Physical Vapor Deposition of Nanorods from Science to Technology

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The transition from nanoscience to nanotechnology is dependent on a level of scientific maturity. After over 6 decades of nanoscience, this level of maturity has only recently been approached. In this work we first present the current state of nanoscience and nanotechnology in the context of nanofabrication using solution syntheses, chemical vapor deposition and physical vapor deposition. To lay the groundwork for scientific investigation into these three, we choose physical vapor deposition as the prototype due to its high purity and elimination of interfering variables. We then present the emergence of a new level of scientific understanding of nanorod growth from physical vapor deposition, realized through the synergy of experiments, theory and simulation, and of fast diffusion on these nanorod surfaces. Throughout, we discuss the pioneering engineering advances in physical vapor deposition that lead to this realization. Further, as a true technological impact, this new level of scientific understanding has enabled the realization of room temperature metallic bonding and sealing. Moving beyond low temperature bonding, we discuss the realization of several new morphologies which may offer even more real technological impact. We close with a discussion on the importance of completing the scientific understanding of nanoscale growth from all three mechanisms- solution, chemical vapor and physical vapor- and the technologies that are primed for this impact.
Physical Vapor Deposition of Nanorods from Science to Technology

Stephen Peter Stagon

B.S., University of Connecticut, 2009

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
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Stephen Peter Stagon
Doctor of Philosophy Dissertation

Physical Vapor Deposition of Nanorods from Science to Technology

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<tbody>
<tr>
<td>Å - Angstrom</td>
<td>Angstrom</td>
</tr>
<tr>
<td>°C – degrees Celsius</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>λ – Wavelength</td>
<td>Wavelength</td>
</tr>
<tr>
<td>γ – Interfacial energy</td>
<td>Interfacial energy</td>
</tr>
<tr>
<td>Ag- Silver</td>
<td>Silver</td>
</tr>
<tr>
<td>Al- Aluminum</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Ar- Argon</td>
<td>Argon</td>
</tr>
<tr>
<td>Au- Gold</td>
<td>Gold</td>
</tr>
<tr>
<td>BCC- Body center cubic</td>
<td>Body center cubic</td>
</tr>
<tr>
<td>BSE- Back scattered electron</td>
<td>Back scattered electron</td>
</tr>
<tr>
<td>c – Speed of light</td>
<td>Speed of light</td>
</tr>
<tr>
<td>C\textsubscript{16}TAB-</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CB – Cassie-Baxter</td>
<td>Cassie-Baxter</td>
</tr>
<tr>
<td>CF- Knife edge vacuum flange</td>
<td>Knife edge vacuum flange</td>
</tr>
<tr>
<td>Co- Cobalt</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cu- Copper</td>
<td>Copper</td>
</tr>
<tr>
<td>CVD- Chemical vapor deposition</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DSSC- Dye sensitized solar cell</td>
<td>Dye sensitized solar cell</td>
</tr>
<tr>
<td>EBPVD- Electron beam physical vapor deposition</td>
<td>Electron beam physical vapor deposition</td>
</tr>
<tr>
<td>EELS- Electron energy loss spectroscopy</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>ES- Ehrlich- Schwoebel barrier</td>
<td>Ehrlich- Schwoebel barrier</td>
</tr>
<tr>
<td>EM- Electron Microscope</td>
<td>Electron Microscope</td>
</tr>
<tr>
<td>ETD- Everheart- Thornly detector</td>
<td>Everheart- Thornly detector</td>
</tr>
<tr>
<td>FEG- Field emission gun</td>
<td>Field emission gun</td>
</tr>
<tr>
<td>FIB- Focused ion beam</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>eV- Electron volt</td>
<td>Electron volt</td>
</tr>
<tr>
<td>Ge- Germanium</td>
<td>Germanium</td>
</tr>
<tr>
<td>GLAD- Glancing angle deposition</td>
<td>Glancing angle deposition</td>
</tr>
<tr>
<td>HCP- Hexagonal close packed</td>
<td>Hexagonal close packed</td>
</tr>
<tr>
<td>He- Helium</td>
<td>Helium</td>
</tr>
<tr>
<td>IBS- Ion bombardment sputtering</td>
<td>Ion bombardment sputtering</td>
</tr>
<tr>
<td>In- Indium</td>
<td>Indium</td>
</tr>
<tr>
<td>ITO- Indium- Tin Oxide</td>
<td>Indium- Tin Oxide</td>
</tr>
<tr>
<td>K- Kelvin</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LAM- Lone atom model</td>
<td>Lone atom model</td>
</tr>
<tr>
<td>LKMC- Lattice-kinetic Monte Carlo</td>
<td>Lattice-kinetic Monte Carlo</td>
</tr>
<tr>
<td>LN- Liquid Nitrogen</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>N- Nitrogen</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ni- Nickel</td>
<td>Nickel</td>
</tr>
<tr>
<td>Nm- Nanometer</td>
<td>Nanometer</td>
</tr>
<tr>
<td>O- Oxygen</td>
<td>Oxygen</td>
</tr>
<tr>
<td>OAD- Oblique angle deposition</td>
<td>Oblique angle deposition</td>
</tr>
<tr>
<td>Pa- Pascal</td>
<td>Pascal</td>
</tr>
<tr>
<td>Pd- Palladium</td>
<td>Palladium</td>
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<tr>
<td>PLD- Pulsed laser deposition</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>Pt- Platinum</td>
<td>Platinum</td>
</tr>
<tr>
<td>PV- Photovoltaic</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PVD- Physical vapor deposition</td>
<td>Physical vapor deposition</td>
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<tr>
<td>QF- Quick flange</td>
<td>Quick flange</td>
</tr>
<tr>
<td>Rh- Rhodium</td>
<td>Rhodium</td>
</tr>
<tr>
<td>RMP – Revolutions per minute</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>RSDT- Reactive spray deposition technique</td>
<td>Reactive spray deposition technique</td>
</tr>
<tr>
<td>SCCM- Standard cubic centimeter per minute</td>
<td>Standard cubic centimeter per minute</td>
</tr>
<tr>
<td>SE- Secondary electron</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM- Scanning electron microscope</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Si- Silicon</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC- Silicon carbide</td>
<td>Silicon carbide</td>
</tr>
</tbody>
</table>
SnO- Tin Oxide
Ta- Tantalum
TC- Thermocouple
TC_{12}AB- Tetradeclammonium bromide
TEM- Transmission electron microscope
Ti- Titanium
TiN- Titanium Nitride
TiO- Titanium Oxide
Tm- Melting Temperature
ZnO- Zinc oxide
UHV- Ultra high vacuum
VLS- Vapor-liquid-solid mechanism
XEDS- X-ray energy dispersive spectroscopy
XRD- X-ray diffraction
Z- Atomic number
I. Introduction

1. What is nanotechnology and does it even matter?

Classically, nanotechnology has been defined as the study of condensed matter with a dimension less than 100 nanometers (nm). Nanotechnology encompasses both pure scientific research, which we will call nanoscience, and the application of the nanoscience in real technology. In terms of science, nanoscience is incredibly interesting and insightful. Most importantly, the phenomena that we struggle to experimentally verify and theoretically understand on a bulk scale is more easily viewed and better understood when the matter in our system goes from square meters to square pico meters! Technologically, nanoscale matter is advantageous because of unique properties, that differ from bulk, that emergence only as the dimension shrinks due to the combination of quantum confinement and the relative increase in surface atoms. However, there exists an important distinction between materials on the order of 100 nm and those on the order of 10 nm. Nanomaterials on the order of 100 nm have been realized for several decades and have functionalities that are similar to their dense thin film counterparts, with the advantage of increased surface area. These early nanomaterials have made little impact on real technology despite receiving tremendous effort and resources. Only recently has attention been shifted to realizing functional nanomaterials with dimensions on the order of 10 nm.

Where did this all begin? A spark hit some loose tinder in 1959 when American physicist Richard Feynman laid his famous lecture There’s always room at the bottom upon the world. In the decades since, countless discoveries of things on the nanoscale have been held in high esteem
by both the scientific community and the general public. Among these are the invention of the
scanning tunneling microscope in 1981 by Binning and Rohrer of IBM\(^1\), the discovery of the
“Buckey Ball” by Richard Smalley at Rice in 1985\(^2\) and the realization of graphene by Geim and
Novoselov at Manchester University in 2004\(^3\). At every step, scientists have envisioned a future
shaped by incredible technological breakthroughs enabled by nanoscience. However, some 54
years after Feynman’s call to action, there are only a handful of niche products that are actually
utilizing nano components or concepts. After billions of dollars of investment and decades of
research, have any of the early, and continuously renewed, promises of nanotechnology
materialized to improvements in our lives? If not, how as we as engineering scientists make
this a reality.

While these questions remain to be answered, it forces one to think about two key points:
(1) Has our investigation into nanotechnology and nanoscience been misdirect, and (2) are we
trying to answer the problems of tomorrow with nanotechnology rather than meeting the needs of
today’s relevant technologies?

Have the past decades of nanotechnology and nanoscience research been misguided?
Perhaps, but not by all. A glut of literature has been presented in a fashion of mixing up the
variables, phenomenological observation with modern sophisticated equipment, speculation and
reporting. This approach, while perfectly valid, it misses a critical piece of the puzzle-understanding of the underlying science. However, when scientific understanding of a
phenomenon is put as the goal then true achievement may result. For example, the realization of
the scanning tunneling microscope has enabled profound advancements in the semiconductor
industry since its conception. This evidence motivates science based exploration with an
emphasis on understanding and illuminating the underlying mechanisms, as opposed to phenomenological “cooking”.

While it is critical for us to look far forward as engineers and scientists, perhaps reaching too far forward has been a hindrance to improvement. While much is to be said for the first experimental realization of a potentially world changing phenomenon, not every realization can be this way and not every researcher can reach for this goal. Diving into our engineering problem solving methodology and borrowing from the lean manufacturing mindset, perhaps consistent incremental improvement may be more pertinent in some cases. As engineers we learn to solve the practical problems and cannot lose this sense of direction. A poignant example of overshooting the target is the dye sensitized solar cell (DSSC). The DSSC was pioneered by Gratzel and his group and first presented in literature in 1991, with the introductory paper having been cited over 14,000 times at the writing of this dissertation. The technology has been publicized as an extremely simple and low cost alternative to the conventional silicon photovoltaic (PV) device with promises of similar efficiencies and dollar per watt ratios that rival fossil fuels. Researched set off for two decades of exploration to find ways of increasing the efficiency, which was about 10% in 1991. After several decades, and perhaps 14,000 publications, the efficiency is yet to break 12%, compared to 20% or so for silicon PV. However, a little pesky problem was overlooked- there is no effective way to seal the DSSC which uses a liquid or gel electrolyte. Even worse, the gel electrolyte has a lifetime of only several years, while 10 + years is necessary for the implementation of such a device. While a few have looked at this, a majority have worked tirelessly for meager improvements to efficiency. At this moment in time, there are no mass produced DSSCs. Alternatively, a simpler technology has benefited hugely from nanotechnology; sunblock cream. In an effort to provide better
protection from the harmful carcinogenic rays of the sun, sunscreen manufacturers turned to nano-sized zinc oxide (ZnO) particles in suspensions to scatter the light of the sun and decrease the intensity reaching the skin. The technology has gained serious traction and is now of the premier means to block the harmful rays of the sun due to its relatively low cost and non-toxicity.

Nanostructures may be fabricated using physical vapor deposition (PVD), a growth method that has clear scientific advantage over other methods of nanofabrication, and becomes the prototype for investigation in this work. Mainstream nanofabrication is composed of three main synthesis genres being: physical vapor synthesis, chemical vapor synthesis and reactive solution synthesis. While they have their relative strengths, and are outlined in this dissertation for completeness, both solution synthesis and chemical vapor synthesis necessitate a chemical reaction. A level of scientific maturity has not yet been reached in the understanding of complex multi-component chemical reactions and current computational power is insufficient to perform the mass of calculations necessary for systems of a meaningful size. In physical synthesis, all chemical reactions are eliminated and nanostructure growth, in this case generally a crystal, is governed nearly entirely by thermodynamics and surface kinetics. The scientific understanding of single, or simple multi-element thermodynamics, and, to a somewhat lesser extent, surface kinetics is both mature and simple enough to create a meaningful interpretation of nanostructure growth from physical processing. Modeling efforts on a meaningful size and time scale have also become possible within the last decade.

2. Review of PVD of nanostructures

Before moving into new advances in PVD of nanostructures, the methods of this investigation and the technological impacts that result, we first provide a comprehensive
overview of existing theoretical and fabrication knowledge in the PVD of nanorods to establish the motivation of this work. Within PVD, the main method to fabricate nanostructures has been glancing angle deposition (GLAD) or oblique angle deposition, where vapor flux impinges and condenses on a substrate oriented at an oblique angle relative to the source of the flux. In the following section we will establish the current state of nanofabrication from OAD and GLAD and present three challenges of science which we will answer in this work.

Nanostructures originate from the shadowing effect in oblique angle deposition which was discovered in 1959 by Knorr, Hoffmann\textsuperscript{8} and Smith\textsuperscript{9} during evaporation experiments with anisotropic source flux. In these early experiments, high surface roughness and directional anisotropy of magnetic properties were noted with dependence on the orientation of the substrate relative to the source vapor flux. Early work on this phenomenon was by vacuum deposition scientists whose primary interests laid in the unique properties that resulted from deposition of films at an oblique angle. Some early observations included magnetic anisotropy in iron (Fe), nickel (Ni) and cobalt (Co)\textsuperscript{10} thin films created with oblique angle deposition (OAD); a process that was eventually used in metal evaporated video tape of the 1980s\textsuperscript{11}. Beyond magnetic anisotropy, electrical and optical anisotropy\textsuperscript{12} were also studied by the pioneers of OAD, and the investigation still continues to very recently\textsuperscript{13-17}, in the hopes of landing upon technologically interesting properties or empirically mapping the “design space” to find the recipe for attractive properties. Early investigate aimed to correlate things like column width and pitch relative to the substrate and source flux, but largely left the growth thermodynamics and kinetics uninvestigated. Often, the columnar structure that formed was periodic on the nanoscale and was composed of each column being a single or poly-crystal. Due to the mindset of the pioneers of OAD, fabrication knowledge quickly matured and very sophisticated geometric control emerged
within the last decade with excellent engineering groups like that of Michael Brett at Alberta. However, the scientific understand of OAD did not mature as quickly as the fabrication knowledge, and up until the author’s group’s work, there did not exist a cohesive closed form theory on the growth of any structures from OAD. In this section we will first outline nearly 6 decades of fabrication knowledge and then put it in context of theoretical understanding. The thermodynamics of crystal growth will be briefly touched on here, but can be found more exhaustively in the methods section.

As mentioned earlier, fabrication knowledge began with magnetic metals and has since progressed to very complex materials systems like organic long chain polymers and may be classified by the respective bonding type: metallic, ionic, covalent, and organic molecules occupying a diverse range of bonds from ionic to van der Waals.

Pure metallic structures from OAD are among the first and most widely studied and vary in dimension from very small, ~15nm diameter, nanorods to large micron sized columns and complex shapes like zig-zags, chevrons and helixes. As mentioned before, the first effects of OAD were realized with Fe, Co and Ni metals being deposited from a thermal or electron beam PVD source with obliquely inclined substrates. It was quickly realized that very collimated flux is necessary for well-defined shadowing conditions. If thermal evaporation or electron beam sources (methods will be discussed in detail in the following methods chapter) are used the flux is well collimated if the distance between the source and substrate is sufficiently far. Metals are very easily deposited and well controlled from thermal and electron beam evaporation sources, but magnetron sputtering may be employed. In the case of sputtering with a background gas, the source flux is generally less collimated and more difficult to achieved well defined shadowing. Angles of inclination of previous studies for metals have ranged from nearly perpendicular to the
flux ($\alpha = 0^\circ$) to nearly parallel to the flux ($\alpha = 90^\circ$) in the case of perfect geometric shadowing. Such large angles are rarely used as the amount of flux reaching the substrate, the real deposition rate $\Phi_{\text{eff}}$, is geometrically defined as $\Phi \cos(\alpha)$, meaning as the oblique angle approaches $90^\circ$ the flux rapidly trails off to null. In application, if several hundred nanometers of film thickness is desired at a perpendicular deposition rate of about 1.0nm / s, the real deposition rate to the substrate drops to only 0.01nm / s, making the deposition time several hours.

From the beginning forward, the growth of metallic nanostructures from OAD begins with either heterogeneous nucleation on a flat substrate or forced nucleation on seed or defect sites. Aside from the oblique angle at which flux reaches the substrate, the most critical condition governing the resulting morphology is the nucleation condition of the film but it has largely been overlooked thus far in both fabrication knowledge and theoretical approximation of OAD and GLAD growth. First, island formation or extreme atomic roughness is necessary for the oblique shadowing to take effect. However, it has largely been overlooked that substrate temperature, deposition rate, and adsorption of residual gasses like $\text{H}_2\text{O}$, O and N greatly affect diffusion on the substrate and drastically\textsuperscript{19,20}. Until recently, very little thought had been given to these conditions and it was largely accepted that the heterogeneous nucleation was a constant (we later return to this and show that this step is extremely critical to the resulting morphology). In heterogeneous nucleation, small non-wetting clusters serve as seeds for the shadowing, and are generally only several nm high and wide and are several nm apart. As growth continues, the oblique angle, deposition rate and substrate temperature will dictate how many of the islands continue to grow and if incoming adatoms (adsorbed flux atoms) are able to diffuse to the sides of the cluster or even off of the cluster to the substrate. Conversely, in seeded or forced nucleation, nucleation occurs on select sites such as nanoparticles or features etched into the
substrate through lithography, and the developing nucleation can be controlled beyond the natural wetting condition. However, it is necessary and critical to note that the length scale of seeds is often at best ~100nm, while non-wetting clusters can be as small as only a few atoms in diameter, limiting the lower limit of features realized through seeded nucleation.

As growth in the vertical direction begins after nucleation both the oblique angle and diffusion of adatoms on surfaces begin to dominate the resulting structure. First, it has been largely speculated that because the flux comes in at a steep glancing angle that there must be conservation of momentum in the direction of the incoming flux which dictates the direction that the column grows in depending on the amount and direction of kinetic energy of the incoming flux. As we will later discuss, in most metals at room temperature this is largely overwhelmed by ample diffusion of on terraces (if it exists at all was debated until only recently and has been ruled out with molecular dynamics simulations and another mechanism was postulated). Therefore, the angle of inclination is governed nearly entirely by the geometric condition. As the shadowing is not absolute, the angle of attack is generally less than 85° so the deposition does not take days to complete, if there is spacing between columns flux will land on the side near the source. At room temperature, there is fast diffusion on most atomically flat metal surfaces so the incoming adatoms should be mobile to diffuse on the top terrace and up and down the sides of the nanorods. If the deposition rate is sufficiently low, this may cause the broadening and eventual coalescence of columns into a dense film if the growth continues long enough. If the deposition rate is sufficiently high, the columns will continue to maintain their diameter because the trapping of adatoms occurs very quickly. As cleared up by modern simulation work, classical approximations of the diffusion barriers of adatoms on a metal surfaces is often over estimated and the surface diffusion was originally thought to be minimal on forming columns or rods and
that the diameter of the rod was largely dictated by the geometric condition\textsuperscript{11}. However, as we will learn later, the geometric condition gives the smallest possible rod diameter and through surface diffusion this may increase.

If substrate rotation or movement is added during the growth, entering the regime of GLAD, different structures may be realized. If the flux angle, $\alpha$, is held constant “slanted posts” are formed at an inclined angle $\beta$ relative to the substrate. These slanted posts are known as nanorods if their diameter is on the order of 100s of nm or less. If the diffusion is low, as is the case over very high Tm metals like magnesium (Mg)$^{21}$ and chromium (Cr) (unpublished Stagon and Huang 2013) these posts may form fans or other somewhat complex and anisotropic structures due to geometric conditions and little movement of adatoms from the location where they land. If the substrate is rotated at a constant angular velocity, expanding vertical columns or vertically aligned spirals may be created based on the angle of attack of the flux and the rotational velocity. If the diffusion is relatively low, very complex structures may be realized because incoming atoms generally stick in place as soon as they land. Although it is not widely acknowledged, complex structures in general cannot be made for low to moderate melting temperature metals because of the low diffusion barrier and relatively high diffusion over steps and edges giving rise to smooth large features. These very interesting features often require very high melting temperature metals, like Cr, molybdenum (Mo), tungsten (W) or tantalum (Ta)$^{13,14}$. If the substrate remains sufficiently close to room temperature during deposition, the homologous temperature of these metals is much lower and thermally activated diffusion is minimized. As we will touch on later, covalent systems and ionic systems tend to be the best prototype materials for working with these complex geometries as they often have extremely high melting temperatures$^{22}$. 
While these structures from GLAD are very interesting, their technological implementation has largely been lacking due to properties that largely resemble bulk. This derives from the relatively large size of these structures, often increasing in diameter over a micron, and the associated bulk behavior that comes with a decrease in surface curvature and large ordered domains. However, islands and thin columns often form when the substrate is not rotated and they may have diameters as small as a few nm. These structures have become known as nanorods from PVD and may have technological impact.

Several trends showing dependence on processing conditions have commonly been reported through fabrication of metallic nanorod or columns from oblique angle deposition. With the motivation of very small structures and all of their properties, a group led by T. M. Lu at RPI moved to fabricate small metallic nanorods of Cu in the early 2000s\(^{23-26}\). Working on the existing fabrication knowledge and minimal theoretical modeling of column growth from OAD, this group was able to realize well separated nanorods of Cu on the order of 100nm in diameter and then a very tight fiber texture with diameter of about 20nm with no spacing being columns. At this stage of understanding, this was believed to be the lower limit of nanorod diameter. As the deposition rate is increased, the diameter of the resulting columns decreases, as does the spacing between rods. When the deposition rate is increased past a critical point, the rods are no longer separated and no longer have unique properties. With the spacing limitation, the smallest metallic nanorods realized from PVD were about 30nm in diameter.

Many different metals have been used in OAD with different results but none have resulted in nanorods smaller than about 30 nm in diameter. We will present an exhaustive list of the materials that have been deposited and the result here with only surface analysis and reserve further analysis for the later chapters. First, Cu is the prototype material of many investigations
into metals and has been fabricated on the order of 30nm is separated fashion and on the order of several hundreds of nm using seeding\textsuperscript{27-32}. Some unique features like anisotropic broadening and bifurcation have been shown with such large Cu fabricated at room temperature. Little has been done to show the effects of substrate temperature on the forming Cu rods. Aluminum is a common engineering material but has a lower melting temperature than Cu and has not been shown to form rods at room temperature through OAD (unpublished Stagon and Huang 2010). However, if the substrate temperature is decreased, it has been reported that columns form, although there have been no micrographs showing this result\textsuperscript{33}. This result is possibly due to fabrication at a homologous temperature that approached 0.3Tm, the same range as Cu at room temperature, when the substrate temperature is dropped to 77K. Co films have been fabricated several times from OAD with angles of less than 50°, which resulted in columnar thin films with angularly oriented nanograins, and nanorods of Co have not yet been fabricated, although they may be interesting for catalysis\textsuperscript{15}. Silver (Ag) has resulted in well separated nanorods from OAD, with columns on the order of 100nm deposited at a high deposition rate at room temperature. It was also found that this generally originates from a film that lies under the Ag rods\textsuperscript{34,35}. Iron (Fe), a classical engineering material with magnetic properties has been studied using OAD and has been shown to form spanning fans reaching diameters of a few hundred nm when grown at $\alpha = 75^\circ$. The columns have wide separation and this causes the flux to land on the side of columns and ultimately leads to the expansion of the diameter\textsuperscript{36}. The BCC structure makes Fe different than the other commonly deposited engineering metals that are largely FCC with relatively low diffusion barriers. Magnesium, a hexagonal close packed structure, has been shown to form large anisotropic blades under OAD, and it has been speculated that preferential or direction surface diffusion along specific directions or over specific types of steps may be the
origin of this, but this has not been directly verified\textsuperscript{37}. Many other metals like Palladium (Pd)\textsuperscript{38}, iridium (Ir)\textsuperscript{39}, and platinum (Pt)\textsuperscript{40} but these investigations largely revolved around creating structures with substrate rotation and have little attention to the small columns that result when the substrate is held stationary. This necessitates further investigation into these engineering materials to uncover the useful morphologies that are possible from PVD with an oblique angle as the dimension of the structures that will result at a steep glancing angle and no substrate rotation should be an order of magnitude smaller than those created with rotation.

