Growth of Y-Shaped Nanorods through Physical Vapor Deposition

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ABSTRACT

This work presents a proposed mechanism for fabricating Y-shaped nanorods, demonstrates the feasibility of the proposal through classical molecular dynamics simulations, and validates the simulations through magnetron sputter deposition experiments. The proposed mechanism relies primarily on the formation of stacking faults during deposition and to a lesser degree on diffusion kinetics and geometrical shadowing. Applications of the proposed mechanism may enable the design of nanorod arrays with controlled branching.

Going from nanoscience to nanotechnology, it is essential to be able to manufacture sophisticated nanostructures from simpler nanostructures or even from single atoms.¹ Using chemical processes, one may start from a vapor and use a liquid or solid catalyst to grow one-dimensional nanowires. The introduction of catalyst nanoparticles onto grown nanowires and the subsequent continuation of nanowire growth results in branched nanowires or nanotrees.² It is also feasible to grow branches using crystal polymorphisms.³ A nanoparticle of cubic crystal structure has four {111} planes. On each of the four planes, a noncubic polymorph of the crystal may develop into a branch. These branches together form a tetrapod.³ Both nanotrees and tetrapods are the result of chemical processes.

In parallel to chemical processes, various physical processes have been employed to fabricate simple one-dimensional nanostructures, such as nanorods and nanosprings. The glancing angle deposition (GLAD) technique,^{4–6} which exploits the shadowing effects, is used widely in fabricating these nanostructures. Accompanying the simplicity of physical processes is the lack of controllability. In particular, there is no catalyst to guide the growth of sophisticated structures. However, the intrinsic crystal properties, such as stacking faults, have led to the formation of interesting nanostructures. As a result of either low stacking-fault formation energy or insufficient atomic diffusion, twins are common in nanoparticles of face-centered cubic (FCC),^{7–9} body-centered tetrahedral (BCT),¹⁰ and diamond cubic structures.^{11,12} Our previous studies using molecular dynamics

simulations and magnetron sputter deposition have shown that Cu nanorods can be faceted and zigzag in shape.^{13,14}

Here we propose a mechanism for fabricating Y-shaped nanorods by exploiting the stacking faults. The starting point is a series of $\langle 110 \rangle$ Cu nanorods (Figure 1a), which could develop during magnetron sputter deposition.¹⁵ The top of the rods are covered with high-symmetry (and low formation energy) surfaces, {111}, {100}, and {110}. The relative dimensions of these surfaces are close to those from a Wulff construction. During deposition, stacking faults develop on the {111} surfaces. Two branches develop from the two {111} surfaces because of the stacking faults, and they have different crystal orientations. A grain boundary forms at the intersection of the two branches as shown in Figure 1b. The grain boundary provides energetically less preferred incorporation sites for subsequently deposited atoms. Consequently, a gap forms between the two branches, typical of grooving during thin-film deposition. When shadowing effects are strong, such as in GLAD, the gap deepens and two branches develop, as shown in Figure 1c. Each of the two branches is faceted and zigzag in shape.¹³

The proposed mechanism for the Y-shaped formation, as illustrated in Figure 1, bears both similarities and differences with the growth mechanism of tetrapods.³ Both mechanisms rely on the four {111} planes in cubic crystals. While the tetrapods grow through chemical processes, the Y-shaped nanorods develop through physical processes. Further, the four branches of a tetrapod exhibit different crystal structures compared to the seed, which is cubic; in contrast, branches of the Y-shaped nanorods have the same cubic structure as the seed.

