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Cost-Effective Systems for Atomic Layer Deposition

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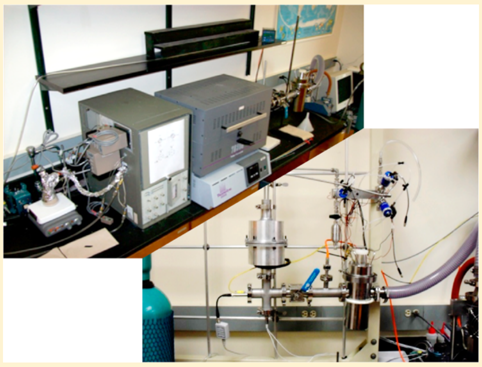
Ⓢ *Supporting Information*

ABSTRACT: Herein, we describe the design and testing of two different home-built atomic layer deposition (ALD) systems for the growth of thin films with sub-monolayer control over film thickness. The first reactor is a horizontally aligned hot-walled reactor with a vacuum purging system. The second reactor is a vertically aligned cold-walled reactor with a quartz crystal microbalance (QCM) and a vacuum purging system. This latter reactor was also built to be capable of the addition of liquid- or solution-phase precursors, including the addition of a solution-based precursor containing nanoparticles. Each system cost less than $10,000, and they were used to deposit aluminum oxide thin films using trimethylaluminum and water/isopropyl alcohol as coreactants. Whereas the horizontal hot-walled system was able to deposit alumina thin films at a growth rate of 1.2−1.4 Å/cycle, the more sophisticated vertically aligned reactor deposited films at 0.95−1.1 Å/cycle, which is comparable to commercial systems costing $100,000 or more. Most importantly, both systems were fabricated entirely by M.S. and undergraduate students at Central Michigan University.



KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Analytical Chemistry, Chemical Engineering, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Laboratory Equipment/Apparatus, Materials Science*

In atomic layer deposition (ALD), a sequence of alternating pulses of chemical reactants (referred to as "precursors") and purging−evacuation cycles are used to deposit a thin film onto the surface of a substrate (Figure 1).[1] An organometallic precursor reacts with surface species on the substrate to produce an initial thin film of a chemisorbed monolayer. The remaining gas-phase precursor molecules are then purged from the system, so there are no gas-phase reactions with the subsequent coreactant pulse. This two-step reaction cycling is self-limiting, allowing for direct control over film thickness during deposition cycles. The presence of gas-phase reactions during the coreactant injection step would cause the addition of granular impurities to the growth of the thin film. This would often cause the film to be uneven or poorly adhered to the substrate. The coreactant injection phase returns the surface chemistry to a similar state as was present during the first addition of the precursor.

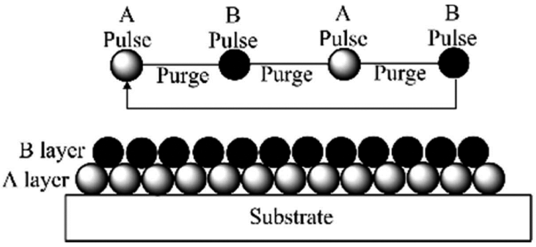


Figure 1. Schematic of atomic layer deposition, which features the surface saturation of one precursor, followed by the self-limiting surface reaction of a second precursor.

Deposition via ALD can be compared to chemical vapor deposition (CVD), which also affords thin film growth via delivery of gas-phase precursors. However, rather than sequential pulsing of precursors separated by purging cycles, CVD uses a continuous flow of an organometallic precursor(s).[2] While being much slower than CVD for thin film deposition, the control of film thickness is the largest advantage for ALD. The self-limiting growth allows for the thickness of the resultant film to be controlled at the angstrom level. The high temperatures needed to remove ancillary ligands of the organometallic precursor compounds also limit CVD reactions from being used to deposit films onto temperature-sensitive substrates.

Whereas CVD may be accomplished on a laboratory scale with a rather inexpensive apparatus of a tube furnace and associated tubing and quartz reaction vessel, atomic layer deposition requires a more complicated experimental system. Commercial ALD systems are priced from $100,000+,[3] which must include injection valves for the precise control of coreactant vapor pulses into the reaction chamber. Herein, we report the student-fabricated and testing of two ALD systems, each costing less than $10,000 and able to compete with commercial systems with regard to deposition rates. For testing purposes outlined herein, aluminum oxide film deposition using trimethylaluminum (TMA) and either water or isopropanol coreactants was chosen as this is a standard ALD reaction that has been reported in multiple sources. The extreme reactivity of TMA and $H_2O/{}^iPrOH$ necessitates the use of careful pulse−purge cycling protocols and tubing configurations to prevent extensive gas-phase reactions and resultant film granularity or even a dangerous explosion.

