

Hollow nanostructures based on the Kirkendall effect: Design and stability considerations

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In nanoscale interdiffusion and reaction, a Kirkendall void in the core of a nanocrystal has been proposed to explain the formation of hollow nanosize particles in recent literature. We present here a simple kinetic analysis of the reaction in nanoparticles, including the effect of the Gibbs–Thomson potential. A general discussion on how to form hollow nanostructures utilizing the mechanism of the Kirkendall effect is given. Furthermore, we show that a hollow nanosize particle is thermodynamically unstable; a high-temperature aging will drive thermal vacancies to the outer surface and transform the hollow nanocrystal to a solid nanocrystal. © 2005 American Institute of Physics. [DOI: 10.1063/1.1873044]

There has been keen interest in controlling the shapes and sizes and materials of nanostructures. Solid nanocrystals, nanorods or wires as well as nanotubes with varying core-shell structures have been fabricated. There is also a deep interest in methods to fabricate hollow nanostructures, especially hollow nanospheres. One intriguing fabrication route recently demonstrated is compound formation in solution starting from solid nanoparticles of one of the constituents.¹ The formation of the void in the center of the particle is attributed to the Kirkendall effect^{2,3} associated with the different diffusion rates of the atoms moving in and out of the sphere. Several examples of hollow nanocrystals of Co_3S_4 and CoO have been presented,¹ but no kinetic analysis of the formation was given, neither was the stability of hollow nanocrystals considered. This letter deals with thermodynamic and kinetic aspects of this effect which might contribute to the design, fabrication route, and materials of hollow nanostructures. We will present a comparison of the growth between planar interfaces and curved interfaces, including the Gibbs–Thomson effect of curvature. At the end we will show that a hollow nano-scale crystal may not be thermodynamically stable.

The Kirkendall effect was originally observed in bulk diffusion couples of Cu and CuZn. Markers which were placed at the original interface had moved into CuZn, indicating that the Zn flux (J_A) is greater than that of Cu (J_B). The unbalance of atomic fluxes is balanced by a flux of vacancies,

$$J_V = J_A - J_B \quad (1)$$

which may lead to void formation. In the classical kinetic analysis of interdiffusion by Darken,³ no void formation by the vacancy flux is necessary provided that equilibrium vacancy concentration can be maintained everywhere in the diffusion couple. In other words, the sources and sinks for vacancies in the entire sample are assumed to be fully operative, hence no supersaturation of vacancies can occur and in turn no nucleation of a void can happen. This is not so in a nanosphere. The confinement of vacancies within the spheri-

cal shell structure will enable vacancies to accumulate, reach supersaturation, and condense into a void.

To apply the Kirkendall effect to form hollow nanostructures, it is more sensible to choose a diffusion couple which forms a compound rather than solid solutions as in the Cu/CuZn case. One of the reactants is a spherical solid particle of “A” and the other reactant “B” may be supplied from a gas phase, or liquid phase or by a solid shell of B around the core particle of A. The resultant compound $A_\alpha B_\beta$ forms between A and B. Examples are silicide formation of $2\text{Ni} + \text{Si} \rightarrow \text{Ni}_2\text{Si}$, or $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$, or the cases reported in Ref. 1. In solid/solid reactions, A and B may interchange as core and shell, e.g., both a nickel-coated silicon core and a silicon-coated nickel core are possible starting configurations. It is obvious that the formation of an empty core will only occur if the out-diffusion of atoms is faster than the in-diffusion. Below, we will use the case of the Ni/Si reaction as an example and we compare the reactions with planar interfaces to curved interfaces.

Figure 1(a) shows a planar layered structure of Ni/Ni₂Si/Si. When a bilayer structure of Ni/Si is annealed around 200 °C, a Ni₂Si layer forms at the Ni/Si interface.⁴ In order to break the covalent bonds of Si at such a low temperature, interstitial Ni in Si is needed below the Ni₂Si/Si interface. This criterion demands Ni to be the dominant diffusing species during the growth of Ni₂Si. The formation of Ni₂Si remains the same even in samples of a thickness in the nanometer range of the Ni film on single crystal Si.⁵