Molecular Dynamics Simulations. As a first step of examining the feasibility of the proposal, we use classical

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Figure 1. Mechanism of Y-shaped Cu nanorod formation. (a) Periodic array of $\langle 110 \rangle$ nanorods with coordinates and crystal orientations; θ is the incident angle, and ϕ is the azimuthal angle. (b) Branching upon the formation of stacking faults. (c) Fully developed Y-shaped nanorods. The red spheres represent atoms in stacking faults, the purple spheres indicate $\{100\}$ facets, and the light-gray spheres represent $\{111\}$ facets.

molecular dynamics simulations to mimic an idealized environment of physical vapor deposition, GLAD. The 2×2 periodically repeated image of the simulation cell is the same as the configuration in Figure 1a. The molecular dynamics simulations depend critically on four elements: (a) interatomic potential, (b) setup of simulation cell, (c) temperature control, and (d) results analyses. The interatomic potential of Cu is in the form of the embedded atom method,²⁰ calibrated to reproduce ab initio values of stacking fault and twin formation energies.²¹ This potential has produced reliable results on surface diffusion^{17,18} and surface elasticity.²² The simulation cell is set up for the best representation of the pattern of substrate prepared in experiment. We adopt the periodic boundary in horizontal directions to represent a periodic array of nanorods. At the start, the nanorods are of $\langle 110 \rangle$, that is, their $\langle 110 \rangle$ direction points upward. The dimensions of the substrate in the horizontal directions are about $18 \times 18 \text{ nm}^2$. The initial nanorod is 3.5 nm in height and 5 nm in diameter; 5 nm is also approximately the diffusion distance of adatoms in the simulations. The substrate is 2.5 nm in thickness. The atoms in the bottom region, about 1.2 nm in thickness or twice the cutoff of the interatomic potential, are fixed to mimic an infinitely large bulk region. The other atoms in the substrate region are controlled under a constant temperature²³ in order to serve as a thermal bath. The nanorod is free from temperature control to avoid

Figure 2. Growth processes of Y-shaped Cu nanorods in molecular dynamics simulations. (a) Stacking-fault formation on $\{111\}$ planes. (b) Grain boundary formation and grooving as two stacking faults meet. (c) The second stacking fault forms in each branch. (d) Multiple stacking faults form in each branch. (e) Expanded view of the top section of b, with a slightly different perspective.

potential artifacts of random forces. The substrate temperature is maintained at 700 K to ensure sufficient diffusion without eliminating the diffusion anisotropy. The deposition is performed at the incident angle, θ , of 84° , and the shadowing effect is considered based on periodic geometry. Atoms deposited away from columns are not shown in our results for neatness. The deposition rate is chosen to be one atom every 250 integration steps as a compromise of computational cost and sufficient diffusion. The deposited atoms carry no more than 0.40 eV kinetic energy to minimize surface heating. The result analysis is performed by using the common-neighbor technique.²¹ Atoms in the stacking-fault layers have 12 nearest neighbors forming 6 sets of 421 and 422 configurations, FCC atoms have 12 nearest neighbors but form 12 sets of 421 configurations.

As shown in Figure 2a, stacking faults develop on the two $\{111\}$ planes. The intersection of the two stacking faults triggers the gap formation (Figure 2b). As deposition continues, multiple stacking faults develop in each branch, shown in Figure 2c and d. A series of simulations as a function of deposition angle show that the Y-shaped nanorods (Figure 2d) will develop as long as the incident angle, θ , is

greater than 78° . Below this angle, the columns become mushroom-shaped, as observed in our previous experiments.¹⁵

In addition to demonstrating the proposed mechanism of Y-shaped nanorod formation, the molecular dynamics simulations also reveal the contribution of kinetic barriers between facets. The facets develop on each branch, as shown in Figure 2e. Incident atoms land primarily on $\{111\}$ surfaces as a result of geometrical shadowing. To reach the grain boundary, they have to diffuse from the $\{111\}$ to a $\{100\}$ facet. This diffusion process has a large three-dimensional Ehrlich–Schwoebel barrier of 0.40 eV,^{17–19} which is insurmountable during room-temperature deposition with a typical deposition rate of micrometers per minute. This diffusion barrier results in, or at least contributes substantially to, the complete separation of the two $\{111\}$ branches.