One common theme among metals is that they almost always form crystalline structures when fabricated at room temperature by OAD. Understanding the nature of metals, they quickly relax into crystalline structures as soon as they are brought to room temperature to characterize, even if they are fabricated at temperature at which they may form crystals with high lattice strain\textsuperscript{41}. It is however possible that coating very small structure with strongly interacting materials, like oxygen or carbon for example, may prevent long range order from forming. However, through this exhaustive literature review there have not been any metallic structures reported that were not crystalline, even those fabricated at cryogenic temperatures.

If a complete theoretical understanding is set aside, there exists a massive body of work that remains uninvestigated; this is the growth of metallic nanorods from steep oblique angles using technologically interesting materials. However, metals are not the only materials that are technologically relevant, with ionic systems (like metal-oxygen) and hard covalent systems like Si, C and Ge, that may produce nanorods with excellent mechanical properties.

Ionic systems have been fabricated a moderate amount but the fabrication knowledge and (especially) the theoretical understanding lag far behind. Among these systems, a majority of fabrication knowledge has been towards large smooth structures that form via rotation of the
substrate, although there has been very recent work towards understanding more thoroughly the contribution of process parameters with a stationary oblique angle. As recently as 2011, a large amount of work was began by the Brett group at Alberta to understand how deposition rate, oblique angle and substrate temperature effect the morphology and crystallinity of ZnO films deposited using sputtering at low vacuum, 0.1 Pa\textsuperscript{7,42}. In this study it was found that nanorods formed larger crystals when the deposition rate was higher and smaller crystals when the deposition rate was lower. Regardless of rate used, the growing columns were generally polycrystalline in nature. Brief calculations on surface diffusion showed that it was highly unlikely that adatoms were able to diffuse before being buried. While no mechanism was presented for the increased crystal order, it is likely that local heating of the crystal lattice enabled increased relaxation and solid and surface diffusion, beyond the argument of diffusion based on substrate temperature. Further, a major limitation exists to understanding this growth in that the diffusion barriers are largely unknown and molecular dynamics potentials are largely unable to capture the complex interaction between Zn and O.

Common covalent systems are those of Germanium (Ge) and Silicon (Si) which have been shown to generally form amorphous structures due to the extremely high Tm. The diffusion barrier on these surfaces is estimated at about 20% of the energy of escape from the source vapor, and this is potentially insurmountable at room temperature\textsuperscript{11}. Expanding columns have been formed with Si at relatively low attack angles, showing potential for smaller columns with closer spacing it the angle is increased\textsuperscript{22}. When Ge was deposited at room temperature it also formed large amorphous structures. However, when the substrate temperature was increased to 230°C it formed very small well separated nanorods on the order of 10s of nm\textsuperscript{43}. As the substrate temperature is increased to 330°C the nanorod diameter increases to over 100nm. At room
temperatures, very small fibers are present between larger bundles, and it is unclear how
diffusion, both on the Si substrate and on the Ge itself, plays a role in generating the geometric
condition. As the temperature is increased the Ge appears to form non-wetting clusters on the Si,
generating a condition of geometric shadowing. Due to the increased temperature the diffusion
may become sufficiently high to allow for smooth features on the nanorod surfaces.

Early theoretical models of OAD are very limited and are largely built upon modeling of
the angle of the growing column in the context of surface diffusion and crystal growth kinetics.
As we will thoroughly discuss a new closed form theory later on in this work, we will only
briefly discuss the early theory before moving onto a conversation on kinetics. Early discrete
continuum models empirically related the geometric condition to the angle of the forming
column as a function of oblique incidence. Here, the column angle $\beta = 0.5 \tan \alpha^{11}$. Other models
aim to determine the bundling of adjacent columns and the spacing in between
the bundles but
no models have been robust enough to capture the behavior of a wide range of materials or
conditions.

When surface kinetics are brought into discussion, even less scientific knowledge exists
for OAD. Two major limitation of understanding the kinetics of crystal growth are the lack of
diffusion barrier data and the instability of multiple layer atomic steps$^{44}$. First, the diffusion
barrier on flat surfaces will definitely play a role in the inclination or tilt of the forming column,
as well as the diameter, as adatoms that strike the side of the column due to incomplete
shadowing may either stick in place or may diffuse over the surface. If the atoms stick in place in
a purely ballistic deposition model then the column tilt will only be a function of geometric
spacing and height of competing columns. If there is diffusion, the column tilt will decrease as
the adatoms will diffuse nearly evenly over the entire rod length if the diffusion on a flat surface
is sufficiently high. As the kinetics of surface diffusion are in the form of an Arrhenius equation, even a small change in diffusion barrier may be the difference between the adatom taking no diffusion jumps before burial or thousands of diffusion jumps before burial. Further, if the surface of the rod is composed of only monolayer surface steps, multiple-layer atomic steps were believed to be unstable until very recently, then adatoms that hit that top will quickly diffuse to the sides of the rod and the rod diameter will expand. If multi-layer steps are indeed stable, this may be a mechanism of the diameter of nanorods stabilizing as the rod continues to grow, rather than rapid expansion, in the case of nearly perfect geometric shadowing at steep glancing angles.

Within the early models of OAD, conservation of parallel momentum is strongly relied upon to explain the fact that the tilt of the columns is not equal to the attack angle. It has been speculated that adatoms have a strong kinetic energy in the direction of the incoming flux and therefore continue in that direction even after collision with the surface. However, through molecular dynamics simulations this has been largely discounted. The reason for this discount is that the kinetic energy of the adatoms is relatively low and when the adatom approaches the surface there is nearly no difference in substrate approach angle as a function of oblique angle. Nearly all of the adatoms approach the surface of the growing angle in a perpendicular fashion, as shown early molecular dynamics simulations. This phenomenon can be more simply explained by purely ballistic deposition onto the front of growing nanorods and fast diffusion along the largely flat sidewalls, or conversely little surface diffusion. Further, the flux is assumed to be entirely collimated, which it generally is not unless there is a very large throw distance, and even a small deviation from direct flux may have a strong effect on the column pitch.

The lack of theoretical modeling of growing nanorods or nanocolumns from PVD with an oblique angle necessitates a call to action. Insights from a strong theoretical understanding may
motivate the experimental realization of the smallest nanorods from PVD. In chapter IV of this work we show the strength of the synergy between closed form theoretical modeling, simulation to determine the action of the major factors, and experiment to validate, expand and realize the structures that have been the goal of a field for decades.

3. Motivation for this study – Three clear challenges

With the understanding of the existing fabrication and scientific knowledge of OAD and GLAD, there are three clear challenges which stand in the path of fabricating metallic nanorods on the order of 10 nm with nano-length scale features, leaving other challenges aside for discussion in future work. (1) The first challenge is the understanding and subsequent fabrication knowledge to control the spacing between forming columns or nanorods. Again, if the columns are too close together then they will coalesce and separate rods will not form. Previously, to drop the nanorod diameter deposition rate was increased resulting in non-wetting clusters coming too close together. Currently, little investigation has been given into the spacing between non-wetting nuclei on the substrate or the spread between size of nuclei – and therefore the % of them that survive to mature height- and how that affects the diameter of the fully developed rod. If the spacing or disparity between two forming nuclei is too great then they will have flux deposited onto their sides and will broaden. (2) The second challenge is to determine how surface diffusion affects the forming rods and ultimately the diameter of the rods. The surface diffusion is a function of the temperature and deposition rate so a closed for theory is necessary to determine how these factors interplay and to give insights into how to fabricate nanorods of the smallest possible diameter. Therefore, knowing the lower limit of surface diffusion under ideal shadowing conditions the goal of the smallest nanorods from PVD may be set. (3) The third challenge is to complete the framework of nanorod growth from physical vapor deposition or a wide range of
materials and determine what the lower limit is for respective materials, with or without the existence of a complete set of diffusion barriers. This is essential to increasing the fabrication knowledge for technological applications. This is not a small task as every metal has a different melting temperature and different interatomic bonding giving rise to different diffusion lifetimes at a given temperature. Some materials may need to be fabricated at depressed temperatures to decrease diameters to the minimum while others may need to be heated, depending on the geometric shadowing condition.

With the motivation clear, this work, *Fabrication of Nanorods from Physical Vapor Deposition and Length-scale Enabled Technologies*, aims to be a cohesive work on the fabrication of nanostructures using a technologically relevant process, physical vapor deposition (PVD) and culminates in a real application, hermetic sealing at room temperature with metallic nanorods. We begin this work by setting the stage of nanofabrication and the current state of characterization paying attention to both science and engineering through touching on contributions to both device design and scientific understanding. Next, we highlight our contribution through an advancement in the scientific understanding of nanorod growth; the realization of the smallest and most well-separated nanorods from physical vapor deposition enabled by a complete theory of nanorod growth. We next move to the investigation and uncovering of a new scientific understanding of the fast diffusion that these nanorod surfaces have at incredibly low temperatures- even at room temperature for metals that we conventionally view as stable. We culminate in a new relevant technology- *room temperature hermetic metallic bonding*. In closing, we present what this approach promises to realize in the near future in terms of engineering science and technology.
Motivated by attractive properties on the nano-length scale, it is easy for one to create a structure in one’s mind, or on a sheet of paper that ought to have incredible world changing properties. However, as important as imagination is, the limiting factor is “how may we physically realize this structure?” As macro-fabrication is necessary to realize a new gas turbine blade, nanofabrication is necessary to realize nanoblade. Mankind has been mastering the art of macrofabrication for several thousands of years and we have arrived at quite a sophisticated set of skills and knowledge. A conventional thinker may simply attack the nanofabrication problem with all of the same tools that they have used for their macrofabrication problems. With a level of dexterity, and perhaps some luck, it has indeed been possible to create nanostructures from these techniques. As an example, top down machining aims to take a large piece and create one part from the larger piece. It is certainly possible to mill, either with a machine tool, ions or electrons, to create a nanostructure. However, it is not very technologically meaningful to build a single attractive structure from precisely placing atoms into their desired positions, so a more sophisticated approached is necessary. While not the focus of this thesis, top down milling or etching to create nanostructures from bulk is a legitimate method and has resulted in many valuable scientific and technological realizations\textsuperscript{45}. However, this method is limited in resolution and effort. Generally, an ion or electron beam is used to work away from the bulk and while the resolution is perhaps a few 10s of nm at the time of this work (it will of course continue to drop over the coming decades), the major limitation is the time and effort required to create an array of meaningful size\textsuperscript{46}. Hypothetically (with order of magnitude estimations to illustrate), using a
top down lithography approach it may take 10s of hours to create a few square microns of nanostructured array at a cost of $10,000s, while technology necessitates square centimeters or meters in minutes and cost $10s\textsuperscript{46}. The approach to fabrication must therefore be more sophisticated and utilize knowledge of chemistry and physical processes.

Growing nanostructures from the bottom up, bottom up self-assembly, has gained velocity as the preferred means of nano fabrication due the ability to rapidly create large volumes of nanostructures at costs that can hit technologically relevant levels. These methods rely on either local chemical reactions to precipitate or condense matter onto catalysts and seeds or on physical deposition processes which kinetic limitations leading to roughness, and therefore features, on the nanoscale. Each of the three methods has inherent strengths and weaknesses and each deserves appropriate attention in discussion.

1. Solution Synthesis

It can be argued that the true study of chemistry began many centuries ago with the medieval alchemists, and its maturity is evident through the modern ability to synthesize metal and metal oxide nanoparticles through solution synthesis methods- among many more truly great things like modern medicine and synthetic oils. At the heart of solution based syntheses, a chemical reaction takes place in a liquid bath containing dissolved metal. The reaction thermodynamically favors the precipitation of solid phase metal from the solution\textsuperscript{47}. With the inclusion of chemical agents which preferentially bind to certain metallic surfaces, and likely do not bind to others, complex structures like nanorods, stars, etc. may be grown from solution synthesis\textsuperscript{47}. Aside from a millennium of chemistry knowledge, investigation into solution synthesis is motivated by technological viability of solution synthesis methods. Overall, the
method of solution synthesis is relatively inexpensive when compared to other methods, chemical vapor deposition (CVD) and PVD, and is scalable for large scale applications\textsuperscript{48}.

However, solution synthesis has several limitations that must be addressed to cross the threshold between scientific investigation and technological application, deriving from a lack of critical scientific understanding. While it is speculated that crystal capping agents preferentially bind to surfaces, this interaction is not well understood\textsuperscript{49}. Also, the amount of variables at play in a wet chemical system are nearly infinite and to control only one, without changing others, to determine scaling trends and basic scientific phenomenon is a nearly insurmountable challenge.

In the following section we will discuss the solution syntheses of metallic nanorods and nanoparticles. It is importantly noted that metal oxide nanoparticles can also be fabricated from largely the same mechanisms.

![Figure 1: Schematic of solution synthesis of metallic nanorods and nanoparticles.](image)

Under the umbrella of solution based synthesis of nanostructures there are two main processes which result in small nanorods; they are electrochemical synthesis and seeded solution synthesis, with seeded solution synthesis being shown schematically in Figure 1. The simplest and best scientifically understood method is electrodeposition into a porous membrane, which can later be dissolved leaving small rods in a suspension\textsuperscript{50}. To avoid the constraint of the
template, organic solvents, surfactants and sonication are added to keep the metal from depositing to the platinum cathode and aggregating; through optimization of conditions the result is a suspension of small metal nanorods and nanoparticles. The second method of small nanorod synthesis from solution is the seeded synthesis method. In seeded synthesis, small metallic nanoparticles seed the growth of nanorods through the reduction of metal salts in the presence of crystal capping agents, such as cetyltrimethylammonium-bromide (C\textsubscript{16}TAB)\textsuperscript{52} or tetradecylammonium bromide (TC\textsubscript{12}AB)\textsuperscript{53}.

In more detail, templated electrochemical growth of nanorods is achieved through the electrodeposition of metal into a nano-porous template\textsuperscript{51,54}. The concept of electrodeposition was first pioneered by Italian physicist Luigi Brugnatelli in 1805, borrowing from the voltaic pile of Alessandro Volta five years prior\textsuperscript{55}. Within the concept of electrodeposition, an electrical current is passed through an electrochemical cell with a sacrificial anode and the cathodic substrate. The metal anode is oxidized and ejects a metal cation into solution, which may join with an anion in the electrolyte. The metal is then transported to the cathode through diffusion driven by a concentration gradient with overabundance at the anode. Once at the cathode the molecule is reduced and the metal joins the cathode while the anion returns to the electrolyte and drives to the anode by diffusion. To realize nanorods, the process begins with the creation of a nano-porous template, most commonly alumina, on a conductive substrate. These pores must be selected carefully as they the deposited metal will precisely will in the empty space. A thin layer of conductive metal, gold (Au) or copper (Cu), is vacuum sputtered into the alumina pores to act as a conductive contact (unfortunately, later on this may be difficult to remove). The substrate and template are placed into a liquid electrolyte filled electrochemical cell with a sacrificial anode, shown in the top portion of Figure 2. Metal is then deposited by passing a current through
the cell, with the rate of deposition being governed by the current and the conductivity of the electrolyte and the duration of the deposition controls the thickness. After removal from the electrochemical cell, everything but the metal nanorods – substrate, alumina support, sputtered conductive layer - is removed through wet-chemical etching. However, it is important to note that this is not a viable means of creating nanorods that can also be etched away with the template and under layer. Therefore, this method lends itself mostly to non-reactive noble metals. The dimensions of the resulting nanorod are a function of the pore diameter, which directly dictates the diameter of the nanorod, and deposition time, which directly dictates the length, although the hard limit is the pore length. The major limits of this method to technological viability are the dimensions of the template and the yield of the process. The ability to create a template of the desired dimensions is reliant on the ability to create the nanoporous template with the correct dimension. The dimensions of such a template are limited to the ranges available by various top down or bottom up techniques of fabricating non-conductive regularly porous media. More importantly, the ability to make a large scale template, and therefore a lot of nanorods, is lacking. The yield of this process is prohibitively low and template electrochemical synthesis has not gained velocity outside of the laboratory.
Figure 2: Electrochemical growth of small nanorods with the template method top, and sonication method, bottom.

Still within an electrochemical cell, small nanorods can be synthesized through the addition of surfactants and organic solvents to the electrolyte solution and passing current through the cell in the presence of mechanical agitation. This is possible through placing the entire electrochemical cell in a sonication bath, as shown schematically in the bottom of Figure 2. Here, the electrochemical cell is composed of a sacrificial metal anode and platinum cathode within a multiple component electrolyte solution. The base components of the electrolyte are a cationic surfactant which may also act as an aggregation blocker, commonly C_{16}TAB, a more hydrophobic rod induction cationic surfactant, such as TC_{12}AB, acetone to loosen the micellar framework of the cationic surfactant and cyclohexane to enhance the formation of long C_{16}TAB micelles. Without the surfactant, or carbon based micellar capping agent, this process does not work. A current is then passed through the electrochemical cell while the entire cell is mechanically agitated in a sonic bath, shown schematically in Fig. 2b. The proposed mechanism of formation is thought to be the formation of metal-Br_{4}^{-}, such as Au, at the anode and reduction at the cathode, nucleating metallic nanoparticles in the solution. It is not clear if nucleation takes
place on the cathode and the sonication is necessary to break forming particles off or if nucleation occurs in the solution near the cathode. It has been demonstrated that sonication is a necessary condition to prevent aggregation of the forming rods. The addition of C$_{16}$TAB is also necessary to produce nanorods; it has been proposed that C$_{16}$TAB may selectively bond to specific crystal orientations of the forming metal nano-particles blocking growth in the coated directions resulting in rod growth, Fig. 3. By inserting a silver (Ag) metal plate into the electrolyte solution near the platinum (Pt) anode some aspect ratio control may be gained, but the mechanism of action is not well understood. This method is severely limited to great advancement due to a lack of scientific understanding of the governing mechanisms. Without the understanding of the mechanism, there variables at play in this which are responsible for the end morphology are numerous and require wide reaching systematic study.

The second method of growing metallic nanostructures is through the precipitation of seed nanoparticles into solution through reduction of metal salts and then preferential growth through chemical capping agents. First, metallic nanoparticle seeds are formed in solution, generally with diameters on the order of several nm. Often, these seeds are amorphous and are the product of nearly random nucleation as the metal is slowly precipitated out of solution through a reduction reaction. This method was pioneered by Turkevich in 1951, when he and his group created 10-20nm Au nanoparticles through the reduction of an Au ion by a citrate ion. The resulting nanoparticles have a citrate cap and are crystalline in nature. An alternative method was realized in 1994, Brust and his group realized nanoparticles through the reduction of Au colloid by NaBH$_4$ in the presence of a phase change agent. Without a capping layer on the nanoparticles, instability would allow them to aggregate quickly, leading to the necessity of a capping layer for handling the nanoparticles on a laboratory scale. To induce the formation of
rods or other more complex structures, crystal surface capping agents, such as C_{16}TAB^{58}, tetraoctylphosphineoxide^{65}, and oleic acid^{66}, amongst others, are added to the solution and are proposed to preferentially bond to select crystal surfaces. Growth of nanorods propagates in the direction that is not coated with a crystal capping agent, Figure 3. Au metal salts and a weak reducing agent are added to the solution and nanorods of various morphologies and aspect ratios can be achieved through the modification of processing conditions, such as temperature and pH^{49}. A further level of control is added by the addition of Ag ions, also considered a crystal surface capping agent, in the form of AgNO_{3}^{67}. Through extensive parametric modification, the fabrication knowledge of small Au nanorods from seeded synthesis is mature but the scientific understanding lags behind until the mechanism by which the surface capping agents and Ag ions act emerge. This method is also technologically limited by the presence of the organic capping agent. This capping agent generally requires annealing to above 150°C for removal, once removed the nanorods aggregate and reshape quickly due to fast surface diffusion on the crystalline surfaces at elevated temperatures^{68}. Further, technologically these nanostructures are difficult to attach to a substrate due to the capping agent.

![Figure 3: Seeded solution synthesis of small Au nanorods.](image)

A common theme amongst the reactive solution processes is the overall inability to control and directly monitor the rate of reaction. In this case, the reaction rate may dictate the resulting structure due to fast diffusion on surfaces and will have a profound effect on the resulting structure. With this limitation, the structure that results is dependent on the transport
and reaction kinetics of the reactants in the solution, which, while extensively studied and empirically modeled by chemists, it is not well understood scientifically.

2. Chemical Vapor Deposition (CVD)

Similar to solution syntheses, chemical vapor deposition of metallic and metal oxide nanostructures is driven by a chemical reaction. However, rather than precipitating directly from solution, the source material (in our case metals and metal oxides) is first converted to the vapor phase and then condensed onto a substrate when thermodynamically preferable, with or without a catalyst to act as a preferential nucleation site or lower the energy threshold for condensation. It should be noted that the fabrication of metallic nanostructures that are not noble metals is very difficult due to the rapid reaction of metals with oxygen at elevated temperatures which are generally necessary to vaporize metals. Therefore, CVD is ideal so for the fabrication of stoichiometric metal oxide thin films and nanostructures. Chemical vapor deposition has been utilized for decades in the semiconductor industry to create thin films of metals, metal oxides and transition materials. Some of the strengths of chemical vapor deposition are the ability to grow very pure crystals with excellent crystallinity that are not possible with higher vacuum processing due to an inability to get the stoichiometry of the components correct, or where the substrate temperatures necessary for epitaxy are higher than possible inside a ultrahigh vacuum (UHV) chamber. In terms of fabrication of nanostructures, CVD has been widely investigated for over a decade for oxide and carbide nanostructures- like silicon carbide (SiC)\textsuperscript{69} and ZnO\textsuperscript{70}. The process is overall very similar to crystal growth from physical processes with the exception of the possibility for the addition of a catalyst to preferentially nucleate a new crystal and a general slug flow of reacts (compared to line of sight deposition for even very high vacuum physical
However, with the addition of the chemical reaction and the catalytic sites, the scientific understanding of CVD lags behind that of PVD.

a. CVD Fabrication Overview

The process for fabrication of nanostructures from CVD is very generic but has several parameters of control that may dictate the resulting morphology. In a generic sense, the process is held in an enclosed reactor. The reactor may be at atmospheric pressure, a pressure slightly greater than atmosphere or a sub atmospheric pressure (low vacuum, high vacuum, or UHV). At any given pressure level the atmosphere may be air or purified inert gas. The chamber may have an inlet for ambient air to enter, may be completely closed off and stagnant, or may have an inlet and outlet for the flow of an inert or reactive gas. A schematic of a basic heated tube reactor can be found in Figure 4. To begin the reactive process, some source materials are placed inside the system, in Figure 4 this is the source material loaded at the center of the reactor. Depending on the desired results, the source materials may be solution phase metals or metal oxides or solid phase powders or slugs. To get the metals into the vapor phase, a combination of vacuum and increased temperature are generally used. Most often, powders are placed in the center of a tube, made of alumina or quartz, with the source at one local and another region where the substrates are some distance away at a different temperature. The reactor may have a single heated region or several different heated zones to more precisely control the temperature profile, like the one in the bottom of Figure 4. As the tube heats up, the metals enter the vapor phase above the source. If the tube is stagnant, there may be some natural convective flow or concentration gradient driven diffusion of the source reactants to other regions of the reactor. If the source is open to atmosphere, there will be a more complex flow of cool ambient gasses into the entirety of the reactor and reaction of the gasses in air with the high temperature vapor. If a vacuum method is
used, generally there will be a carrier or reactive gas piped into the reactor from one end creating a slug flow of the reactants to the substrate (deposition) region of the reactor, left of Figure 4\textsuperscript{71}. Some new reaction configurations are emerging to meet the needs of CVD in mass production. For example, the reactive spray deposition technique (RSDT) pioneered by Maric and Roller at the University of Connecticut, relies on a combustion reaction for the precipitation or vaporization of metals and metal oxides from a stream of liquid\textsuperscript{72}.

