

Semiconductor Nanocluster Growth within Polymer Films

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Models for semiconductor nanocluster growth within polymer films are presented. The models assume a diffusion–aggregation mechanism of nanocluster growth, where the semiconductor molecules aggregate to form primary particles, which then aggregate, giving larger particles. Reaction–diffusion and equilibrium models based on scaling analyses have been developed. Both of the models qualitatively explain the experimentally observed effects of various processing parameters on the final nanocluster size. The models also make quantitative predictions of the variation in the final nanocluster size on varying these processing parameters. Experiments are proposed to determine whether the two models represent an accurate picture of nanocluster growth. Such models of nanocluster growth may enable a rational exploration of parameter space and guide experimentalists aiming to synthesize monodisperse semiconductor nanoclusters in polymer films.

1. Introduction

There is a fundamental interest in understanding the size-dependent properties of nanoclusters. The interest in these materials is also driven by a number of applications where the utilization of nanoclusters is expected to result in improved performance. Since any experimental investigation of the properties or device applications of nanoclusters requires a source of nanoclusters, the synthesis of nanoclusters is an important field of research.

Semiconductor nanoclusters (particles with diameters between 1 and 10 nm) have been the subject of numerous investigations in recent years. The size-dependent properties of semiconductor nanoclusters make it important to control the particle size distribution. The quality of the particles synthesized (crystallinity/surface passivation/polydispersity) determines both the devices in which the nanoclusters can be used and the size-dependent properties that can be studied. Numerous methods have been developed to synthesize nanoclusters. There are two principal strategies used for the condensed-phase synthesis of monodisperse semiconductor nanoclusters. The best current method was developed by Murray et al.¹ and later modified by Bowen Katari et al.² This method draws on diffusion models developed by La Mer et al.,³ who showed that the production of a series of monodisperse colloids depends on a temporally discrete nucleation event followed by slow growth. The nucleation is achieved by starting out with a supersaturated solution of the cluster-forming species. The depletion of species during nucleation can prevent further nucleation and result in controlled growth. Murray et al.¹ achieved a temporally discrete nucleation event by injecting organometallic reagents into a hot coordinating solvent. Pyrolysis of the reagents

resulted in a discrete nucleation event. Controlled growth, followed by size-selective precipitation, resulted in samples with an extremely narrow size distribution (<5% rms in diameter).

An alternative attractive strategy involves the sequestering of semiconductor precursors within confined domains, followed by uncontrolled growth, leading to one semiconductor nanoparticle in each confined domain. If each confined domain contains the same number of precursors, this strategy will lead to monodisperse nanoclusters. This principle motivates nanoparticle synthesis in reverse micelles,⁴ vesicles,⁵ zeolites,⁶ and block copolymer microdomains.^{8–20,47} There are problems associated

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with each of these methods. Micelles in solution are dynamic entities characterized by an exchange of both surfactant units and micellar contents.⁷ This exchange is not ideal for the synthesis of highly monodisperse nanoparticles. While zeolite pores can be used to synthesize fairly uniform particles, one cannot make particles of arbitrary sizes.

We have been working on the synthesis of semiconductor nanoclusters with controllable sizes and narrow size distributions within the microphase-separated domains of block copolymers synthesized by ring-opening metathesis polymerization. Previously, semiconductor nanoclusters were synthesized within microphase-separated diblock copolymer films by a scheme in which metal complexes were attached to one block of the copolymer before microdomain formation.^{8–12} An alternative approach involves the selective sequestering of metals into the preformed microdomains of a block copolymer film.^{13,14,47} Once loaded, these metal-containing domains serve as localized reaction sites for cluster synthesis, for example via reaction with H₂S to form metal sulfides.^{13,14} Other groups have also used the block copolymer approach to synthesize nanoclusters.^{15–20}

The block copolymer approach has several advantages. Living polymerization techniques such as anionic polymerization or ring-opening metathesis polymerization can be used to synthesize block copolymers with low polydispersities. The uniformity of the microdomain sizes of block copolymers is much greater than the uniformity of their molecular weights,²¹ implying that the packing of molecules in the domain counteracts the molecular weight distribution. The problem of micellar exchange is non-existent in block copolymer films and is suppressed in block copolymer micelles.²⁰ In the case of metal nanoparticles, the synthesis of one nanoparticle per micro-

domain has been reported.^{17,22} The primary drawback of the block copolymer approach is that it usually produces more than one semiconductor nanoparticle per block copolymer microdomain. In such situations, since the uniformity of the microdomains has not been used, the particle size distribution is relatively broad.