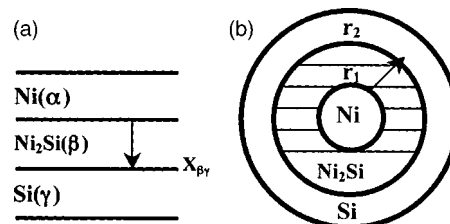


FIG. 1. (a) A schematic diagram of the cross section of a layered structure depicting the growth of Ni₂Si between Ni and Si. Ni is the dominant diffusing species. (b) A schematic diagram of the cross-section of a spherical nanoscale structure of Ni/Ni₂Si/Si. Ni is in the core and the out-diffusion of Ni to react with Si to form Ni₂Si will lead to void formation in the core of the nanostructure.

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The kinetics of thickening of the planar layered structure has been given,⁶ and there is no change of interfacial area during the growth. Assuming a diffusion-controlled process, the layer thickening rate is governed by Fick's first law of diffusion or the flux equation. Considering the dominant flux in a single layer growth as shown in Fig. 1(a), we have the velocity of the interface between Ni₂Si and Si to be given as

$$\frac{dx_{\beta\gamma}}{dt} = - \frac{D_{\beta}}{(C_{\beta\gamma}^{\text{eq}} - C_{\gamma\beta}^{\text{eq}})} \frac{dC_{\beta}}{dx}, \quad (2)$$

where $dx_{\beta\gamma}/dt$ is the velocity of the interface between Ni₂Si and Si, D_{β} is the diffusivity of Ni in Ni₂Si, $C_{\beta\gamma}^{\text{eq}}$ and $C_{\gamma\beta}^{\text{eq}}$ are equilibrium concentrations of Ni in Ni₂Si and in Si, respectively, near the interface of Ni₂Si/Si, and dC_{β}/dx is the concentration gradient of Ni at the Ni₂Si/Si interface. The layer thickening rate of Ni₂Si is obtained by combining the interfacial velocities of its two interfaces. Under the assumption of diffusion-controlled growth, a parabolic dependence of layer thickness on time was obtained.⁷ Using implanted noble gas elements such as Xe as a diffusion marker, Ni has been identified to be the dominant diffusing species, and in addition the atomic fluxes of Ni and Si have been measured, which in turn gives their difference or the vacancy flux.⁸

Figure 1(b) shows the cross section of a spherically layered Ni/Ni₂Si/Si, with Ni in the inner core. The out-diffusion of Ni to grow the Ni₂Si will lead to the formation of a void in the core. The thickening of a shell of Ni₂Si will change both its interfacial areas. More significantly, when we deal with nanosize spherical particles, we must consider the effect of Gibbs–Thomson potential on the growth rate as in the theory of ripening.^{9–11} If we just consider the out-diffusing species (Ni in this case), the growth rate of the spherical interface at r_2 will approximately be governed by

$$\frac{dr_2}{dt} \approx \frac{D_{\beta}}{kT} \left(- \frac{\Delta\mu_{\beta}}{\Delta r} \right) \quad (3)$$

where

$$\begin{aligned} \Delta\mu_{\beta} &= \Delta G_{\text{silicide}} + \left(\frac{2\gamma_2\Omega}{r_2} - \frac{2\gamma_1\Omega}{-r_1} \right) \\ &= \Delta G_{\text{silicide}} + 2\Omega \left(\frac{\gamma_2}{r_2} + \frac{\gamma_1}{r_1} \right) \end{aligned} \quad (4)$$

and $\Delta r = r_2 - r_1$. r_2 and r_1 are the radius of the outer and inner surface of Ni₂Si, respectively, γ_2 and γ_1 are the interfacial energy per atom of the interface between Ni₂Si and Si and between Ni₂Si and Ni, respectively, Ω is the atomic volume of the atom under consideration, and $\Delta G_{\text{silicide}}$ is the formation energy of Ni₂Si per atom. Since the term $\Delta G_{\text{silicide}}$ is negative and the second term is always positive the curvature leads to a lower flux of nickel. In the extreme case of very high values of γ and very small values of r_2 and r_1 , as can be expected for nanoscopic structures, the Gibbs–Thomson effect may potentially completely prevent the out-diffusion flux.

