one particular system, the pressure at the sample can deviate from the pressure one might expect based on the total system differential pressure. Using a protocol that measures the pressure at the sample within the TEM enables the implementation of reproducible experimental conditions and reporting of results across the multiple existing platforms—as well as any potential future platforms—for *in situ* TEM experiments in gas environments.

7. Acknowledgments

This work was performed in the Environmental Molecular Sciences Laboratory (EMSL), a national science user facility sponsored by the Department of Energy's Office of Biological and Environmental Research, and located at Pacific Northwest National Laboratory. The authors would also like to acknowledge the support of the EMSL William Wiley post-doctoral fellowship, and assistance of the Materials Characterization Lab at Penn State University for followup tests. Thanks are extended to L. Kovarik for a number of helpful discussions, and to Roar Kilaas for updates to MacTempas that simplified defocus measurement.

Figure 2: Using EFTEM, the effective t/λ can be measured from the ratio of (a) an unfiltered image and (b) a zero-loss-filtered image. Gold nanoparticles were deposited on the upper window as a model sample: the scattering from the gas is calculated by measuring the areas between particles. (c) To measure t , the Fourier transform of filtered image (b) is fit to the contrast transfer function of the microscope. The electron beam is focused slightly above the sample, such that both top and bottom amorphous SiN windows are at a measurable defocus. The upper left quadrant of (c) is the raw fast Fourier transform (FFT), while the remainder as been averaged around the center of the FFT. The local thickness of the gas is then $t_{\text{gas}} = \Delta f_2 - \Delta f_1 - t_{\text{SiN}}$, where, t_{SiN} , is the thickness of one window.

Figure 1: To achieve atm-level pressures within a high vacuum TEM, gas is delivered to the sample through a very narrow channel that is separated from the vacuum of the microscope column by a pair of semi-electron-transparent windows. (a) For the results shown in this study, gas flow rate is regulated at the input by a mass flow controller (MFC), and pressure is regulated at the outlet. This system uses two input MFCs, e.g. to mix a reactive gas with a non-reactive carrier gas (e.g. N_2). A two-way-valve is situated just before the holder, to seal the system for transport or allow purging of the gas lines without exposing the sample to gas. (b) A cartoon of an unsealed holder tip with only the bottom Si/SiN chip in place, diagramming the main channel (defined by the chips and patterns on the chip surface) and the bypass channels (formed by the small space between the chips and the holder). (c) A cross-sectional schematic of the two Si/SiN chips after assembly: the thickness of the gas is defined by the spacing between the two SiN windows, which bow outward under the applied gas pressure.

Figure 4: The local pressure is measured from ~1.0–2.2 atm (15–33 PSIA) in N_2 gas, with ~0.2 atm (3 PSI) steps. From the polar average of the FT for each image summarized in (a), one can see that the spacing of the outer set of Thon rings (upper window) increase with increasing pressure, while the spacing of the inner set of Thon rings decreases slightly (the spacing changes non-linearly with Δf , and most dramatically as $\Delta f \rightarrow 0$). Energy filtered images are recorded for a fixed focal plane set above both windows, such that the bulging with increased pressure is expected to bow the upper window closer to focus and the lower window to greater defocus. (b) The pressure at the sample is calculated by combining t and t/λ with equation 6 (inset, green text), plotted against the outlet pressure (top axis) and an estimated pressure within the tip calculated from the differential pressure (see text). The best-fit line for P as a function of P_{est} is unique to this particular setup. The data shown in (b) are averaged from the circuit of 15–33–15 PSIA.

Figure 3: Gases such as N_2 have characteristic low-loss signals observable with EELS. Spectra are recorded while switching from 1 atm Ar gas to 0.5 mL/min flowing N_2 gas at slightly greater than 1 atm. The Ar features disappear and the N_2 gas feature ceases increasing within 10 minutes of switching to flowing N_2 . Monochromation (~0.4 eV) helps to separate the gas features from the large plasmon features contributed by the SiN windows centered about ~22 eV (inset). The spectra for one SiN membrane is included (gray line) to demonstrate that the features are indeed contributed by the gas. Spectra were recorded with a dispersion of 0.05 eV/pixel, are smoothed (Gaussian, 3 pixel), and normalized to the plasmon peak intensity for ease of comparison.