A number of processing parameters can be used to change the size of the nanoclusters produced within the block copolymer microdomains. In the case of the synthesis of metal sulfide nanoclusters from metal carboxylate precursors in microphase-separated block copolymer films,^{10,14} it was found that performing the reaction with H₂S at higher temperature or in the presence of coordinating solvents can result in larger nanoclusters. It is important to understand how these processing parameters influence the nanocluster growth process. Understanding the growth process and why the growth stops at a particular nanocluster size is essential for developing a rational synthesis of monodisperse semiconductor nanoclusters within block copolymer microdomains.

2. Aggregative Growth Mechanism

The nanocluster growth starts with the reaction of the metal carboxylate groups in the block copolymer microdomains with H₂S-producing metal sulfide (MS) molecules. This reaction is assumed to be very rapid. This assumption is consistent with previous tests of the reaction of H₂S with organometallic monomers¹⁰ and with the fast reaction of H₂S with aqueous metal carboxylates. Within each domain, cluster formation therefore occurs from a homogeneous solution of MS molecules in the polymer.¹⁰ A diffusion–aggregation mechanism of nanocluster growth is assumed in this work, where MS molecules aggregate to form primary particles, which in turn aggregate, giving larger particles.

Aggregative growth has been invoked in a number of other instances. On the basis of twinning structures observed in gold sols prepared by the reduction of auric acid by citrate, Uyeda et al.²³ suggested that the final gold sols are formed by agglomeration of small primary particles. Zukoski et al.²⁴ have noted that a number of precipitation reactions appear to follow a path where primary particles are formed and remain in solution for an appreciable period of time prior to aggregating to form the final precipitate. Murphy et al.²⁵ demonstrated this aggregation of primary particles to be the mechanism of growth for iron oxide particles under some conditions. A number of particles formed in the precipitation studies of Matijevic et al.^{26–28} are spherical agglomerates of crystallites. Bogush et al.²⁹ have developed an aggregative growth model for the formation of uniform silica particles from silicon alkoxides. Assuming that particles grow solely by aggregation, the model provided good estimates of final particle size distribution parameters from silicon alkoxide reaction rates.

Alternate mechanisms of nanocluster growth within the polymer film are possible, including a nucleation and growth mechanism. However, there is evidence that aggregative growth does occur in these films. In one experiment, where a film containing small PbS nanoparticles (yellow) was exposed to vapors of methanol, the film turned orange-red. Since the PbS nanoparticles had already been synthesized prior to the methanol exposure, growth on preformed nuclei cannot explain the increase in nanoparticle size. The increase in particle size can however be explained by the diffusion and aggregation of small PbS nanoparticles.

One must also consider the possibility of growth by Ostwald ripening. There are some situations where

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ripening may well be the dominant growth mechanism. Schneider et al.¹⁹ synthesized PbS nanoclusters within amphiphilic block copolymer micelles composed of polystyrene-poly(4-vinylpyridine) and found that particle growth could be induced by gradually adding small amounts of HCl in diethyl ether. In this case, nanoparticle growth may be occurring by Ostwald ripening, since HCl can dissolve metal sulfide nanoparticles,³⁰ resulting in coarsening of the particles. However, for the most part, nanocluster formation in our experiments occurs in polymer films, not in aqueous or acidic solutions. Free ions in the film will not be well solvated, and the activation energy for Ostwald ripening is expected to be high. The nanoclusters, once synthesized, are extremely stable, and no change in the particle size distribution was observed over a period of several months. Furthermore, growth by Ostwald ripening cannot explain the distribution of nanoparticle diameters within a single domain and the increase in nanoparticle size on carrying out the reaction with H₂S at higher temperatures.

One may think that the nature of the growth mechanism would be apparent by looking at the morphology of the growth product. Aggregative growth may be expected to result in open dendritic structures with characteristic fractal dimensions. Such dendritic structures are expected when the diffusion-limited aggregation model³¹ is applicable. The structure of the agglomerate formed is determined by a competition between the collision rate and the coalescence rate.^{32,33} When collision rates are much faster than coalescence rates, fractal-like structures can be formed. When the coalescence rate is high, coalescence can occur almost on contact and produce larger spherical particles. In the case of small semiconductor nanoclusters, the coalescence rates can be affected by the large melting point depression. For instance, CdS nanoclusters with 24 Å diameters were found to melt at 573 K,³⁴ much below the bulk melting point of 1678 K. The melting point would be even lower for smaller CdS nanoclusters. A similar depression is expected in the melting points of other metal sulfide nanoclusters. The melting point of bulk PbS is 1391 K,⁴⁸ considerably lower than that of bulk CdS. The melting point depression for small clusters can result in facile coalescence and the formation of single-crystalline nanocrystals even by an aggregative growth mechanism. For larger particles though, polycrystallinity may be a result of such a growth process.