■ HORIZONTAL HOT-WALLED ALD SYSTEM

System Design

The development of a hot-walled horizontally aligned ALD reactor is a solid base for understanding how to develop an ALD reactor. This is because a hot-walled reactor is simple to build, as it requires basically only a quartz tube and a tube furnace. By using this design, it simplifies the development of the system reducing many complexities that can be found in other types of reactor systems. This also allowed us to design a system at low cost by repurposing existing equipment.

The system was composed of three primary components (Figure 2). The first component was a simple 50 mL Schlenk flask containing the coreactant (either H_2O or ${}^iPrOH$) that was immersed in a sand bath for temperature control of the evaporation of the liquid (A in Figure 2). Argon served as the carrier gas and was introduced to the flask via Tygon tubing fashioned to a glass tube. The vapor that was generated by this bubbler system was transferred to the reaction chamber through the side arm of the Schlenk flask. In order to prevent recondensation of the coreactant en route toward the deposition chamber, the transfer tubing was wrapped with glass wool and aluminum foil.

Figure 2. Photos of the horizontal hot-walled ALD system, composed of the (A) coreactant ($H_2O/{}^iPrOH$) injection system, (B) precursor oven−injection system, and (C) deposition chamber. The sand bath used to heat the coreactant flask (A) is not shown in the image.

The second component in the system was contained within the oven of a repurposed HP 5710A gas chromatograph (B in Figure 2; Figure 3). This included the control valves, the precursor sample vessel, the injection port, and the tubing for switching and transferring precursor and coreactant materials into the reaction chamber. The gas chromatography (GC) furnace was simply used as a heating source to maintain the precursor and valves at the desired temperature. Although an antiquated instrument from the department surplus was used, inexpensive used GC ovens may be found online through LabX or eBay listings. Alternatively, the precursor flasks, valves, and associated tubing could be wrapped with heating tape (<$100; Fisher Scientific) in order to vaporize the precursor and coreactant. The existing fittings within the GC oven were removed, and the openings were drilled through the sides to run the valves and injection ports into the oven. The Valco E90 valves ($2,000) used for precursor and coreactant vapor pulsing were electrically driven and controlled via a Valco serial valve interface controller ($630). These valves were chosen for their easy integration into the system, their ease of setup, and low cost. However, the minimum on−off pulsing rate of the valves was 1 s, and the valves tended to overheat after 100 cycles or so of deposition.

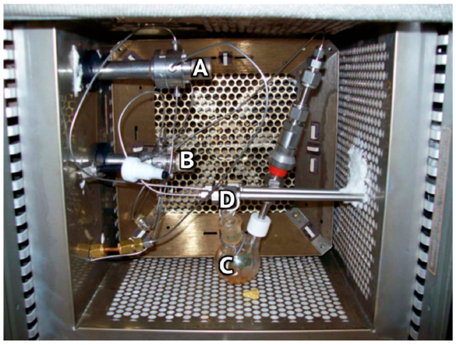


Figure 3. Photograph of the precursor vessel and reactor valve chamber. Pictured is the inside of the GC oven showing several of the main components of the reactor: (A, B) Valco 2-way injection valves for the precursor and coreactant vapors that were connected via capillary tubing to 1/4 in. stainless steel transfer lines to the (D) deposition chamber, and (C) a precursor sample vessel, which is a 10 mL two-neck round-bottom flask. Alternatively, a 40 mL electropolished stainless steel sample cylinder with top and bottom openings could be used ($200, Swagelok).

The final component of the simple system, the deposition chamber, is shown in Figure 4 and C in Figure 2. This consisted of a Thermolyne 79300 tube furnace[4] and a quartz tube where the deposition reactions took place. This system regulated the reaction temperature at which the surface-based reaction occurred, and the tube furnace allowed for easy temperature control of the sample. A quartz tube[5] with stainless steel end connectors (Ace Glass and A&N Corp., respectively; $600) was used because it allowed for the reaction to be visibly monitored during the reaction cycle and could be used at temperatures well above those required for ALD reactions. The waste gas line from the deposition chamber was sent to a chemical fume hood. In order to facilitate the purging of precursor and coreactant vapors from the chamber between sub-monolayer