The advantage of using the Kirkendall effect to generate hollow nanostructures is the wealth of information on the diffusion rate in hundreds of materials in bulk or in thin film form, and especially concerning the silicides which have been well investigated for applications as contacts and gates in microelectronic devices. In silicide formation, there are cases in which the metal is the main diffuser (as in Ni₂Si), so

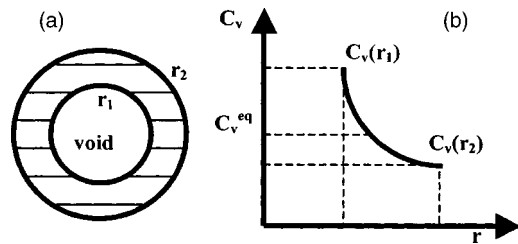


FIG. 2. (a) A schematic diagram of the cross section of a hollow nanocrystal, in which r_1 and r_2 are the inner and outer radius, respectively. (b) A schematic diagram of vacancy gradient across the shell of hollow nanocrystal. C_v^{eq} indicates the equilibrium vacancy concentration near a planar surface.

the core has to be metallic in order to form hollow silicide structures. There are also silicides in which silicon is the main diffuser, so the starting core should be silicon as in the case of WSi₂ formation.

Let us turn to gas reactions. If we restrict ourselves to silicon cores again, it is obvious that the oxidation of Si particles in oxygen atmosphere will not lead to hollow SiO₂ spheres since oxygen diffuses inwards.¹² In contrast, nitridation of a solid silicon sphere should lead to a Si₃N₄ hollow sphere since silicon is moving out faster than nitrogen is moving in, by judging from the thin film case in which nitridation of silicon leads to vacancy injection.¹²

Instead of compound formation, a dissociation reaction with appropriate diffusional fluxes may also lead to hollow spheres. It is well known that at high temperatures, the reaction of Si+SiO₂→2SiO is predominant in the absence of O₂.¹³ This is why thin SiO₂ layers on silicon wafers evaporate in MBE reactors above about 900 °C, which is used for generating clean silicon surfaces. Therefore, an oxidized silicon core annealed in vacuum should show the generation of SiO which diffuses out of the SiO₂ shell, consuming the Si in the core, and leaving an empty SiO₂ shell.

Because the radius in a nanoparticle is very small, we consider its stability. In the limiting case when all the Ni and Si, as shown in Fig. 1(b), have been reacted, we obtain a hollow shell of Ni₂Si. In a planar structure, a sheet of free-standing Ni₂Si of nano thickness will be thermodynamically unstable. This is because it tends to reduce its surface area by becoming a sphere. In classical metallurgy, it is known that a lamellar pearlite will transform to a spherical pearlite upon aging. A hollow nanoparticle also turns out to be thermodynamically unstable.

In Fig. 2(a), the cross section of a hollow nanosize particle of single element phase is shown. If we assume that the inner and outer radii are r_1 and r_2 , respectively, the chemical potential of surface atoms on these two surfaces will be

$$\mu_1 \left(= \mu_0 + \frac{2\gamma}{-r_1} \Omega \right) < \mu_2 \left(= \mu_0 + \frac{2\gamma}{r_2} \Omega \right), \quad (5)$$

where μ_0 refers to the chemical potential of the atoms in the bulk material. Under the potential gradient atoms tend to diffuse from the outer surface to the inner surface, finally leading to an elimination of the void and to a compact nanosphere. This result is in accordance with an energy conservation based on the total surface area. By conservation of volume, we have for the transformation from a hollow sphere to a solid sphere, $\frac{4}{3}\pi r_2^3 - \frac{4}{3}\pi r_1^3 = \frac{4}{3}\pi r_0^3$, where r_0 is the

radius of the solid particle. The reduction in surface area will be $4\pi r_0^2 < 4\pi(r_2^2 + r_1^2)$, where $r_2 > r_0 > r_1$.

