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Visualization of the Coalescence of Bismuth Nanoparticles

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Abstract: Coalescence is a significant pathway for the growth of nanostructures. Here we studied the coalescence of Bi nanoparticles *in situ* by liquid cell transmission electron microscopy (TEM). The growth of Bi nanoparticles was initiated from a bismuth neodecanoate precursor solution by electron beam irradiation inside a liquid cell under the TEM. A significant number of coalescence events occurred from the as-grown Bi nanodots. Both symmetric coalescence of two equal-sized nanoparticles and asymmetric coalescence of two or more unequal-sized nanoparticles were analyzed along their growth trajectories. Our observation suggests that two mass transport mechanisms, i.e., surface diffusion and grain boundary diffusion, are responsible for the shape evolution of nanoparticles after a coalescence event.

Key words: liquid cell TEM, in situ TEM, coalescence, surface diffusion, grain boundary diffusion

INTRODUCTION

Coalescence of nanoparticles, where two or more nanoparticles attach by chance and grow into one particle, frequently occurs during nanoparticle growth. It often arises from the fact that nanoparticles are unstable under many circumstances due to the large surface-to-volume ratio and they tend to form a single particle by collisions to reduce the total surface energy. Coalescence, as an important alternative pathway to monomer attachment, has been utilized to synthesize complex nanostructures (Zheng et al., 2009; Richards et al., 2010a; Liu et al., 2013; Ustarroz et al., 2013), such as nanoflakes (Vaughn et al., 2011), nanorods (Liu et al., 2011), nanowires (Liao et al., 2012), nanoflowers (Vaughn et al., 2012), and so on. On the other hand, the coalescence of nanoparticles can also lead to degradation of their physical properties, such as the loss of catalytic activities, band gap changes, and so on.

There have been many studies on coalescence mechanisms both theoretically (Zhu & Averback, 1996; Lewis et al., 1997; Eggers, 1998; Zachariah & Carrier, 1999; McCarthy & Brown, 2009) and experimentally (Bonevich & Marks, 1992; Dai et al., 2001; Palasantzas et al., 2006; Lim et al., 2009; Ingham et al., 2011). Typically, coalescence occurs via one or more of the four mass transport modes (Kuczynski, 1949): hydrodynamic flow, evaporation-condensation, volume diffusion, and surface diffusion. According to early studies, when particles are smaller than 1 μ m and at a temperature below their bulk melting point, surface diffusion is normally considered as the dominant mass transport route (Mullins, 1957). A characteristic power law $r \sim t^a$ is expected, where *r* is the radius of the contact neck of the particle after

Received October 1, 2013; accepted January 23, 2014 *Corresponding author. hmzheng@lbl.gov coalescence, *t* is time (*t*), and *a* is a constant. For the surface diffusion, the constant *a* is $\frac{1}{7}$ (Kuczynski, 1949) or $\frac{1}{6}$ (Mullins, 1959; Nichols & Mullins, 1965; Eggers, 1998). McCarthy & Brown (2009) estimated a higher *a* value of $\frac{1}{3}$ for coalescence at the early stage and a lower *a* value of $\frac{1}{6}$ at the intermediate stage based on Monte Carlo simulation of the coalescence of fcc nanoparticles. The higher *a* value at the early stage can be attributed to the highly curved neck region which could provide high coordination sites for material diffusion and redistribution.

Progress has also been made in experimental studies of nanoparticle coalescence by in situ techniques, including in situ transmission electron microscopy (TEM) imaging (Palasantzas et al., 2006; Lim et al., 2009; Zheng et al., 2009; Simonsen et al., 2010; Grogan et al., 2011; Liao et al., 2012; Yuk et al., 2012; Liu et al., 2013), real-time X-ray diffraction and small-angle X-ray scattering (Ingham et al., 2011), and in situ X-ray absorption fine structure spectroscopy (XAFS) measurements (Harada & Kamigaito, 2011). Among these techniques, in situ TEM, which can visualize particle evolution in liquids with high spatial resolution (Zheng et al., 2009; Liao et al., 2012; Yuk et al., 2012; Liao et al., 2013; Niu et al., 2013), has attracted a lot of attention. There has been increasing interest in using liquid cell TEM to study nanoparticle growth mechanisms, where coalescence has been identified as playing an important role (Zheng et al., 2009; Grogan et al., 2011; Li et al., 2012; Liao et al., 2012; Yuk et al., 2012; Liu et al., 2013). Despite all of these accomplishments, our understanding of the coalescence of nanoparticles is still limited and a systematic study of coalescence is needed.

