

Review

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Syntheses and applications of small metallic nanorods from solution and physical vapor deposition

Abstract: Metallic nanorods have a wide range of important technological applications. Fabrication of metallic nanorods of ~100 nm using physical vapor deposition (PVD) has been commonplace for several decades. On this length scale, nanorods have similar functionalities to bulk thin films with the advantage of increased surface area. When the lateral dimension is decreased to ~10 nm new functionalities emerge that are not present in thin film counterparts, such as catalysis. Small metallic nanorods, those ~10 nm, have classically been made through solution-based synthesis. Alternatively, recent advances in scientific understanding, a framework of nanorod growth, have opened the door to the fabrication of small nanorods through PVD. Growing small nanorods through PVD offers technologically relevant advantages over solution-based processing like direct control of aspect ratio, pure high-vacuum processing, and oriented attachment to a substrate. Among materials, gold (Au) has a wide range of technological applications and is a good prototype for understanding the behavior of common face center cubic metals. This article reviews solution processing and PVD of small metallic nanorods using Au as a prototype, in terms of scientific understanding and fabrication knowledge, and further compares and contrasts the two approaches.

Keywords: glancing angle deposition; nanofabrication; nanorod; physical vapor deposition; solution synthesis.

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1 Introduction

Over the past several decades, nanomaterials have become a major focus of scientific research. This emphasis

is largely due to the emergence of unique and technologically useful properties of materials that emerge as at least one dimension shrinks and surfaces become dominant. Conventionally, the distinction of “nano” has been reserved for materials where one dimension is on the order of ~100 nm or smaller. On this length scale, material functionalities are largely similar to their thin-film counterparts. The most significant technological gain on this length scale is an increase in surface area over thin films and bulk. In most materials, it is necessary to drop the lateral dimension to ~10 nm before size effects begin to become dominant and deliver a qualitative change in properties [1]. Among objects on this length scale, small metallic nanorods, those that are ~10 nm in diameter in comparison to larger metallic nanorods that are ~100 nm in diameters, have emerged as technologically important, and their fabrication has been widely reported in the literature [2–7].

Small metallic nanorods have many important technological applications that rely on functional properties that are due to their small diameter, as illustrated by three examples. As the first example, small copper (Cu) nanorods reduce the thermal budget for low-temperature three-dimensional wafer bonding [3]. In applications where it is desirable to stack integrated circuit wafers on top of one another, wafer-to-wafer bonding is necessary [8]. Because of their delicate doping profile, integrated circuit wafers are particularly sensitive to high temperatures and the management of “thermal budget” is necessary [9]. More specifically, if the impregnated wafer is heated too high, the profile of the dopant molecules may be disturbed. Due to improved conductivity and electromigration properties over conventional aluminum (Al) interconnections, industry is shifting to Cu for interconnections and wafer-to-wafer bonding [3]. To maintain the thermal budget, small Cu nanorods from physical vapor deposition (PVD) are used as a bonding medium. As the diameter drops to 30 nm, when external pressure is applied, Cu nanorods coarsen and coalesce to a dense film at a

temperature that is ~50% of bulk Cu melting temperature [3]. Using this property, arrays of Cu nanorods can bond integrated circuit wafers at temperatures lower than possible, with dense Cu thin films thus protecting the dopant profile. As the second example, small silver (Ag) nanorods increase the sensitivity of surface enhanced Raman scattering (SERS) sensors by orders of magnitude [10–12]. In SERS, a laser probe induces vibrations in target molecules on surfaces. In some applications, the vibration may be too small to accurately measure. Small Ag nanorods are then used as scaffolds onto which the target molecules are attached. The vibration signal is enhanced by orders of magnitude as the laser interacts with electrons in plasmonic oscillations, which only emerge at small dimensions, of the surfaces of the Ag nanorod scaffolds. The magnification is a result of the resonance of valence electrons in the nanorods that are excited at their natural frequency by incoming photons from the SERS laser probe. As the third example, also relying on surface plasmon resonance, which emerges at small sizes, gold (Au) nanorods are used for the hyperthermic destruction of cancer cells and bioimaging [13–16]. The biocompatibility of Au and the small diameter enable Au nanorods to be retained inside the cancer cell [17]. Once in the cancer cell, the nanorods are targeted with light – near-infrared (NIR) light can pass deep into the tissue. Rapid heating occurs through surface plasmon resonance due to the excitation of the valence electrons of the nanorod at their resonant frequency by incoming photons. By changing the aspect ratio, the wavelength of light that induces plasmonic resonance can be modified to the NIR range for better tissue penetration [14, 18]. Bioimaging is enhanced through two-photon luminescence (TPL) of Au nanorods with deep penetrating NIR light. Like surface plasmon resonance, TPL is also dependent on the small size and is coupled to the Au nanorods ability to sustain surface plasmon resonance with minimal damping [14]. In TPL, two photons of NIR light excite an electron within the nanorod. When electrons from the sp band recombine with holes in the d

