IOP PUBLISHING NANOTECHNOLOGY

Nanotechnology **20** (2009) 085613 (5pp) doi:10.1088/0957-4484/20/8/085613

Gold bead-strings in silica nanowires: a simple diffusion model

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Received 12 November 2008, in final form 18 December 2008
Published 3 February 2009
Online at stacks.iop.org/Nano/20/085613

Abstract

Silica nanowires grown from gold droplets deposited on the surface of a silicon crystal sometimes develop within them a regular series of gold beads distributed along the wire axis in what is often called either a bead-string or a pea-pod structure. This is generally attributed to a 'Rayleigh instability' driven by the surface free energy of the included gold core. Here a new model is proposed in which quasi-conical gold inclusions are developed by the diffusion-limited growth process and are subsequently modified to spherical shape by another diffusion process that is driven by surface free energy. This model provides a possible basis for detailed numerical calculations.

1. Introduction

Amorphous silica nanowires can be grown on a crystalline silicon substrate by first depositing a thin metal film on its surface and then heating the system to elevated temperatures (>1000 °C) in an inert ambient (e.g. N_2 or Ar) containing trace amounts (3–5 ppm) of oxygen [1, 2]. During heating the metal film breaks up into nanometer-scale islands and reacts with the silicon substrate to form molten droplets of gold–silicon eutectic composition. These droplets absorb gas-phase reactants in the form of O_2 and SiO, produced by reaction between the O_2 and the Si wafer, until they become supersaturated, at which point solid precipitates of secondary phases (e.g. Si or SiO_2) can form within the droplet. These precipitates then grow and extend from the droplets to form nanowires. During subsequent growth the liquid eutectic droplet simply acts as a preferential absorption site for the gas-phase reactants and as a rapid transport medium for diffusion to the growing nanowire. The diameter of the nanowires depends upon the size of the gold droplets, which is itself influenced by the thickness of the original gold film.

In the process described above, the gold-rich droplet remains in contact with the substrate, at the base of the growing nanowire. However, in an alternative process, where a secondary source of SiO vapor is provided above the metal layer by covering it with a second silicon wafer, as in figure 1, the gold-rich particles remain at the tip of the growing nanowire. Moreover, while the geometry of the nanowire is normally uniform, under some conditions it develops a strange pea-pod structure with a string of nano-sized gold beads distributed with nearly regular spacing along its axis, as shown in figures 2(a) and (b). Typical annealing conditions for the growth of such a structure are 60 min at 1100 °C. Growth of similar structures under somewhat different conditions has reported by Wu *et al* [3] and more recently by Hu *et al* [4]. The prevalence of such bead-strings in the silica nanowires depends critically upon growth conditions and may vary between about 1% and 80% even on a single wafer. This variation is understandable for the growth regime shown in figure 1, since oxygen diffuses in from the sides of the space between the wafers. The pea-pod structure is not unique to gold but has also been observed for nickel on silicon.

Exactly how such a pea-pod develops is at present a matter for conjecture, the generally favored view being that a cylindrical core of liquid gold is for some reason included in the growing wire, and that this core then develops a 'Rayleigh instability' [5], such as that experienced by a uniform stream of flowing liquid, and is converted to a stream of uniform droplets by the process of minimization of surface free energy. The separation of the nano-beads is indeed close to that which would be expected from this process, namely about two to three times the original core diameter.

While this explanation is possibly true, it raises questions when examined in more detail because it requires first the development of a long uniform cylindrical gold core within the wire. In an early paper on the subject [3], however, the authors state that 'the driving force $\cdots$ might occur from periodic

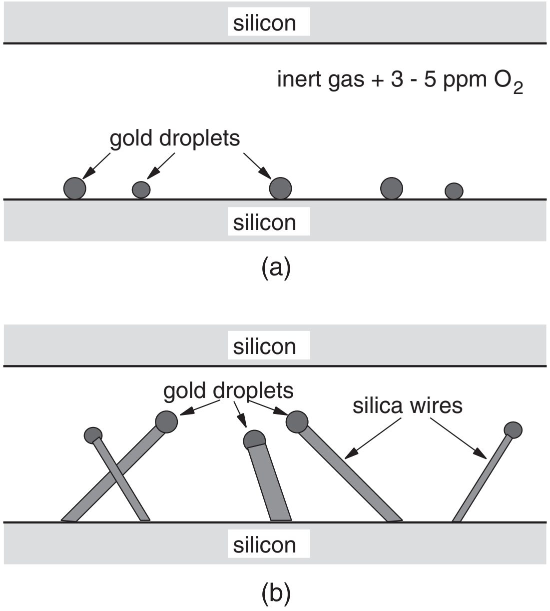


Figure 1. Growth technique for the nanowires described here. (a) The space between two silicon wafers is filled with an inert gas with a small concentration of oxygen, and a thin gold film deposited on one of these wafers has converted to droplets. (b) With annealing at higher temperatures, silica nanowires grow with the gold droplets at their tips.