Bismuth (Bi) nanoparticles are widely used as catalysts for the growth of semiconducting nanowires (Fanfair & Korgel, 2005; Dong et al., 2007*a*, 2007*b*, 2008). There are also several previous reports on the synthesis of Bi nanoparticles (Wang et al., 2008; Richards et al., 2010*b*). Herein, we studied the coalescent growth of Bi nanoparticles by following individual nanoparticle growth trajectories using *in situ* liquid cell TEM. The coalescence of different pairs of nanoparticles is compared side-by-side. Two types of coalescence, i.e., asymmetric coalescence of different sized nanoparticles and symmetric coalescence of similar sized nanoparticles, have been observed. Coalescence of multiple nanoparticles has also been captured, by which nanorods or irregular shape particles are achieved. We propose that both surface diffusion and grain boundary diffusion are involved for mass transport during relaxation of the coalescend nanoparticles.

MATERIALS AND METHODS

In situ Liquid Experiments

Chemicals including bismuth neodecanoate, oleylamine and pentadecane were obtained from Sigma Aldrich. The reaction precursor solution was prepared by dissolving 0.5 M bismuth neodecanoate into the mixture of pentadecane and oleylamine (7:3 vol/vol). *In situ* growth and imaging of the Bi nanodots were carried out in homemade liquid cells, where liquid precursors were sandwiched between two ultrathin silicon nitride membranes (15 nm in thickness). Liquid cell fabrication and liquid loading procedures were described in our previous publications (Zheng et al., 2009; Niu et al., 2012).

TEM Imaging

All imaging results were acquired in a JEOL 2100 with a high-resolution pole piece (Cs = 1 mm) and a LaB₆ filament. A Gatan Orius CCD camera was used for *in situ* imaging. The electron beam (200 kV; beam current density of about 500 electrons/Å²·s) passes through the silicon nitride window ($3 \times 50 \mu$ m), and induces growth of Bi nanoparticles in the liquid layer. The movie was recorded at a rate of 5 Fr/s by the open-sourced software VirtualDub embedded in the DigitalMicrograph software. The as-recorded movie was compressed to reduce the file size (480×480 pixels), and the play speed of Supplementry Movies 1 & 2 is 12 times faster than the original movies.

Supplementary Movies 1 and 2

Supplementary Movies 1 and 2 can be found online. Please visit journals.cambridge.org/jid_MAM.

Results

Overview of the Coalescence Events

Nucleation and growth of the Bi nanoparticles were initiated by electron beam casting onto the liquid precursor layer inside a liquid cell with the electron microscope. A current density of about 500 electrons/Å² s was maintained during growth. Growth of Bi nanoparticles with significant coalescence events was observed. We tracked the growth trajectories of nanoparticles by coalescence, including symmetric coalescence of two equal-sized Bi nanoparticles, asymmetric coalescence of unequal-sized Bi nanoparticles, and coalescence of multiple nanoparticles.

Figure 1 shows the growth of Bi nanoparticles with the significant influence of coalescence events. The sequential TEM images display that average particle size increases and the number of nanoparticles decreases within the field of view as growth proceeds (Fig. 1a). Small nanoparticles prefer to attach to nearby large particles, and coalescence of multiple nanoparticles occurs frequently (Movie S1). An area with typical multiple coalescence events is highlighted, as shown in the sequential images in Figure 1b. Two types of coalescences, i.e., asymmetric coalescence of two unequal-sized particles and symmetric coalescence of two equal-sized particles, are confirmed. Figure 1c shows the evolution of particle size distribution with time. At the early stage (1-20s), there are two distinct populations of nanoparticles with average sizes of 2.1 and 4.5 nm (highlighted by arrows in Figure 1c). Then, the number of smaller clusters decreases and average particle size increases to 5.5 nm at 40 s. Small nanoparticles < 2.1 nm mostly vanish at the later stage and large Bi nanoparticles with an average size of 9 nm are eventually obtained. Nucleation and preferential disappearance of the primary nanoparticles indicate that coalescence is a significant route for Bi nanoparticle growth.