Overall, due to the high temperature nature of CVD, it is relatively difficult to hold a high vacuum to the temperatures some reactions necessitate. Therefore, it is nearly impossible to grow pure metals that are reactive with this method. For example, at these vacuum levels the vapor pressure of Cu is well above 1000°C and our experiments have shown that a clean Cu surface will oxidize at even 10^{-7} Torr at only 225°C. Alternatively, ZnO takes temperatures above 800°C at pressures of 0.1 to 200 Torr to vaporize. Often, it is necessary to add a reactive gas to get the proper stoichiometry in the desired crystal\textsuperscript{73}.

![Figure 4: Schematic of CVD growth (top) with representative single zone temperature profile (bottom).](image-url)
The crystal growth in CVD is almost entirely based on thermodynamics, with little contribution from kinetics, with the exception of adequate source vapor and supersaturation at the substrate, and may be modified by the addition of a catalyst particle. In CVD, the fast growth direction, or the low energy state crystallographic plane, nearly always results. For example, ZnO <0001> is nearly always the direction of crystal growth as these are the low energy planes. This stands as a major limitation for multiple reasons. First, if this direction is not the desired growth direction then there is little that can be done to modify this growth. Second, if there is an epitaxial mismatch between a surface and the deposited material then polycrystalline growth may result. A Polycrystalline film will result because local defects on the surface of the substrate, or spots like kink sites etc., may act as preferential nucleation sites because they have higher surface energies than their smooth counterparts. As the temperature or saturation increases to a level where nucleation on the desired surfaces becomes thermodynamically possible, before complete coverage is reached from the non-desired spots, a polycrystalline film with multiple orientations and high roughness may result.

With the addition of a catalyst, acting in either solid or liquid phase, the spacing between these nucleation sites, crystal diameter, and the resulting crystalline orientation from the catalyst spot may be roughly controlled. Carbon has been used as a common catalyst for the CVD growth of nanostructures. Nanoparticles of carbon are often either sputtered onto the substrate or added to the source material. The carbon acts to begin the precipitation of metal or oxide from the vapor phase to the solid phase, but the precise mechanism of this reaction is not well understood. When deposited on the substrate, it is generally clear that the carbon stays in its position and the vapor is transported through the reactor to the carbon and reacts in the lower temperature substrate position. In the case where the carbon is added to the source material the
mechanism is far less clear. In this case, it is possible for the carbon to begin the reaction with the source material before the carbon and structure fall to the substrate, allowing for several directions of growth and very complex surfaces. Even further complicating the process, a combination of both in possible. An example of a complex structure grown from carbon catalyzed CVD of ZnO is the nanoflower seen in Figure 5.

![ZnO nanoflower grown from carbon catalyzed CVD.](image)

**Figure 5: ZnO nanoflower grown from carbon catalyzed CVD.**

When a metal catalyst is used the mechanism, known as the vapor-liquid-solid mechanism (VLS), is more clear. This method was first pioneered as early as 1964 by Wagner and Ellis of Bell Labs, when they demonstrated the VLS growth of Si nanowires using Au, Pt,
palladium (Pd), Ag, Cu and nickel (Ni) catalyst\textsuperscript{79}. In this situation, a metallic thin film is sputtered, or an array of nanoparticles is drop or spin coated, onto the substrate. Au is the most commonly used catalyst material as it is free of oxide formation near its melting temperature and acts strongly as a catalyst in the liquid state. When in the thin film form, the Au forms non-wetting liquid droplets in the chamber, left of Figure 6. The limitation in this case is that the melting temperature of Au must be surpassed by the substrate temperature. This completely eliminates the possibility of lower melting temperature ($T_m$) substrates (no chance for flexible electronics here!). The temperature of reaction is generally lower than the melting temperature of the catalyst because a eutectic alloy is generally formed between the catalyst and the source material\textsuperscript{80}. To lower the temperature a bit, tin (Sn) has also been shown to act as a catalyst in some cases, but the melting temperature of Sn is still beyond the glass transition temperature of a lot of technologically important materials\textsuperscript{81}. Again, the substrate temperature can only be dropped so low as the vapor will condense before reaching the substrate if it is in a region too far from the source.

Continuing, once the carrier gas is turned on and the source vapor is transported down the reaction chamber to the substrate, the vapor is then incorporated into the liquid metal droplet and a liquid alloy forms, middle of Figure 6. Once there is a liquid droplet, the liquid may become saturated with the source material and it precipitates out onto the substrate, right of Figure 6. It is unclear of how the precipitation occurs. It is speculated that, as in the early crystal growth theory, that a screw dislocation drives the growth of the solid\textsuperscript{80}. As it is driven purely by thermodynamics, the fast growth direction of the precipitating material nearly always wins out.
Figure 6: The vapor liquid solid mechanism of nanowire growth.

Many interesting structures have been grown with either the VLS or catalytic growth CVD mechanisms. Early work in the area was into ZnO, pioneered largely by ZL Wang, SiC, Silicon (Si), titanium oxide (TiO), tin oxide (SnO), titanium nitride (TiN), and germanium (Ge) amongst many others. Some more recent work has investigated metal nanowires from CVD, for example the growth of an Au whisker from a catalyst particle\textsuperscript{82}.

It should again be noted that one of the major limitations of CVD is the inability to directly monitor and control deposition rate and overall deposition length. While deposition rate is a function of vapor pressure and carrier gas concentration it is not well understood and may affect the resulting morphology. More importantly, the overall amount of deposited mass is not well controlled in primitive laboratory systems (a quartz crystal microbalance may be utilized in a sophisticated semiconductor system) and the end morphology of the resulting nanostructures is difficult to control.
b. The CVD Reactor

Briefly, a CVD reaction chamber was developed at the University of Connecticut in house by the author, and produced some interesting (and so far unpublished) results which will be briefly mentioned here for future documentation. First, the system and its capabilities will be outlined and then the results will be briefly overviewed.

The in house system, shown below in Figure 7, is a cylindrical tube reaction chamber contained within a tube furnace (MTI Corporation). The tube is heated with electrical resistance heaters equipped with electronic PID controller and feedback monitored by B type Pt –Rhodium (Rh) with a thermocouple (TC) junction composed of two Pt alloys, 30% and 13%. However, the limits of this TC are between about 100° C and 1800° C, so lower temperature CVD reactions require modification. Also, since the range of the thermocouple is so wide, the resolution at a given temperature is several degrees C, but this precision is more than acceptable. The heating chamber can accept reaction tubes ranging from very small to 10 cm in diameter. The center heated region of the tube is about 25 cm long and the tube is placed into the chamber in any desired heating configuration. The resistance heaters have a maximum of 5 kW of power output and can heat a 3” alumina tube at rates up to about 20° C / min at maximum power. However, it is important to keep in mind thermal expansion and phase change in the tube material, so the maximum heating and cooling rate is generally limited to about 5° C / min to minimize strain rate from thermal expansion and allow for phase change in the alumina tubes. Quartz tubes have a maximum temperature of about 1200°C before they begin to soften and misshape and alumina can withstand cycling up to 1600°C if the tube is generally defect free. The ends of the tube can be capped with stainless steel vacuum flange. The flange works by providing compression onto high temperature silicon o-rings that seal against the outside of the tube. These fixtures both have globe valves with Teflon seats to provide a relatively good seal to the tube if demanded.
We will now move to the vacuum system on this and allow sufficient explanation for future researchers looking to replicate or modify such a system. To the left of the tube there is also an in line full range pressure- vacuum bourdon tube gauge. The bourdon gauge, first realized in the early 1800’s, relies on a C shaped tube which elastically deforms as pressure is increased or decreased and this movement is shown on a calibrated scale magnified by a gear ratio between the actuation and the bourdon tube. This is used to determine if the digital gauges may be reading anomalously and for redundancy. Beyond this, a metal or low permeability plastic tube is run to a series of vacuum components. The vacuum components are all low vacuum components and have Viton o-ring seals in quick flange (QF) configuration. The
first component is a metal mesh filter to prevent any large particles or CVD deposition from getting into the gauges and pump. Next, the system runs into a 4 way cross made of stainless steel. On the adjacent sides of the cross there are two digital vacuum gauges to monitor the system. In CVD, the system is generally first allowed to base out for several hours to remove oxygen and moisture from the system to assure that the reaction is as anticipated. The system may even be back filled several times with inert gas to assure that there is no left over contamination as iterations of vacuum are pulled. Depending on the desired base pressure, different pumps and gauges are employed. On our system, we use an Edwards mechanical roughing pump to bring the chamber down to a desired based pressure of $1.0 \times 10^{-2}$ Torr and therefore need to have a fine gauge to measure this range. In our case, we chose a “wide range combination gauge” to assure that we have the ability to accurately measure. On the upper end of the range, a Pirani gauge is employed. A Pirani gauge measures vacuum by heating a resistor with a driving voltage and then measuring the change in resistance from its default configuration. As the temperature changes, the resistance changes. This is very accurate but is limited in measuring from about 0.5 Torr to $10^{-4}$ Torr. The gauge also has an inverted magnetron, in case we ever chose to decrease pressure further. This gauge has a very powerful magnet and an anode post surrounded by a cylindrical cathode. When an atom enters into the strong magnetic field it is stripped of its electrons and an ion is left while the electrons are gathered by the cathode and are measured. This only works at lower vacuum levels, perhaps $10^{-3}$ Torr down to UHV levels of about $10^{-9}$ Torr with good certainty (above this range the detector is saturated and below there is insufficient signal). Many companies specialize in these systems as they are very relevant to technology. The following Figure 8 shows the range of gauging for measurement, which we will certainly return to later for UHV PVD.
On the other side of the tube furnace there is a low permeability plastic tube connected to a carrier gas source with an inline mass flow controller. The mass flow controller has an electronic PID controller and a flow meter which measures the flow rate via a pressure drop across an orifice. Some common carrier gasses are Argon (Ar) or Nitrogen (N). Additional gasses may be added in to react with the contents of the reaction chamber such as oxygen (O) and require an additional mass flow controller and care as they may feed combustion reactions if combustion begins in the reaction chamber.

In the early work of this student, CVD synthesis took the lead role in growing nanowires of ZnO for applications in solar cell; unexpectedly there were interesting results in both wettability (by liquid water) and morphology that emerged that are presented in the following section.

3. Physical Vapor Deposition (PVD)

Physical vapor deposition is a process in which a source material (metal, metal oxide, or even polymer) is vaporized under vacuum and freed vapor phase atoms travel throughout the
vacuum enclosure to create a thin film, Figure 9. The process is extremely versatile, bolstered by its simplicity, and has been around since at least 1838 when Michael Faraday used a primitive thermal vacuum deposition system to coat components for his interesting devices. Within physical vapor deposition there are many techniques to excite the source atoms to the vapor phase from their previous phase, generally solid but conceivably liquid, each having relative strengths and weaknesses.

**Figure 9:** A representative PVD chamber. The source is vaporized, the vapor travels through the chamber to substrate, and the vapor condenses to solid phase on the substrate.

The first method we will investigate is sputtering, where the source atoms are released through the bombardment of high energy atoms and are then freed into the vacuum chamber with a wide range of energy levels. It should be noted that although it has its strengths, sputtering is sometimes difficult to rate control and due to the random bombardment angle may make things like masking and geometric shadowing difficult.

The most common method of sputtering is Magnetron sputtering in which an extremely strong magnetic and electrical field is generated behind the source material and high ions of inert gas are rapidly accelerated at the target, Figure 10. The inert gas, usually Ar, is inserted into the chamber very near to the target and as it passes through the strong magnetic field it is stripped of
electron(s) and becomes ionized. The ions are then rapidly accelerated towards the target through the strong magnetic field. When the rapidly moving ions hit the target surface atoms are knocked off the surface of the target. Due to the fixed nature of the magnets at the rear of the target “race tracks” are etched into the surface of the target and the utilization of the target is not uniform. In somewhat insulating materials, radio frequency (RF) sputtering is possible in where the polarity of the magnets behind the target is rapidly switched, generally at about 13.5 MHz, to assure that the surface of the target does not become charged. Magnetron sputtering is particularly useful in systems were thermal oxidation is an issue and can be used to deposit high purity metallic and metal oxide films in relatively low vacuum levels. The source does not always require water cooling and the system has fewer parts than other physical vapor deposition systems.

![Magnetron sputtering diagram](image)

**Figure 10:** Magnetron sputtering diagram showing the magnetic field generated in front of the target that ionizes sputtering gas causing substrate bombardment and vaporization.

In magnetron sputtering, the deposition rate is roughly a function of the sputtering power, that is, the energy of the magnetic field, and the flow rate of the gas. It is potentially difficult to closely control the deposition rate, but it is much more controllable than solution synthesis and
chemical vapor deposition. Here the deposition rate can be monitored by a quartz crystal microbalance. The quartz crystal microbalance is a system in which a thin crystal is placed perpendicular to the flux from the target and as mass is added to the crystal the vibrational frequency will change. The change in vibrational frequency is then associated with the additional deposition onto the microbalance and thickness and rate can be solved for by knowing the mass of the incoming atoms.

![Diagram of Ion Beam Bombardment PVD](image)

**Figure 11: Ion beam bombardment PVD. High energy ions from a dedicated ion source impact a target. Ion energy levels can be directly controlled for accurate rate control.**

Alternatively, a high energy ion source can be created separate of the target to avoid the formation of “race tracks”, known as ion bombardment deposition or ion beam sputtering (IBS), Figure 11. The major advantage of IBS over magnetron sputtering is that the energy of incoming ions and the total flux can be changed independently, resulting in more control over deposition rate and energy of deposited adatoms which will ultimately dictate the resulting film, or nanostructure, morphology. However, due to the relative impurity of the gas compared to UHV
chambers, the volume of gas that enters the chamber may potentially lower the vacuum level and introduce impurities into the chamber, this is an issue for both Magnetron and Ion sputtering systems, and contamination grows with deposition rate.

Within the framework of sputtering, there is the opportunity to add a secondary modification source, such as secondary ion bombardment to the substrate or an addition of reactive gasses or ions into the vacuum chamber, Figure 12. Ion bombardment of the substrate allows for a decrease in the overall roughness of the film or implantation of ions into the solid to effectively dope the resulting film. For example, ion beam assistance can change the growth mode of a film from polycrystalline to epitaxial. Ion bombardment to the substrate is generally not very useful for the fabrication of nanostructures as it generally decreases the surface roughness and re-sputters the small features. When reactive gasses are added to the chamber, either impregnated near the source or near the substrate, there may be a reaction that occurs as the atoms are moving through the chamber. This is useful for the deposition of complex oxides, such as indium-tin oxide (ITO), which is both transparent and conductive when the stoichiometry is correct but black and completely non-transparent when oxygen deficient.
Figure 12: Ion assisted deposition where a secondary dedicated ion source may be added to bombard the growing film to improve step coverage.

A second, less prevalent, method of physical vapor deposition is cathodic arc deposition which is the preferred method for depositing very hard thin film coatings on things like machine tools (and apparently Cold War Soviet weaponry!). Briefly, a very high current low voltage arc is generated between the target, in this case the cathode, and a fine tipped “igniter” in a high vacuum system. The beam is only a few microns in size, so it locally heats the area of the target extremely high vaporizing it very quickly. After the heat dissipates the vapor deposition quickly extinguishes. Some of the same materials can also be done from other deposition systems but generally yields a less hard film because the velocity of the vapor is lower, as the temperature is lower.
Figure 13: In pulsed laser deposition (PLD) a high energy laser strikes the target causing the local vaporization of source material. PLD results in excellent step coverage and maintenance of vacuum condition.

A third vacuum physical vapor technique is pulsed laser deposition (PLD) where a target is hit with a high energy laser in regular intervals and a plume of vapor, as well as other matter from the target, is locally ejected in a plume, Figure 13\textsuperscript{88}. The deposition technique is relatively simple in comparison to the other methods in terms of instrumentation, but the physical process is much more complex due to the interaction between the laser and the solid. PLD can be performed in either UHV/ HV environments or in a reactive environment to form oxides, but the interaction of the reactive environment and the laser must be accounted for. When the laser, which is composed of photons, strikes the metal or metal oxide target, it must first interact with the matter and generate phonons and excited electrons. The area of the target is then heated and vaporizes and a plume of electrons, ions, molecules, nanoparticles, melted clusters is ejected. This is a potential complication of the system. Further, as the energy level of the laser is somewhat difficult to control the deposition rate may be difficult to control. Locally within the
plume of ejected material there is intense super saturation of atomic species leading to a higher nucleation density on the substrate. This high nucleation rate lends itself to epitaxy, rather than the growth of nanostructures as nearby nucleation sites will generally coalesce as growth continues\textsuperscript{88}.

![Diagram of substrate and plume of ejected material.](image)

**Figure 14:** In thermal evaporation a coil or boat is resistance heated under high vacuum past the vapor pressure leading to vaporization. The lack of super heat leads to lower temperature of source atoms and less step coverage.

A fourth method of PVD is known as simple thermal evaporation in which a material is heated inside a vacuum chamber by a conductive heating element and due to the vacuum condition vaporizes and transports across the chamber, Figure 14\textsuperscript{89}. Next to sputtering, this is one
of the most easily implemented and low cost systems. Most university research laboratories that work in materials science or similar fields will own an evaporative deposition system. This evaporation technique must generally be performed in high to UHV conditions because the vapor atoms will not leave the liquid melt if the vapor pressure requirements are not met. In this case, the resulting film may not be incredibly pure because a large region of the chamber becomes very hot and may outgas during deposition decreasing the vacuum and the conductive heating element may also outgas. Beyond this, the number of materials that may be deposited suffer because of the limitations on maximum temperature of the thermal element and the necessary high vacuum condition- oxides cannot be deposited because they will outgas and degrade the vacuum. In this deposition method there is generally line of site deposition, because the vacuum level is generally a bit lower than other deposition systems, and because of the low velocity of atoms in the vapor due to the low energy relative to other methods. This leads to poor “step coverage”, before finishing an atomic layer a new layer nucleates, and higher surface roughness, most recently known as nanostructures\textsuperscript{90}. With thermal evaporation through resistance heating, the deposition rate is relatively difficult to control due to a lag between the control input and the change in thermal energy.
Under the motif of “thermal” type evaporation is electron beam physical vapor deposition in which a high energy electron beam, a few mm in size, strikes the thermal evaporation source and creates local vaporization, Figure 15. Electron beam physical vapor deposition has wide versatility when compared to other PVD techniques. Because of the local electron beam heating and potential for very high energy densities, a very wide range of materials can be deposited. High purity metals can result in very high purity films if the chamber has adequate pumping and a long slow melting outgas of the source material is used. Alternatively, modern systems are made so that the arc will not extinguish (or strike the chamber wall) at vacuum levels as poor as $10^{-2}$ Torr so that oxides may be deposited. An additional ion or gas source may be added to the chamber to allow for reaction to reach desired stoichiometry. The actual electron beam system is very easy in construction composed of only a filament creating an arc between an anode and
cathode which passes through a water cooled crucible which houses the source material. The power level is easily adjustable in nearly real time and through a PID controller monitoring with a quartz crystal microbalance the deposition rate can nearly be controlled in real time. Due to its extreme versatility and relatively easy implementation, the electron beam PVD (EBPVD) system is generally regarded as the workhorse of research labs worldwide. Realizing all of these advantages, we chose to design and build a capable EBPVD system at the University of Connecticut, which is outlined in the next section.

4. The electron beam PVD system

In the following section we will detail the design, development and implementation of an EBPVD system by the author at the University of Connecticut. Within the main vacuum chamber there is an electron beam source at the bottom of the chamber, the substrate somewhere above the source and with cooling water for several components in a HV or UHV chamber with external controls. A cooled quartz crystal microbalance is passed through into the chamber near the substrate to measure the deposition rate. A shutter may be utilized on either the substrate or the source to allow a set deposition rate to be reached before the substrate is coated.

The most crucial part of every vacuum system is the vacuum containment unit, known as the chamber or the tank, as shown beautifully in Figure 16. The preferred material for the walls of the vacuum chamber is stainless steel because of its excellent resistance to oxidation and corrosion and high impermeability. The oxidation resistance of chamber walls is necessary because any retained oxygen will slowly enter the pumped region of the vacuum chamber and contaminate the vacuum. The chamber is a large cylinder of about 25 cm diameter and 50 cm in height. The size of the chamber is dictated by the size of the electron beam source unit, the desired substrate size and the desired distance between the source and the substrate. Classically,
empirical knowledge suggests that a longer throw distance is preferable because more laminar flow of source atoms is achieved further from the beam to achieve an even coating on the substrate and direct impingement\textsuperscript{92}. The geometry selected allows for the throw distance to be nearly 40cm, which is considered to be a very far throw distance. Onto the main chamber there are several vacuum flanges welded to allow instrumentation to be passed through into the system. There are two main types of vacuum gaskets, polymer and metal, each capable of different vacuum levels. Polymer o-rings are generally capable of reaching the high $10^{-8}$ Torr range when they are new and have air leak rates of around $1 \times 10^{-5}$ sccm / s. Metallic o-rings are capable of reaching deep into UHV range and have air leak rates of less than $1 \times 10^{-9}$ sccm / s when installed properly. The difference is due to the permeability of gases through the polymer, which ultimately limits the quality of the vacuum. In our system we chose to use Viton o-rings on most of the components as the vacuum level of $10^{-9}$ Torr is more than sufficient for nearly all basic science investigations aside for the deposition of very reactive metals. Several additional flanges utilizing copper, or knife edge, gaskets are used to allow for the addition of UHV instrumentation. The top plate has a rotary motion feed through to allow for multiple substrates and shuttering. There are large flanges on the chamber to allow for a quartz viewport to see inside the chamber during deposition and for a large turbomolecular pump to be placed on the back of the chamber.
The next basic requirement is selection of the pump to pull the chamber down to the desired vacuum level, in this case UHV in the range of $10^{-8}$ Torr. The first pump that must be selected is the mechanical or roughing pump. Low vacuum pumping is required to get most of the air out of the system so higher vacuum pumps may take over and remove the remainder down to the desired level. These higher vacuum pumps cannot handle the load that low vacuum pumps can and bog down when trying to operate near atmosphere. The roughing pump must be large enough in displacement to pump down the entire chamber in a quick time. A quick time is desired between cycles so that a high throughput of low purity samples can be quickly fabricated for first line testing if desired. Due to the size of the chamber, the Leybold D8B pump is chosen.
with a pumping capacity of 9.7 m$^3$/hr. This pump is able to evacuate the chamber to $1.0 \times 10^{-2}$ Torr within 10 minutes. The next requirement is to determine the high vacuum pump.

Keeping the requirement of $10^{-8}$ Torr, pump down speed and ultimately cost in mind, we choose to compare a diffusion pump, ion pump, turbomolecular pump and cryogenic pump. The diffusion pump acts to pull a vacuum by the motion of a high speed jet of gas pulling against the molecules in the chamber. The high speed jet is generated by the boiling of oil at the bottom of the pump. This is perhaps the earliest concept of high vacuum pump, developed in 1915 by Wolfgang Gaede and used on the enormous mass spectrometer in the Manhattan Project. Some of the shortcomings of this pump are the long startup time, as one must wait for the oil to begin to boil, a long shut down time because the oil must cool before being exposed to air or risk burning and the potential for the oil to back feed into the system and contaminate the chamber. To work around this, a complex ballast system is possible but this will magnify the cost and complexity of a system as require several gate valves (on the order of $2000$ each), ionization gauges ($1000$ each) and an auxiliary chamber ($10,000$ +).

A second pump, the ion pump acts by creating a strong magnetic field, on the order of 1000 to 2000 Gauss, to ionize atoms in the chamber and get them to stick to a cathode. The major issue with the ion pump is that it is very delicate to pumping conditions and requires roughing to $1.0 \times 10^{-3}$ Torr, which is lower than can be expected for a mechanical pump- so a turbo pump is required anyway. The cryogenic pump uses a very low temperature working fluid, generally compressed helium, to capture atoms onto a cold trap and is capable of very low vacuum levels but also requires extremely low roughing values and suffers from very slow pumping speeds.
A third type of pump, the turbomolecular pump, the newest among the bunch invented in 1958 by Becker, is simply a series of blades driven by an electrical motor used to give molecules a velocity towards the outlet of the pump. Although relatively low powered, the speed of the rotor with blades is very high and often operates at 90,000 rpm. In terms of pump speed, the turbomolecular pump is generally regarded as the fastest and best capable of handling cycles, so this immediately brings favor to this pump with an ultimate base pressure nearing $10^{-10}$ Torr. With the constraint of cost, the turbomolecular pump is the lowest costing pump also. However, due to the constant moving parts and high rotation velocity, the turbomolecular pump generally does not last as long between maintenance as other pumps and is ideal for applications where it may easily be exchanged for a rebuilt unit. Therefore, for this chamber a Leybold Turbovac 151 with a pumping speed of 145 l/s was selected.