In the hollow shell structure as shown in Fig. 2(a), we cannot define the equilibrium concentration of vacancies. This is unique in a hollow nanoscale particle. Since there are two surfaces with different potentials to serve as references for source and sink of vacancies, no equilibrium vacancy concentration can be given. The inner surface is under a negative pressure, so the vacancy concentration near it will be higher than that near the outer surface which is under a positive pressure. In Fig. 2(b), a vacancy concentration gradient across the hollow shell is shown. We note that we could assign a concentration corresponding to the equilibrium vacancy concentration, C_v^{eq} , with respect to a planar surface in a bulk sample as indicated in Fig. 2(b). If we anneal the hollow nanocrystal at a high temperature to increase its thermal vacancy concentration, these vacancies will go to the sink on the outer surface and will be replenished from the inner surface, resulting in the disappearance of the void at the core of the particle.

To estimate the time scale for the filling of a hollow particle at elevated temperatures, the hollow shell structure as shown in Fig. 2(a) is assumed a single element phase, instead of a compound phase, for simplicity. We define the vacancy concentration near the inner surface, r_1 , and the outer surface, r_2 , respectively, to be

$$C_v(r_1) = C_v^{\text{eq}} \left(1 + \frac{\beta}{r_1} \right), \quad (6)$$

$$C_v(r_2) = C_v^{\text{eq}} \left(1 - \frac{\beta}{r_2} \right), \quad (7)$$

where $\beta = 2\gamma\Omega/kT$, and γ is the surface energy per unit area, Ω is the atomic volume of a vacancy, and kT has the usual meaning. In spherical coordinates and if we assume a steady state process, we can solve the concentration profile of vacancies as,

$$C_v(r) = C_v^{\text{eq}} \beta \left(\frac{r_2 + r_1}{r_2 - r_1} \right) \frac{1}{r} + C_v^{\text{eq}} \beta \left(-\frac{2}{r_2 - r_1} \right) + C_v^{\text{eq}}. \quad (8)$$

Using Fick's first law, we obtain the flux of vacancies leaving (or atoms arriving at) the spherical surface of r_1 . Then the time needed to fill the void can be estimated to be

$$t \cong \frac{kT}{A\gamma D\Omega} r_1^3, \quad (9)$$

where A is a constant of the order of ten, and D is the self-diffusion coefficient of the atoms in the particle.

Let us take Au as an example since we know its surface energy and diffusivity very well; $\gamma = 1400 \text{ erg/cm}^2$ and $D = 0.1 \times \exp(-1.8 \text{ eV})/kT \text{ cm}^2/\text{s}$. Assume a hollow nanoparticle having $r_1 = 30 \text{ nm}$ and $r_2 = 60 \text{ nm}$, it will take about $5 \times 10^3 \text{ s}$ at $400 \text{ }^\circ\text{C}$ to transform the hollow particle into a solid particle. In case the hollow particle has $r_1 = 3 \text{ nm}$ and $r_2 = 6 \text{ nm}$, the required transformation time is only a few seconds.

The formation of Kirkendall voids by interfacial reaction and the annihilation of these voids by a subsequent aging have been observed in the reactions between a thin film of Cu and molten eutectic SnPb solder.¹⁴ Reacted near $220 \text{ }^\circ\text{C}$ for a short time of 1 min, Kirkendall voids were observed to form within a cluster of tiny Cu_3Sn grains. Yet with a prolonged reaction to 10 min, these Kirkendall voids disappeared, accompanied by the transition of Cu_3Sn to Cu_6Sn_5 . The in-diffusion of Sn to convert Cu_3Sn to Cu_6Sn_5 may have consumed the vacancies in the void.

While our analysis is about spherical nanocrystals, we expect an analogous behavior in nanotubes. No doubt, a single wall nanotube (e.g., a carbon nanotube) will not have the stability problem we discussed here, but a thick wall nanotube should have the same behavior. The nanoscale Kirkendall effect can be used to form hollow nanotubes or hollow cylindrical objects, although instability may lead to a string of voids instead of a hollow cylinder.

Generally speaking, Kirkendall void formation is a nuisance in technology since it weakens the mechanical properties of the structure. This has been a reliability issue in those technologies where an interfacial reaction is associated with a manufacturing step, as in solder joints.¹⁵ The finding that Kirkendall void formation may be a general method to produce hollow nanocrystals has cast a positive light on this classical phenomenon. Because of the potential applications of hollow nanostructures, more study of this phenomenon will be needed. It is clear that many kinds of hollow nanoparticles and tubes can be fabricated using the Kirkendall effect, regardless of whether the final structures consist of a compound or a solid solution.

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