Average particle size and the number of particles as a function of time are plotted in Figures 1d and 1e. Intriguingly, both plots show rate (slope of the plot) changes around 78 s (marked by arrows). Since asymmetric coalescence is dominant at the beginning, with smaller nanoparticles coalescing to the nearby bigger ones rapidly, a much faster decrease of the number of particles is achieved. The growth rate appears to be slightly faster as well. As the consequence of coalescence, the size of particles increases and the density of particles become lower. This results in lower collision possibilities between nanoparticles, thus a slower decrease in the number of particles at the later stage of growth, as shown in the right side of plots in Figure 1e. The two types of coalescence will be discussed in more detail as below.

Asymmetric Coalescence

We compare six sets of nanoparticles that have undergone coalescence events. Each set of nanoparticles has a larger nanoparticle with the diameter of about 7 nm and a smaller nanoparticle with the diameter varying from 3 to 5.6 nm. Each set of these nanoparticles coalesce and relax into a single spherical nanoparticle. Figure 2a shows sequential images of the processes of coalescence, shape reorganization, and formation of a sphere. The smaller particle is more mobile than the larger one (7 nm) in each pair and the smaller particle tends to migrate towards the bigger nanoparticle. We measured the speed of migration as a function of their inter-particle distance. As shown in Figure 2b, when the



Figure 1. An overview of the coalescence of Bi nanoparticles during growth in a liquid cell. **a**: Low magnification transmission electron microscopy (TEM) image series showing the growth of Bi nanoparticles. **b**: Magnified TEM image series showing the coalescence of ten Bi nanoparticles. The arrows indicate those particles involving coalescence events. **c**: Particle size distribution at different stages of growth. **d**: The average size of the nanoparticles as a function of time. **e**: Evolution of the number of particles with time. Scale bar: (a) 20 nm, (b) 10 nm.

particles are far from each other, the small particle moves randomly. When the interparticle distance is around 1.5 nm, there is a net drift velocity that leads to coalescence of two nanoparticles. The dipole-dipole electrostatic interaction between two nanoparticles can be responsible for the observed nanoparticle coalescence (Liao et al., 2012). It is noted that the range of interaction in this system appears to be smaller than the previously reported Pt-Fe system (Liao et al., 2012). This could result from the higher viscosity of liquids and less interaction from ligands (i.e., lower ligand density) in the current system.

Relaxation time for the coalesced dumbbell particle to form a spherical particle is drastically different when the particle size varies. The smaller particle deforms when it reaches the bigger nanoparticle. When the particle is very small where the volume ratio (small particle/large particle) is < 28%, there is no obvious "necking" process after two particles coalesce. Only when the volume ratio of two particles reaches 40% or higher, such as the pair "4", "5", and "6" in Figure 2a, a short-time "necking" process occurs after coalescence. The "necking" process corresponds to a plateau in the relaxation plot (Fig. 2c). Details of the "necking" are shown in Figure 3, the high resolution TEM images of two Bi nanoparticles, where two nanoparticles are connected and a neck with diameter of 4 nm is observed. Relaxation time (*t*) increases with the particle size (*d*, diameter of the smaller particle in a pair) following a power law relationship, $t \sim d^a$ and $a = 3.3 \pm 0.4$ (Fig. 2d). It is clear that the smaller the particle, the less time it takes for the particle to relax. It is obvious that the mass transport time is less when the



Figure 2. Asymmetric coalescence of Bi nanoparticles. **a**: Transmission electron microscopy (TEM) image series of the coalescence of six pairs of Bi nanodots. In each pair, a large particle of 7 nm coalesces with a smaller nanoparticle. The starting time of each coalescence event is arbitrary. **b**: The speed of the smaller nanoparticle changes as it approaches the larger nanoparticle in each pair as a function of interparticle distance. **c**: Length (L) evolution of the coalescing nanoparticles. **d**: The relaxation time of the six pairs of coalesced Bi nanoparticles. Scale bar: (a) 5 nm.

particle is smaller; however, theoretical simulation is needed to interpret the quantitative relationship.