To measure the pressure inside the vacuum gauge a combination of a Pirani, inverted magnetron and ionization gauge are used. The Pirani gauge, as described in earlier sections, is used to measure pressures down to $10^{-2}$ Torr. Beyond $10^{-2}$ Torr an inverted magnetron is used in redundant configuration with a hot filament ionization gauge. The ionization gauge operates through heating a filament near a charged cage. Electrons are pulled from the hot filament and drive towards the cage. Before reaching the cage, most hit molecules in the chamber and cause ionization. A center ion collection post inside the gauge has a negative voltage bias and collects the ions. The rate of ion bombardment is measured and calibrated to the pressure level. The ionization gauge is very accurate down to $10^{-11}$ Torr, but often burns out due to the fragile hot filament, causing the need for redundancy.

Within the chamber, several things are added to increase the functionality of the chamber. First, the substrate holder is deeply recessed into the chamber to allow for the use of either liquid
nitrogen cooling or resistance heating of the substrate making the effective temperature range of the substrate from -269°C (liquid helium) to 300°C. The substrate may also be mounted so that it has computer controlled rotation on a stepper motor or precise positioning at a predetermined angle, glancing angle, relative to the incoming vapor flux. In the author’s knowledge this is the first application where a substrate may be taken from cryogenic temperatures to high temperature without breaking vacuum while being held at a glancing angle.

5. Materials Characterization on the Nanoscale

Perhaps equally as important as the ability to fabricate nanostructures is the ability to characterize what you have created. Before moving onto introducing new growth mechanisms we must first outline the tools available to investigate materials on the nanoscale- without this there is no chance of scientific advancement. Until the invention of the electron microscope in the 1930s, indirect spectroscopy had to be employed to determine things like morphology, composition and crystallinity. Today, researchers have a sophisticated tool set at their disposal to accurately characterize materials down to the atomic level. Within this tool set the most important tools are electron microscopy (EM), X-ray diffraction (XRD), energy dispersive or loss spectroscopy. In the following section we will discuss the implementation and background of each of the respective methods.

Before the invention of electron microscopy, the resolution of optical microscopy had become a major limitation to the study of condensed matter. Due to the relatively large wavelength of light, ~550 nm at its smallest visible regime, green light, the maximum resolution of visible light microscopy is limited to about 200 nm. The resolution is a function of wavelength and goes by

\[ d = \frac{\lambda}{2NA} \]  \hspace{1cm} (19)
Where \( d \) is the resolution limit, \( \lambda \) is the wavelength of the imaging beam and \( NA \) is the numerical aperture which is a function of the index of refraction of the material and the angle of interaction. Motivated by the quest to directly observe individual atoms and atomic structures, early researchers pushed to increase the resolution of the microscope, eventually looking to other mediums to achieve this goal.

In electron microscopy, high energy electrons are used to generate an image through interactions with the specimen. (As the author took a class with the author of one of the foremost electron microscopy texts, the text will be used extensively throughout this section as a reference) Electron microscopy was pioneered by Max Knoll and Ernst Ruska in 1931 at the Technical University of Berlin, Germany when they realized the first electron lens enabling the transmission electron microscope. Until this time, the behavior of electrons was not well known and it was generally accepted that electrons behaved like high energy particles. Even with this belief, the German group set out to show that electrons could be controlled through an electromagnetic coil, with the electron source being a cathode ray oscilloscope and a small metallic specimen being placed near the anode with an electroluminescent screen placed below. Largely unknown to these pioneers, the nature of the electron is both as a particle and as a wave, first proposed by French physicist Louis De Broglie in 1924. Proposed by De Broglie, the wavelength of an electron is

\[
\lambda = \frac{h}{P} \tag{20}
\]

Where \( h \) is planks constant and \( P \) is the relativistic momentum. When the electron is accelerated by a potential field, like in electron microscopy, accounting for relativistic effects due to velocities approaching 0.7c, the wavelength becomes

\[
\lambda = \frac{h}{\sqrt{2M_0eU} \left[ \frac{1}{1 + \frac{eU}{2M_0c^2}} \right]} \tag{21}
\]
Where $M_0$ is the mass of the electron, $e$ is the charge of the electron, $U$ is the voltage of the potential field through which the electron is accelerated and $c$ is the speed of light. Electron acceleration voltages commonly used today in scanning electron microscopy (SEM) are generally on the order of 10 KeV, resulting in a wavelength of 12.2 pm, (yes, that is pico meters, or $10^{-12}$) and in transmission electron microscopy (TEM) are on the order of 200 KeV resulting in a wavelength of 2.5 pm. Compared to the resolution of several hundreds of nm from visible light, electrons are clearly advantageous.

The two forms of electron microscopy, SEM and TEM, share several common themes, but differ in hardware and operating principle. The commonalities between the two are that a high energy electron beam is generated by an electron gun in HV or UHV, a point source which ejects electrons, and are then accelerated and shaped through a series of electromagnetic lenses and apertures. The electrons then strike the sample and depending on the sample morphology and the velocity of the electron the electron may either pass through the sample, transmission, or penetrate then deflect back, scanning. A detector, ranging from an inline CCD camera to a faraday cage and scintillator (E-T detector), is used to generate an image from the electrons. While an image tells us so much valuable information, there is much more information to be had from analyzing different “byproducts” that result from the interaction between the high energy and mater, like x-rays. The potential of this spectroscopy is multiplied by the high resolution positioning and ability to control the region of measurement with high selectivity and precision.

In transmission electron microscopy, electron transparent samples are placed amidst a series of electromagnetic lenses and apertures, shown below in Figure 17, and struck by a high energy, 50 to 1000+ KeV, stream of electrons. To achieve electron transparency, when operating at a normal acceleration voltage of 200 KeV, the sample must be on the order of 50 nm thick,
otherwise the electrons may be trapped inside the solid. As the electrons pass through the material they interact with the nucleus and electron clouds of the solid and are scattered at low angles following Bragg’s law. The main type of detector is a phosphorescent screen or a digital CCD camera detector placed at the bottom of the stack to intercept the electrons that have passed through the sample. In a TEM the electron source may be either a thermal emission source like lanthanum hexaboride \( \text{LaB}_6 \), where electrons are emitted from the entire crystal through heating, or a field emission source (FEG), where electrons are emitted from crystal through a strong electromagnetic field across the crystal. The electron source is held under UHV to reduce contaminant build up on the source. Some FEG sources, Schotchy assisted, utilize a heated tip to keep contamination from forming on the tip and keep the longevity of the tip while decreasing the necessity of UHV conditions at the gun. For example, heated FEG tips can operate at \( 5 \times 10^{-9} \) Torr. The first electron lens, the Wenhelt, is used in thermal emission to accelerate the electrons away from the source and begin to focus the electrons. In a FEG, the first electron lens acts to accelerate the electrons away from the source and begin to focus the electrons. Continuing down the column, in a high vacuum or UHV condition, the electron beam is then condensed by a series of lenses and is intercepted by a condenser aperture to limit the beam size and get rid of the electrons at the highest angles. These high angle electrons actually introduce aberrations into the image which limit the resolution of the microscope. Chromatic aberrations are those that are from non-uniform electron energy emission from the source and are difficult to remove, but more recently a monochromator electron lens may be added to sophisticated microscopes. Spherical aberrations result from the outer electrons of the electron beam and are a result of focusing differences between the interior and exterior of the electron lens. This aberration is decreased by inserting a small condenser aperture, to get rid of the outside electrons, and
operating at a higher acceleration voltage. At higher acceleration voltages the electrons are “bent” less by the electron lens and travel down the column straighter. Next the electrons reach the sample and pass through. After the sample the electrons interact with an objective lens and objective aperture to increase the resolution by decreasing the overall information reaching the detector and shedding the electrons with the highest scattering angles. Depending on the focal plane, either an image can be cast on the detector- when the focal plane is the sample, or a diffraction pattern from the electrons can be cast- when the focal plane is the crossover point of the objective lens giving a spot pattern corresponding to the regular Bragg refraction. A selected area aperture may be put in place further down the column to decrease the area that is being viewed in diffraction mode, right of Figure 18; to block the electrons that are coming from other spots in the sample. Several more lenses then follow this aperture to increase the magnification of the image. Due to the small scattering angles, magnification up to 1,000,000 x are possible from very high acceleration voltage instruments.
Figure 17: Schematic representation of the column of a transmission electron microscope. On the left the microscope is focused on the specimen and forms an electron image while on the right the microscope lenses are focused on the back focal plane of the objective lens and a diffraction pattern is in focus.

The image from regular bright field TEM (other more advanced methods will not be discussed here but can be found in the references) shows contrast from the interaction of the electrons and matter as they pass through, like the one on the left of Figure 18. It is important to remember that the TEM image is actually a 2D projection of a three dimensional image, so thickness changes are important to account for. Thickness contrast is a primary means of contrast in the electron image. Simply, the more matter the beam passes through the less electrons that will reach the detector. The bright regions of a TEM sample are regions where the electrons are scattered less and head more directly to the detector (or they may be regions where the electrons are all scattered to, it is important to try to determine which it is) and the dark regions are caused
by heavy scattering and interaction. If there are dislocations or other impurities within a sample a dark or light region will result because there is a local difference in stacking leading to a more or less dense region in the sample. Different materials and phases will also result in different scatter, with high Z elements resulting in more scattering of electrons and therefore less brightness on a TEM image. If the detector is changed to pick up areas where there is scattering, a dark field image, then specific crystallographic orientations will all refract the electrons the same and local orientation may be determined. Dark field imaging is useful for aligning the sample for advanced techniques and creating maps of polycrystalline samples based on orientation.

![Figure 18: A bright field TEM micrograph of an Au nanorod on a carbon support grid with Au nanocrystals on the substrate (left) and the respective selected area diffraction pattern (right).](image)

Transmission electron microscopy lends itself very well to the high resolution imaging of thin crystalline samples but is limited by the samples it may accommodate and cannot give any 3-dimensional topographic information. The first constraint is that the sample be electron transparent and no larger than the stage of the TEM, which requires the sample be about 3 mm x 3 mm x 50 nm or smaller. Handling such a thin sample brings about the first constraint, as it is
very delicate. The sample is placed onto a copper or carbon grid to be placed into the TEM column. Preparing such a sample is often very difficult and briefly a few techniques to achieve this are directly fabricating the sample (in this case it has to be nanoparticles, nanorods etc. or a very thin film) onto the TEM grid, mechanical wafering and polishing, focused ion beam milling (FIB), looking at the tip of a sharp cleaved edge or many, acid etching, and many other sophisticated techniques. Often, it is difficult to create a TEM sample without destroying the object you are trying to image as they are very delicate. A prime example of this is the imaging of metallic nanorods on silicon wafers by this student. Even doing FIB milling, the nanorods are quickly destroyed; meaning the only way to have a proper image is to directly deposit the nanorods onto the TEM grid. A second constraint is that the material must be able to withstand HV conditions without degradation and must not burn up under the strong electron beam. In this case, the TEM imaging of polymers and biological samples is very difficult. Further, if you hit a polymer sample with a high energy electron beam the degradation will contaminate the vacuum with hydrocarbons that will float about near the sample and deflect the incoming electrons prior to reaching the sample. One of the first samples used in the TEM by Knoll and Ruska was a cotton fiber which quickly burned up under the electron beam. If information is desired without destructive sample preparation, like for a component that was removed from a jet engine for example, or if surface information is desired, then the TEM is not the preferred characterization method and SEM should be employed.

Scanning electron microscopes operate by bombarding a sample with high energy electrons with velocity on the order of .5 to 30 KeV and recording secondary electrons (SE) and back scattered electrons (BSE). Like the TEM, at the top of the column in a UHV enclosure, generally pumped down with Ion getter pumps after being roughed by a turbomolecular pump
and a roughing pump, an emission source releases electrons. In modern microscopes a FEG is used to have a very small high energy electron beam. Further down the column there sits a condenser lens to further reduce the spot size of the beam. An aperture is then put in place of varying diameter to decrease aberrations of the image. Below the aperture there sits the focusing lens, known as the pole piece, which is the final lens and dictates the focal distance. In SEM, the beam is focused to cross over precisely on the sample surface. Often the chamber of the SEM may be held at lower vacuum levels than the column meaning that for strong electron feedback the sample should be as close as possible the pole piece. Generally, the same for SEM can be very large and the chamber it sits in can vary in vacuum level from “environmental”, 0.1 Torr or so, all the way to UHV chambers for very high resolution imaging. The sample chamber may be large to accommodate bigger samples as there are no lenses or detectors behind the specimen there does not need to be maintenance of such a high vacuum level and linearity of the beam as in TEM.

In the SEM, when the electron beam strikes the surface of the sample the electrons interact with the mass in several ways. First, some electrons are released from the very surface of the sample as Auger electrons because an inner shell electron is knocked free resulting in the ejection of an outer shell electron. These electrons are generally not used for imaging in the SEM. As some electrons penetrate a bit further, maybe 10’s of nm into the sample, ionization occurs and electrons are shed by the material. These electrons are called secondary electrons and are generally of an energy level of 50eV or less. Further, some beam electrons may penetrate deep into the sample and then return from the sample due to refraction, or back scattered electrons. The highest energy backscattered electrons come directly back towards the beam and the greater the energy loss the greater the angle of refraction. In SEM imaging the SE give
excellent information on topography and very high resolution as they do not penetrate far into the sample. So see the difference between these electrons, Figure 19, is presented as a schematic representation.

Figure 19: As electrons from a high energy beam strike a thick solid they interact in a variety of ways and originate from different amounts of physical sample space.

In terms of achieving the maximum resolution with an SEM, the beam is rastered quickly across the sample to excite the surface and give off electrons. The resolution is a function of the size of spot used to excite the atoms and the energy at which the electrons are striking the sample. If the spot size is too large then there is too much information returning back for any given position and features cannot be discerned. Alternatively, if the spot size is too small and the scan is too fast then there is not enough information coming back to the detector to
get adequate information. The energy level of the electrons also dictates the resolution because at lower accelerating voltages the electrons have more aberrations and larger scatter angles when they interact with the atoms in the chamber between the sample and the pole piece. Therefore the very best resolution from an SEM is achieved when the detector is getting the “right” (subjective) amount of information and the electrons are interacting as little as possible with the chamber. The electrons would then enter the sample directly parallel and excite all regions of the sample evenly giving rise to even levels of ionization, and ejection of secondary electrons, from equivalent sample mater.

The SE and BSE electrons are gathered by distinctly different detectors inside the SEM to form images. The SE images are generally collected by Everhart-Thornly detectors (ETD) in modern microscopes. The ETD is composed of a charged Faraday cage and a scintillator with a high acceleration voltage. The Faraday cage sucks in the low energy secondary electrons and allows them to pass through to the scintillator where they are accelerated by as much as 10 KeV to cause the discharge of light. This light discharge is then recorded via CCD camera. If the signal is weak, due to low beam current in an attempt to get a high resolution image, the ETD can function for a long duration without saturating, with the CCD camera iteratively collecting data to compose an image. It is worth noting that the richness of topographic information from the ETD is because of the charged Faraday cage- nearly 3 dimensional images are achieved because the electrons from all over the excited region are collected by the ETD and there is nearly no shadowing. BSE are detected by an annular solid state detector near the pole piece. The highest energy BSE come back towards the energetic beam at the lowest angles, leading to bright spots in the image. BSE images offer less resolution than SE images because of a larger excitation volume – electrons can come back from a large area due to scattering and there are
large areas of overlap. However, Z contrast information is readily available from BSE imaging because the scattering is directly dependent on interaction with nuclei. Therefore, complex phase or grain mapping can be achieved using BSE imaging. A comparison of the two detection methods, BSE and SE, is shown in Figure 20.

![Figure 20: BSE SEM image (left) and SE SEM image (right) of the same region of a Ti-alloy particle at 2000X Magnification.](image)

Using both SEM and TEM, several different types of analysis may be performed to determine chemical composition. In both TEM and SEM, X-ray energy dispersive spectroscopy can be employed. When high energy electrons hit matter and penetrate deep into it, electrons are often knocked from the conduction band to the valence band. When these electrons jump back they release the extra energy as a characteristic X-ray. These X-ray levels are unique to each element and even each jump between bands. This method is often called XEDS or EDS, and should never be called EDX, as it often is, as that is simply the name of the most widely produced name brand. In SEM, the large area of the sample creates a very large excitation volume for X-rays to emerge from. The resolution of XEDS in SEM is therefore on the order of a few microns, so it is very useful for large phase analysis, but not very useful for nanostructures.
In the TEM, XEDS only excites an area the size of the beam spot, maybe a bit larger, so very precise XEDS analysis can be performed. Also in TEM, electron energy loss spectroscopy can be employed where the energy loss between the direct beam as it comes off the source to when it is detected below the source can be determined as correlated to passing through a material of a given Z. EELS is very precise as it collected electrons passing directly through the desired region down to a few nm certainty.

Another method of characterization which will be briefly mentioned in X-ray diffraction (XRD), in which an X-ray beam interacts with the material in question and scatters back at regular patterns due to interaction with the structure of the material. XRD is particularly useful for the quick characterization of large samples and powders to determine the crystalline orientation and even crystallite size. In XRD, an X-ray beam with a known energy and wavelength is scanned across the sample at varying angles. A detector is placed at a similar angle on the opposite side of the sample. The X-rays refract at specific angles due to interaction with the regular planes of the atomic structure of the material being studied. From this, using Bragg’s law, the spacing between planes can be determined. Further, with an understanding of the width of the peak, a rough approximation of domain (crystal in a film or particles size in powder) size can also be determined. For the characterization of nanostructures XRD is useful for determining the orientation of regular arrays or their mean crystallite size as a quick approximation. Additional references can be found in the works cited\textsuperscript{116,117}. 
III. Scientific State of Nanostructures from Physical Vapor Deposition

1. Thermodynamic Crystal Growth Primer

Before we may understand how nanostructures form from physical vapor deposition it must be briefly understood how crystals grow in general. As with any other process, the only way a phase change will begin, in this case from solution or vapor, if it is thermodynamically preferable. The crystal growths begins through nucleation, that is the formation of a cluster of a critical stable size. Once a cluster has nucleated the crystal growths through a four step process: (1) mass, vapor, is transported to the surface, (2) the atom attaches, or is adsorbed, onto the surface, (3) the adatom moves on the surface and (4) the adatom either nucleates a new layer or incorporates to a edge of kink site. Unlike other forms of crystal growth, it is important to realize that PVD, especially moderate to high vacuum PVD, is always in a state of supersaturation. For comparison, solution systems may have a supersaturation of 0 to ~10%, while CVD may have as much as 100% and PVD may have as much as 1000%. This means that nucleation is almost always preferred, eliminating the problem of nucleation of the next layer present in early crystal growth theory\(^93\).

As first proposed by Connecticut’s own Gibbs in 1877, the Gibbs free energy of the vapor phase must be higher than Gibbs free energy of the solid crystal and the remaining vapor for a nucleus to form on a surface\(^94\). More recently, Mullins described crystal growth as the change in chemical potential, \(\Delta \mu\) as the measure of free energy response to atoms transferring from one phase to another which a greater chemical potential representing a greater driving force\(^95\). In this case, the governing equation becomes:
Putting in thermodynamic variables:

\[ \Delta \mu = \mu_{vapor} - \mu_{crystal} \]  \hspace{1cm} (14)

Here \( K \) is the Boltzmann constant, \( T \) is the absolute temperature and \( S \) is a measure of supersaturation. When \( \Delta \mu \) is \( > 0 \), the system is supersaturated and crystal growth is preferred. The work to form a cluster, or nucleate a new cluster on a surface is:

\[ \Delta G = -n\Delta \mu + 4\pi r^2 \sigma \]  \hspace{1cm} (16)

Where \( n \) is the number of atoms in the cluster, \( r \) is the radius of the cluster and \( \sigma \) is the surface free energy. Therefore, at a given supersaturation level the critical radius of a stable cluster is then:

\[ r^{\text{crit}} = \frac{2\sigma V}{kT \ln S} \]  \hspace{1cm} (17)

Where \( V \) is the volume of the forming cluster. This nucleation may occur at either random spots for an atomically smooth substrate or may occur at locations on the substrate that have locally higher surface free energy and nucleation of a cluster would reduce the overall free energy of the system.

After nucleation the crystal grows by a 4 step process and the growth mode may be limited by kinetics. The first step is mass transport to the crystal surface and the adsorption of the adatom to the crystal surface. Once on the surface the adatom encounters a diffusion barrier and makes diffusion jumps based on its thermal energy and the barrier it faces. Both the thermal energy and diffusion barriers the adatom faces will dictate its final position. If it has sufficient energy to continue diffusing, it will move to a low energy position, such as a kink or edge site, as shown in Figure 21 below.
To make a diffusion jump on a surface to reach a new configuration an adatom must overcome a diffusion barrier, which varies based on the atomic configuration. The adatom jump rate, \( r \), goes as

\[
\Gamma = \nu e^{-\frac{E}{kT}}
\]  

Where \( \nu \) is the atom vibrational frequency, \( E \) is the energy barrier of diffusion and \( KT \) is the thermal energy in absolute temperature, \( T \). It takes some real finite time for an atom to diffuse across a terrace. If the adatom does not have sufficient thermal energy it may be limited to its diffusion area. For example the barrier may be too large. Discovered in the early 2000’s the barrier for an adatom to diffuse over a monolayer step compared to a multiple layer step – that is that the monolayer step is a that of a single atomic layer and a multiple layer is more than one atomic layer- is perhaps two to three times smaller\(^{96,97}\). This increases the chance for surface roughness.

Within this classical framework surface roughness can be explained, beyond intrinsic roughening that occurs at elevated temperatures. First, if the deposition rate is high then an
adatom on the top terrace may come in contact with an additional atom from deposition before it may diffuse off of the top terrace to a lower energy site along the step. In this case, the two adatoms form a dimer and the diffusion barrier for a dimer is much higher than that for a single adatom and the mobility is extremely limited. Therefore, at a high deposition rate the diffusion lifetime is limited and the surface roughness increases because three dimensional growth becomes more dominant. The second means of increasing roughness is to decrease the temperature. By decreasing the temperature the thermal mobility of the adatoms is kinetically limited by the diffusion barrier necessary to make jumps. At low temperature, meaning low energy of adatoms, or high deposition rate three dimension growth can also become dominant.

Figure 22: Thin film growth modes. (I) Layer by layer, (II) layer - by -layer and islanding and (III) islanding.

Three modes of growth may result from a substrate, with two giving rise to rough films, as illustrated in Figure 22. This model is in contrast to the Kossel model that assumes nearly complete substrate coverage. In Frank-van der Merwe growth the interaction between substrate and developing film is very strong and complete coverage is achieved by the first layer, left of Figure 22. After the first layer nucleates the diffusion of adatoms on the film is ample and adatoms are able to find low energy sites. In this case, the strong interaction between the substrate and the growing film blocks the formation of multiple layer surface steps and the largest barrier adatoms face to move is the 2D diffusion barrier over a mono-layer. If the
substrate–film interaction is strong but the film-film interaction is also strong, the deposition rate is very high, or if the diffusion barrier is too strong to be overcome – either because the diffusion barrier itself is too high or because the energy of adatoms is too low to overcome the barrier-then adatoms will not be able to overcome mono-layer steps before a new layer nucleates. This condition gives rise to Stranski-Krastanov growth, middle of Figure 22. The final growth mode comes from a non-wetting substrate, right most of Figure 22, and is dominated by multiple layer surface steps. This growth mode may come about if the deposition rate is very high and a new layer is nucleated before complete coverage, if the substrate – adatom interaction is much weaker than the adatom – adatom interaction, or if the diffusion barrier is very high – again as a function of actual barrier or temperature. In the case of non-wetting substrate, the adatom-adatom interaction is stronger than adatom-substrate, once a cluster of two layers forms the diffusion barrier transitions from 2D to 3D and adatoms now face a significantly larger barrier to move from the tops of islands. In combination with geometric shadowing either of the two modes that result in roughness may result in nanostructures from PVD. In the following section we will discuss this growth in detail.