Experimental Validation. To validate the proposed mechanism, we deposited Cu nanorods in an ultrahigh vacuum glancing angle magnetron sputter deposition system with a base pressure of 10^{-9} Torr. To obtain the isolated Cu nanorods, we initially patterned Si(001) substrates using a monolayer of 500-nm-diameter polystyrene spheres that self-assemble from colloidal suspensions into a hexagonal close-packed array as described in detail in ref 16. Sputtering was then carried out in 2 mTorr 99.999% pure Ar using two 7.5-cm-diameter Cu targets (99.999% pure), mounted at an angle of 180° with respect to each other and with their surfaces being perpendicular to the substrate surface. As discussed above, the large incident angle assists the formation of Y-shaped branched structures because of atomic shadowing. In our experiment, the average incident angle, θ , is controlled by the relative positions of the targets, the substrate and a collimating plate, and was chosen to be 84° , consistent with our molecular dynamics simulations, with a spread from 83° to 88° .¹⁶ During deposition, the substrate was rotated continuously about the polar axis with a speed of 60 rpm so incident atoms arrive at the substrate from azimuthal angles. No external substrate heating was applied. However, plasma heating increased the growth temperature from room temperature to 96°C , as measured by a thermocouple in the substrate holder. Film microstructures were investigated using a ZEISS SUPRA55 scanning electron microscope operated at 5 kV, an extractor current of $182\ \mu\text{A}$, and the e-beam incident normal to the substrate surface. We took more than 100 micrographs from multiple samples. The nanorods exhibit various orientations and can be classified into three categories: Y-shaped $\langle 110 \rangle$ nanorods, single crystal $\langle 111 \rangle$ and $\langle 001 \rangle$ nanorods, and polycrystalline nanorods. From the information obtained in the SEM images, it is accurate to declare that the proposed branching mechanism works well for nanorods that are $\langle 110 \rangle$ oriented.

The micrograph in Figure 3a shows that many Cu nanorods branch out. Analyses of 96 comparable micrographs indicate that three categories of nanorods exist. One of the three is of $\langle 110 \rangle$ type before branching, as outlined in the figure. Figure 3b is a higher-magnification micrograph of a Y-shaped Cu nanorod outlined in Figure 3a. It exhibits two hexagonal facets that represent the $\{111\}$ growth fronts of

Figure 3. SEM images of Y-shaped Cu nanorods in large area (a) and zoom-in region (b). The broken lines and labels in b are drawn to help visualize the facets.

the two branches, with the same configuration as the schematic of Figure 1b. In addition to these terminating facets, the micrograph also shows the faceted side-walls of the branch, $\{100\}$ and $\{111\}$ facets. The dark contrast at the origin of the branches is likely due to a depression in the nanorod walls associated with the interception of the stacking faults. Furthermore, the sequence of changing facets, each of the family $\{111\}$ but with different normal directions, clearly indicates the position of the stacking fault.

It is worth noting that we have observed branching in the experiment for only a fraction of the nanorods. This fractional

nature may be ascribed to the fact that the initial nanorods are not all perfectly $\langle 110 \rangle$ -oriented and the stacking-fault nucleation and shadowing processes have random natures. However, in principle, the nanorod orientation as well as the degree of shadowing, defined by the geometric relation to the neighboring nanorods and the deposition flux direction, can be controlled. In that case, one can envision devising strategies to create arrays of nanorods with controlled branching using this simple process.

In summary, we have proposed a mechanism for fabricating Y-shaped nanorods using physical vapor deposition. The classical molecular dynamics simulations demonstrate that the proposal is feasible. Furthermore, these simulations show that stacking-fault formation is the necessary factor and that the large three-dimensional Ehrlich–Schwoebel barrier and geometrical shadowing are also important factors. The accompanying magnetron sputter deposition experiments provide positive confirmation to the proposed mechanism and the subsequent molecular dynamics simulations.

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