Symmetric Coalescence

Besides the asymmetric coalescence as described above, there are also symmetric coalescence events that occur when two nanoparticles of the same size coalesce. We compare the coalescence processes of five sets of nanoparticles with different sizes, 3.46, 4.65, 5.94, 6.60, and 7.30 nm (Fig. 4). It shows the same trend as the above that the smaller the particle, the less time it takes for the coalesced particle to relax into a sphere. When the particles are smaller than 5 nm, i.e., set "1" and "2" in Figure 4a, there is no obvious "necking" after coalescence. However, when particles are larger than 5 nm, such as the set "4" and "5", the "necking" process is dominant in the relaxation process (Fig. 4b). Compared to asymmetric coalescence, the "necking" period for particles with similar particle sizes is much longer (Fig. 4b). The relaxation time (t) increases with particle size (d) following a power law relationship $t \sim d^a$ and $a = 3.1 \pm 0.3$. Since the symmetric coalescence of larger nanoparticles is pronounced in the later part of growth, the lower average growth rate can be achieved (see the plot after 78 s in Fig. 1d). It is noted that the tumbling motion is not significant for the selected nanoparticle pairs (without significant angle changes) thus the necking kinetics can be measured without bias.

Coalescence of Multiple Nanoparticles

When coalescence of multiple nanoparticles occurs, the relaxation process and morphology of the relaxed nanoparticle can be largely influenced by the nature of coalescence. Figure 5a shows two different scenarios where three nanoparticles agglomerate together. In the first scenario, two similar sized nanoparticles coalesce first and another smaller particle joins in. After these sequential coalescence events, the whole particle gradually relaxes into a sphere. In the second scenario, two similar sized nanoparticles coalesce, and another particle of comparable size joins in before the particle is relaxed. Then, the whole particle becomes elongated and forms a nanorod.

Similarly, two different scenarios appear in the coalescence of four nanoparticles (Fig. 5b). When four nanoparticles of different sizes approach each other from four directions, they agglomerate first and relax into a spherical particle at a later stage (see the trajectories of the four particles in Figure 5c). In the second scenario, when four nanoparticles with similar sizes are attached together a branched nanoparticle is obtained after 220 s. The relaxation processes are interrupted in cases where multiple similar sized nanoparticles are agglomerated, because there is a long period of "necking" associated with the coalescence of each set of similar sized nanoparticles (as discussed in the above symmetric coalescence). It could take a very long time for these nanoparticles to relax into a sphere. These nanorods or branched shaped nanoparticles could be stabilized by surfactants covering the surface (Liao et al., 2012).

The relaxation processes after three different types of coalescence, i.e., asymmetric coalescence, symmetric coalescence and coalescence of multiple particles, are summarized in Scheme 1 (I). Both surface diffusion and diffusion through grain boundaries are highlighted. The possible mass transport directions are also marked. Different morphology can be achieved after the coalescence events.

Coalescence versus Collision

Since coalescence is a critical pathway for the growth of nanostructures, there have been a lot of previous studies on coalescence in different circumstances (Dong et al., 2004; Hawa & Zachariah, 2004, 2006; Simonsen et al., 2010; Harada & Kamigaito, 2011; Ingham et al., 2011; Ustarroz et al., 2013). In colloidal synthesis, many factors, including temperature, solvent viscosity, particle size, and concentration of nanoparticles, can influence coalescence from which distinct nanostructures have been achieved (Zheng et al., 2009; Ingham et al., 2011; Liao et al., 2012; Liu et al., 2013; Ustarroz et al., 2013).

Generally, the morphology of the final particle after coalescence events is determined by the competition between the coalescence time ($\tau_{coalescence}$, the time for the particle to attach and relax into a spherical particle) and collision time ($\tau_{collision}$, we refer to an effective collision that lead to particle agglomeration). If the coalescence time is less than the collision time, the particles could relax before another collision event takes place and thus a spherical particle can be achieved. However, if the coalescence time is longer than the collision time, the relaxation can be interrupted by the collision from another particle and particle agglomerates of complex morphologies can be produced (Hawa & Zachariah, 2004):

 $\tau_{\text{coalescence}} < \tau_{\text{collision}} \rightarrow \text{spherical particle},$ $\tau_{\text{collision}} < \tau_{\text{coalescence}} \rightarrow \text{particle agglomerate}.$

Our *in situ* observation is consistent with the above model. Under the current liquid cell condition, movements of nanoparticles are significantly slower than those in bulk liquid, therefore, the collision frequency of the migrating nanoparticles should also be much lower. Therefore, most coalesced nanoparticles are relaxed into spherical particles as shown in Scheme 1. However, the concentration of nanoparticles in the liquid cell experiments is high, which enhances nanoparticle collisions (Figs. 2c and 4b. We also observed



Figure 3. High resolution transmission electron microscopy images of two unequal-sized Bi nanodots, the volume ratio (smaller/larger) is about 0.42. The initial stage of the necking is highlighted by arrows. Scale bar: 5 nm.

some nanoparticle agglomerates resulting from coalescence of multiple nanoparticles, where larger particles are involved (Figs. 5a and 5b). The coalesced nanoparticle needs a long time to relax, it forms an irregular shaped nanoparticle since it collides with another particle before relaxation (see Fig. 5b and Scheme 1).