With knowledge of this kinetic limitation and deposition rate dependence, one may envision a scheme of growing very rough films, perhaps even with nanoscale surface roughness. If adatoms preferentially land on the top terraces and not the side terraces, perhaps through geometric shadowing in line of sight deposition in PVD, and are limited to the top terraces through high deposition rate or low mobility then a three dimensional structure will result. This method of realizing nanorods from physical vapor deposition is utilized throughout this body of work and is described in more detail in the next section.
2. Glancing and Oblique Angle Deposition in PVD

The methods of high vacuum PVD have been around since the 1900s. Over the last ten decades, there has been much progress in fabrication technology and many advanced methods of PVD have emerged. In particular, two of these methods, glancing angle deposition (GLAD)\(^{13,17}\) and oblique angle deposition (OAD)\(^{98}\) have enabled the growth of metallic nanorods using PVD. The glancing angle deposition method was pioneered, in its modern sense, by Michael Brett and his group at the University of Alberta, Canada, in the early 1990’s- his group and several of his students are still very active today. In GLAD the source, generally UHV EBPVD or RF magnetron sputtering, are held stationary in the vacuum chamber and the substrate is manipulated to be set up at an angle so that the direction of the incoming flux is not perpendicular to the substrate. If the substrate is held stationary only high points, which generally come about from either substrate patterning or a non-wetting condition, receive the incoming flux. As the technique has become more mature, very complex structures like the helix and chevron have been fabricated through the addition of substrate rotation\(^{16}\). In OAD, the source flux is moved in relation to the substrate, so the angle of attack can be changed in real time during deposition. This method was pioneered by several groups at RPI in the late 1990’s. In both methods, geometrical shadowing is used to limit the deposition of new flux to the top of geometrically high locations, peaks, while the only flux that geometrically low locations, valleys, receive is from atoms having diffused down from peaks. Using the method of geometrical shadowing, it becomes possible to fabricate metallic nanorods using PVD, Figure 23.
Figure 23: Schematic of growth under GLAD. First surface roughness originates, left, followed by geometric shadowing and growth of tall spots of the film, middle. As the film grows the high spots dominate and rods form.

While experimental realization of very rough films and metallic nanorods was common place, scientific understanding of the growth was only possible after the stability of multiple layer surface steps and the 3D Ehrlich-Schwoebel (ES) barrier emerged. Within classical crystal growth the growth of surfaces advances by incorporation of adatoms into kink or edge sites and the crystal grows both laterally and upward, driven by a screw dislocation on the top of the crystal. In metals, adatoms diffuse over monolayer surface steps and across surfaces met by very low barriers, so within this framework very smooth films should form. In terms of diffusion, the motion over a step site is usually through exchange between a step atom and the atom that approaches the step and the diffusion on a surface may be through hopping across the surface or by switching between a bulk atom and the surface atom. An early work, Mullin 1990’s, aimed to explain the high surface roughness of some metallic films, at this time deposited without a glancing angle, and used a “wedding cake” model, showing how a steep bunching of mono-layer
surface steps may result in high roughness, but the feature size of such roughness should be very large, on the order of microns\textsuperscript{95}.

Although on the correct path, the wedding cake model still could not explain the length scale of metallic nanorods developing from GLAD and OAD, so a new model was necessary. Under GLAD and OAD, small non-wetting clusters may form on the substrate and only the tops of these clusters receives additional flux. If these clusters are entirely composed of mono-layer surface steps, diffusion top the top of clusters should be fast for metals and adatoms from the top should quickly diffuse down the sides of the cluster and the cluster should expand to coalesce into a dense film. From the experiments it is however evident that this is not happening. Investigation under high resolution SEM and TEM shows that the sides of the nanorods are nearly straight and smooth and those that form from non-wetting substrates are in fact take the shape of an inverted tower and not a wedding cake\textsuperscript{41}, Figure 24. The smooth surfaces suggest that there must be multiple layer surface steps, which had been considered unstable since the early works of Ehrlich and Schwoebel in the 1960’s\textsuperscript{44,101}. In the early 2000’s our group worked on DFT Ab-initio calculations to determine if there was a different barrier faced by adatoms to diffuse over a multiple layer surface step, compared to a monolayer\textsuperscript{96}. It was then realized that, indeed, the barrier an adatom faces when it diffuses over a multiple layer step is much larger than that of a monolayer step. With this new realization work was done to show that the diameter of nanorods that comes from a wetting substrate, that is that monolayer and multiple layer steps naturally compete, that is they arise from Stranski-Krastanov growth, is on the order of 100 nm, finally giving rise to an explanation for how nanorods may grow without continuous expansion\textsuperscript{19}. As adatoms land on the top during glancing angle deposition they are kinetically limited to the top terrace by the large 3D barrier – multiple layer steps come about due to the random nature of
growth- and a new layer may be nucleated even if it is not thermodynamically preferable compared to incorporation into a step or kink.

Figure 24: A TEM micrograph of Au nanorods on a carbon support. The Au nanorods have smooth side walls.

Recently, the group also showed, through lattice-kinetic Monte Carlo (LKMC) simulations, that multiple layer surface steps are indeed stable but also exhibit positive feedback which has strong implications for the growth of nanorods. Multiple layer steps give rise to more multiple layer steps as they bunch together and the strong diffusion barrier becomes active. Even in cases of incomplete geometric shadowing, multiple layer surface steps in 2 dimensions may
confine adatoms on the sides, giving rise to the shape of the inverted tower, rather than the wedding cake.

On a non-wetting substrate the non-wetting clusters may be bounded by multiple mostly layer surfaces steps, giving rise to nanorods of a smaller diameter from Volmer-Weber growth. Under the condition of glancing angle deposition these nanorods may maintain a small diameter because the dominance of multiple layer surface steps begin at the nucleation of the rod and the 3-D diffusion barrier becomes more active.

This is the beginning of the framework and accompanying theory of the growth of nanorods, and illustrates that there are two modes of growth, Mode I from a wetting substrate which gives rise to nanorods with both multiple layer and monolayer surface steps and Mode II which originates from a non-wetting substrate and may be dominated by multiple layer surface steps and has a very small diameter. This framework and theory is at the core of this thesis and is explained in detail in later sections.

With this basic scientific understanding, the fabrication of metallic nanorods using GLAD and OAD has become commonplace for two decades, and fabrication techniques have become mature. The first reported structures grown from PVD were metal and metal oxide nanorods, among other complex geometrically sculpted thin films, in 1994\textsuperscript{102}. Building from this early fabrication knowledge, the fabrication of nanorods from a wide range of metals, such as Cu\textsuperscript{27,103,104}, Ag\textsuperscript{34,35,105}, tantalum (Ta)\textsuperscript{106}, Pt\textsuperscript{40}, and Cr\textsuperscript{15} amongst others, has been reported in the literature. Unlike solution processing, direct morphological control is possible in PVD. As more mass is deposited to the substrate, the nanostructure will grow predictably. Unlike solution processes, where complex chemical reactions take place, all of the atomic motion within PVD is physical; ballistic deposition or diffusion (metal-substrate or metal-metal) are the only two
means by which atoms may move. By modifying deposition rate and substrate temperature, the mobility of adatoms on the substrate and metal surface can be predictably altered. With the addition of substrate rotation and dynamic angular adjustment, flux can be added to the substrate from nearly any direction. The result is the ability to engineer complex structures such as helixes, chevrons, zig-zags and fans\textsuperscript{13}.

Our motivation for choosing metallic systems as the prototype of study is clear as they have many technological applications and scientifically growth of pure metal crystals is well understood. However, materials from other bonding systems are equally as technologically relevant but their growth mechanisms are not as clearly defined due to more complex electronic structures. In the following section we will make the brief transition from metallic systems to ionic, covalent and amorphous systems to survey the current body of knowledge to set the stage for further investigation.

When the author entered the field of nanofabrication from PVD, this knowledge base was established and the technological drive to reach smaller diameters was the motivating factor. To begin this realization, conventional wisdom of crystal growth was utilized and anomaly of film porosity dependence on deposition rate gave insight into the necessity for a comprehensive theory of nanorod growth and the completion of the framework\textsuperscript{103}. This work was done using Cu, and is outlined in Section IV.

Again, experimental realization preceded scientific understanding when Au nanorods of small diameter and excellent spacing were realized. Au nanorods are interesting for biological applications due to their strong plasmonic resonance and have been used for things like cancer sequestration because they are chemically inert and non-toxic\textsuperscript{107-111}. Until recently, Au nanorods had not been widely investigated using PVD\textsuperscript{41}. Using electron beam PVD in high vacuum with
glancing angles from 85 to 88°, different substrates, and sample cooling our group has realized Au nanorods with diameters of 10 nm, Figure 25. The rods in Figure 25 have diameters of 10 nm and are grown on highly non-wetting adhesive tape (3M Copper Conductive Tape 1182, 3M Corporation, St. Paul, MN) at a deposition rate of 0.1 nm/s, a glancing angle of 88° and liquid nitrogen cooling. This realization motivated the complete experimental exploration and further fueled interest and efforts into the theoretical formulation.

Figure 25: SEM image of small Au nanorods from PVD, originating from a non-wetting substrate.

In section IV we return to growth of metallic nanorods and first outline the new and complete theory of nanorod growth from physical vapor deposition and show how it has enabled the realization of the smallest, and most technologically relevant, nanorods from physical vapor deposition to date.
IV. A New Scientific Contribution: The Smallest Metallic Nanorods from Physical Vapor Deposition

As we introduced in the beginning of this dissertation, there is the technologically driven necessity to realize nanorods of ~10nm. The following section outlines this pursuit and culminates in the realization of the smallest nanorods ever from physical vapor deposition and the scientific understanding of why they grow.

1. Anomaly of film porosity dependence on deposition rate

Metallic thin films of variable porosity are useful for a diverse range of applications, and more importantly, metallic nanorods (a film with extreme porosity) can be very technologically important if their dimension shrinks to ~10nm in diameter. To reiterate, some examples of these applications are the use of Copper (Cu) nanorods in three-dimensional (3D) wafer bonding\(^\text{28}\), metallic and bi-metallic nanorods as catalysts in chemical reactions\(^\text{118,119}\), and nanorod coatings for enhanced boiling\(^\text{29}\). 3D wafer bonding is an emerging technology which enables wafer level 3D integration of electronic systems\(^\text{28,120}\). Cu thin films have been used for wafer bonding, but integrated damage may occur at the high temperatures required to melt or drastically increase surface and solid diffusion of Cu thin films; bulk Cu has a melting temperature of 1085° C\(^\text{120}\). Cu nanorods begin to coarsen, which initially misinterpreted as melting as we address in the next section, at temperatures as low as 400° C presenting an alternative to destructive high temperature processing\(^\text{23}\). As catalysts, Pt nanorods have shown high catalytic activity due to their increased surface area and speculation of catalytically preferred surface orientation when
compared to bulk. Bi-metallic nanorods may also be made, such as Cu-Pt, which offer similar catalytic activity but with the use of less Pt, which has prohibitively high cost. In boiling applications, porous Cu nanorod films offer a significantly higher amount of boiling nucleation sites compared to micro and bulk films; up to a 30 fold increase. In all applications, control of film porosity is desirable. Further, in all of these applications, a common theme is metallic nanorods that are on the order of 30nm in diameter and that are very close together. Therefore, the goal is to decrease the critical dimension, the diameter, to further improve properties like depressed coarsening temperature, catalytic activity and surface area. If spacing between rods is also increased the properties may impact a wider range of applications as these structures may coarsen or even behave as their thin film counterparts if the rods are too close together – we will bring substance to this claim in the next section of this dissertation.

The control of film porosity and nanorod diameter is feasible through control of diffusion kinetics; that is, the competition of surface diffusion and geometrical shadowing during physical vapor deposition, when conventional theory is accepted. Reducing surface diffusion, through depressed temperature or increased deposition rate, and enhancing geometrical shadowing leads to higher film porosity and should lead to smaller diameter nanorods as the roughness of the film increases. By geometrical shadowing, atomic flux from physical vapor lands on elevated surface regions. Further, by limiting the diffusion lifetime or distance of adatoms, the deposited atoms do not reach depressed regions of the surface. As a result, elevated regions grow more elevated while depressed regions do not receive flux as deposition progresses. According to this scenario, the porosity of thin films goes up as the deposition rate goes up, since the diffusion time of adatoms goes down with increasing deposition rate.
In this section, we report an anomaly in the dependence of film porosity on deposition rate. As the deposition rate goes up from 1 nm / sec to 6 nm / sec, the porosity goes down, and the film morphology changes from separated nanorods to a more uniform film. Further, we identify a mechanism for the anomaly, by considering the interplay of substrate non-wetting, nucleus density on the substrate, and the minimum diameter of nanorods. This offers the first insight to the critical dimensions governing nanorod growth and sets the stage for the emergence of an overall framework of nanorod growth.

Before presenting the results, we briefly describe the experimental methods of growth and characterization. Cu films are deposited on SiO₂ - or a layer of native oxide on top of Si(111) - substrates using electron-beam evaporation physical vapor deposition. The vacuum chamber, a cylinder of roughly 50 cm diameter and 75 cm tall (note that this is a chamber at Los Alamos National Lab and not the in house chamber that was built at the University of Connecticut) is first evacuated to a base pressure of $5 \times 10^{-8}$ Torr and held for several hours to remove impurities from the chamber. During deposition, working pressure is about $5 \times 10^{-7}$ Torr. The chamber is pumped down with mechanical roughing pump first, then a turbomolecular pump and achieves high vacuum through a large ion pump. The substrate and chamber are not temperature controlled, and deposition occurs with chamber temperatures ranging from 20° C to 45° C as measured by a K type thermocouple fed through into the interior of the chamber. The source materials is 99.997% copper and is installed in the vacuum chamber before deposition. The substrate is 40 cm away from the source. To achieve geometrical shadowing, the substrate is oriented approximately 85° from the top of the chamber, which is parallel to the source. Source materials are then vaporized using a high power electron beam arc. Varying deposition rate from 0.1 nm / sec to 6 nm / sec, films are grown to thicknesses up to 500 nm. The deposition rate is
measured perpendicular to the flux using a quartz crystal deposition monitor. Due to the significant angle of inclination, the actual deposition rate is lower than measured. Samples are removed from vacuum and characterized using a FEI Quanta 250 FEG field emission scanning electron microscope. Crystallographic orientation is characterized using a Bruker DB8 Advance Diffractometer System, both instruments are located at the University of Connecticut Center for Clean Energy Engineering. To transport the nanorods between fabrication and imaging a vacuum desiccation system is built and samples are shipped express from LANL to Uconn. Further, as we will see later, Cu nanorods rapidly form a thin oxide shell and the shape of the nanorods becomes very stable at room temperature without any discernible morphological change. Imaging of the nanorods was performed in high vacuum mode with an acceleration voltage of 10 KeV and a spot size of “3” corresponding to a moderate spot size of a few nm.
Figure 26: Scanning electron microscopy (SEM) images of Cu films deposited at (a) 1 nm/sec and (b) 6 nm/sec.

As shown in Figure 26, the Cu film has large porosity at the deposition rate of 1 nm/sec, and separated nanorods are identifiable. At this deposition rate, there is some agglomeration of rods next to one another. This is due to a relatively shallow glancing angle allowing for some deposition to occur between adjacent rods. The large features also result from a low deposition rate allowing for more complete coverage before the next layer nucleates, as Cu is relatively mobile over the first layer at room temperature. As the deposition rate increases from 1 nm/sec to 6 nm/sec, the film porosity decreases and a more uniform film develops. The decrease of porosity with increasing deposition rate is anomalous with respect to the conventional
understanding. Conventional understanding infers that as the deposition rate increases the diffusion lifetime on surfaces will be decreased and the roughness increases. This should mean smaller nanorods, but this is not the case. In the following we design experiments to determine why this is the case.

We suggest a mechanism for the anomaly, based on the interplay of substrate non-wetting, nucleus density, and the minimum diameter of nanorods. First, due to non-wetting of Cu on SiO₂, according to literature reports, 3D nuclei of Cu form at the early stage. Second, a higher deposition rate leads to a higher density of nuclei, and forces a complete coverage of the non-wetting substrate before nanorods develop. This critical separation of nanorods is a critical component of understanding the entire framework of nanorod growth and formulating the theory of nanorod growth from physical vapor deposition. This deposition rate anomaly changes the growth mode of the film from non-wetting, in which small nanorods have been shown to result, to wetting in which nanorods do not result from copper. The coverage of a non-wetting barrier layer by Cu in the metallization of integrated circuits is based on the same principle. Third, as the separation of nuclei is smaller than the diameter of Cu nanorods - which is on the order of 30 nm at these conditions, according to our groups preexisting theoretical formulations under the condition that surface steps are always multiple-layer - the porosity between nuclei disappears and a uniform film develops. This means that there is a critical cross over point at which the smallest nanorods at a given glancing angle and temperature condition (among other control variables that will later be formulated into the theoretical framework) where there is a transition from nanorods to dense film with increasing deposition rate. Based on recent studies, multiple-layer steps are kinetically stable, in contrast to earlier understanding. When the initial diameter of an island is smaller than the critical cross over point, the overwhelming dominance
of multiple-layer step is feasible as the island expands laterally from bottom to top; this is the condition provided by the non-wetting condition.

Figure 27: Scanning electron microscopy (SEM) images of Cu films deposited at 0.1 nm/second, (a) without indium and (b) with 5 nm indium pre-deposition; with the inset being an SEM image of the indium nuclei on an area of 500 nm X 500 nm of SiO2.
To validate the suggested mechanism, we have designed two experiments. In the first experiment, we use a deposition rate of 0.1 nm/sec, which is 10X lower than that of Figure 26(a). The critical deposition rate that separates a large-porosity film and a uniform film is between 1 and 6 nm/sec. Further lowering the deposition rate from 1 nm/second to 0.1 nm/sec should also lead to well-separated nuclei and thereby nanorods, according to our suggested mechanism. By decreasing the deposition rate, there should be further separation between nanorods than the ones that occur at 1.0 nm / s, which is indeed the case. As shown in Figure 28:
the film consists of nanorods that are similar to those in Figure 26(a). This similarity indicates that the suggested mechanism is valid. In the second experiment, we pre-deposit indium (In) of 5 nm in thickness on the SiO$_2$ substrate, before Cu deposition. 3D nuclei of In on the substrate (as shown in the inset of Figure 27(b)) serve as preferential nucleation sites for Cu, due to the strong In-Cu interaction$^{123}$. This heterogeneous nucleation of Cu islands further promotes their separation, and should lead to better separated nanorods than without In pre-deposition, if the suggested mechanism is valid. As shown in Figure 27(b), the Cu nanorods indeed are better separated than those in Figure 27(a) and much better separated than those in Figure 27(a). This offers insight into a way that smaller nanorods may be achieved. By defeating the L$_s$ constraint, the deposition rate can be further decreased to reach the smallest cluster size, improve the dominance of 3D surface steps and decrease the effective temperature.

Having presented the anomaly and a feasible mechanism, we next examine how the films will develop further as deposition continues, and what texture dominates. As shown in Figure 28(a), the large-porosity film develops into nanorods of very small diameter, on the order of 30 nm, that is comparable to the minimum diameter of Cu nanorods$^{19,20}$. From the uniform film of Figure 28(b), nanorods still develop as deposition continues, due to the geometrical shadowing at glancing angle incidence. The density of Cu nanorod nuclei on the film surface of Figure 26(b) derives from growth of Cu on Cu, and non-wetting disappears. As a result, the nuclei of Cu nanorods are not bounded by overwhelmingly multiple-layer steps. Since the realization of the minimum diameter of Cu nanorods depends on the dominance of multiple-layer steps, the diameter of Cu nanorods is larger than the minimum. As an indication of out-of-plane texture, the XRD shows both films have the $<111>$ texture, as most Cu films do$^{28-30}$. 
In summary, in this section we report an anomaly in the dependence of film porosity on deposition rate, suggest a mechanism for the anomaly, and provide two pieces of evidence to validate the suggested mechanism. On a non-wetting substrate, 3D nuclei form at the early stage, and geometrical shadowing at a glancing angle promotes further 3D growth leading to porous films. As the separation of nuclei is larger than the minimum diameter of nanorods, well-separated nanorods develop and porosity is large. However, when the separation is smaller than the minimum diameter, the nanorods will not have space to develop, uniform film develops and the porosity is low. This insight shows that there is an extreme need to develop a framework of nanorod growth to differentiate clearly between growth from a wetting and non-wetting substrate, before and after cross over or an innately wetting substrate, and to fully understand the roll of spacing between nanorods and the resulting diameter as a function of all of the processing conditions. With this understanding, the push to nanorods of ~10nm in diameter may become possible and the realization of such nanorods would again do what was regarded as impossible (paralleled first to the realization that nanorods are possible compared to crystal growth theory from the 1950s, second that multiple layer surface steps are not only possible but kinetically stable and now reducing the size below 30nm).

2. Emergence of a framework of nanorod growth (JOM)

The mechanisms controlling the diameter of metallic nanorods have recently emerged through a theoretical framework\textsuperscript{20,41,124}. The framework is the first piece of a cohesive theory of nanorod growth. The framework serves as the groundwork for the theory of nanorod growth and aims to determine the limiting conditions and all of the variables which dictate the growth of nanorods. The theory is developed from the ground up, starting with the nature of the substrate. In mode I of growth, the left half of Figure 29, nanorods develop from a wetting substrate and
take the shape of towers. This is the classical Stranski-Kranstanov growth with extreme roughness and kinetic limitations. Nanorods that develop from mode I are \( \sim 100 \) nm in diameter. Nanorods come about from mode I through the dominance of geometric shadowing and intrinsic surface roughness. The competition of monolayer and multiple-layer surface steps, that is nanorods have both monolayer and multiple layer surface steps, leads to the diameter of the resulting nanorods stabilizing around 100 nm\(^9\). This mode is the classical mode of nanorod diameter that has been studied for several decades. However, the existing theory lags if the temperature is changed, for example low temperature growth, or if the 2 dimensional diffusion barrier is sufficiently high. As this dissertation is being drafted research continues on low temperature growth from this mode, termed Mode 1’, which shows small nanorod diameters on the order of 30 nm for Ag and Au, but not smaller.

Of particular technological interest is nanorod growth in mode II, the left of Figure 29. In mode II, a non-wetting substrate results in well-separated islands growth. At high glancing angles, meaning a majority of adatom flux lands on the top of the island, or the developing nucleus, it is suspected (at this point in investigation) that the resulting nanorods may be as small as \( \sim 10 \) nm in diameter, taking the shape of a cylinder or an inverted tower as they grow tall. In this mode, multiple-layer surface steps are dominant, which necessitates the recent development that multiple-layer surface steps are indeed kinetically stable\(^9\). When the diffusion barrier of adatoms over the multiple-layer steps, the geometric shadowing condition and the deposition rate are all sufficiently large, the diameter of nanorods grows very slowly as the length of the nanorod increases\(^9\). At a given incidence angle, as deposition rate or diffusion barrier increase, the diameter of the resulting nanorod decreases. This scaling law will become evident as the theory is completed in the next section. The smallest diameter of nanorod is reached when the
surface diffusion is lowest; that is, surfaces are nearly entirely multiple-layer steps and the diffusion barrier is large, and the deposition rate is maximized. In the case of very sparse nanorods, shadowing in three-dimensions is not complete and flux may reach the substrate. Due to the extreme non-wetting condition of the substrate, atoms diffuse to the base and sides of the existing small rods.