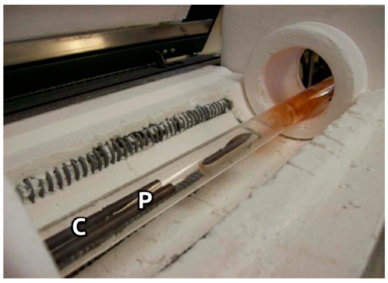


Figure 4. Photograph of the deposition chamber consisting of a quartz tube inside a tube furnace. The injection lines for the precursor (P) and coreactant (C) vapors can be seen near the bottom of the chamber, and a sample in a ceramic boat at a typical distance from the injection port is pictured near the center of the chamber.

pulsing, a Welch 1400 dual seal rotary vane pump ($3,000) was employed.[6] The pressure inside the chamber was monitored using a Hastings dual sensor vacuum gauge model 2002 ($1,200), which was capable of monitoring pressures between 2 Torr and 1×10^{-4} Torr. In order to protect the vacuum pump, a liquid nitrogen trap from A&N Corp. ($685) was used.

System Testing

To test the system, the reaction of trimethylaluminum with water to produce a thin film of alumina on the surface of a silicon wafer was examined. This is one of the most widely tested ALD reactions, because these coreactants are explosively incompatible and hence must be controlled in order to deposit suitable thin films. After systematically varying the precursor, reactant, and purging times, the best conditions for conformal, homogeneous aluminum oxide deposition were 10 s injections for both the precursor and coreactant, with each pulse separated with a 20 s purge cycle. *Ex situ* film thickness measurements using a Filmetrics F20 thin film analyzer showed a thickness of 18−21 nm after 150 cycles, corresponding to an average deposition rate of 1.2−1.4 Å/cycle. Energy-dispersive spectroscopy (EDS) analysis showed the presence of aluminum (Figure 5). Scanning electron microscopy (SEM) showed that the surface was smooth, with only minor defects in the film (Figure 6).

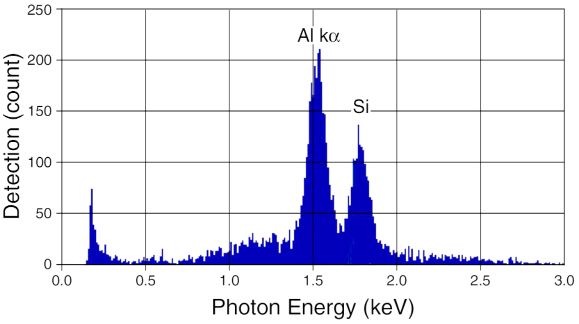


Figure 5. EDS spectrum of a representative Si wafer coated with alumina using the horizontal hot-walled ALD system.

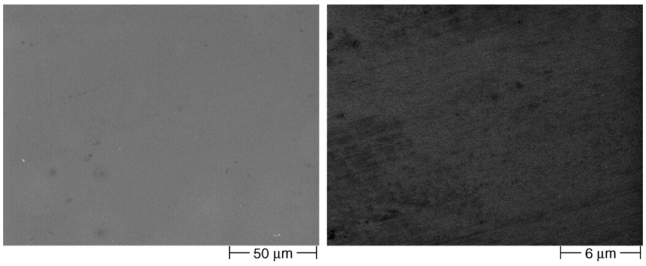


Figure 6. SEM images of a Si wafer after growth of aluminum oxide using the horizontal hot-walled ALD system. The images were taken at 550× magnification (left) and 4000× magnification (right). All images were taken using a working distance of 15 mm, accelerating voltage of 6.0 kV, and probe current of 6×10^{-11} A.

■ VERTICAL COLD-WALLED ALD SYSTEM

System Design

To address the problem with relatively slow pulsing and overheating of the Valco GC valves and lack of an *in situ* film thickness monitor, a second reactor was designed and built. This reactor features a vertically aligned cold-walled reactor with a high-temperature quartz crystal microbalance (QCM) stage that is capable of monitoring film thicknesses *in situ* at temperatures up to 200 °C (Colnatec, $1,800). A simple plug-and-play Q-pod transducer (Inficon, $500) was used to interface the QCM to a PC for real-time film thickness measurements. The QCM system used herein is a standalone unit that was purchased specifically for this application. However, it should be noted that this functionality is an optional add-on to this system; that is, the film thickness could easily be determined *ex situ* following a particular deposition run, which was the case in the horizontal hot-walled system.