Considering the electron beam effect on particle motion, a higher beam current density of about 1,000 electrons/Å² s was applied on the as-formed Bi nanoparticles. It can be seen that the electron beam can expedite the motion rate of the nanoparticles (Supplementary Movie 2). However, the particle size effect is stronger than the beam effects on the coalescence process within the range of electron beam intensity being used, i.e. from 500 to 1,000 electrons/Å² s (see Supplementary Figures 2 and 3).

Supplementary Figures 2 and 3

Supplementary Figures 2 and 3 can be found online. Please visit journals.cambridge.org/jid_MAM.



Figure 4. Symmetric coalescence of two Bi nanoparticles where two equal-sized nanoparticles attach and relax into a sphere. **a**: transmission electron microscopy image series showing the evolution of five pairs of Bi nanoparticles. **b**: Length evolution of the particle pair after coalescence until a spherical is achieved. The effective statistic point of the length starts when the distance between the two approaching nanoparticles is about 0.85 nm. **c**: The relaxation time of the five pairs of coalescing nanodots until they merge into a round particle. Scale bar: (a) 5 nm



Figure 5. Coalescence of multiple Bi nanoparticles. **a**: Transmission electron microscopy (TEM) image series showing the coalescence of three Bi nanoparticless. One scenario is the formation of a spherical nanoparticle, and the other formation of a nanorod. **b**: TEM image series of the coalescence of four Bi nanoparticles. One scenario is formation of a round nanoparticle and the other one is formation of a nanorod. **c**: Trajectories of two-dimensional motion (positions of the center of mass) of the four nanodots in (**b**) before they contact each other.



Scheme 1. Schematic diagrams of the coalescence processes. (I) Asymmetric coalescence of two unequal-sized nanoparticles. (II) Symmetric coalescence of two equal-sized nanoparticles. (III) Coalescence of three nanoparticles resulting in a nanorod. The green, red and black arrows highlight particle movement before coalescence, atom diffusion and surface tension, respectively. A spherical nanoparticle is achieved when coalescence time ($\tau_{coalescence}$) is smaller than the collision time ($\tau_{collision}$). Nanorods or other irregular shaped agglomerates are generated when coalescence time ($\tau_{coalescence}$) is larger than the collision time ($\tau_{collision}$).

Mass Transport Mechanisms of the Coalescence

It is well known that surface diffusion can be the dominant mass transport mechanism for nanoparticles below their bulk melting temperature. In our case, since the coalescence time is largely dependent on particle size (close to $t \sim d^3$, estimated from Fig. 4c), solid state coalescence can be considered. Therefore, we assume that surface diffusion is the main mass transport mechanism for coalescence.

We measured changes in the neck diameter and particle length of six pairs of equal-sized Bi nanodots, see Figures 6a and 6b. From the neck evolution as the function of time, two distinct power laws, in the form of $d_{neck} \sim t^a$, with estimated a to be of 0.73 ± 0.16 and 0.25 ± 0.03 were achieved for the coalescence events at the early and late stages, respectively (Supplementary Figure 1). The relationship $d_{\text{neck}} \sim \bar{t}^{0.73 \pm 0.16}$ at the early stage of coalescence is obtained, which is distinctively different from the relationship $d_{\text{neck}} \sim t^{0.16}$ predicted by the classical continuum theory (Kuczynski, 1949; Mullins, 1957). This might be due to atoms on the Bi nanoparticle surface being highly mobile when affected by the electron beam, and that the highly curved neck, which gives high coordination sites for material diffusion, could then facilitate the fast neck evolution. The relationship $d_{\text{neck}} \sim t^{0.25 \pm 0.03}$ at the late stage, which is slightly different

from the power law $d_{\text{neck}} \sim t^{0.16}$, can be considered as mainly resulting from surface diffusion. On the other hand, since the length evolution displays a gradual decreasing feature, surface diffusion should not be the single mechanism for particle relaxation. The grain boundary diffusion along the contact plane of the two particles should also be considered (Zhang & Schneibel, 1995; Zhang & Gladwell, 1998).