band, photons are emitted from the nanorod, which are also in the NIR region and thus easily pass back through tissue to be detected [16]. Due to the relative importance of Au in technology and the mass of research presented in the literature, it is fitting to choose Au as a prototype material of investigation in this review. Having demonstrated the need, the question at hand is then: how does one fabricate small, ~10-nm-diameter nanorods?

Both solution and physical processing have been used to fabricate small Au nanorods. Under the umbrella of solution processing, the left of Figure 1, the main methods to achieve small Au nanorods are electrochemical synthesis [5, 19, 20] and seeded solution synthesis [21–25]. Within electrodeposition, there are two schemes of creating small Au nanorods; they are template electrodeposition [19] and electrochemical synthesis with agitation in the presence of surfactants [5, 20]. The electrochemical template method is the most straightforward means of synthesizing nanorods from solution processing. In this method, Au is electrodeposited into the gaps of a nanoporous membrane in a liquid electrolyte-based electrochemical cell. The second means of electrochemical synthesis relies on the addition of mechanical agitation and a surfactant – organic solvent solution to the electrochemical cell. In this method, the nanoporous membrane is replaced with a platinum cathode. Alternatively, seeded solution synthesis has emerged in the literature as the most mature, in terms of fabrication knowledge, and offers a facile means of producing Au nanorods suspended in a solution. Generally, seeded synthesis operates through the reduction of Au salts in the presence of seed nanoparticles and surface capping agents, which block growth on select crystal faces [20, 23, 24]. By altering processing conditions and the additive concentration of Ag ions, seeded growth can produce a range of aspect ratios and yields [26]. Because of the complex chemical interactions in solution-based methods, scientific understanding faces challenges.

In contrast to solution-based processes, the fabrication of nanorods using PVD involves only physical

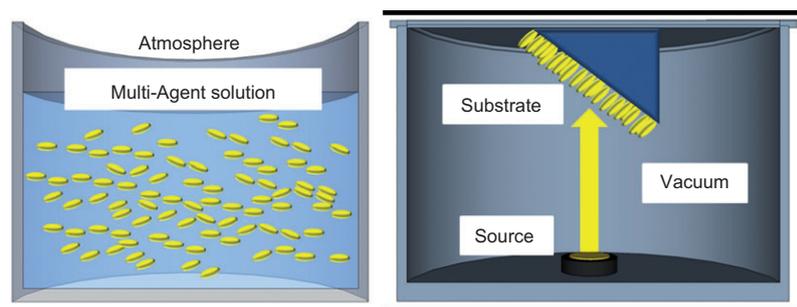


Figure 1 Methods for small nanorod growth with solution-based synthesis (left) and PVD (right).

processes and is less difficult to scientifically understand. In particular, a framework of nanorod growth through PVD [27] has emerged, leveling fabrication knowledge and scientific understanding. For several decades, PVD has been used to fabricate sculpted metallic and metal oxide thin films with features ~ 100 nm [28]. As examples, Cu [3, 29], tantalum (Ta) [30], Ag [10, 11], and chromium (Cr) [31] nanorods, zigzags, and spirals have been widely demonstrated in the literature [28, 32]. To achieve ~ 100 -nm nanorods, which are generally a single crystal [29], the incoming physical vapor is generally deposited onto the substrate at an incidence angle, right of Figure 1, using the methods of glancing-angle deposition (GLAD) or oblique-angle deposition (OAD). When on the order of 100 nm, nanorods from GLAD are the result of a wetting substrate and incoming flux reaching the geometrically high locations of the growing film. On this length scale, large heterogeneous nucleation sites have also been used to act as geometrically high spots onto which nanorods grow. Building off of this, nonwetting substrates have been used to create small nanorods using GLAD. Small nanorods, which are generally a single crystal and have been realized to diameters ~ 7 nm [7], develop in a different manner: the initial deposition on the substrate results in island formation and the islands are geometrically higher than the surrounding substrate. With the high incidence angle, the top of the islands receive a majority of incoming flux.