¹ P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, *Science*. **295** (2002) 2053–2055.

² P.A. Crozier, R. Wang, and R. Sharma, *Ultramicroscopy* **108**, 1432 (2008).

³ R. Sharma and K. Weiss, *Microsc. Res.*

- ²¹ P.A. Crozier and S. Chenna, *Ultramicroscopy* **111**, 177 (2011).
- ²² J.F. Creemer, S. Helveg, P.J. Kooyman, A.M. Molenbroek, H.W. Zandbergen, and P.M. Sarro, *Journal of Microelectromechanical Systems*, **19**, 254 (2010).
- ²³ L. Mele, F. Santagata, G. Pandraud, B. Morana, F. Tichelaar, J. Creemer, and P. Sarro, *J. Micromech. Microeng.* **20**, 085040 (2010).
- ²⁴ D.B. Williams and C.B. Carter, *Transmission Electron Microscopy* (Springer, 2009).
- Tech. **42**, 270 (1998).
- ⁴ J.B. Wagner, F. Cavalca, C.D. Damsgaard, L.D.L. Duchstein, and T.W. Hansen, *Micron* **43**, 1169 (2012).
- ⁵ R. Sharma, P.A. Crozier, *Environmental transmission electron microscopy in nanotechnology*, (2005) 531–565.
- ⁶ J.R. Jinschek, S. Helveg, *Micron*. **43** (2012) 1156–1168.
- ⁷ J.S. Warner, *J. Electrochem. Soc.* **114**, 68 (1967).
- ⁸ H. Zhang, J. Gromek, G.W. Fernando, H.L. Marcus, and S. Boorse, *Journal of Phase Equilibria* **23**, 246 (2002).
- ⁹ D. Zemlyanov, B. Klötzer, H. Gabasch, A. Smeltz, F.H. Ribeiro, S. Zafeiratos, D. Teschner, P. Schnörch, E. Vass, M. Hävecker, A. Knop-Gericke, and R. Schlögl, *Top Catal* **56**, 885 (2013).
- ¹⁰ I.M. Abrams and J.W. McBain, *J Appl Phys* **15**, 607 (1944).
- ¹¹ G.M. Parkinson, *Catal Lett* **2**, 303 (1989).
- ¹² T.L. Daulton, B.J. Little, K. Lowe, and J. Jones-Meehan, *Microsc Microanal* **7**, 470 (2001).
- ¹³ T. Kawasaki, K. Ueda, M. Ichihashi, and T. Tanji, *Rev Sci Instrum* **80**, (2009).
- ¹⁴ T. Yokosawa, T. Alan, G. Pandraud, B. Dam, H. Zandbergen, *Ultramicroscopy*. **112** (2012).
- ¹⁵ S.B. Vendelbo, P.J. Kooyman, J.F. Creemer, B. Morana, L. Mele, P. Dona, B.J. Nelissen, S. Helveg, *Ultramicroscopy*. **133** (2013) 72–79.
- ¹⁶ L.F. Allard, S.H. Overbury, W.C. Bigelow, M.B. Katz, D.P. Nackashi, and J. Damiano, *Microsc Microanal* **18**, 656 (2012).
- ¹⁷ H.L. Xin, K. Niu, D.H. Alsem, and H. Zheng, *Microsc Microanal* **19**, 1558 (2013).
- ¹⁸ R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 3rd ed. (Springer, New York, 2011).
- ¹⁹ J.B. Wagner, F. Cavalca, C.D. Damsgaard, L.D.L. Duchstein, T.W. Hansen, *Micron*. **43** (2012) 1169–1175.
- ²⁰ L. Reimer and H. Kohl, *Transmission Electron Microscopy* (Springer, 2008).