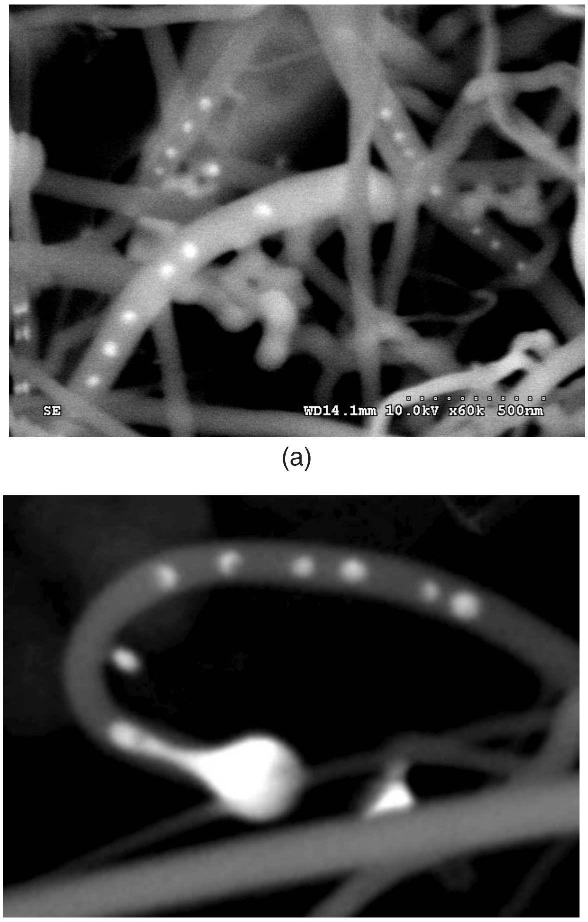
instabilities in the growth process' which is very different. It is the purpose of the present paper, therefore, to propose such an instability mechanism that is governed by simple diffusion and that generates isolated beads in uniform succession as the growth proceeds.

2. The diffusion mechanism

While it would be possible in principle to carry out a numerical solution of the diffusion equation for the whole system, including diffusion of SiO and O_2 in the surrounding gas, its dissolution in the gold droplet and conversion to SiO_2, diffusion through the gold to the growing interface with the nanowire, and deposition there, this is very complicated and, even if successful, would not reveal much about the underlying physical mechanisms. In this short paper, therefore, a series of simple approximations will be adopted to describe in a semi-quantitative manner the various stages involved in the growth of gold beads within the nanowire. First, however, let us examine the possibility of a detailed solution, because some of the results will be used in the later simple theory.

Taking the center of the gold droplet as origin, and the concentration of SiO_2 in the system to be $\psi(r, \theta, \phi)$ with $r = 0$ at the center of the gold droplet, and $\theta = 0$ along the axis of symmetry towards the growing wire, as shown in figure 3(a), the steady-state equation to be solved within the droplet is $\nabla^2\psi = 0$. The general solution to this equation in spherical polar coordinates (r, θ, ϕ) can be shown [6] to have the form

$$\psi(r, \theta, \phi) = \sum_{n,m=0}^{\infty} A_{nm} r^{-1-n} Y_n^m(\theta, \phi) + \sum_{n,m=0}^{\infty} B_{nm} r^n Y_n^m(\theta, \phi) \qquad (1)$$



(a)

(b)

Figure 2. (a) Typical nearly regular growth of gold bead-strings within silica nanowires. The width of the image is 2 μm. (b) Here the gold droplet at the end of the wire is clearly visible and the geometry of the growing gold core near the droplet supports the model described in the present paper.