Supplementary Figure 1

Supplementary Figure 1 can be found online. Please visit journals.cambridge.org/jid_MAM.

Regarding coalescence of two equal-sized nanoparticles (Supplementary Figure 4), the mass flow due to surface diffusion can be estimated. According to Fick's law, the flux J_s induced by surface curvature can be written as

$$J_{\rm s} = -\frac{\delta_{\rm s} D_{\rm s} \Omega \gamma_{\rm s}}{kT} \frac{\partial K}{\partial \gamma} \tag{1}$$

where D_s is the surface diffusion coefficient, γ_s is surface free energy per unit area, δ_s is the surface diffusion thickness, Ω is the atomic volume, k is Boltzmann's constant, T is absolute temperature and K is the principal curvature of the surface.



Figure 6. The evolution of diameter and length of the neck after each pair of Bi nanoparticles are coalesced. **a**: The evolution of neck diameter as a function of time. **b**: The decrease in length versus time during particle relaxation.

Another route of mass redistribution is through grain boundary diffusion and the flux J_{gb} is driven by the gradient of stress σ normal to the boundary. It can be given as

$$J_{\rm gb} = -\frac{\delta_{\rm gb} D_{\rm gb} \Omega}{kT} \frac{\partial \sigma}{\partial y}$$
(2)

where D_{gb} is the grain boundary diffusion coefficient, δ_{gb} is the grain boundary diffusion thickness and *y* is the position on the grain boundary. Based on previous numerical studies (Zhang & Schneibel, 1995; Zhang & Gladwell, 1998), when a grain boundary meets a free surface, it reaches equilibrium between J_{gb} and J_s . There is a balance between surface tension γ_s and grain boundary tension γ_{gb} , and the chemical potential continuity. Consequently, mass transport during the coalescence is dependent on the ratio of two diffusion processes $\frac{D_s \delta_s}{D_{gb} \delta_{gb}}$ and competition between surface tension and grain boundary stress $\left(\frac{\gamma_s}{\sigma \gamma}\right)$. Moreover, the dihedral angle 2θ could be determined by: $\cos \theta = \frac{\gamma_{gb}}{2\gamma_s}$ (see Scheme 1 and Supplementary Figure 2). From our *in situ* observation, the dihedral angle 2θ of $110 \pm 10^\circ$ is achieved for Bi nanoparticles with symmetric coalescence. Consider the surface tension of Bi nanodot γ_s is 0.43 N/m (Eustathopoulos, 1983), the grain boundary stress is calculated to be $\gamma_{gb} = 0.49 \pm 0.06$ N/m.

Supplementary Figure 4

Supplementary Figure 4 can be found online. Please visit journals.cambridge.org/jid_MAM.

CONCLUSION

In this paper, we studied coalescence of Bi nanoparticles during growth using in situ liquid cell TEM. Two types of coalescence, i.e., asymmetric coalescence and symmetric coalescence were observed. Coalescence of multiple nanoparticles was also identified. Morphology of the nanoparticles after coalescence was largely determined by size of the primary nanoparticles, the time for coalesced particles to relax, and collision frequency. From shape evolution of particles after coalescence, we found that neck growth follows a power law relationship $(d_{neck} \sim t^a)$. Two stages of growth were identified, and the exponent a of 0.73 ± 0.16 and 0.25 ± 0.03 were achieved. Both surface diffusion and grain boundary diffusion can be involved for mass transport during relaxation of the coalesced particles. Considering the surface tension of Bi nanodot γ_s is 0.43 N/m (Eustathopoulos, 1983), the grain boundary stress is calculated to be $\gamma_{gb} = 0.49 \pm 0.06$ N/m.