The aggregative growth model is assumed to apply in the rest of the discussion. However, such a diffusion-aggregation mechanism does not by itself explain why nanocluster growth stops at a particular size. It is assumed in this work that the nanoclusters are stabilized by interactions between the nanocluster surface and polymer ligands (such as carboxylic acid groups present in the polymer microdomains). The interaction can be considered to be a reversible reaction between the ligand (L) and the cluster surface (Cs), with (#LCs) representing the number of cluster-ligand bonds.



Nanocluster growth stops when (#LCs)_r cluster-ligand bonds are formed and trap the nanoparticle in an energy well. If ΔH is the enthalpy change on the formation of a ligand-cluster bond, an alternate way of stating this constraint is that growth stops when

$$-(\#LCs)_r \Delta H \gg kT \quad (2-2)$$

At the same time, for a nanoparticle of a certain size (with

a specified number of surface atoms) at a certain temperature, there will be an equilibrium number of cluster-ligand bonds (#LCs)_{eq}. If (#LCs)_r > (#LCs)_{eq}, nanoparticle stabilization will not take place, and growth will continue. To explain the stabilization at a particular particle size, two models may be invoked. The first one is a reaction-diffusion model, which implies a competition between a reaction time (time required to form (#LCs)_r cluster-ligand bonds) and a diffusion time (time required for particles to collide and coalesce). The second possible model is an equilibrium model, which would be valid if the cluster-ligand reaction is fast but if (#LCs)_r is initially greater than (#LCs)_{eq}. In this case, growth will proceed until the nanoparticle reaches a size for which (#LCs)_r ≤ (#LCs)_{eq}. Since both of these models involve particle diffusion in polymer films, the next section discusses diffusion in polymer matrixes. This section is followed by a discussion of the two models. The models are based on a simple scaling analysis which nevertheless provides valuable insights into the growth process.

3. Diffusion in Polymer Matrixes

Diffusion in polymer matrixes has been an active area of research,³⁵⁻⁴² with applications in areas such as controlled drug delivery and size-exclusion chromatography. The diffusion of sufficiently large probe molecules in polymer films may be coupled to fundamental chain relaxations,³⁵ such as those associated with cooperative segmental motions occurring near the glass transition temperature *T_g*. The diffusivity *D* of a sphere is usually described by the Stokes-Einstein relation

$$D = \frac{kT}{6\pi\eta R} \quad (3-1)$$

where *T* is the temperature, *R* is the sphere radius, and *η* is the zero-shear-rate viscosity of the medium in which the sphere is suspended.⁴² This relation assumes that the medium can be treated as a continuum on the length scale of *R*. While this relation is valid for non-interacting spheres in a small-molecule solvent, its applicability in polymer solutions or polymer films is questionable. Nevertheless, particles in polymer films will undergo Brownian diffusion and will experience viscous forces associated with the polymer. The parameter *η* in eq 3-1 may be considered to be the effective viscosity experienced by the particle. However, since the motion of large particles will involve cooperative segmental motions of the polymer, the polymer viscosity is a reasonable first guess for the viscosity of the medium. The variation of the polymer viscosity with temperature can be determined using the WLF equation⁴³

$$\log\left(\frac{\eta(T)}{\eta(T_g)}\right) = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (3-2)$$

where *C*₁ and *C*₂ are constants and *T_g* is the glass transition temperature of the polymer. The variation in the diffusivity of the particle with temperature can be determined using eqs 3-1 and 3-2. The diffusion of metal particles in polymer films has been studied.^{44,45} Shull et al.⁴⁵ measured diffusion coefficients for ~150 Å gold particles within poly(2-vinylpyridine) films. The diffusion of the gold particles was found to be coupled to the bulk viscosity of the polymer.

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4. Nanocluster Growth Models

The above discussion illustrates that both particle diffusion in films and the aggregative growth of colloidal particles have been observed. These phenomena can be combined to develop the nanocluster growth models. Relationships between particle size and processing conditions will be derived for the special case of particles growing in a spherical microdomain of radius R_d . The scaling of the final particle radius with temperature and the presence of coordinating solvents are however generally applicable for any copolymer morphology.

At a particular point in the growth process, let the microdomain contain N particles of radius R_p . The particle diffusivity D is related to the particle radius and temperature by the Stokes–Einstein relation 3-1. R_f is the radius of the final particle that would be formed if all of the particles in the microdomain aggregated to give one particle. K is the equilibrium constant for the reversible reaction 2-1 between the ligands and the cluster surface, and k_f and k_r are the rates of the forward and reverse reactions, respectively.