where A_{nm} and B_{nm} are constants and $Y_n^m(\theta, \phi)$ is a spherical harmonic function. The situation is somewhat simpler than this here because it is axially symmetric, so that only functions with $m = 0$ need be considered. If this solution, denoted by ψ_1, is taken to apply within the gold droplet, then a similar solution ψ_2 with different coefficients $A'_{n,0}$ and $B'_{n,0}$ will apply in the surrounding region out to infinity. The necessary condition that ψ_1 remains finite within the gold droplet requires that $A_{n,0} = 0$ for all n, while the condition that $\psi(\infty)$ has a constant value ψ_∞ requires that $B'_{0,0} = \psi_\infty$ and $B'_{n,0} = 0$ for $n > 0$. The matching conditions on the gold surface at $r = R$ are that

$$\psi_1(R, \theta) = \beta\psi_2(R, \theta) \qquad \text{for } \theta > \theta_0 \qquad (2)$$

where the numerical factor β is determined by the free energy of dissolution of silica in gold, and

$$\left.\frac{\partial\psi_1}{\partial r}\right|_{r=R,\theta>\theta_0} = \gamma \left.\frac{\partial\psi_2}{\partial r}\right|_{r=R,\theta>\theta_0} \qquad (3)$$

where γ is the ratio of diffusion coefficients for the active silica in gold and in the vapor. There is a further boundary condition

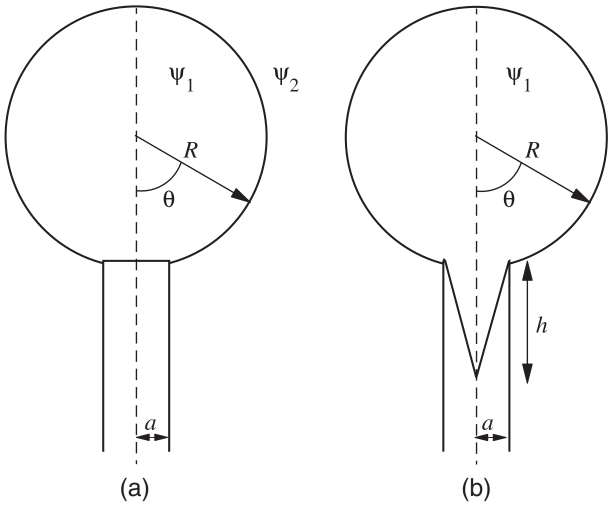


Figure 3. (a) Geometry of the growing wire at an early stage; (b) geometry at a later stage.

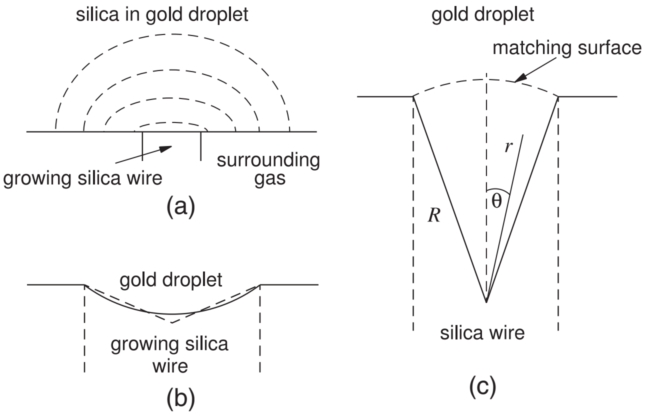


Figure 4. (a) Simple initial approximation with a growing disc, representing the interface between the silica wire and the gold droplet, on an inert flat plane. Broken curves are contours of equal ψ. (b) Diffusive growth leads to a central depression that can be approximated as conical. (c) Coordinates for analysis of conical growth. The solution inside the cone must be matched to the solution in the droplet on the matching surface.

on the exposed cylindrical surface of the wire. Physically, this surface is inert so that the gradient of ψ_2 normal to the surface must be zero.

The first configuration, shown in figure 3(a), represents the initial stage of wire growth when the interface between the gold droplet and the growing silica wire is taken to be planar. The second configuration, shown in figure 3(b), represents a later stage of growth with a conical interface, which we will return to consider later. Unfortunately even this initial situation is virtually impossible to solve analytically [6], while the situation shown in figure 3(b) could only be solved numerically, and even this would be difficult, so we shall resort to a much simpler approximate approach.