![Figure 29: Growth modes of nanorods showing a wetting substrate, left, and a not wetting substrate, right.](image)

The technological push to reach nanorods of a small diameter may be realized when the smallest diameter of nanorods, $L_{\text{min}}$, is combined with an understanding of the minimum spacing between nanorods, $L_c$. Intuitively, even if the diameter of a growing nanorod is very small, they must be spaced sufficiently far apart so as to remain separate. That is, if the minimum spacing between nanorods is smaller than the diameter of the growing nanorod, for a given set of deposition conditions, a dense film will result. The separation of nanorods on a non-wetting substrate is governed by the separation of first layer nucleation sites. Our recent formulation shows that the minimum spacing between nanorod nuclei, and therefore resulting nanorods,
scales as \( L_s = 1.9 \left( \frac{12 V}{7\pi F} \right) \), where \( V \) is the relevant diffusion barrier of adatoms on the substrate and \( F \) is the deposition rate\(^{20}\). With this formulation in place, the substrate conditions may be realized that allow for sufficient spacing between nanorods and the smallest diameter, this remains to the next section to be formulated, as the cross over from the anomaly must be formulated. As the deposition rate increases, the minimum diameter of nanorods decreases but the minimum separation decreases even faster. The point where \( L_{\text{min}} \) is only marginally less than \( L_s \) will result in nanorods of the smallest possible diameter. Under real geometric shadowing conditions this is estimated to be on the order of ~12 nm for Au due to its higher 3D diffusion barrier than Cu\(^{41}\). However, this small size has never been achieved before in a well separated fashion; when nanorods grow very small they must be very close together due to the constrain of \( L_s \). Due to the very natural statistical spread in diameter and spacing of growing nanorods, well separated rods only occur when \( L_s \) is much larger than \( L_{\text{min}} \). Without adequate separation, a fiber texture occurs and it is possible that some of the unique properties that come about from the small diameter are negated as the nanorods coalesce into a dense polycrystalline film.

3. The smallest nanorods from physical vapor deposition

To reiterate, it is only when a dimension is dropped to the order of 10 nm that material properties begin to change. Again, this is the reason why we aim to push the diameter of nanorods from physical vapor deposition to ~10 nm. Classically, the diameter of a nanorod is less than 100 nm, while the length may range from tens of nanometers to several microns. Fabrication of nanorods from physical vapor deposition (PVD) with diameters of about 100 nm which are strongly attached to substrates has been commonplace for several decades. Due to very clean processing conditions and simple directly observable controlling mechanisms, PVD crystal growth has become scientifically well understood. While scientifically interesting to those
growing crystalline thin films, little technological impact has resulted because the properties of the 100 nm rods are predominantly the same as their continuous thin film counterparts with the small advantage of increase surface area. When compared to PVD, solution processing has grown nanorods with diameters of about 10 nm, which are randomly oriented and dispersed in fluid\textsuperscript{35,58,67}. On this length scale, properties such as catalysis\textsuperscript{125,126} and plasmonic resonance\textsuperscript{109,127} emerge that are absent in bulk and thin film configurations and have enabled new technologies like the detection and hyperthermic destruction of cancer cells with infrared light. This begs the question, why have nanorods on the order of 10 nm in diameter not been fabricated from PVD? What is the smallest diameter than can be reached with PVD? If they can be fabricated, what new or improved technologies can be demonstrated as proof of concept?

Keeping this goal and question in mind, in this section we first present the culmination of the theory of nanorod growth, that is: the development of the framework, the formulation of separation of nanorod nuclei and the diameter of the smallest nanorods, and then go on to use the insights gained from the newly completed theory to realize the smallest diameter of metallic nanorods ever.

For the theoretical formulation, the conceptual framework of nanorod growth serves as the starting point\textsuperscript{124}. In contrast to the theories for the growth of large crystals\textsuperscript{95}, this framework recognizes that multiple-layer surface steps are kinetically stable in contrast, the classical theory predicts that such steps are kinetically unstable. Further, these multiple-layer surface steps dictate the diffusion of adatoms during nanorod growth. Under this framework, metallic nanorods grow in two modes – I and II (Figure 29). In mode II, the growth takes place on non-wetting substrates and nanorods have the shape of a cylinder (or of an inverted tower if they grow sufficiently tall).
Because of the complete, or nearly complete, dominance of multiple-layer surface steps over monolayer surface steps, growth mode II results in the smallest diameter of nanorods.

![Figure 30: Evolution of a nanorod as a function of time for mode II.](image)

Focusing on growth mode II, we first describe our physical model of nanorod growth; the mathematical formulation then turns the model into a closed form theory. The model starts with nucleation on a non-wetting substrate [snapshot \( t_1 \) in Fig. Figure 30(b)]. Due to non-wettability, the critical size of nucleating the second layer is one atomic diameter. As nanorods grow, they receive atomic flux only on the top due to complete geometrical shadowing. Once the deposited atoms overcome the large diffusion barrier of multiple-layer steps, they experience much smaller diffusion barriers on the sides and therefore tend to distribute equally along the vertical direction. As a result, they have the shape of a cylinder [snapshot \( t_2 \) in Figure 30(b)]. Since the diameter of the nanorods is small, only one adatom will be on top most of the time, and a new layer nucleates once two adatoms present simultaneously; this is also called the lone adatom model (LAM). The snapshot \( t_2 \) in Figure 30(b) shows the configuration with the nucleus of a new layer. Aiming at the smallest diameter, we consider the complete geometrical shadowing condition – that is, atoms are deposited onto only the top of nanorods, not onto the sides. With the small diameter of
nanorods and the large diffusion barrier at the multiple-layer steps or edges of the nanorods, the newly nucleated layer will grow to full coverage before any deposited atoms diffuse to the side. The snapshot $t_3$ in Figure 30(b) shows the configuration when the coverage of one layer is complete. The snapshot $t_4$ in Figure 30(b) is similar to the snapshot $t_2$, except with one extra layer on top of the nanorod.

As shown in detail in our very recent publication, *Smallest metallic nanorods from Physical Vapor Deposition*” In volume 110 of Physical Review Letters, the formulation of the theory for the smallest diameter, $L_{\text{min}}$, arrives at $L_{\text{min}} \approx \left[ \frac{(10/\alpha^2) \ln(n/2)}{(v_{3D} / F_c)} \right]^{1/5}$ for cases of complete geometrical shadowing and under cases of incomplete geometrical shadowing goes as $L_{\text{min}} \propto (v_{3D} / F)^{1/5}$.

Having verified the theory we now use the experimental results of the film porosity anomaly to validate it. In our experiment performed in collaboration with the Center for Integrated Nanotechnology at Los Alamos National Lab, Cu nanorods of ~30 nm in diameter grow under a deposition rate of 1 nm/s with an incidence angle of 85°; the substrate temperature is uncontrolled but is within 300-350 K. By increasing the deposition rate to 6 nm/s, the growth of nanorods transitions into the growth of a dense film. By including the theoretical separation of nanorod nuclei $L_s$ in Figure 30(b), our theory explains this anomalous transition as the following. The crossover of $L_{\text{min}}$ and $L_s$ occurs at ~20 nm. As deposition rate increases, both $L_{\text{min}}$ and $L_s$ decrease. When they reach ~20 nm, $L_s$ becomes smaller than $L_{\text{min}}$, so there is no space for separate nanorods to exist. Because of random nucleation, some nanorods are separated at a smaller distance than the theoretical value $L_s$. As a result, nanorods bridge and merge even if $L_s > L_{\text{min}}$, provided they both are still close to ~20 nm. That is, $L_s$ makes it nearly impossible to
grow well separated Cu nanorods that are smaller than ~30 nm; beyond our own experiments, others have also reported only nanorods of ~30 nm or larger but not smaller. The fact that the theory explains the anomalous experimental results serves as a validation.

Now that the theory has been verified and validated, we use it to guide the pursuit of the smallest nanorods. The first insight from the theory is that $L_s$ is the limiting factor of growing smaller nanorods. If we can eliminate the constraint of $L_s$, it may become possible to grow smaller and well separated nanorods of diameter $L_{\text{min}}$. It is possible to change $L_s$, with minor impact on $L_{\text{min}}$, by using substrates of different wettability or heterogeneous nucleation, or to change $L_{\text{min}}$ with minor impact on $L_s$ by using different substrate temperatures. Putting this insight into action, we apply four strategies. (1) By using large incidence angles, we lower the effective deposition rate to promote the relationship $L_s > L_{\text{min}}$; (2) by using lower substrate temperatures, we take the advantage of larger activation energy in $L_{\text{min}}$ to promote the relationship $L_s > L_{\text{min}}$; (3) by using substrates with heterogeneous nucleation, we make $L_s$ ineffective; and (4) by using highly non-wetting substrates, we increase $L_s$ to promote $L_s > L_{\text{min}}$. Since the last three strategies are apparent, we use Fig. 2(c) to show the feasibility of only the first strategy. As the incidence angle becomes larger, while keeping the nominal deposition rate constant, $L_{\text{min}}$ becomes larger but $L_s$ becomes even larger. Indeed, the increase of incidence angle promotes $L_s > L_{\text{min}}$.

The second insight is that a decrease of $\nu_{3D}$ (by an increase of the diffusion barrier of adatoms over multiple-layer surface steps) can be effective to reduce the diameter of nanorods according to $L_{\text{min}} \propto (\nu_{3D}/F)^{1/5}$. Putting this insight into action, we use quantum mechanics...
calculations to identify a metal with a large diffusion barrier of adatoms and therefore small \( \nu_{1D} \).

Our calculations show that the relevant energy barrier of adatoms diffusion down a multiple-layer surface step in Au is 0.52 eV, much larger than the 0.40 eV in Cu or 0.12 eV in aluminum (Al)\^{27,96,123}; this barrier is in contrast to the Ehrlich-Schwoebel barrier of adatoms diffusion down a monolayer surface step. With this set of data, the second insight suggests that we can reach an even smaller diameter for Au nanorods than for Cu nanorods.

![Figure 31: Scanning electron microscopy (SEM) images of well-separated (a) Cu and (b) Au nanorods at an early stage; the insets with the same scale show the morphologies of substrates.](image)

Using the first insight from the theory, we design the growth of Cu nanorods as the following; with additional details on the derivation available in our PRL paper\^{41}. We use a large incidence angle of 88°, a substrate with heterogeneous nucleation sites of SiO\(_2\), and a low substrate temperature of about 250 K; the deposition rate is 0.1 nm/s. The experiments indeed confirm that well-separated Cu nanorods of \( \sim 20 \) nm in diameter grow, Figure 31, as the first theoretical insight suggests. This represents the smallest well-separated Cu nanorods that have ever been reported using PVD. Using both the first and the second insights from the theory, we
grow Au nanorods using a large incidence angle of 88°, a substrate that is highly non-wetting (3M Copper Conductive Tape 1182, 3M Corporation, St. Paul, MN), and a low substrate temperature of about 250 K; the deposition rate is also 0.1 nm/s. The experiments indeed confirm that well-separated Au nanorods of ~10 nm in diameter grow Figure 31, as the two theoretical insights suggest. In fact, some of the Au nanorods are as small as 7 nm in diameter. Once again, the Au nanorods of ~10 nm in diameter are the smallest well-separated metallic nanorods that have ever been reported using PVD.

As the well-separated nanorods continue to grow beyond ~800 nm in height, they start to form new architectures. For the case of Cu, bridging occurs but nanorods generally remain separated. In contrast, nearly complete merging of nanorods occurs without the heterogeneous nucleation sites Figure 32. For the case of Au, branching has occurred beyond ~800 nm, but the small diameter and the separation of nanorods both persist. In contrast, a dense columnar Au film grows when the substrate is a regular Si {100} substrate with native oxide Figure 32.

Figure 32: SEM images of (a) Cu and (b) Au nanorods at a later stage when nanorods are about 1000 nm long; the insets with the same scale show surface morphologies of nanorods when conventional substrates are used.
With this new framework, new morphologies for technologically interesting materials can be realized and understanding of the resulting growth as part of the theory is possible. In the following section, we begin filling in the “data points” of different FCC metals and see how they fit into the framework as a function of diffusion barrier. We next move to modify $L_\alpha$ and $L_{\min}$ through changing temperature, deposition rate and substrate type, among other things.
In this section we present results for the deposition of well separated and small metallic nanorods from a wide range of metals on different substrates and at different temperatures. We aim to show how FCC metals fit into the framework and that there is the necessity for expansion of the framework to accommodate materials of different crystal lattice structure, like body center cubic (BCC) and hexagonal close packed (HCP).

1. **FCC metal systems (Pt, Ni, Al, Ag)**

   The previous section presented the growth of only two metals, Au and Cu. While they are very technologically relevant, there are many other FCC metals which are equally relevant and require due attention. Unlike Au and Cu, the respective diffusion barriers, 2D and 3D, are unknown for Pt, Ni, and Ag. The barrier knowledge is available for Al, but within the old framework, nanorod growth should not result from PVD because the diffusion barriers are too low. However, under the new framework this may not be the case and will be investigated.

   The first metal results presented are those of Pt, which is technologically important for catalysis and high temperature sensing applications due to its very high melting temperature$^{118,119,129}$. Within the framework, the homologous substrate temperature for Pt is much lower than that of Au and Cu with the substrate at room temperature. This means that nanorods of Pt at room temperature should have a smaller diameter than Au and Cu at room temperature. Also, it is possible that Pt has a higher 2D and 3D diffusion barrier than Au, working to further decrease the diameter of the resulting nanorods.
Briefly, the deposition experiments are carried out in house in the EDPVD deposition system on ultrasonically clean Si <100> substrates with no temperature control of the substrate. The source material is 99.995% Pt from Kurt J. Lesker Co. and is deposited from a graphite crucial liner. The substrates are wafer chips mounted on a precision angle stub with a calculated glancing angle of 86.5° from the normal of the source. The chamber is pumped down for several hours and based to 1.0 x 10^-7 Torr while working pressure is in the range of 5.0 x 10^-6 Torr. The vacuum level drops during deposition because of the high amount of power necessary for the deposition of Pt, as the chamber grows hot and some areas of the wall reach 100°C and begin to release molecules trapped in the layers of predeposition. Deposition is carried out at a rate of 0.3nm / s to a thickness of 150 nm first and then 250 nm as the second set of results.

As the results for Pt, the interaction between Pt and Si with native oxide is non-wetting, as shown in Figure 33, and has substantial spacing at room temperature.
Figure 33: Pt nanorods beginning to grow on Si substrate at room temperature and a glancing angle of 86.5° with a non-wetting substrate condition.

As seen in Figure 34, the nanorod nuclei have very small diameters, on the order of only a few nm, and relatively close spacing when compared to Au and Cu at similar conditions. Due to the steep shadowing however, spacing increases as the growth continues as taller bundles win out over shorter ones. With this spacing, as growth continues, branching must occur because additional flux begins to land on the side of the rods. This flux is not very mobile at this low temperature, even on the flat rod sides, and intern new “leads” form at the same small diameter as the main rod. Figure 35 is the same area with increased magnification to further show the morphology.
Figure 34: PT nanorods grown to 250nm of total thickness at a glancing angle of 86.5°.
While not pictured here, alternative substrates have been used and the results have been similar morphologies. These substrates include PET and Nafion. An example of Pt deposition onto PET is seen below in Figure 36. Due to the plastic substrate the image has poor quality due to charging, but the rod morphology can be seen through the charging. The wetting condition of the PET substrate is different than that of the Si with native oxide which results in a different spacing or density of nanorod nuclei and closer spaced rods.
Figure 36: Growth of Pt nanorods on PET substrate at 86.5° glancing angle, room temperature and a deposition rate of 0.3 nm/s.

The second metal introduced here is Ni, which is regarded as chemically very similar to Pt with the exception of a lower melting temperature and relatively less inertness and catalytic activity\(^{26,118,126,130}\). Ni is technologically important as a lower cost catalyst than Pt for various applications. The diffusion barriers for Ni are unknown at this time but due to the higher Tm and lower homologous substrate temperature the results of Ni are expected to be rods on the order of 10-30nm in diameter.

Briefly, like Pt, Ni nanorods were deposited using EBPVD under high vacuum conditions onto Si \(<100>\) wafers with native oxide layer. Source material, 99.99% Ni, is loaded into a
graphite crucible liner and the chamber is pumped down to $5.0 \times 10^{-7}$ Torr base for several hours. During deposition the power is roughly the same as with Au and the chamber and substrate remain below 50$^\circ$ C. Deposition is performed with a measured glancing angle of 86.5$^\circ$ held in the precision angle mount at a rate of 0.2 nm/s and deposition is held out to 300nm. As seen in Figure 37, the Ni nanorods are substantially larger in diameter than Pt and therefore do not experience branching as they are sufficiently close for a majoring of incoming flux to land on the top of forming nanorods. The Ni nanorods grow about ~25nm in diameter and do not wet the substrate. The surfaces of the Ni nanorods appear to be significantly rougher than those of Cu, Au while the roughness of Pt cannot be determined due to the extremely small rod diameter. The roughness may derive from the high $T_m$ of the Ni.
Figure 37: Ni Nanorods grown at a glancing angle of 86.5°, deposition rate of 0.2 nm / s, a total film thickness of 300nm.

Ag has many technological applications including anti-microbial surfaces and surface enhanced Raman scattering (SERS) and Ag has been investigated previously using GLAD at lower incidence angles\textsuperscript{34,35,105}. The diffusion of barrier is between that of Cu and Au, unpublished in house \textit{Ab-initio} calculations, and a slightly lower Tm meaning that the resulting rod diameter for Ag should be slightly larger than that of Au. However, in practice it has been discovered that the morphology is Ag is very dependent on deposition rate and substrate temperature. If a long deposition is performed at a low rate the morphology approaches a film but at the same glancing angle if a high deposition rate is used small diameter rods result. Further
on we will show that there is very fast diffusion on Ag nanorods at low temperatures, as low as 50°C, which is likely a predominant factor in the transfer to film at low deposition rates because the substrate temperature may reach in excess of 50°C as the electron beam is on for long durations.

Here, Ag nanorods and films were fabricated at glancing angles of 86.5° and deposition rates of 0.1 nm/s and 1.0 nm/s, respectively. The chamber was allowed to reach a base pressure of 5.0 x 10^{-7} Torr for several hours prior to deposition and the source material was 99.995% pellets from Kurt J. Lesker Co. Films were grown to thicknesses of 300nm and during deposition the substrate temperature was measured at <50°C for the deposition rate of 1.0 nm/s and >50°C for the deposition rate of 0.1 nm/s at the end of the deposition because it heats for longer. Figure 38, below, shows Ag nanorods grown at a rate of 0.1 nm/s where it is clear that there is strong coalescence between adjacent rods. It is also clear through the area of low deposition to the right that Ag forms 3D non-wetting clusters on the Si substrate so growth here is mode 2. However, when compared to Figure 39, the density of clusters at the lower deposition rate on the substrate is higher, and the overall cluster size is larger. As the temperature increases diffusion on the substrate also increases after the initial deposition, leading to agglomeration across the entire thickness.
Figure 38: Ag nanorods grown at a glancing angle of 86.5 ° to a thickness of 300 nm at a rate of 0.1 nm / s.

When the deposition rate is increased to 1.0 nm /s on the same substrate rods form, which is against the intuition gained from the anomaly reported earlier on. This indicates that the temperature is the major factor here and that there is fast diffusion on the surfaces as the temperature increases at the low deposition rate. The nanorods from the high deposition rate are on the order of 50 nm in diameter, as the homologous temperature is higher than Cu and Au, as shown in Figure 39 below. The large spacing between rods is also a constraint on the diameter as material is definitely deposited onto the side of the rods as the rods continue to grow tall
contributing to the thickness. The minimum diameter is maintained by some of the nanorods, which are clearly much thinner than other, because they are largely shadowed by their neighbors.

Figure 39: Ag nanorods grown at a glancing angle of 86.5° a deposition rate of 1.0 nm / s to a total thickness of 750nm.

Unlike the other materials presented in this section, we choose Al as another FCC prototype because it has very low diffusion barriers, the 3D barrier of Al is about half of that of Cu 0.15 eV compared to 0.3 eV respectively, and in previous theory Al should not form nanorods, but rather a dense film. However, in the new theory, it is possible to grow Al nanorods and they should be on the order of 100 nm in diameter if there is sufficient spacing between
adjacent rods. Here, we realize the room temperature growth of Al nanorods for the first time (a truly interesting piece of scientific realization).

Al nanorods are again fabricated using the in house EBPVD system on Si <100> wafers with native oxide layer. Source material is 99.995% Al from Kurt J. Lesker company and is deposited from a graphite crucible. As an aside, it is largely accepted that the liner should be boron nitride for Al deposition because the Al must be superheated to reach a vapor pressure. However, in this work the graphite liner has been shown to work better to contain the Al and keep it from spitting and sculling from the crucible. Unlike with other materials, the vacuum level during deposition is very important for the deposition of aluminum so the chamber was allowed to base out at $1.0 \times 10^{-7}$ for 12 hours and a cold finger at liquid nitrogen (LN) temperature was used to maintain the vacuum in the $10^{-7}$ Torr range during working. The Al was first heated slowly to allow the surface of the source pellets to outgas and held in light melt configuration, with the substrate shuttered, for 1 hr. The vacuum was then allowed to return to base pressure before deposition began. Substrate temperature was measured and was maintained $< 50^\circ$ C through the entire deposition. The deposition rate was held at 0.7 nm / s during deposition and a total thickness of 700 nm was deposited.
Figure 40: Al nanorods fabricated at a glancing angle of 86.5° with a deposition rate of 0.7 nm/s and a total film thickness of 700 nm.

The results of deposition are shown in Figure 40. Al rods of roughly 100nm in diameter with large spacing between adjacent rods. The rods range in diameter from about 50 nm to over 100 nm and are spaced on average 100 nm apart. This is the first time ever that Al has been grown in rods from physical vapor deposition and marks an important milestone in scientific knowledge of nanorod growth.
2. Engineering diffusion barriers – Low temperature growth

In this section, we begin by presenting preliminary work on the low temperature growth of common FCC metals and analyze the results within the theory of nanorod growth from mode II. Within the scaling of \( L_{\text{min}} \) and \( L_s \), a decreased temperature should drastically reduce the diameter of the growing rod and should also reduce the spacing between rods but to a lesser extent. However, because the structures are fabricated at 77 K, once they are brought to room temperature to image, they may experience fast surface diffusion and reshape or they may experience rapid chemical reaction with ambient and form an oxide shell. Here we present the preliminary data on several metals deposited at 77 K with a glancing angle of roughly 86.5°.

The overall deposition process is the same for all of the materials as will be briefly outlined here. Substrates, either ultrasonically cleaned Si <100>, Si <111> or corning glass, are placed at the top of the chamber at a measured glancing angle of 86.5°. Source materials are purchased from Kurt J. Lesker Company and range in purity from 99.95% to 99.995% and are deposited from graphite liners (In, Cu) or vitrified carbon over graphite (Au, Ag). In all cases the chamber is pumped down to at least \( 2.0 \times 10^{-7} \) Torr and allowed to remain there for at least 3 hours. Source materials are then preheated with the samples shuttered and are allowed to outgas for about 15 minutes before allowing to cool and letting the vacuum recover before deposition. LN is added to the external LN chamber and the temperature of the substrate is measured with K type thermocouple until the thermocouple reaches its lower limit. The LN cools the substrate for 30 minutes prior to deposition and the substrate temperature should remain close to 77 K for the entire duration of the deposition. After the deposition is complete the LN is drained from the external tank, or allowed to evaporate off if time allows, and the system is allowed to return to room temperature through ambient heating.
As the first material we will present indium (In) metal deposited at LN temperatures. In films deposited at room temperature and a glancing angle are generally flat films with large crystals due to a very low diffusion barrier of In on itself. However, when deposited at LN temperatures, the effective diffusion barrier for In grows and rod formation is possible. Interestingly, if the rods are brought to ambient before being allowed to warm to RT, they will maintain their rod structure, likely due to the formation of an oxide capping layer. When they are allowed to warm under vacuum they simply form a rough globule like structure and are not very interesting scientifically or technologically. The following Figure 41 and Figure 42 are of In deposited at LN temperatures, as described above. Extremely fast surface diffusion is still apparent on these rod structures even when the oxide layer is allowed for form. Perhaps they can be stabilized by flooding the chamber with O₂ during the vent process.
Figure 41: In deposited at LN2 temperatures and a glancing angle of $86.5^\circ$ and a deposition rate of 0.2 nm/s to a thickness of 250nm.
Figure 42: In deposited at LN2 temperatures and a glancing angle of 86.5° and a deposition rate of 0.2 nm / s to a thickness of 250nm.