4.1. Reaction–Diffusion Model. Nanocluster growth is governed by a competition between a diffusion time τ_D and a reaction time τ_R . Growth stops for $\tau_D \gg \tau_R$, or when the Damkohler number $Da \gg 1$ ($Da = \tau_D/\tau_R$). The diffusion time can be estimated as

$$\tau_D \approx \frac{L^2}{D} \quad (4-1)$$

where L is the mean half-separation between nanoparticles. Recalling that R_d is the radius of a spherical microdomain, R_p is the particle radius at a given point in the growth process, and R_f is the radius of the final single particle in the microdomain, we have

$$L \approx \frac{\beta R_d}{1/N^{1/3}} - R_p = R_p \left(\frac{\beta R_d}{R_f} - 1 \right) \quad (4-2)$$

using

$$NR_p^3 = R_f^3 \quad (4-3)$$

where β , whose value is close to 1, is related to the assumed packing of the particles within the domain. The expression in parentheses in eq 4-2 is related to the volume fraction of particles in the domain. Combining eqs 4-1 and 4-2, we get

$$\tau_D \approx \frac{R_p^2}{D} \left(\frac{\beta}{\phi^{1/3}} - 1 \right)^2 \propto \frac{R_p^2}{D} \quad (4-4)$$

where the proportionality holds for cases where the volume fraction of particles in the domain is a constant, as would be the case in determining the effect of various processing conditions on the final particle size reached within a given domain.

The diffusion time can be alternately considered to be the characteristic time for doublet formation during Brownian flocculation.⁴⁶ While the exact form of the expression is slightly different, the scaling of the characteristic time with R_p and D is identical to that in eq 4-4. It is interesting to determine the order of magnitude estimates of the diffusivities of PbS nanoparticles during nanocluster growth in block copolymer films. During a typical PbS nanocluster growth experiment at room temperature, the absorption edge was found to shift from 450 to 550 Å over a 45 min interval. This shift could be

considered to arise from the diffusion and aggregation of two particles approximately 10 Å in diameter by diffusing over a distance of ~ 10 Å. Equation 4-1 gives us a diffusivity in this case of $\sim 3.7 \times 10^{-18}$ cm²/s. Shull et al.⁴⁵ measured diffusivities between 10^{-15} and 10^{-16} cm²/s for 150 Å diameter gold particles in poly(2-vinylpyridine) at ~ 140 °C. Although their particles were much larger, their temperature of measurement was considerably greater than the glass transition temperature (104 °C)⁴⁹ of poly(2-vinylpyridine). The monomer composing the minor block of our block copolymer was 2-norbornene-5,6-dicarboxylic acid (NORCOOH). Poly(NORCOOH) is glassy at room temperature (the temperature of the measurement). While poly(NORCOOH) will be plasticized by the reacting H₂S, given the low temperature of the reaction, the order of magnitude estimate of the diffusivity is fairly reasonable.

The characteristic reaction time τ_R can be considered to be given by

$$\tau_R \approx \frac{(\#LCs)_r}{\left. \frac{d(\#LCs)}{dt} \right|_{t=0}} \quad (4-5)$$

where $(\#LCs)$ is the number of ligand–cluster bonds per nanoparticle. As ligand–cluster bonds form, the rate of new bond formation will in general decrease with time, but eq 4-5 works well as an order of magnitude scaling estimate.

In general the reaction rate expression in the denominator depends on the rates of both the forward and the reverse reactions. However, if the rate of the reverse reaction is neglected,

$$\tau_R \approx \frac{(\#LCs)_r}{k_f[L](\#Cs)} \propto \frac{(\#LCs)_r}{k_f[L]R_p^2} \quad (4-6)$$

since $(\#Cs)$, the number of unreacted surface sites per nanoparticle, is initially equal to the total number of surface sites and is therefore directly proportional to the square of the radius of the nanoparticle. In eq 4-6, $[L]$ refers to the number of ligands per unit volume. From eqs 4-4 and 4-6, we get

$$Da \propto \frac{k_f[L]R_p^4}{D(\#LCs)_r} \propto \frac{k_f[L]R_p^5\eta}{T(\#LCs)_r} \quad (4-7)$$

using the Stokes–Einstein relation 3-1.