In this review, we will first present the primary methods of growing small Au nanorods – solution-based and physical processes – and discuss fabrication knowledge and scientific understanding of each method, respectively.

2 Primary methods of growing small Au nanorods

2.1 Fabrication of small nanorods using solution-based processing

Under the umbrella of solution-based processing, there are two main processes that result in small Au nanorods: electrochemical synthesis and seeded solution synthesis. The simplest and best scientifically understood method is electrodeposition into a porous membrane, which can later be dissolved, leaving small rods in a suspension. To avoid the constraint of the template, organic solvents, surfactants, and sonication are added to keep the Au from depositing to the platinum cathode and aggregating; through the optimization of conditions, the result is

a suspension of small Au 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 Au salts in the presence of crystal capping agents, such as cetyltrimethylammonium bromide ($C_{16}TAB$) [25] or tetradodecylammonium bromide ($TC_{12}AB$) [33].

Templated electrochemical growth of small Au nanorods is achieved through the electrodeposition of Au metal into a nanoporous template [19, 34]. The process begins with the creation of a nanoporous template, most commonly alumina, on a conductive substrate. A thin layer of conductive metal, Au or Cu, is vacuum sputtered into the alumina pores to act as a conductive contact. The substrate and template are placed into a liquid electrolyte-filled electrochemical cell with a sacrificial Au anode (shown in Figure 2A). Au is then deposited by passing a current through the cell, with the rate of deposition being governed by the current and the duration of the deposition controls the thickness. After removal from the electrochemical cell, everything but the Au – substrate, alumina support, sputtered conductive layer – is removed through wet chemical etching. 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.

Still within an electrochemical cell, small Au 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 [5, 20]. Here, the electrochemical cell is composed

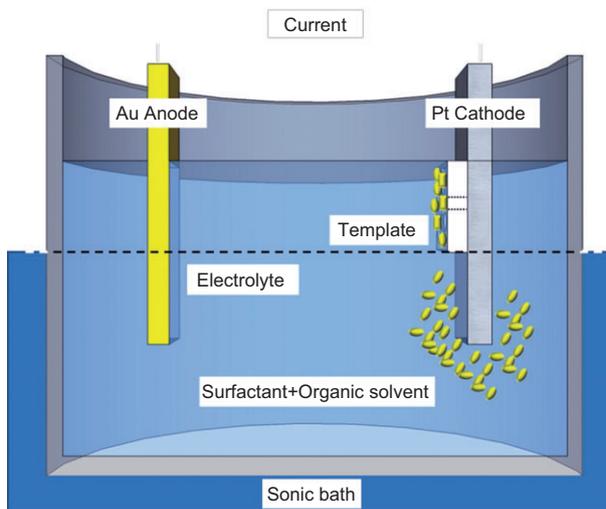


Figure 2 Electrochemical growth of small nanorods with the template method (top) and sonication method (bottom).

of a sacrificial Au 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. A current is then passed through the electrochemical cell while the entire cell is mechanically agitated in a sonic bath (shown schematically in Figure 2B). The proposed mechanism of formation is thought to be the formation of $AuBr_4^-$ at the anode and a reduction at the cathode, nucleating Au metal nanoparticles in the solution. It is not clear if nucleation takes place on the cathode, and 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 the 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 nanoparticles, blocking growth in the coated directions and resulting in rod growth (Figure 3). By inserting an Ag metal plate into the electrolyte solution near the Pt anode, some aspect ratio control may be gained, but the mechanism of action is not well understood [26].

The seeded synthesis of small metallic Au nanorods is based on the reduction of metal salts in the presence of seed nanoparticles and crystal surface capping agents [21–25, 33, 35–37]. First, metallic nanoparticle seeds are formed in the solution, generally with diameters on the order of several nanometers [38]. To induce the formation of rods, crystal surface capping agents, such as $C_{16}TAB$ [21–24, 39], tetraoctylphosphineoxide [33], and oleic acid [25], among others [37], are added to the solution and are proposed to preferentially bond to select crystal surfaces. 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 [39]. A further level of control is added by the addition of Ag ions,



Figure 3 Seeded solution synthesis of small Au nanorods.

also considered a crystal surface capping agent, in the form of $AgNO_3$ [35]. 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.