The next material of interest presented here is Ag. When deposited under LN conditions a deposition rate dependence is demonstrated. When deposited at a low deposition rate of 0.1 nm / s, Figure 43, the Ag forms a very fine close packed nanorod structure with very small diameter that is maintained as a single column through the entire length. The surfaces appear to be transforming under the increased temperature to ambient due to increased surface diffusion and signs of Rayleigh instability, or the formation of regular spherical droplets from a long slender solid rod through surface diffusion, appear to be forming.
Figure 43: Ag nanorods at LN temperature and a glancing angle of 86.5° at a deposition rate of 0.1 nm/s and a total thickness of 800 nm.
Figure 44: Ag nanorods at LN temperature and a glancing angle of 86.5° at a deposition rate of 1.0 nm/s and a total thickness of 800nm.

As the deposition rate is increased to 1.0 nm/s from 0.1 nm/s, Figure 44 above, the morphology of the nanorods changes to more sparse rods with increased diameter and branching. The increase in diameter is a function of the wide spacing; flux must land on the side of the nanorods. The increased spacing is likely due to a lack of mobility on the surface and a greater variation between the height and size of the nucleation clusters than those grown with the low deposition rate that may have some substrate mobility.
Figure 45: Au deposited at LN temperature and a glancing angle of 86.5° with a deposition rate of 0.1 nm / s and a total thickness of 500nm.

Next, Au is deposited at the same low and high deposition rates and results are similar to those of Ag; there is a morphological dependence on deposition rate. When fabricated at 0.1 nm / s deposition rate very small Au fibers form, some with diameters of only a few nm, Figure 45. The structure likely originated from mode II growth and due to mechanical instability groups of adjacent rods or fibers had to come together to collectively support their vertical growth. Amazingly, little surface diffusion was seen in this morphology and it remained stable at room temperature in ambient for several months. While there is no sight of oxide formation on the X-
ray diffraction, it is possible that at this small diameter the Au has transitioned from inert to reactive and formed an oxide capping layer that is not evident when the diameter is roughly 5 times larger in room temperature fabrication.

Figure 46: Au deposited at LN temperature and a glancing angle of 86.5° with a deposition rate of 1.0 nm / s and a total thickness of 500nm.

When the deposition rate is increased to 1.0 nm / s the separation between adjacent bundles of Au nanorods increases, in similar fashion to Ag, Figure 46. However, unlike with Ag there is not expansion of individual rods as growth is continued and the bundle diameter appears to remain roughly the same from substrate to tip. The nanorods may grow as complete competing
units, and the flux continues mostly on the top of bundles compared to on the side for Ag. This difference must arise from a

When Cu is grown under LN conditions the results vary greatly from other similar FCC metals. At the low deposition rate of 0.1 nm / s well-spaced rods on the order of 30 nm diameter form, Figure 47. The spacing of the rods appears greater than those seen in Ag and Au. As the rods grow they appear to have even expansion from bottom to top.

Figure 47: Cu deposited at LN temperature and a glancing angle of 86.5° with a deposition rate of 0.1 nm / s and a total thickness of 500nm.
When the deposition rate is increased from 0.1 nm/s to 1.0 nm/s the rods come closer together and the diameter shrinks, Figure 48. This gives weight to the theory that the spacing of adjacent rods is responsible for the relatively large diameter of the rods formed at 0.1 nm/s. To completely understand this phenomenon initial nucleation and early growth analysis with electron microscope is necessary.

Figure 48: Cu deposited at LN temperature and a glancing angle of 86.5° with a deposition rate of 1.0 nm/s and a total thickness of 500nm.
Figure 49: Al deposited at LN temperature and a glancing angle of 86.5° with a deposition rate of 0.7 nm/s and a total thickness of 750 nm.

Al produces very scientifically interesting results when fabricated at LN temperatures, Figure 49. Wide fans form as the rods grow tall due to increased spacing between rods. The mechanism governing the formation of fans is unclear because the diffusion barrier of Al is much lower than its FCC counterparts Cu, Au and Ag. Further, this fan result is very interesting when compared to Ag, which has broadening of rods at high deposition rates, because rather than form a broad rod separate side fans form. Further adding to the complexity is the fact that the homologous temperature is higher for Al than it is for Ag at 77 K. Like Cu, Al oxidizes very
easily. In-situ characterization of the growing rods is necessary to determine if surface oxide is coming into play and artificially increasing the diffusion barrier— as has been done in previous studies\textsuperscript{23}.

3. \textbf{Non-FCC metals extension necessary in scientific understanding to meet up to fabrication knowledge (Cr, Co, Si)}

Unlike FCC metals, the diffusion barriers for BCC and HCP metals are not well investigated and may result in different grown morphologies than those seen in FCC metals. Another major difference is that the melting temperature of common non-FCC metals is much higher than that of FCC metals, for example the melting temperature of Cr is 1907°C compared to about 1000°C for Ag, Au and Cu. This shows that some of the first work that must be done to complete the scientific understanding of nanorod growth is to determine the diffusion barriers of common engineering metals like Cr, Cobalt (Co), and Si. Figure 50 shows the growth of Cr nanorods on a corning glass substrate at a deposition rate of 1.0 nm / s with no substrate temperature control. Anisotropic blades form which are very different than the rods seen in FCC metals, likely as a result of a relatively low homologous temperature of the substrate and large spacing between adjacent rods. The crystallographic formation is of scientific interest.
Figure 50: Cr deposited at RT temperature and a glancing angle of 86.5° with a deposition rate of 1.0 nm / s and a total thickness of 500nm- showing anisotropic fan formation.

Similar to Cr, Co forms blade like structures when fabricated at a glancing angle of 86.5° with a deposition rate of 1.0 nm / s, Figure 51. Cobalt nanorods may be of technological interest because of the catalytic capabilities of Co and the scientifically interesting BCC crystal structure.
Figure 51: Co deposited at RT temperature and a glancing angle of 86.5° with a deposition rate of 1.0 nm/s and a total thickness of 500nm.

Even Si may be grown into nanorods using GLAD, as seen in Figure 52. Due to the very high melting temperature of Si, it is expected that crystalline Si will not form from PVD at RT and that an amorphous structure which rapidly transforms into SiO$_2$ would result. However, XRD indicates that the Si nanorods from GLAD are indeed crystalline and likely have a thin SiO$_2$ shell. These results have potential to impact photonics and further scientific exploration is necessary.
Figure 52: Si deposited at RT temperature and a glancing angle of 86.5° with a deposition rate of 1.0 nm/s and a total thickness of 500nm.
VI. From Nanoscience to Nanotechnology

With the new properties that are realized as materials dimensions shrink to ~10nm, nanotechnology can impact existing technologies or meet the needs of technologies that are currently limited from expanding due to certain major milestones that conventionally engineered materials cannot meet. In this section we present one such example, low temperature hermetic sealing with metallic nanorod array. This sealing serves as an example of the advancement that is necessary for emerging technologies to escape from the laboratory to the storefront and that can only become possible when nanoscience becomes mature. In this example, the flexible and organic electronics industries could not progress because they lacked a low cost low temperature seal that is compatible with the components of their devices and has adequate impermeability to oxygen and moisture.

1. Low temperature metallic bonding

Metallc bonding can be advantageous as sealing, but the bonding process has not been possible below 100°C, above which plastics in solar cells and flexible electronics may degrade. Here, we show for the first time metallic bonding below 100°C, with excellent sealing and mechanical properties. Our approach benefits from a recent scientific breakthrough in growing small well-separated metallic nanorods. We first coat plastic substrates with well-separated Ag nanorods, and pressed the two substrates together with a pressure of 20 mega Pascal (MPa) at temperatures ranging from room temperature to 150°C. The electron microscopy characterizations reveal dense bonding structure. Further, the leakage tests reveal that the bonding performs better than the plastic environment, and the mechanical tests reveal shear
strength of more than 10 MPa, at which the substrate breaks or delaminates from the bond. The leakage resistance, coupled with the low bonding temperature, will likely lead to the widespread applications of metallic bonding in organic solar cells and flexible electronics.

To start, we examine what metallic bonding approaches have been explored, and more important analyze why they did not work below 100°C. For metallic bonding at low temperatures, sufficient solid diffusion is necessary, and fast surface diffusion of nanomaterials has been the focus of multiple attempts. Nanoparticles and nanorods (including longer and slimmer nanowires) can maintain large surface areas when they fit between two substrates. However, either a capping layer or poor separation can render the nanoparticles and nanorods ineffective in the low temperature bonding.

Ag nanoparticles are resistant to oxidation, and yet sufficiently inexpensive to have been used in low cost anti-microbial applications\textsuperscript{56,131}. The solution processing of Ag nanoparticles leaves an organic capping layer on them, and such layer does not disintegrate below 160°C\textsuperscript{68,132}. As a result, the Ag nanoparticles will consolidate into a continuous film only above this temperature of 160°C. Using an organic solvent, it is possible to open up the capping layer to allow nanoparticle sintering even at room temperature\textsuperscript{68}. However, this method is not compatible with organic and flexible electronics because it will also dissolve the active components. Further, the sintered Ag nanoparticles are in porous form, which may be useful for electrical conduction but the porous structure cannot function as seal. Along a different line, the nanorods from physical vapor depositions do not have to face the challenge of organic capping layer. However, the Cu nanorods attempted are not well-separated, and they coarsen into dense film before bonding\textsuperscript{28,120}. As a result, the bonding temperature of Cu nanorods is 400°C, which is similar to
that of Cu thin films. We note that the Cu nanorods likely have an untended capping layer of oxide since Cu is prone to oxidation.

While previous attempts of metallic bonding using nanoparticles and nanorods have not led to a feasible bonding process below 100°C, they have offered very important insights. If we can generate well-separated Ag nanoparticles or nanorods with no capping layer, their surfaces will not easily oxidize and surface as fast diffusion path for low temperature bonding. That “if” has become reality recently, through the development and guidance of theoretical framework for nanorod growth.41

In the following, we first identify the necessary pressure and temperature for fast surface diffusion, then use heated press to bond two plastic substrates at this temperature; and also bond two silicon substrates to facilitate imaging after focused ion beam (FIB) milling. In characterizing the quality of the bonds, we employ three techniques: scanning electron microscopy (SEM) imaging of cross-section morphology of the bond, leakage rate measurement of a vacuum that is sealed with the bond, and mechanical measurement of shear strength of the bond.

Conceptually, Figure 53 shows how the bonding process may work at low temperatures, including room temperature. Ag nanorods cover a plastic substrate with a metallic thin film layer to promote adhesion. As two such substrates are brought together (left of Figure 53), they are under a compressive pressure and then heated (middle of Figure 53). This hot press leads to a dense metallic bonding (right of Figure 53). Using an example organic solar cell133,134, Figure 53 illustrates that a non-degrading metallic bonding can block the leakage of oxygen and moisture into the solar cell (left), in contrast the leakage of an ordinary plastic sealing that degrades and leaks (right). As a consequence of the leakage, the solar cell core decomposes.
As the first set of results, we determine the necessary temperature for sufficient diffusion. We begin by determining the necessary temperature for the fast surface diffusion on three prototype metals that should produce the best bond due to their electronic, mechanical and chemical properties—Au, and Cu. Considering that most bonding processes take about an hour, we anneal the nanorods for 60 minutes. We begin with the annealing of Cu nanorods to determine the temperature at which they coarsen under high vacuum to prevent the surface oxidation. Figure 54 shows Cu nanorods as fabricated and annealed at 500°C for 1hr. Lower temperature annealing resulting in very little change and the change first became evident at 500°C. However, Cu forms an oxide shell very rapidly, even under high vacuum conditions\textsuperscript{135,136}. This is shown through a lack of morphological change observed after heating of Cu nanorods in the fabrication chamber to a temperature of 225°C for 1hr without breaking high
vacuum. Therefore, Cu should not serve as the ideal prototype material for low temperature bonding due to the oxide shell that will always form in real applications.

Figure 54: Well separated Cu nanorods before sintering (top) and after vacuum annealing at 500°C for 1 hr.
Figure 55: Au annealing progression in ambient with (top left) as fabricated, (top right) annealed at 115°C for 1hr, (bottom left) annealed at 150°C for 1hr, and (bottom right) annealed at 200°C for 1hr.

To eliminate the oxide formation and prohibited surface diffusion of Cu, Au is chosen as the next material of investigation due to its chemical inertness. Figure 55 shows the annealing progression of Au nanorods in ambient conditions. The top left panel shows the as fabricated Au nanorods with a well separated nature. The top right panel shows the nanorods after annealing at 115°C for 1hr. After 1hr at 115°C the nanorod surfaces have become smoother and some
diffusion has allowed rods to begin to come together. The bottom left panel shows annealing at 150° C for 1hr and increased surface diffusion is evident due to the smooth surfaces and agglomeration of neighboring nanorods. By increasing the annealing temperature to 200° C large amounts of diffusion have transformed the nanorods into spherical particles on the surface of the substrate. It is clear that this is not melting because the small particles on the substrate still exist and have not re-evaporated or moved as a liquid across the substrate to join to larger clusters.

Figure 56 shows as synthesized Ag nanorods, and they coarsen but remain separated after heating at 50°C for 60 mins, Figure 56. However, heating at 75°C for 60 mins converts the well-separated Ag nanorods into a dense film, as shown in Figure 56c. Heating at an even higher temperature of 100°C, Figure 56d, also leads to the conversion except that the grains of the film are larger than in Figure 56d. We note that the diffusion process is so fast at 75°C that the conversion of nanorods to film is nearly complete in merely 5 minutes resulting in a morphology identical to Figure 56c. This fast conversion may allow for fast bonding, but this point will be left for future exploration in order to compare and contrast with conventional bonding practices.
Figure 56: SEM images of Ag nanorods (a) before annealing from a tilted top view, with the titled cross-section view as inset, (b) after annealing at 50°C for 60 mins, (c) after annealing at 75°C for 60 mins, and (d) after annealing at 100°C for 60 mins.

Figure 57: Ag nanorods as fabricate (left) and after 2 weeks under low vacuum at RT (right). Diffusion fills in large gaps between rods.
Even more pertinent to very low temperature bonding is the coarsening and diffusion of Ag nanorods that occurs at room temperature. Figure 57 compares the as fabricated Ag nanorods and nanorods that were held in low vacuum desiccation for two weeks at room temperature, about 20°C. The difference is remarkable in that the spacing in between nanorods is completely eliminated due to fast surface diffusion. It is highly likely that under pressure there is local heating due to regions of high pressure and sliding friction leading to fast diffusion. Therefore, the bond achieved at room temperature may also result from fast diffusion.

Having identified the diffusion characteristics at different temperatures for our best prototype material, Ag, we next show the bonding results at a series of temperatures. Figure 58a shows that even at room temperature very brief (less than one minute) mechanical compression of 20MPa alone leads to well-connected bonding, although voids exist. Under this compression, heating at 75°C for 60 minutes leads to a dense bonding (Figure 58b); the few gaps are ~5nm in dimension and are much smaller than those from bonding of Cu nanorods at 400°C. As an exploration, Figure 58c shows the bond that results from heating to 100°C under mechanical compression. There are nearly no voids present and the bond is continuous with the nanosize grains of the nanorod largely remaining, as indicated by the contrast in the cross sectional SEM. Further heating of the cross section leads to recrystallization across the bond. Although we were unable to determine a difference in strength at this stage, our bonds were limited by the shear strength of our substrates in this initial exploration; the bond strength will definitely change as a function of crystal structure and may actually decrease with grain growth.
Figure 58: SEM images of bond cross sections under mechanical compression (a) at room temperature for less than one minute, (b) at 75°C for 1 hr, (c) at 100°C for 1 hr and (d) at 150°C for 1 hr.

Figure 59: Leak testing and failure mechanisms of the bond.
Going beyond the morphologies of the bonds, we now put them to test for leakage resistance and mechanical properties. Figure 59a shows that the pressure in a vacuum increases at the rate of 0.007 Torr CC/ m, or 0.5 sccm / s, when the seal is completely plastic, and this rate is reduced to 0.005 Torr CC / m, 0.4 sccm / s, when the seal is the metallic bond of Figure 58a. That is, the Ag bond has better leak resistance than the plastic itself. While this difference in leak rate is impressive, it is not adequate for the protection of components in flexible electronics like organic semiconductors and it is not air tight. This is due to the use of plastic substrates and the overall leaking of the plastic hose that is used in the low vacuum system. Here, this leak rate measured for the Ag seal the baseline of our low vacuum system; therefore an alternative method is devised.

Currently, helium (He) is used to test for leaks in air tight seals because of its small size and rapid motion through cracks. Our next test is a high vacuum He leak down test where two knife edge (CF) gaskets are sealed together with either polymer or Ag nanorods. The major limitation to the implementation of organic semiconductors is the high permeability of their substrates and sealants. On this level, it is estimated a device must have a hermetic seal with a leak rate on the order of $1 \times 10^{-9}$ sccm / s or less of air$^{133,138}$. In this leak test, the seals are placed into a CF flange and normal CF bolt loads are applied. In the first iteration, the atmosphere outside of the bond is air and the vacuum chamber is pumped down under a constant power condition. After pumping for 1hr, the single Cu CF gasket and the Ag bonded double gasket perform identically while the plastic seal performs substantially worse. The 1hr pump down results indicate that baseline and Ag reach $4.0 \times 10^{-6}$ Torr while the plastic reaches $7.5 \times 10^{-6}$ Torr. This gives a minimum leak rate of $1.5 \times 10^{-5}$ sccm / s for the plastic seal, on par with normal permeability of plastics. The leak rate calculated here is the minimum possible leak rate,
as the vacuum pump operates more efficiently at higher pressures. However, the major limitation to this method is directly observing the leak rate of the respective seals. The observed leak rate of the plastic seal is far above the seal needed for organic solar cells, so we must dive further.

To directly observe the leak rate to the seals a vacuum the chamber must be pumped down and then the vacuum pump must be either turned off or valved off under a He environment. An ion gauge predictability measures the increase is pressure in an He environment, as calculated by a comparison of the relative mass of he and air. In this test we use all CF flanged components, which have low leak rates of $1 \times 10^{-9}$ sccm/s of he to completely eliminate any issues with the baseline, and therefore the resolution of our measurement, being too high. To create a He environment, a plastic containment unit is placed around the sealed flange and Ion gauge and a positive pressure of He gas is achieved. A small leak of He assures that there is little air in the He environment.

Going beyond the morphologies of the seals, we now put the seal of Figure 4a to the test of air leak; see section of the S4 Supplemental Materials for details of setup and measurements.

According to direct measurement of pressure degradation as a function of time inside a sealed vacuum, we determine the air leak rate to be less than $6.7 \times 10^{-10}$ cm$^3$ atm/s, taking into account a very conservative error bar. To appreciate how small this leak rate is, we compare it with (1) the leak rate of polymeric adhesive, and (2) the desired standard of the OSC and OLED industries. First, repeating the leak test with polymeric glue, we determine the leak rate to be at least 1000 times higher than that of the metallic seal. Second, when it comes to the industry standard, the requirements of leak resistance are $1 \times 10^{-3}$ cm$^3$ atm/m$^2$/day for O$_2$ to $1 \times 10^{-4}$ cm$^3$ atm/m$^2$/day for H$_2$O vapor, for a reference configuration of 1 m x 1 m square solar panel [1]. For such a reference configuration, the air leak rate of our metallic seal is equivalently $1.5 \times 10^{-3}$ cm$^3$
atm/m²/day. Considering that 21% of typical air is O₂ and 3% is H₂O vapor (in volume), the corresponding leak rate of O₂ is 3.2 x 10⁴ cm³ atm/m²/day and that of H₂O vapor is 4.5 x 10⁵ cm³ atm/m²/day. These are several times better than the industry requirements for both O₂ and H₂O vapor [1]. We note that this better-than-required leak rate is achieved at room temperature under small mechanical pressure of 9.0 MPa, and also in ambient environment. Since the seal from room temperature processing suffices, here we will not pursue the test of seals from higher temperature processing.

As an additional step, we have examined the mechanical shear strength of the metallic seal. Using lap shear pull tests, we determine the lower limit of the shear strength of the seal in Figure 4a to be 8.9 MPa; see Supplemental S5 for details of measurements. Repeating the tests using seals formed under mechanical pressure of about 5 MPa, we find that the air leak rate does not change by more than 10% but mechanical delamination occurs between the seal and the polymeric substrates. That is, for both air leak resistance and mechanical strength, the mechanical compression of up to about 10 MPa is appropriate.

In terms of mechanical strength, the bond fails in two modes, substrate fracture at full strength or delamination at partial strength, Figure 59b. When bonded at room temperature, bonds fail in delamination under pressures up to 10MPa and bond strength is a function of applied pressure, Figure 60. After the bond pressure reaches 10MPa, the bond strength reaches a maximum of 12MPa as the substrate fractures. Further testing, either as a scholarly pursuit or as an industry company, is necessary to determine the true strength of the bond on stronger substrates as a function of microstructure – or nanostructure in this case as the bond cross section is only 1 micron and crystal sizes are on the order of 10s of nm. This bond strength is in excess
of “super glue” which has an advertised bond strength of ~7MPa for bonding plastic\textsuperscript{139}. As a function of temperature, using 150°C and 700KPa of bonding pressure and bonding duration of only 5 seconds results in the bond achieving full mechanical strength. At room temperature, bonding can also be performed in 5 seconds, or potentially less with a rapid punch often used in industry, and full mechanical strength is reached. This technology should prove to have remarkable implications for technology.

![Figure 60: Bond Shear Strength when performed at room temperature and varying bonding pressure.](image)

To put our low temperature metallic bonding in perspective, we compare and contrast it with similar bonding/welding methods based on eutectic or nanoscale melting. Some soft metallic alloys, such as lead- tin (Pb-Sn), have eutectic melting temperature below 100°C\textsuperscript{140}. However, the use of Pb is banned or in the process of being banned in developed countries\textsuperscript{141}. Even without the concern of Pb toxicity, these bonds are very soft and do not carry much mechanical load\textsuperscript{142}. As a result, eutectic melting does not help in the low temperature bonding of organic solar cells or flexible electronics. The nanoscale melting – melting of nanomaterials at substantially lower temperature than the bulk melting temperature – has been cited in the
literature\textsuperscript{143,144}. However, both experiment\textsuperscript{145} and modeling\textsuperscript{146} results show that nanoscale melting is prominent (or below 50\% of the bulk melting temperature) only when the dimension of nanomaterials is below 5 nm or so. At this small dimension, the nanomaterials will become chemically active even if they are Au or Ag. Such chemical reactions may not be completely eliminated, even in costly vacuum. That is, eutectic melting and nanoscale melting do not enable the low temperature metallic bonding. By contrast, the low temperature bonding reported here is feasible at room temperature and in ambient air environment instead of high vacuum.

In summary, in this section we report the first metallic bonding at room temperature, in ambient air environment, by using well-separated Ag nanorods. We show that the low-temperature bonding is a result of pronounced surface diffusion of small nanorods. Our characterization shows that the metallic bond is nearly void free, has an air leakage rate superior to polymer adhesives, and has a mechanical strength higher than that of plastics. This low-temperature metallic bonding technology will have direct impacts to the sealing of organic solar cells and flexible electronics.

Briefly, we include our methods of fabrication and characterization for future reference.

Introduction

Here we present supporting material to the key results in the main text. This supplement includes the experimental methods of fabrication, annealing, characterization and sealing; as well as the calculations used in the determination of the leak rate of the seals.