If the reaction–diffusion model is applicable, nanocluster growth will stop for $Da \gg 1$. The effects of changes in processing conditions may be determined by assuming that the expression on the right-hand side of eq 4-7 remains constant at the point at which nanocluster growth stops. While T appears explicitly in the denominator of the expression for Da , it should have a much greater effect through the temperature dependence of k_f and η . Particularly in the case of polymer films near the glass transition temperature, the changes in viscosity with temperature (given by eq 3-2) should dominate. Expression 4-7 therefore implies that the increase in nanoparticle size on performing the H₂S reaction at higher temperatures is a consequence of the lower viscosity of the polymer. The expression also describes the form of the variation in particle size with temperature, which can be tested by experiments. The increase of cluster size when the reaction is performed in the presence of coordinating solvents can

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also be explained by the resulting decrease in the viscosity of the plasticized polymer and a possible decrease in the rate of the forward reaction due to the competitive binding of the solvent either to the ligand or to the cluster surface or to both.

4.2. Equilibrium Model. This model assumes that although the ligand cluster reaction is fast, nanocluster stabilization is prevented by the fact that the number of required cluster–ligand bonds $(\#LCs)_r$ is greater than the initial equilibrium value $(\#LCs)_{eq}$. Nanocluster growth stops once the particle reaches a size for which $(\#LCs)_r \leq (\#LCs)_{eq}$. Now, the equilibrium constant K is given by

$$K = \frac{[LCs]}{[L][Cs]} \quad (4-8)$$

where the quantities in parentheses refer to the number of species per unit volume. Assuming that the concentration of the ligands in the domain is essentially constant during the growth process,

$$K \propto \frac{[LCs]}{[Cs]} = \frac{(\#LCs)}{(\#Cs)} \propto \frac{(\#LCs)}{R_p^2} \quad (4-9)$$

When nanocluster growth stops, $\#LCs = (\#LCs)_r$, implying that

$$\frac{KR_p^2}{(\#LCs)_r} = \text{constant} \quad (4-10)$$

Now if ΔH is the enthalpy change per ligand–cluster bond, the change in the equilibrium constant with temperature is given by

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4-11)$$

Neglecting the smaller variation in $(\#LCs)_r$ with temperature, eqs 4-10 and 4-11 give

$$\ln\left(\frac{R_{p2}}{R_{p1}}\right) = \frac{\Delta H}{2k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4-12)$$

for the variation of the nanocluster radius with reaction temperature. If this model is applicable, the increase in cluster size with increasing temperature is a result of the weaker interaction between the ligand and the cluster at higher temperatures, as is expected for an exothermic attractive interaction between the cluster and the ligands. The effect of coordinating solvents is to reduce $[L]$ or $(\#Cs)$ by binding to the ligand or the cluster surface.

5. Discussion

Both of the above-mentioned models can qualitatively explain the effect of the various processing parameters on

the final nanocluster size. Particularly in the case of the effect of temperature, both of the models contain an exponentially activated parameter (viscosity in the reaction–diffusion model and the equilibrium constant in the equilibrium model). Careful experiments will have to be designed to determine which of the two models represents the accurate picture of nanocluster growth. One possible experiment involves synthesizing block copolymers where the minor block is a random copolymer of a carboxylic acid containing monomer and an inert monomer which can act as a diluent. By choosing different inert monomers with substantially different homopolymer glass transition temperatures, one can create microdomains with the same ligand concentration but very different viscosities. By synthesizing semiconductor nanoclusters within these different microdomains, one will be able to distinguish between the two competing models of nanocluster growth. For example, one could synthesize two block copolymers having methyltricyclododecene (MTD) as the major block, one with the minor block consisting of a random copolymer of MTD and NORCOOH, and the other one with the minor block consisting of a random copolymer of norbornene and NORCOOH. The compositions of the minor block should be chosen in such a way that the carboxylic acid concentration is identical in the microphase-separated domains of the polymers. If the equilibrium model is applicable, the final nanocluster diameter should be identical in both polymer films, whereas if the reaction–diffusion model is applicable, larger clusters will be produced in the less viscous norbornene–NORCOOH microdomain.

Another possible way of discriminating between the two models is to perform the nanocluster growth for two different metal loadings (i.e. two different volume fractions of particles) within the domain. Decreasing the metal loading should not affect the final particle size for equilibrium-limited growth, whereas it will increase the diffusion time and lead to smaller particles in the case of diffusion-limited growth.

These models of nanocluster growth can serve to guide experimentalists whose objective is to synthesize monodisperse single nanocrystals per block copolymer microdomain. The variables that may be efficiently modified to increase the nanocluster size include temperature, coordinating solvents, and the choice of monomer. The most effective strategy may involve the judicious choice of a monomer or combination of monomers resulting in a lower viscosity and weaker binding to the cluster surface in the microphase-separated domain. A rational exploration of parameter space will enable the synthesis of monodisperse nanoclusters which may then be incorporated into novel devices.

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