As shown in Figure 7, this system includes specially designed ALD diaphragm valves and electrical connections to control the valves via PC (LabView, $100), along with the precursor and coreactant sample cylinders (Swagelok, $217). The second component is the reaction chamber, the heating element, and the quartz crystal microbalance (B in Figure 7); the vacuum system (C in Figure 7) was the only component that was unchanged from the previously described horizontal hot-walled system.

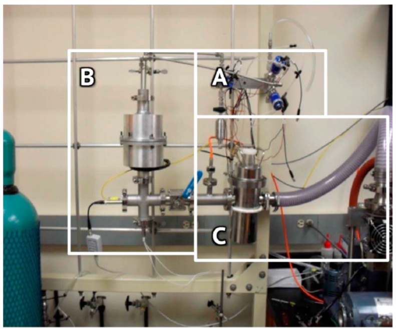


Figure 7. Photograph of the vertically aligned ALD system, showing (A) the placement of the valve components, (B) the reaction chamber, and (C) the vacuum system. Electrical connections to the QCM and yellow thermocouple cable are visible at the bottom left of the reaction chamber; electrical connections for the heated sample stage are seen immediately below the reaction chamber. Not shown is heat tape that was used to heat the transfer lines from the precursor and coreactant valves, so condensation would not occur prior to injection into the deposition chamber.

The valves are pneumatically actuated diaphragm valves specifically designed to maximize cycle life.[7] The length of cycles that could be run on the original reactor had been a limiting factor, because the electric motors tended to overheat after prolonged cycling. These valves also have a much faster switch rate of 5 ms compared to the ca. 1 s switching time of the electrically actuated valves used in the original reactor. In addition, the valves were also specially designed to minimize the entrapment area to reduce valve clogging, which could disrupt the deposition process. As shown in Figure 8, the valves were mounted vertically with the sample cylinders below the valves, so that precursor and coreactant liquids could not be siphoned directly into the system, causing severe damage by clogging the valves. The purge gas (Ar or N_2) was attached through a direct connection to a gas cylinder via Tygon tubing. A fourth optional valve (Figure 9; Swagelok, $1,614) that was specially designed for liquid aerosol injection into an ALD reactor may be mounted directly above the reaction chamber. This may be used for the introduction of nanoparticles via suspensions in liquid solvents or for nonvolatile precursors or coreactants.

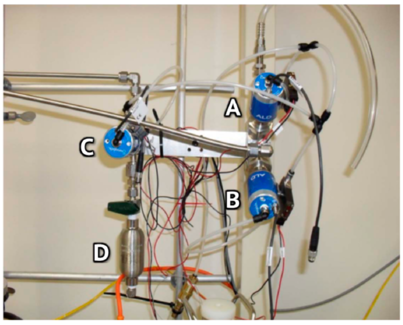


Figure 8. Three of the four valves of the vertically aligned ALD system are shown: valve A is used for gas assisted purging, valve B is used for injection of the precursor, and valve C is used for the injection of the coreactant. The coreactant stainless steel cylinder, D, is shown below valve C. Not shown is an analogous precursor cylinder that would be placed via Swagelok connections to valve B. The price of these valves was \$3121 for the 2-valve, 3-port system (A and B), and \$1,490 for the 2-port valve (C).[8]

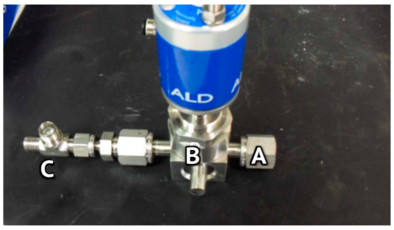


Figure 9. Aerosol injection valve: (A) the input for the sample cylinder, (B) the opening for the addition of a gas for a gas-assisted aerosol spray of the precursor, and (C) the output into the reactor.

The clamshell-type reactor in this design was produced from a solid block of aluminum metal (\$100), utilizing equipment housed by the College machine shop. Both halves were produced with the interior milled to the same sizes and specifications. The main difference between the two halves is that one half had a thicker flange and a notch milled into the flange for a sealing O-ring. The other had a thinner flat flange used to compress the O-ring to maintain a strong vacuum seal on the chamber (Figure 10). The two-tube injection port from the first reactor was used in this reactor as well. A major change in the heating system had to be developed as the original hot-walled reaction chamber was placed inside a tube furnace. To produce a cold-walled reactor, a separate heating element that would only heat the reacting surface needed to be developed. This consisted of a round aluminum wafer, which was connected to a Minco CT16A temperature controller. Although the walls of the reactor increased from ambient due to the heat evolved from the enclosed sample stage, this system is still referred to as "cold-walled" because no active heating of the sidewalls was included in the design.[9]