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References

- BONEVICH, J.E. & MARKS, L.D. (1992). The sintering behavior of ultrafine alumina particles. *J Mater Res* 7, 1489–1500.
- DAI, Z.R., SUN, S.H. & WANG, Z.L. (2001). Phase transformation, coalescence, and twinning of monodisperse FePt nanocrystals. *Nano Lett* 1, 443–447.
- DONG, H., MOON, K.-S. & WONG, C.P. (2004). Molecular dynamics study on the coalescence of Cu nanoparticles and their deposition on the Cu substrate. *J Elec Mater* 33, 1326–1330.
- DONG, A., TANG, R. & BUHRO, W.E. (2007a). Solution-based growth and structural characterization of homo- and heterobranched semiconductor nanowires. *J Am Chem Soc* **129**, 12254–12262.
- DONG, A., WANG, F., DAULTON, T.L. & BUHRO, W.E. (2007b). Solution-liquid-solid (SLS) growth of ZnSe-ZnTe quantum wires having axial heterojunctions. *Nano Lett* 7, 1308–1313.
- DONG, A., YU, H., WANG, F. & BUHRO, W.E. (2008). Colloidal GaAs quantum wires: Solution-liquid-solid synthesis and quantumconfinement studies. J Am Cheml Soc 130, 5954–5961.

- EGGERS, J. (1998). Coalescence of spheres by surface diffusion. *Physl Rev Lett* **80**, 2634–2637.
- EUSTATHOPOULOS, N. (1983). Energetics of solid/liquid interfaces of metals and alloys. *Int Metals Rev* 28, 189–210.
- FANFAIR, D.D. & KORGEL, B.A. (2005). Bismuth nanocrystal-seeded III-V semiconductor nanowire synthesis. Cryst Growth Des 5, 1971–1976.
- GROGAN, J.M., ROTKINA, L. & BAU, H.H. (2011). In situ liquid-cell electron microscopy of colloid aggregation and growth dynamics. *Phys Rev E*, **83**, 061405.
- HARADA, M. & KAMIGAITO, Y. (2011). Nucleation and aggregative growth process of platinum nanoparticles studied by in situ quick XAFS spectroscopy. *Langmuir* **28**, 2415–2428.
- HAWA, T. & ZACHARIAH, M.R. (2004). Molecular dynamics study of particle-particle collisions between hydrogen-passivated silicon nanoparticles. *Phys Rev B* **69**, 035417.
- Hawa, T. & ZACHARIAH, M.R. (2006). Coalescence kinetics of unequal sized nanoparticles. J Aerosol Sci 37, 1–15.
- INGHAM, B., LIM, T.H., DOTZLER, C.J., HENNING, A., TONEY, M.F. & TILLEY, R.D. (2011). How nanoparticles coalesce: an in situ study of Au nanoparticle aggregation and grain growth. *Chem Mater* 23, 3312–3317.
- Kuczynski, G.C. (1949). Study of the sintering of glass. *J Appl Phys* **20**, 1160–1163.
- LEWIS, L.J., JENSEN, P. & BARRAT, J.L. (1997). Melting, freezing, and coalescence of gold nanoclusters. *Phys Rev B* 56, 2248–2257.
- LI, D., NIELSEN, M.H., LEE, J.R.I., FRANDSEN, C., BANFIELD, J.F. & DE YOREO, J.J. (2012). Direction-specific interactions control crystal growth by oriented attachment. *Science* 336, 1014–1018.
- LIAO, H.-G., CUI, L., WHITELAM, S. & ZHENG, H. (2012). Real-time imaging of Pt_3Fe nanorod growth in solution. *Science* **336**, 1011–1014.
- LIAO, H.-G., NIU, K. & ZHENG, H. (2013). Observation of growth of metal nanoparticles. *Chem Commun* 49, 11720–11727.
- LIM, T.H., MCCARTHY, D., HENDY, S.C., STEVENS, K.J., BROWN, S.A. & TILLEY, R.D. (2009). Real-time TEM and kinetic Monte Carlo studies of the coalescence of decahedral gold nanoparticles. ACS Nano 3, 3809–3813.
- LIU, L., LI, X., WU, X., CHEN, X. & CHU, P.K. (2011). Growth of tin oxide nanorods induced by nanocube-oriented coalescence mechanism. *Appl Phys Lett* **98**, 133102–133103.
- LIU, Y.Z., LIN, X.M., SUN, Y.G. & RAJH, T. (2013). In situ visualization of self-assembly of charged gold nanoparticles. J Am Chem Soc 135, 3764–3767.
- McCARTHY, D.N. & BROWN, S.A. (2009). Evolution of neck radius and relaxation of coalescing nanoparticles. *Phys Rev B*, **80**, 064107.
- MULLINS, W.W. (1957). Theory of the thermal grooving. *J Appl Phys* **28**, 333–339.
- MULLINS, W.W. (1959). Flattening of a nearly plane solid surface due to capillarity. *J Appl Phys* **30**, 77–83.