First consider the situation shown in figure 4(a), which is meant as an approximation to the initial stage of wire growth shown in figure 3(a). Instead of the complex geometry and physics of a liquid gold droplet surrounded by a source vapor, we imagine the radius of the gold droplet to be infinitely large compared with the wire diameter, so that the gold can be taken to occupy the whole upper half-plane. The solute concentration ψ is taken to be the saturation value at the surface of the growing disc and to increase to a constant supersaturation value at infinity. The vapor surrounding the gold droplet should then occupy the lower half-plane with the boundary conditions (2) and (3) applying along the boundary plane. Solution even of this problem is very difficult so, for simplicity again, we assume that most diffusion takes place within the gold droplet rather than across the extended gold/vapor interface, and replace these boundary conditions by the simple one $\hat{\mathbf{n}} \cdot \nabla\psi = 0$ on the surrounding surface of the plane, where $\hat{\mathbf{n}}$ is a unit vector normal to that plane. We then want to solve the steady-state diffusion equation $\nabla^2\psi = 0$ within the gold region above the plane and subject to these boundary conditions, the rate of growth of the disc-like end of the wire at distance r from the origin being proportional to $\hat{\mathbf{n}} \cdot \nabla\psi$ at that point.

The solution for this simplified case is not particularly interesting but it reveals one important feature which can be appreciated by noting that the surfaces of constant ψ are almost planar and parallel to the growing disc surface at small distances but become hemispherical at large distances, with oblate hemispheroids (semi-ellipses in cross-section) being a good approximation at intervening distances, as illustrated in figure 4(a). Allowing a small normal gradient at the gold/vapor interface would not make a great deal of difference. The important result is that the normal concentration gradient $\hat{\mathbf{n}} \cdot \nabla\psi$ across the disc will be smaller near its center than near its edge, so that the disc center will grow more slowly, leading to a concave dish-like shape. For reasons that will become apparent, it is simplest from a computational point of view to assume that this dish shape can be approximated as a shallow conical depression, and it will be shown that such a model leads to a solution that develops to the deeper conical structure shown in figures 4(b) and (c).

Suppose now that we have a conical depression in a plane, as shown in figure 4(c). Within the conical volume the appropriate coordinate system to use is spherical polar (r, θ, ϕ), where these symbols now refer to different quantities from those in figure 3 because the coordinate origin has been moved. Since the system is assumed to have axial symmetry, the coordinate ϕ is actually irrelevant. In such a coordinate system, the equation $\nabla^2\psi = 0$ still applies, and its solution is given by equation (1) with $m = 0$ because of the axial symmetry. Because the apex of the cone is included in the region, this solution must be simplified by requiring that $A_{nm} = 0$ to avoid an infinity at the origin, and can be rewritten as

$$\psi(r, \theta, \phi) = \sum_{n=0}^{\infty} B_n r^n P_n(\cos\theta), \tag{4}$$

where $P_n(\cos\theta)$ is a Legendre polynomial. An examination of the behavior of Legendre polynomials or the equivalent Legendre functions [7] shows that for $\theta < \theta_n$ where θ_n is the first zero of P_n, they behave very nearly as

$$P_n(\cos\theta) \approx \cos\left(\frac{\pi\theta}{2\theta_n}\right) \tag{5}$$

Table 1. Angle θ_n for first zero of $P_n(\cos\theta)$.

n	1	2	3	4	6	10
θ_n	90°	54°	37°	30°	21°	13°

the angle θ_n of the first zero of P_n being shown as a function of n in table 1.

These results can be used to describe, to good approximation, the diffusion field within an infinite cone of semi-angle θ_n as

$$\psi(r,\theta) = \psi_0 + B_n r^n \cos\left(\frac{\pi\theta}{2\theta_n}\right), \tag{6}$$

where ψ_0 is the saturation concentration of silica in gold and B_n is a constant. This expression can be extended to apply to non-integral values of n by simply treating n as a continuous variable and interpolating between the θ_n values given in table 1.