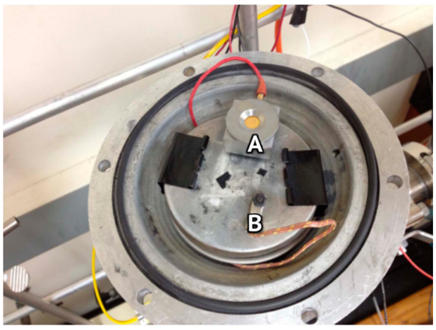


Figure 10. Photograph of the vertically aligned ALD system reaction chamber interior and heating element. Shown is the (A) bottom clamshell reactor, featuring the heating stage with the QCM on its surface. The thermocouple (B) was directly connected to the stage, and substrates to be coated are placed in the middle of the stage (between A and B; small pieces of carbon tape are evident where previous substrates were placed).

The sensor for the QCM was placed alongside the substrates on top of the heating element to keep it in the same reacting environment as the material that is being used for deposition. As shown in Figure 10, the dimensions of the aluminum-heated stage had to be smaller than the inside diameter of the reaction chamber, to allow precursor vapors to be removed *in vacuo* after they interact with the heated substrates on the surface of the sample stage. The two halves of the clamshell reaction vessel, as well as the T-connection underneath that is connected to the vacuum system, are shown clearly in B of Figure 7.

System Testing

Once again, the reaction of trimethylaluminum (TMA) with water or isopropyl alcohol (IPA) was used to produce a thin film of alumina on the surface of a silicon wafer. After the precursor, reactant, and purging times were systematically varyied, the best conditions for conformal, homogeneous aluminum oxide deposition were found to be 500 ms injections for both TMA and H_2O/IPA, each separated by a 3000 ms purge cycle. *Ex situ* film thickness measurements using a Filmetrics F20 thin film analyzer showed a thickness of 95−110 Å after 100 cycles, corresponding to an average deposition rate of 0.95−1.1 Å/cycle. Using the *in situ* QCM sensor, a growth rate of ca. 1.0 Å/cycle (Figure 11) was verified. EDS analysis showed the presence of aluminum (Figure 12).

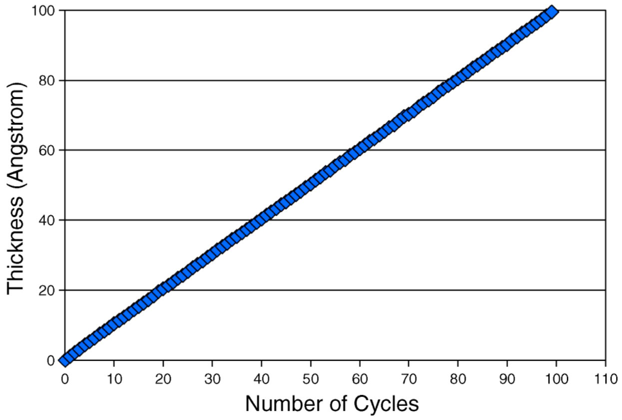


Figure 11. *In situ* film thickness monitoring of alumina thin film deposition using the QCM placed within the reactor.

■ USE IN UNDERGRADUATE COURSES

Two atomic layer deposition (ALD) systems used for the deposition of alumina thin films were student fabricated and tested. Both systems cost less than \$10,000 and were capable of depositing conformal alumina thin films at growth rates comparable to commercial systems. These simple designs should allow this vapor deposition technique to be used more extensively for undergraduate and graduate laboratories, for both pedagogical and research activities.[10] In particular, these

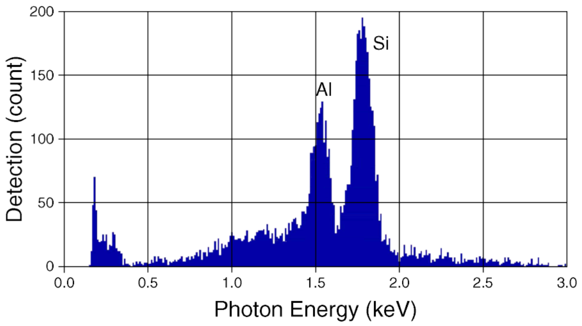


Figure 12. EDS spectrum of a representative Si wafer coated with alumina using the vertical cold-walled ALD system.