- NICHOLS, F.A. & MULLINS, W.W. (1965). Morphological changes of a surface of revolution due to capillarity—induced surface diffusion. J Appl Phys 36, 1826–1835.
- NIU, K., LIAO, H. & ZHENG, H. (2012). Revealing dynamic processes of materials in liquids using liquid cell transmission electron microscopy. J Vis Exp 70, e50122.
- NIU, K.-Y., PARK, J., ZHENG, H. & ALIVISATOS, A.P. (2013). Revealing bismuth oxide hollow nanoparticle formation by Kirkendall effect. *Nano Lett* **13**, 5715–5719.
- PALASANTZAS, G., VYSTAVEL, T., KOCH, S.A. & DE HOSSON, J.T.M. (2006). Coalescence aspects of cobalt nanoparticles during in situ high-temperature annealing. J Appl Phys, 99, 024307.
- RICHARDS, V.N., RATH, N.P. & BUHRO, W.E. (2010a). Pathway from a molecular precursor to silver nanoparticles: the prominent role of aggregative growth. *Chem Mater* 22, 3556–3567.
- RICHARDS, V.N., SHIELDS, S.P. & BUHRO, W.E. (2010b). Nucleation control in the aggregative growth of bismuth nanocrystals. *Chem Mater* 23, 137–144.
- SIMONSEN, S.B., CHORKENDORFF, I., DAHL, S., SKOGLUNDH, M., SEHESTED, J. & HELVEG, S. (2010). Direct observations of oxygen-induced platinum nanoparticle ripening studied by in situ TEM. J Am Chem Soc 132, 7968–7975.
- USTARROZ, J., HAMMONS, J.A., ALTANTZIS, T., HUBIN, A., BALS, S. & TERRYN, H. (2013). A generalized electrochemical aggregative growth mechanism. *J Am Chem Soc* **135**, 11550–11561.
- VAUGHN, D.D., HENTZ, O.D., CHEN, S., WANG, D. & SCHAAK, R.E. (2012). Formation of SnS nanoflowers for lithium ion batteries. *Chem Commun* 48, 5608–5610.
- VAUGHN, D.D., IN, S.-I. & SCHAAK, R.E. (2011). A precursor-limited nanoparticle coalescence pathway for tuning the thickness of laterally-uniform colloidal nanosheets: the case of SnSe. ACS Nano 5, 8852–8860.
- WANG, F., TANG, R., YU, H., GIBBONS, P.C. & BUHRO, W.E. (2008). Size- and shape-controlled synthesis of bismuth nanoparticles. *Chem Mater* **20**, 3656–3662.
- YUK, J.M., PARK, J., ERCIUS, P., KIM, K., HELLEBUSCH, D.J., CROMME, M. F., LEE, J.Y., ZETTL, A. & ALIVISATOS, A.P. (2012). High-resolution EM of colloidal nanocrystal growth using graphene liquid cells. *Science* 336, 61–64.
- ZACHARIAH, M.R. & CARRIER, M.J. (1999). Molecular dynamics computation of gas-phase nanoparticle sintering: A comparison with phenomenological models. *J Aerosol Sci* **30**, 1139–1151.
- ZHANG, W. & GLADWELL, I. (1998). Sintering of two particles by surface and grain boundary diffusion—a three-dimensional model and a numerical study. *Comp Mater Sci* 12, 84–104.
- ZHANG, W. & SCHNEIBEL, J.H. (1995). The sintering of two particles by surface and grain boundary diffusion—a two-dimensional numerical study. *Acta Metallurgica et Materialia* **43**, 4377–4386.
- ZHENG, H., SMITH, R.K., JUN, Y.-W., KISIELOWSKI, C., DAHMEN, U. & ALIVISATOS, A.P. (2009). Observation of single colloidal platinum nanocrystal growth trajectories. *Science* **324**, 1309–1312.
- ZHU, H.L. & AVERBACK, R.S. (1996). Sintering processes of two nanoparticles: A study by molecular-dynamics. *Philos Mag Lett* 73, 27–33.