In this simplified model we do not, of course, have an infinite cone to consider but rather one of finite length. If, however, we are able to make the approximation that the surrounding surfaces of equal concentration $\psi(r,\theta)$ for $r > R$, where R is the oblique depth of the cone, join smoothly onto those described by equation (6) for $r < R$ at the surface $r = R$, as shown in figure 4(c), then the simple solution (6) is applicable within the cone. (This fitting of solutions is by no means a simple matter, as has been demonstrated by Morse and Feshbach [6] for calculation of the potential inside and outside a spherical shell with a hole in it.) For our present purposes the value of the constant B does not matter since we are concerned with geometry rather than overall growth rates. Consider the general situation in which $\theta \approx \theta_n$, so that the concentration within the cone behaves as $r^n \cos(\pi\theta/2\theta_n)$, then the normal gradient above the growing conical surface at $\theta = \theta_n$ is simply proportional to r^{n-1}, and the surface advances in a normal direction at a rate proportional to this gradient.

It has already been shown in the discussion accompanying figure 4 that this description does not work well in the flat-plane limit with $\theta_n = 90°$ and $n = 1$, but we already know that this configuration develops a concave structure as in figures 4(b) or 5(a), and soon the conical approximation will be appropriate with $n \approx 2$ and $\theta \approx \theta_1 \approx 55°$ as in figures 5(b) and (c). Near this stage of evolution, the concentration gradient at the conical walls, and therefore the normal growth rate, will be proportional to r, which implies that a conical shape will be maintained but the cone semi-angle will decrease. Since the diameter of the cone mouth is fixed, this means that the cone, with its enclosed gold liquid, will extend increasingly far along the axis of the growing wire, as shown in figure 5(d).

By extending the approximation, the cone will continue to narrow until its semi-angle approaches $\theta_3 \approx 37°$ with $n \approx 3$. The growth rate now varies as $r^{n-1} \approx r^2$ so that the conical shape will no longer be maintained but the walls will begin to curve in near the mouth, as shown in figure 5(e). The micrograph in figure 2(b) supports this model, since the configuration of the gold core near the droplet closely resembles that shown evolving in figure 5(e). Examination of a large number of micrographs of wires with enclosed bead-strings shows that most of them have a slightly conical extension from the gold bead, though not often as pronounced as in the figure, which was caught at a critical stage of its evolution. This closing near the mouth of the cone will continue as in 5(f) until the mouth is completely closed as in 5(g). A new stage of the process then begins at two levels. Within the enclosed gold droplet, diffusion will take place in order to reduce the surface area, and this will lead to a near-ellipsoidal shape for the droplet as in 5(h), and ultimately to a spherical shape. At the same time, diffusion processes at the interface with the main gold reservoir will reconstruct the shape of the surface so that it matches the original configuration 5(a). The whole process of growth of enclosed droplets to form a bead-string will then repeat, with the beads located at uniform spacing along the axis of the growing wire.

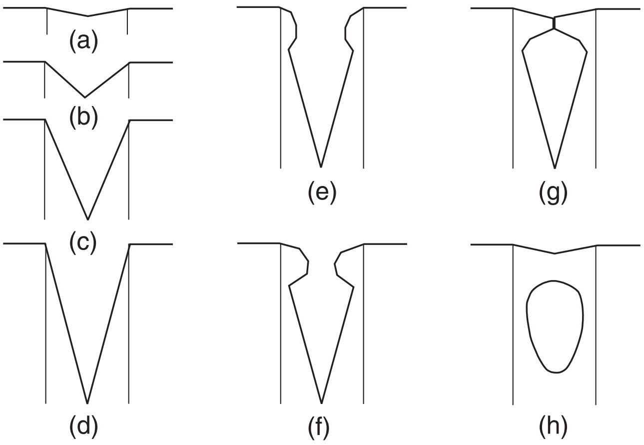


Figure 5. Successive stages in the evolution of a bead within a nanowire. When the stage (h) has been reached, the process repeats from (a).

It is difficult to provide an accurate estimate of the spacing between beads generated in this way, since this depends in detail upon the growth rate of the various stages shown in figure 5, and particularly of the closure stages 5(e) and (f), but a limiting approximation can be attempted. Rapid closure of the cone mouth, as in figure 5(f), begins when $n \approx 3$ and the cone angle is less than about 37°. If the closure were to proceed infinitely rapidly then the ratio of radius to length of the cone would be about $\tan 37° \approx 0.75$. When this enclosed cone changes by diffusion to a sphere, the radius will be about half the cone length. Such an infinitely rapid closure will therefore lead to a string of beads with diameter just equal to their separation. Infinitely rapid closure is, of course, an extreme limit, but it is difficult to estimate just how much growth will occur during the closure stages of figures 5(e)–(g). The conclusion is that the spacing of the beads should be at least enough to separate them, and probably a good deal greater than this and perhaps close to the experimental value which is a little more than three times the diameter.