home-built ALD systems have been employed for a number of undergraduate and graduate (M.S. and Ph.D.) research activities and for a number of modules for laboratory-based classes in the Science of Advanced Materials (SAM) Ph.D. program, which involved diverse groups of students from engineering, physics, and chemistry backgrounds ("Inorganic and Nanomaterials Laboratory" and "Surface Characteriztion Laboratory"). Undergraduate students who did not participate in its design and fabrication have used this instrument for their capstone research projects (see Supporting Information) and were quickly able to understand its operating principle and initiate the testing of precursor and coreactant injection programs for their particular needs. Undergraduate research projects focused on alumina thin film deposition studies, as well as HfO_x thin film deposition, which also included synthetic coordination chemistry to synthesize novel Hf precursor compounds. In addition to research, these systems would also be extremely valuable for ACS-certified undergraduate curricula within materials, physical, or analytical chemistry laboratory modules, for the synthesis of a variety of thin films or nanomaterials.

It should be noted that although thin films were deposited onto silicon surfaces and utilized SEM, EDS, and reflectance spectroscopy for characterization, other characterization techniques may be utilized, depending on their availability at one's home institution. Government laboratories and sites of the National Nanotechnology Infrastructure Network[11] also offer discounted rates for electron microscopy and other characterization techniques for academic users without suitable equipment at their host institutions. Atomic force microscopy (AFM) is now being widely offered in desktop models and is much more affordable than electron microscopy (EM) to determine the overall film topography (but not elemental composition). Also, instead of reflectance spectroscopy used herein, one could also use ellipsometry to determine film thicknesses. Although FTIR would be featureless for alumina thin films, Raman spectroscopy would also be helpful to identify Al−O resonances from the deposited film. Furthermore, the low deposition temperatures used in ALD are amenable for the deposition onto other substrates such as glass or quartz or even temperature-sensitive substrates such as plastics, if desired.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Some examples of capstone undergraduate research projects that employed the ALD systems, summary tables of component costs, additional photos of the vertically aligned system, and CAD diagrams of the clamshell reaction vessel. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(2) For articles published in *J. Chem. Educ.* related to CVD, see: (a) Ahmed, W.; Sein, H.; Rajab, H.; Jackson, M. Chemical Vapor Deposition of Diamond Coatings onto Dental Burrs. *J. Chem. Educ.* **2003**, *80*, 636−641. (b) Vohs, J. K.; Bentz, A.; Eleamos, K.; Poole, J.; Fahlman, B. D. Chemical Vapor Deposition of Aluminum Oxide Thin Films. *J. Chem. Educ.* **2010**, *87*, 1102−1104. (c) Fahlman, B. D. Chemical Vapor Deposition of Carbon Nanotubes: An Experiment in Materials Chemistry. *J. Chem. Educ.* **2002**, *79*, 203−206.

(3) For ALD systems at the lower end of pricing, see: http://www.cambridgenanotechald.com (accessed May 2014).

(4) Although this tube furnace is quite costly (ca. $10,000), used furnaces are available at online auctions at a much lower price. Alternatively, one could simply heat the tube with heat tape (*ca.* $200) to afford thin film deposition.

(5) Due to the low-heat requirements of ALD vs CVD, a glass deposition tube with stainless steel endpieces may be used instead of quartz, at a fraction of the cost.

(6) Especially with the assistance of an inert gas purge, high vacuum is not required for ALD; hence, one is also able to use a lower-capacity pump or even house vacuum lines that would circumvent the use of expensive turbo or oil diffusion vacuum pumps.

(7) The pneumatic activation required additional vacuum tubing to connect the valves to the house vacuum source.

(8) These are retail pricing directly through Swagelok; these exact valves were recently found in good refurbished condition at a fraction of the cost at online auctions (e.g., $130−$150 on eBay).

(9) If the side walls are not heated to a temperature slightly above the temperature of the precursor transfer lines, it may be necessary to heat the walls of the reactor with heat tape or a heating mantle to prevent condensation of vapors and formation of a granular coating onto the walls of the deposition chamber.

(10) Under the guidance of Dr. Fahlman, a student completely designed and fabricated both systems described herein for his Master's degree. The knowledge that was required to design, build, and test these systems was obtained from undergraduate coursework in materials chemistry and familiarity with chemical vapor deposition and specific engineering techniques (machining, identifying, and preparing various Swagelok connections etc.) that was gleaned from prior involvement in related research projects as an undergraduate.

(11) National Nanotechnology Infrastructure Network. http://nnin.org (a NSF-funded initiative to provide low-cost options for

fabrication and characterization of nanomaterials for institutions without suitable equipment) (accessed May 2014).