2.2 Fabrication of small nanorods using PVD

The methods of high-vacuum PVD have been around since the 1950s. Over the last six decades, there has been much progress in fabrication technology, and many advanced methods of PVD have emerged. In particular, two of these methods, GLAD [28] and OAD [40], have enabled the growth of metallic nanorods using PVD. In these methods, either the substrate or source may be rotated in respect to one another to achieve an incidence angle of flux. In both methods, geometrical shadowing is used to limit the deposition of new flux to the top of geometrically high locations (peaks), whereas the only flux that geometrically low locations (valleys) receive is from atoms that have diffused down from peaks. Using the method of geometrical shadowing, it becomes possible to fabricate metallic nanorods using PVD (Figure 4).

Fabrication of metallic nanorods using GLAD and OAD has been commonplace for two decades, and fabrication techniques have become mature. The first reported structures grown from PVD were metal and metal oxide

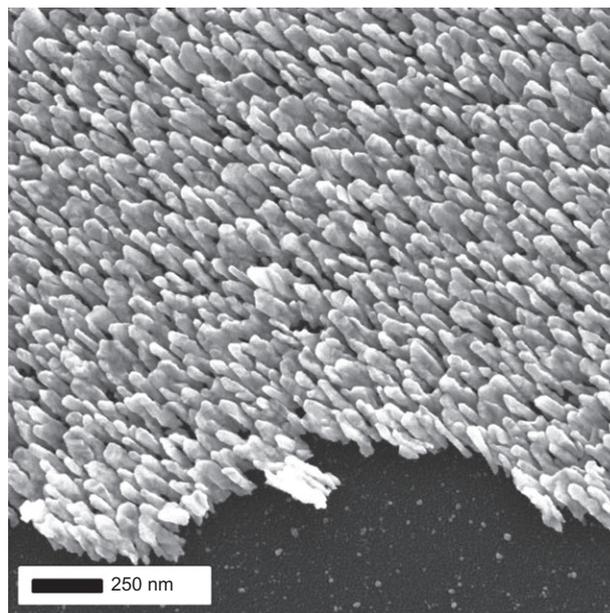


Figure 4 SEM image Au nanorods using PVD with large diameters, originating from a wetting substrate.

nanorods, among other complex geometrically sculpted thin films, in 1994 [28]. Building from this early fabrication knowledge, the fabrication of nanorods from a wide range of metals, such as Cu [3, 29], Au [7], Ag [10, 11], Ta [30], and Cr [31] among 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 and diffusion (metal-substrate or metal-metal) are the only two means by which atoms may move. By modifying the 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, zigzags, and fans [28, 31, 32].

Until recently, Au nanorods had not been widely investigated using PVD [7]. 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 100 and 10 nm (Figures 4 and 5, respectively). The rods in Figure 4 are have diameters of 100 nm and are grown on Si substrates, with native oxide layer, at a deposition rate of 0.2 nm/s,

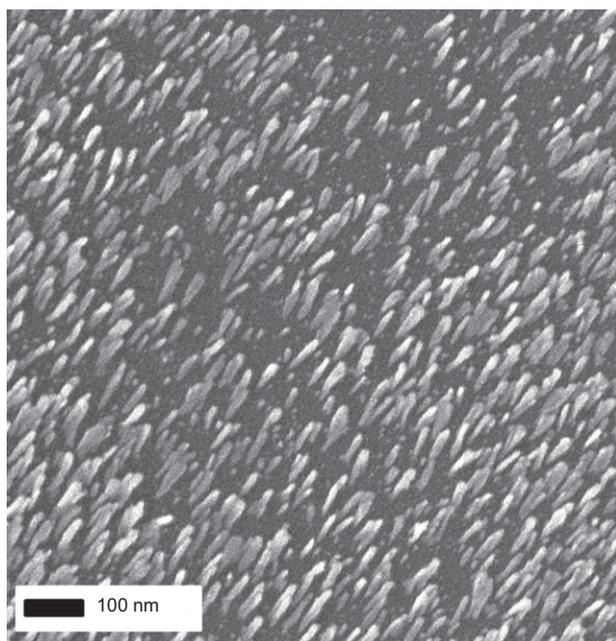


Figure 5 SEM image of small Au nanorods from PVD, originating from a nonwetting substrate.

a glancing angle of 85° , and no substrate temperature control. The rods in Figure 5 have diameters of 10 nm and are grown on highly nonwetting adhesive tape (3M Copper Conductive Tape 1182; 3M Corporation, St. Paul, MN, USA) at a deposition rate of 0.1 nm/s, a glancing angle of 88° , and liquid nitrogen cooling [7]. The variation in diameter and spacing is connected to a difference in substrate and deposition conditions, revealing the controlling mechanisms.