3. Beads, solid wires, or gold cores?

There is, however, a question raised by the analysis, and this is to explain why it is that most wires grow as a solid without an included nano-bead string. Diffusion processes again appear to provide an answer to this question. In the theoretical description outlined above, the only diffusion process considered for most of the growth cycle is that involved in deposition of silica from the gold onto the walls of the growing conical depression. It is only after closure of the mouth of this cone, as in figure 5(g) that another diffusion process is invoked to convert the sealed cone into a nearly spherical bead. This second diffusion process is driven by the need to minimize total free energy, and this is accomplished by reducing the area of the bounding conical surface towards a sphere. It has been assumed that this process, which depends upon surface free energy as its driving influence, proceeds at a rate that is small compared with the growth rate of the conical surfaces, which has the concentration of silica in the gold droplet as its driving influence. This in turn is controlled by the temperature and concentration of SiO in the surrounding gas. There is thus a competition between these two processes. If the external conditions are set so that the wire is growing very rapidly, then the concentration-controlled mechanism will prevail and the nanowire will develop a narrow conical interface with the gold and this will then collapse into a string of beads, as previously discussed. If, however, the external conditions are set in such a way that wire growth is slow, then geometric changes driven by the diffusion effects of surface free energy will prevail and the growth process will stabilize at the stage indicated in figure 5(b), with a dish-like depression at the interface with the gold droplet. There will then be no development of a conical depression and no mechanism for the generation of a bead-string within the wire.

The analysis detailed above raises questions about the possibility that formation of bead-strings might result from a Rayleigh instability in a liquid gold cylindrical core included in the nanowire during the growth process. This follows from the diffusion equation and its solution (6) for a conical inclusion with semi-angle θ. For a cylindrical inclusion, the semi-angle θ_n is essentially zero, and from table 1 this implies that n is very large, leading in turn to the conclusion that the growth of the shell surrounding the core, which varies as r^{n-1} in our simple model, will be concentrated at the aperture where the growing wire meets the gold droplet. This will cause the cylinder to close at this end so that, viewed in another way, it appears to preclude the development of a cylindrical core with length significantly greater than its diameter. Such structures can, however, sometimes be observed, as shown in figure 6. The wire as shown is growing to the right in the figure and gradually decreasing in diameter, as also is the gold droplet at its end. The cylindrical gold core thus developed in the early stages of growth and the bead-string at a later stage.

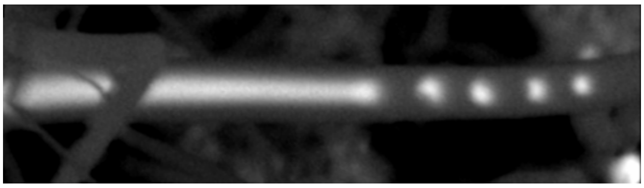


Figure 6. A silica nanowire with a gold core growing upon a silica substrate. The growth direction is towards the right and the wire is capped by a gold bead, which is not included in the image.

The possibility that the cylindrical gold core broke into beads as a result of a Rayleigh instability seems unlikely in this case, since the part of the core to the left in the image has not collapsed to droplets despite its longer time of existence. There are two alternative hypotheses: the first is that growth conditions—temperature, or local supersaturation—changed slightly during the growth process and that this somehow modified the core growth conditions, while the second is that this change may be the result of a decrease in the ratio of terminal gold droplet diameter to wire diameter as gold is removed from the droplet and deposited in the core. The points raised in the previous paragraph, however, appear to rule out development of a simple cylindrical gold core, and an explanation for the formation of such cores must be sought, since they are certainly observed under some conditions. The growth theory developed in the present paper would require great refinement and numerical evaluation before it could approach an analysis of this matter.

4. Conclusion

This paper has presented what can be claimed at best to be a semi-quantitative model for the formation of gold bead-strings within silica nanowires grown by the technique described in section 1. This bead formation process has the conceptual attraction that it does not depend upon instabilities developed in a considerable length of cylindrical liquid gold core, as is the case with models based upon the Rayleigh instability, but proposes instead a simple diffusion mechanism that produces nano-beads individually but in regular succession. It is hoped that this proposal may serve as a basis for a detailed numerical solution of this interesting problem.

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