Fabrication of Nanorods
Nanorods are fabricated using a high vacuum electron beam physical vapor deposition system (PVD). Source materials - 99.95 % or greater purity chromium (Cr) and silver (Ag) (Kurt J. Lesker Co.) - are placed in the base of the chamber in a graphite crucible liner. Ultrasonically cleaned substrates of silicon (Si) (111) with native oxide, polyethylene terephthalate (PET), and mechanically polished 2.75” knife edge vacuum flange copper (Cu) gaskets (Kurt J. Lesker Co.) are placed at an angle of 86.5° relative to the source plane near the top of the chamber. The throw distance between the source and the substrate is approximately 40 cm. The system is closed and pumped down with a turbomolecular pump to a base pressure of 6.5 × 10⁻⁵ Pa and held at this pressure for six hours. During deposition, working pressure remains below 6.5 × 10⁻⁴ Pa. Deposition rates are measured with a quartz crystal microbalance, and electronically controlled through the power of electron beam. To achieve the morphologies in this Letter, Cr adhesion layers are deposited to a thickness of 100 nm at a rate of 0.3 nm / s, and Ag film is deposited to a thickness of 500 nm at 1.5 nm / s; at normal incidence. Afterwards, the chamber is returned to atmosphere so the substrate is oriented at 86.5°. Ag nanorods of nominally 1000 nm thick at 1.5 nm / s are deposited at a working pressure below 6.5 × 10⁻⁴ Pa; this deposition rate is measured perpendicular to the incoming flux. Samples are removed from the chamber and immediately characterized or sealed.

**Characterization and annealing**

Immediately after fabrication, samples are moved to an FEI Quanta 250 FEG microscope for scanning electron microscopy (SEM). Images are taken using secondary electrons in high vacuum mode, at an acceleration voltage of 20 KeV, and at a working distance of 10 mm. Cross
sectional imaging is performed with the sample on a 90° aluminum SEM stub with a stage tilt of 2° to give additional morphological perspective.

Samples are annealed using an electronically controlled laboratory hot plate (Fisher Scientific Isotemp). The hot plate is allowed 15 minutes to come to a steady state temperature. Afterwards, the sample is introduced for annealing. The annealing is not done sequentially; a fresh sample is used in each annealing experiment at respective temperatures. The error in the annealing temperature may arise from the probe, a K-type thermocouple, that is used to track the temperature, which may have an error in measurement of up to 2.2 %, and the tracking temperature of the hot plate is recorded as a maximum of 5 %. The temperature probe is placed directly onto the face of the substrate. The multiplication of the temperature error gives a conservative maximum of 8 % error in measurement. When the desired annealing time is over, the sample is removed immediately to avoid down ramping of temperature. SEM imaging of the annealed samples is performed right after the removal.

**Sealing and Seal Characterization**

Sealing for SEM imagining is performed soon after fabrication on a Carver Co. heated press. The press platens are heated to the desired temperature, ranging from room temperature to 100° C. Again, the conservative possible error in temperature measurement of 8 % derives from the 2.2 % measurement error of the temperature probe and the 5 % tracking error of the digitally controlled heated platens. PET and Si with native oxide substrates with Cr and Ag underlayer and Ag nanorods are placed facing one another between the platens and pressure is added manually via compression of a hydraulic ram over about 10 seconds. Timing begins
when pressure is fully applied. Sample cross sections are 1.25 cm x 1.25 cm and the applied force is 1400 N +/- 200 N. The bonding pressure is then calculated to be 9.0 MPa ± 1.3 MPa. The source of potential error in the force measurement is the resolution on the analog pressure gauge of the heated press. Seals are held at each temperature for five to 30 minutes before pressure is released without allowing for down ramping of temperature.

Seal cross sectional samples are prepared using focused ion beam milling (FIB) (FEI Co.) immediately after the sealing process to create cross sections that are free of contamination or artifact that may arise from mechanical polishing. Before the milling, the seal samples are fractured with rough cross sections. A low power finish cut is used to avoid contamination from the gallium milling beam. SEM imaging is performed using secondary electrons without removing the sample from the milling vacuum chamber.

Set Up for Seal Leak Rate Measurement
**Figure S1: Leak rate test geometry.** (a) Optical image of the vacuum gasket, ionization gauge and vacuum valve; and (b) cross sectional schematic of the vacuum gasket region, boxed area of (a).

The air leak rate of seals is measured by monitoring the high vacuum degradation rate as a function of time. Since our focus is on the leak of metallic bond, we use Cu gaskets as substrates in the measurements. Using polymers as substrates would introduce other leaks that overshadow the targeted measurements. First, two Cu knife edge vacuum gaskets are mechanically polished by hand down to a five micron polishing solution to remove large surface defects. Some defects still exist on the gasket faces, but they are only non-connected pits and do not affect the leak. The Cu gaskets are then ultrasonically cleaned in acetone and DI
H₂O. Using the same method as in S2, we grow Ag nanorods on top of Ag film, which in turn is on top of the Cr adhesion layer. Only the two mating faces of the gaskets are used in sealing, the center of the gasket remains open. The coated gaskets are then used to seal between an ionization gauge and an ultra-high vacuum (UHV) valve. The configuration is shown below in Figure S1 and the only possible leakage is through the sealed region between the two gaskets.

**Seal Pressure Calculation**

Compressive force on the double copper (Cu) gasket seal is estimated from the applied bolt torque. Applied torque is measured with a torque wrench that has a measurement uncertainty of +/- 0.3 Nm. The bolts are SAE grade 5 medium carbon steel and are nominally 0.63 cm in diameter and have 11 threads per cm (1/4 x 28 in the English nomenclature). Torque is applied in three rounds of increasing magnitude in an alternating pattern to a maximum load of 18.6 Nm. The relationship between applied bolt torque and Force is given by Collins [1] as

\[ T \approx \frac{1}{2} \left( \frac{l \cos \theta + \pi d_b \mu_t}{\pi d_b \cos \theta - l \mu_t} \right) + 0.625 \mu_c \right] F d_b \]

Where \( T \) is the applied torque, \( l \) is the height of the thread, \( \theta \) is the thread pitch angle, \( d_b \) is the thread diameter, \( \mu_t \) is the thread frictional coefficient, \( \mu_c \) is the collar frictional coefficient and \( F \) is the compressive force on the seal. Here, we use the values from Collins [1] for the thread and the collar frictional coefficient. As an upper limit, we use the static friction coefficient between hard steel and hard steel of 0.45 and as a lower limit we use the sliding friction of hard steel on hard steel of 0.25. The thread pitch \( \theta \) is also given in Collins as 60° and the height \( l \) is 0.6 mm. Using the upper limit of frictional coefficient, 0.45, the force applied is calculated to be 3875 N and using the lower limit the force applied is calculated to be 6925 N. To determine the
pressure, the area of the bond is measured as that of the gasket in contact; this area has a measured outer diameter of 4.83 cm ± 0.1 cm and an inner diameter of 3.67 cm ± 0.1 cm. The upper and lower limits of pressure may be calculated as 9.0 MPa, corresponding to a frictional coefficient of 0.25, and 5.0 MPa, corresponding to a frictional coefficient of 0.45. Since the upper limit of 9.0 MPa is the conservative value for our results, it is what we cite in the main text; any lower value of pressure would mean that the results are even better.

**Chamber Volume Measurement**

The volume of the chamber that is enclosed by the seal is used to calculate the leak rate. The enclosed volume between ionization gauge and the vacuum valve is for leak measurement. The top section of the enclosed volume, between the ionization gauge and the seal is 16 cm$^3$ as specified by the manufacturer. The bottom section, between the seal and the vacuum valve, is 72 cm$^3$, by measuring the diameter and height using laboratory calipers. The total enclosed volume is 88 cm$^3$.

**Leak Rate Measurement**

The leak rate is an effective value, as the difference of two leak rates: that with the seal, and that with the baseline Cu gaskets. For the baseline measurement, a single Cu gasket is placed in the configuration and a torque of 18.6 Nm is applied to the gasket bolts. The system is pumped down to 6.5 x 10$^{-5}$ Pa and held at this pressure for 24 hours to remove as much background gas and contamination as possible. The system is not baked out, and remains at room temperature, because the later testing of seals must remain at room temperature. The ionization gauge is a Kurt J. Lesker 354 Series Ionization Vacuum Gauge Module (IVG). The manufacturer of the IVG reports a typical accuracy of the IVG as +/- 15% of reading and...
 repeatability as +/- 5% of the reading. As we are comparing the vacuum degradation of the seal to that of the baseline, the repeatability is the most important factor in the determination of the leak rate. The baseline leak rate is measured with the ionization gauge by turning off the pumping and closing the UHV valve, isolating the gasket and the ionization gauge. Data points are taken once per second by an Agilent multiplexing meter. The increase in measured pressure as air leaks through the seal into the chamber is then recorded for nine minutes. This baseline is considered to be the leakage through the interface between the knife edge and Cu gasket and the outgassing of the contamination attached to the area of the isolated valve and the interior area of the gasket. The pressure as a function of time is shown in Figure S2. The leak rate is determined by subtracting the initial pressure from the final pressure, multiplying this by the enclosed volume and then dividing my time. The curve of true pressure always remains below this upper limit estimate, and this reported value is therefore the worst possible leak rate as a function of time. The baseline leak rate is measured as $1.38 \times 10^{-8}$ cm$^3$ atm/ s. Taking into consideration the maximum error induced by 5% uncertainty in repeatability and the final recorded value of baseline pressure, $8.45 \times 10^{-3}$ Pa at nine minutes, the smallest measurable air leak rate with confidence from this method is $6.7 \times 10^{-10}$ cm$^3$ atm/ s.

Next, the double gasket with metallic seal is placed into the same configuration and torqued down with the same compressive force of 18.6 Nm. The measurement is repeated as for the baseline case. At the end of nine minutes, the pressure is $8.45 \times 10^{-3}$ Pa. Using the difference between this pressure and the baseline value of $8.45 \times 10^{-3}$ Pa, we determine the effective leak rate of the metallic seal to be $5.07 \times 10^{-10}$ cm$^3$ atm/s. However, this leak rate is below the resolution limit of the measurement system, $6.7 \times 10^{-10}$ cm$^3$ atm/ s. Therefore, the effective leak
rate should only be regarded as smaller than $6.7 \times 10^{-10}$ cm$^3$ atm/ s, with confidence. This resolution limit is what we use in the main text as the effective leak rate.

In order to compare with industry standard, we convert the leak rate per unit length into that per unit area. The leak rate per unit length of our seal is the $6.7 \times 10^{-10}$ cm$^3$ atm/ s divided by the seal length along the circumference (which is 15.1 cm), and it is $4.4 \times 10^{-9}$ atm cm$^3$/s/m. In the organic solar cell (OSC) industry, a standard configuration as discussed in is a square panel of 1m x 1m, with perimeter of 4m. Multiplying our leak rate of $4.4 \times 10^{-9}$ atm cm$^3$/s/m by the perimeter and converting the time from second to day, we have the leak per unit area as $1.5 \times 10^{-3}$ cm$^3$ atm/m$^2$/day. To correlate the air leak rate with those of oxygen (O$_2$) and water (H$_2$O) vapor, we use the volumetric composition of regular air. Under normal operating conditions for an OSC or organic light emitting diode (OLED), air is composed of 21% O$_2$ and may contain up to 3% H$_2$O vapor when fully saturated. We estimate the leak rate of O$_2$ as 21% of $1.5 \times 10^{-3}$ cm$^3$ atm/m$^2$/day, or $3.2 \times 10^{-4}$ cm$^3$ atm/m$^2$/day. Similar, we estimate the leak rate of H$_2$O vapor as 3% of $1.5 \times 10^{-3}$ cm$^3$ atm/m$^2$/day, or $4.5 \times 10^{-5}$ cm$^3$ atm/m$^2$/day.
Figure S2: Vacuum Pressure Degradation. Vacuum pressure as a function of time for the system baseline (solid black), the metallic seal (green circle), and the polymer adhesive (red solid).

For comparison to the metallic seal, a polymer adhesive is used in the same configuration of leak test. A thin layer of cyanoacrylate is placed onto the surface of a polished Cu gasket and another polished gasket is placed facing the adhesive. The double sealed gasket is put into the vacuum system and torqued down to the same specification as the metallic seal. Low vacuum is applied with a mechanical pump to remove any air pockets which may be present in the adhesive layer and the adhesive is allowed six hours to cure before the high vacuum stage is engaged. Again, the system is allowed to remain at base pressure for 24 hours.
and the degradation of pressure is measured as a function of time, in the same way as for the metallic seal. The measured leak rate of the polymer seal is $6.7 \times 10^{-7}$ cm$^3$ atm / s, which is equivalent to 1.5 cm$^3$ atm/m$^2$/day per unit area basis.

**Figure S3: Polymer Adhesive Cross Section.** Cross sectional image of the polymer adhesive cross section using (a) XEDS mapping of Si and (b) accompanying secondary electron image with the cross sectional thickness marked by the red arrow.

The configuration of the polymer is characterized using SEM microscopy and X-ray energy dispersive spectroscopy (XEDS), Figure S3. The sample is prepared between two Si {111} wafers under the same mechanical pressure as the sealing configuration. The glued Si wafers are then mechanically fractured, polished and coated with several nm of gold (Au) for SEM imaging to prevent charging. Based on XEDS in the FEI Quanta 250 SEM, Figure S3 (a), the gap between the two Si substrates is 3.9 µm by mapping only the characteristic X-rays from the Si substrates. In the accompanying secondary electron SEM image, Figure S3 (b), the polymer seal between substrates is void free and continuous; likely due to the applied pressure of 9.0 MPa. In industrial applications, two factors will worsen the leak of polymer seals. One, without the pressure of 9.0 MPa, the polymer seals likely will contain voids. Two, the thickness of polymer
seals is usually larger than 3.9 µm, and larger thickness leads to more leak; in contrast, only the thickness of the nanorod layers matters in the metallic seal.

**Lap Shear Sealing and Shear Strength Measurements**

To test the mechanical strength, we use polymer substrates since Si substrates break easily; the same adhesion layer and Ag nanorods are deposited on top. Sealing of two PET substrates is performed using a laboratory press with a polished aluminum pressing die to assure even pressure across the seal area. The pressing die is approximately 1.25 cm x 1.25 cm in size and the plastic substrates are placed within the die so that about 1 mm (+/- 0.5 mm) x 10 mm (+/- 1 mm) of seal area overlaps, and will therefore be sealed together. The sealed cross sectional area is therefore about 1 x 10^{-5} m^2. Pressure is slowly added manually and the timing begins when the peak force of 1500N +/- 200N is reached. Dividing this force by the die area gives a sealing pressure of 9.6 MPa +/- 1.2 MPa. The sealing process is maintained for five minutes, and then immediately released as the press is lowered.

The lap shear pull tests are performed after sealing on a computer controlled tensile testing machine. Under these conditions, all 10 samples failed through substrate fracture under an average load of 89 N with a standard deviation of 17 N. Since the seal area is 1 x 10^{-5} m^2, this gives average seal shear strength as more than 8.9 MPa with a standard deviation of 1.7 MPa. The strength of the seal must therefore be greater than this value because the failure is in the weaker link, that is the PET substrate.
VII. Future Exploration and Conclusions

To bring this document to closure, it is very important to discuss what is necessary for further exploration to complete the lifetime of work which has only begun in this document. Returning to the themes from the introduction, which have been echoed throughout, there are three main areas of nanorod synthesis that require completion in scientific understanding: completing the theory of nanorod growth from PVD for BCC and HCP metals, beginning to understand more completely mechanisms of nanorod growth from CVD and beginning to understand more completely the mechanisms of nanorod growth from solution synthesis. As science progresses, transfer from science to technology may become progressively more possible as each layer of understanding is achieved. There are many current technologies that are on the verge of being impacted by nanoscience that we will touch on very briefly in this section.

1. Scientific investigation

As this study has shown, scientific understanding leads to technological advancement, and the pursuit of scientific understanding should be paramount in the career of anyone doing research in engineering science. Within the field of nanorod fabrication, there exists three grand challenges of scientific understanding, listed in order of perceived difficulty, and they are: physical deposition, chemical deposition and solution precipitation.

With the emergence of the theory of nanorod growth from PVD, scientific understanding of the growth of nanorods from physical vapor deposition has become more mature. Among the necessary areas of scientific investigate to bring the scientific understanding to completion include a complete set of 2D and 3D diffusion barriers for FCC, BCC and HCP materials which
nanorods may be grown from. Understanding into the growth of BCC and HCP nanorods from PVD may also have an additional level of complexity when compared to FCC metals and additional growth mechanisms may be uncovered with increased experimental fabrication and atomistic simulation.

One major limitation to the current experimental analysis techniques that the author has faced is the introduction of oxide or other contamination from interacting with the ambient during transfer from the fabrication chamber to the characterization chamber. Also, X-ray diffraction techniques are not possible with current instrumentation under UHV conditions meaning that an oxide layer grows during characterization under light vacuum or ambient. To accurately characterize the growth of nanostructures and thin films from physical processing in-situ analysis is preferred, but “quasi in-situ analysis” may offer nearly as much insight. To realize this, thinking as a true engineering, a sophisticated fabrication and characterization chamber may be created. The hypothetical system would be composed of a UHV chamber with a multi-source magnetron sputtering gun pumped down by the combination of a mechanical pump, a turbomolecular pump and a cryogenic pump to base the chamber out at $10^{-11}$ Torr. Off of the main chamber there may be shuttered gate valves for an electron beam source with electromagnetic lenses and a power supply capable of accelerating electrons ranging in velocity from 1.0 KeV to 200 KeV with raster capabilities and a separate monochromated X-ray source. Below the sample there may be shuttered and valve separated detectors for transmitted electrons and EELS. Above the sample near the source there may be a ET detector for secondary electrons and perpendicular to the X-Ray source there should be an X-ray detector. By having manipulation on the substrate, all of the detectors and sources may be stationary and TEM, SEM and X-Ray diffraction analysis may be performed without moving the detectors. Further, if the
electron source and detectors are shielded from flux from the magnetron gun then in-situ analysis of the growing structures may be performed.

The next grand challenge of scientific understanding of nanorod growth is determining the controlling mechanisms of growth from chemical vapor deposition. The additional complexity in this problem derives from the combination of thermodynamic and kinetic contributions to the growth. Due to the complexity of the process, atomistic simulation lends itself well because within a virtual experiment one may eliminate variables that cannot be eliminated in the laboratory. The path to discovery in this area is then simple atomistic simulation married to fabrication experiments as validation. Within CVD there is generally only a handful of reactants and a catalyst in an inert environment, so the variables are numerous but constrained. It should be noted that while it is not possible at this moment it time, with rapidly expanding computer power, it will soon be possible to simulate the complex chemical reaction as well as the atomistic simulation and develop accurate multi-scale models.

The same approach of atomistic simulation of experimental validate should be taken to learn the underlying mechanisms of solution synthesis of metallic nanorods. The complexity of this problem is now much larger than that of CVD because of the chemical reactions occurring in the multi-component aqueous environment. Considerable computational power is necessary to brute force through all of the variables but it may be necessary to untangle the complex interactions between crystal capping agents, solution and solid.

Overall, a mature understanding of PVD is approaching while the scientific understanding of CVD and solution synthesis are more complex and will require greatly increased computational power synergized with ever advancing experimental techniques.
2. Technology

We again return to the concept of consistent incremental improvement of life, driven by the consistent incremental improvement of technology. Looking back over the last 50 years, the consistent incremental improvement in IC technology has brought incredible computing power and connectivity to everyone living in the first world. In a more concrete sense compared to the science discussed in the last section, the world truly faces grand challenges to continue to maintain our ever growing population. Among the motivators are renewable energy, clean drinking water and expanding and improving medical care.

To meet the energy needs of the world in the midst of dwindling fossil fuel reserves, the issue of global warming set aside for the politicians and climate scientists to discuss, improved efficiency of fossil fuel consumption and increased competency of renewable energies are necessary. By around 2010 solar technology had become relatively mature with many companies having large IP portfolios and strong investment behind them to create low cost, reel to reel, mass produced second and third generation solar cells. For example, Konarka was nearing first production of low cost organic solar panels on plastic substrates. Unfortunately, the convergence of two “waves” extinguished this technological surge. The first wave was peak the global economic crisis and a loss continued investment in solar startup companies and the second was the largely increased production of high efficiency low cost Si solar panels from the Asian market. Konarka then failed after collecting over $170 million of investment capital\textsuperscript{147}, largely due to stopped investment and partially due to miscalculation on the difficulty of solving the problem of sealing the photovoltaic, and left a dark spot on the advancement of renewable energy sources like solar. The recent stability in fossil fuel prices has led to a level of complacency and development of renewable resources has largely returned to the laboratory.
However, it is certain that the price stability will be short lived and continued research will enable some of the next wave of renewable energy technologies to take hold and be cost competitive. This is due to small incremental improvements to simple things like impermeable sealing, as outlined in this thesis.

Continued research is necessary to further improve efficiency of third generation solar panels, like organic polymer and small molecule, and solve problems like the necessity for a solid state electrolyte in the dye sensitized solar cell. Plasmonic nanoparticles and nanorods may be used in solar cells as both hot electron injectors and fast electron transport to improve efficiency. Currently the ability to fabricate ideal structures is either prohibitively expensive or not compatible with low cost manufacturing techniques like reel to reel. Improved understanding is necessary in solution and physical processing to realize structures that may serve these purposes.

Two technologies that are on the verge of progressing from laboratory to life are cancer detection and sequestration with Au nanorods and SERS for the fast and low cost detection of a wide range of biological components like viruses, bacteria and chemicals. Au nanorods are both non-toxic and can be functionalized with materials so that they are preferentially incorporated into cancer cells. Once in the cancer a UV laser may be shown on the nanorods- this wavelength can pass through the skin and flesh of humans up to several cm without causing any harm. The nanorods then heat up due to their plasmonic resonance, resonant oscillation of hot surface electrons due to quantum interactions with the UV photons, when excited by UV light. The cancer cells are then rapidly destroyed and the Au is then easily passed from the body. To further this technology, Au nanorods need to be fabricated to respond to other wavelengths of light that may pass further through human tissue. The plasmonic resonance is a function of the aspect ratio
of the nanorod, and a more complete understanding of nanorod synthesis from solution will enable ideal morphologies to be realized at relatively low cost. The other issue is that the solution synthesis of Au nanorods always results in a toxic organic capping layer. This layer can be avoided through the growth of Au nanorods from physical processes and the recent realization of Au nanorods from PVD may allow for the tune-ability and high purity needed for treatment. The second technology which is on the verge of commercialization is SERS with nanorod substrates. Ag nanorods have emerged at the preferred substrates onto which cells and chemicals are attracted. Through plasmonic oscillation of the nanorods caused by the excitation of the Raman probe, which is a laser, the Raman signal is amplified by a large amount. The amplification allows for the extremely rapid detection of the biological agents that were not discernible from signal noise without the amplification. Among the issues with the large scale implementation of the method are the repeatability between two substrates and stability of the signal over time. As our results on Ag show, Ag nanorods have fast surface diffusion and may coalesce into continuous rough films with sufficient time. Although not discussed here, our group has begun work on creating a stable core shell structure that will have a strong plasmonic response but will also stop surface diffusion on Ag nanorod surfaces to achieve a stable structure for repeatable results over time. The plasmonic response can also be modified through changing fabrication variables, which are well understood within the new theory of nanorod growth. Current nanorod substrates are fabricated with large spaced rods on the order of 100nm in diameter. As seen in this work, the large spacing on Ag nanorods leads to inconsistent size of nanorods and minute changes in flux condition across the substrate will yield a large spread of nanorod morphology. This can be addressed now that the physical understanding has emerged
and smaller, more closely spaced (but still well separated) nanorod arrays can be fabricated with high uniformity of rod diameter, across the entire substrate.

To conclude this work, we began with a discussion of the necessity for increased scientific understanding of nanofabrication and consistent incremental improvement to existing technologies through nanotechnology. We outlined the current state of nanofabrication in terms of both fabrication knowledge and scientific understanding and presented the strengths and weaknesses of the methods of solution synthesis, CVD and PVD. We chose PVD as a prototype for scientific investigation because it is clean and completely controlled by overwhelming kinetic limitations. We then presented the motivation for a new and complete theory of nanorod growth from PVD which enabled the experimental realization of the smallest ever nanorods from PVD. We then showed the growth of many different metals under a wide range of condition and fit the growth into the theory. After exploring the properties of these nanorods and realizing the surfaces have extremely fast diffusion we began the transfer from nanoscience to technology and demonstrated room temperature metallic bonding and sealing for the first time. From here we addressed grand challenges for the science and application of nanotechnology in the future.