The mechanisms controlling the diameter of metallic nanorods have recently emerged through a theoretical framework [7, 27]. The theory is developed from the ground up, starting with the nature of the substrate. In mode I of growth (Figure 6, left), nanorods develop from a wetting substrate and take the shape of towers (the nanorods in Figure 4 are from mode I). Nanorods that develop from mode I are ~ 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 [41]. Of particular technological interest is nanorod growth in mode II. In mode II, a nonwetting substrate results in well-separated islands growth (Figure 6, right). At high glancing angles, meaning a majority of adatom flux lands on the top of the island or the developing nucleus, the resulting nanorods may be as small as ~ 10 nm in diameter, taking the shape of a cylinder or an inverted tower as they grow taller (Figures 5 and 7).

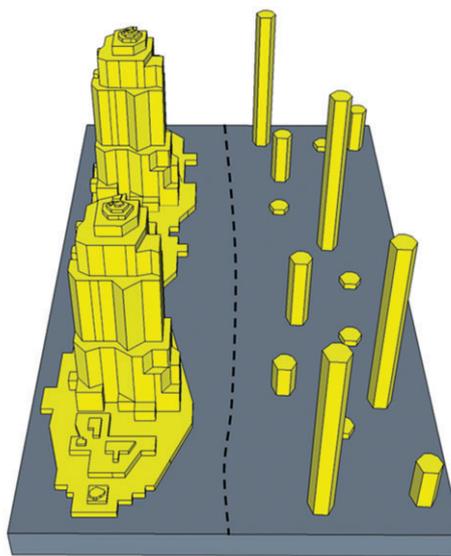


Figure 6 Growth modes of nanorods showing a wetting substrate (left) and nonwetting substrate (right).

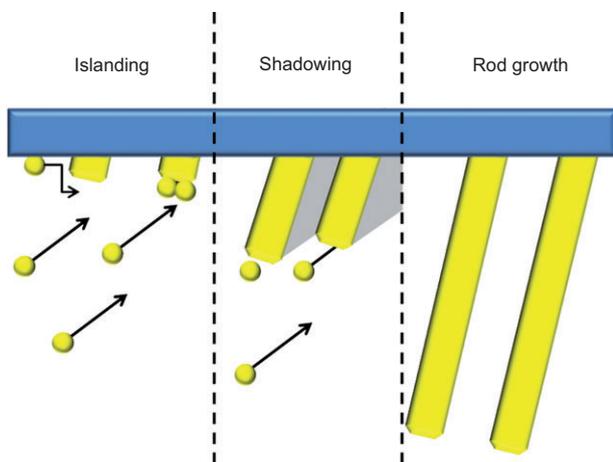


Figure 7 Evolution of a small nanorod from a nonwetting substrate using GLAD in PVD.

From left to right, a nonwetting substrate generates islands creating shadowed regions (in gray) and giving rise to rod development. In three dimensions, the entire substrate is not shadowed, but under nonwetting conditions, atoms that reach the substrate quickly diffuse to the sides of nanorods.

In this mode, multiple-layer surface steps are dominant, which necessitates the recent development that multiple-layer surface steps are indeed kinetically stable [42]. 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 [7]. At a given incidence angle, as the deposition rate or diffusion barrier increase, the diameter of the resulting nanorod decreases, scaling as $L_{\min} \propto (v_{3D}/F)^{1/5}$, here L_{\min} is the minimum diameter of nanorods, v_{3D} is the relevant diffusion barrier of adatoms over multiple-layer steps, and F is the deposition rate. The smallest diameter of the nanorod is reached when the surface diffusion is lowest, that is, surfaces are nearly entirely multiple-layer steps, 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. Because of the extreme nonwetting condition of the substrate, atoms diffuse to the base and sides of the existing small rods.

The technological push to reach nanorods of a small diameter may be realized when the smallest diameter of nanorods, L_{\min} , is combined with an understanding of the minimum spacing between nanorods, L_s . 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 nonwetting 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 [43]. As the deposition rate increases, the minimum diameter of nanorods decreases but the minimum separation decreases even faster. The point where L_{\min} is only marginally less than L_s will result in nanorods of the smallest possible diameter. Under real geometric shadowing conditions, this is on the order of ~ 12 nm for Au [7]. 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 constraint 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_{\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.

By engineering L_s and removing this constraint, the minimum diameter of nanorod has recently been reached. Using the insights gained by the recent theoretical formulation, we have pushed the lower limit of nanorod size. Using a substrate that is nearly completely nonwetting, making L_s much larger than L_{\min} , and using a prototype material with a high three-dimensional diffusion barrier, we have fabricated well-separated Au nanorods as small as 7 nm in diameter [7]. It is likely that diameters on this length scale will spur technological interest and motivate a new direction of research toward engineering nanorods of small diameter using PVD.

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3 Discussion

The respective strengths of solution and physical synthesis methods are complementary, meeting the needs of the full spectrum of technological applications that use small metallic nanorods. The nature of each method introduces inherent limitations, but fortunately, these limitations are not shared by both methods.

Solution-based synthesis of small metallic nanorods has the advantages of high yield, simple methodology, and low equipment overhead, but it also faces significant

scientific challenges, which cause morphology control issues. Compared with physical deposition methods, solution-based synthesis methods require less equipment infrastructure – there is no need for a vacuum environment. For applications that require large yields, whether mass or volume, of small nanorods, the seeded solution approach may be scaled indefinitely in size. On the other end of the spectrum, the same simple methodology allows for small batches of small metallic nanorods to be synthesized in basic educational laboratories. This simple methodology may be attractive, but it is susceptible to the introduction of impurities through atmospheric processing and reagent uncertainty. However, progress may be somewhat slowed due to a lack of scientific insight regarding the mechanisms of rod formation and morphological evolution. Although the interacting chemical agents and processing conditions may be empirically and intuitively optimized, there exists no direct science-guided path between concept and realization for new desirable morphologies.

While working within the advantages and challenges that accompany vacuum processing, the synergy between scientific understanding and fabrication knowledge makes small nanorods from PVD ideal candidates for use in many technological applications. The necessary high-vacuum processing conditions make high purity, both material and crystal, achievable. With the goal of tuning for technological applications, the aspect ratio can be directly controlled, as the process is physical; nanorod length is a function of deposited mass. By engineering L_s , through the substrate wetting condition and deposition rate, and L_{min} , through materials selection or modification of diffusion barriers through the addition of surfactants [44], the diameter and spacing of nanorods can be directly controlled. Further, a major strength of PVD nanorods, when compared with solution synthesis, is that they are fabricated attached and oriented to a substrate, ideal for applications such as sensing and photonics [28]. When applicable, PVD nanorods may be removed from substrate for applications requiring a suspension. PVD faces the challenge of the necessity for a high vacuum and the accompanying equipment costs, which may increase with scaling.

4 Summary

In this review, we have presented the technological importance, fabrication knowledge, and scientific

understanding of small metallic nanorods. On the length scale of ~100 nm, metallic nanorods have the advantage of increased surface area over their dense film counterparts. When this length scale is decreased to ~10 nm, size effects emerge and functionalities that are not present in dense films result. Because of these functionalities, technologists have used small metallic nanorods in applications such as low-temperature wafer bonding, SERS, and cancer cell sequestration, among others. Within metallic materials, Au is chosen as the prototype due to its important technological applications, breadth of fabrication knowledge, and strong representation in the literature.

Two distinct methods of fabricating small metallic nanorods are well represented, although with different levels of scientific understanding and fabrication knowledge, in the literature: solution-based and physical processing. Solution-based synthesis methods, electrochemical and seeded synthesis, are low-cost means of producing large amounts of small metallic nanorods but face challenges of morphological control and immature scientific understanding. When compared with solution synthesis, PVD fabrication of small metallic nanorods is qualitatively equal in fabrication knowledge but is more mature in scientific understanding. Small nanorods are grown using GLAD on nonwetting substrates, and a small diameter is maintained through the dominance of multiple-layer surface steps. A framework of nanorod growth has recently guided the fabrication of well-separated small Au nanorods of ~10 nm in diameter. Using the predictability and controllability of physical processing in synergy with science-based design, investigation into small nanorods of technologically relevant materials and geometries may follow the first 10-nm Au nanorods.

Regardless of the synthesis method, small metallic nanorods have demonstrated technological importance in a wide range of applications, such as wafer bonding, SERS, and cancer therapy. Surely, with the progression of scientific understanding of solution-based processing and through science-guided fabrication using PVD, reaching for smaller shows promise to make a big impact.

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