Supporting Information

Highly Ordered Arrays of Metal/Semiconductor Core-Shell Nanoparticles with Tunable Nanostructures and Photoluminescence

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Methods

Fabrication of ultra-thin alumina masks (UTAMs) and In nanoparticle arrays on Si/SiO₂ substrates (Figure S1)

The UTAMs we used were prepared in a two-step anodization process. High-purity (99.99+%) aluminum foil of about 0.22 mm thickness was used as the starting material. Before anodization, the aluminum foil was first degreased with acetone, and then annealed at 400°C for 4 hours under vacuum conditions to remove mechanical stresses; finally, it was electropolished in a 1:9 solution of perchloric acid and ethanol. After the first anodization step (a) in 0.3 M oxalic acid solution at 40 V in 17 °C for 10 h, the anodic oxide layer was removed in a mixture of H₃PO₄ (6 wt%) and H₂CrO₄ (1.8 wt%) at 60°C (b). This specimen was anodized again for a very short time resulting in a very thin alumina layer (c). Then, a PMMA layer was deposited on the top of the alumina layer from a 6% PMMA/chlorobenzene solution, and baked at 120°C for about 25 min (d). After that, the Al layer was removed in SnCl₂ solution. The removal of the barrier layer and the following pore-widening process was carried out in 5 wt% H₃PO₄ solution, forming an UTAM with a PMMA layer on the top. Then the UTAM/PMMA was mounted on the substrates (Si/SiO₂) (e). The PMMA layer was removed using acetone or chloroform (f), and the UTAM was finally attached on the substrate with the quick drying of the acetone. In nanoparticle arrays were thermally evaporated using the Edwards Auto 306 Evaporator (g); the vacuum is about 5E-6 torr while the evaporation rate is about 0.2-0.3 nms⁻¹. After the preparation of the In nanoparticle arrays, the UTAMs were floated away from the substrates in acetone bath for 1~2 minutes, leaving the highly ordered In nanoparticle arrays on the surface of the substrate (h). The UTAMs prepared by oxalic acid solution are used to fabricate nanoparticles in the size-range of 40-80 nm, we also use sulfuric acid and phosphoric acid solutions to fabricate UTAMs, which are used to fabricate nanoparticles in the size-range of 10-40 nm and 80-100 nm respectively. The area of the

UTAM is about 2.25 cm^2 with our current anodization setup and can be as large as several tens of square centimeters with modified setup.

Figure S1. Schematic outline of the fabrication of ultra-thin alumina mask and highly ordered In nanoparticle arrays.

Detailed analyses of the crystalline orientation of the In and In₂O₃ nanoparticles

In nanoparticles (Figure S2) and In₂O₃ nanoparticles (Figure S3)

Figure S2. Detailed analysis of the cross-sectional HRTEM image (a) of an In nanoparticle in Sample A (same image as Figure 3a₁). a₁ is the low-magnification image. b, b₁ and c are the Fourier transformation patterns of the same-large squared areas b, b₁ and c in a, which are in the In nanoparticle and Si substrate respectively. d and e are the Fourier filtered lattice images of the areas b and c in a. To study the relative orientation relationship between In and Si, we performed the simulation of electron diffraction patterns along the [111] direction of In [Sys: Tetragonal, S. G.: I4/mmm (139)] (f) and the [110] direction of Si (g), both of them have been rotated so that they fit the patterns in b and c exactly. The surface normal of the Si (001) substrate is defined by the arrow in g. We moved the arrow to f and found that the In (101) plane has almost the same direction as the surface normal direction of Si, which indicates that the In (101) plane is parallel to the Si (002) plane. Therefore, the relative orientation relationship between In and Si was identified as In(101)[111]//Si(002)[110]. The white and black parallel lines at the bottom right corner in d and e are the In (101) and Si (002) planes, respectively. There are about 22 lattice distances along the surface normal direction in d and e. Thus the lattice distance ratio of In (101) to Si (002) is about 1:1, which is in good agreement with the standard value of 2.71:2.72. The lattice directions in areas b and b₁ (b and b₁) are about the same.

Figure S3. Detailed analysis of the cross-sectional HRTEM image (a) of an In₂O₃ nanoparticle in Sample H (same image as Figure 3c₁). b, and c are the Fourier transformation patterns of the same large squared areas b and c in a, which are in the In₂O₃ nanoparticle and Si substrate respectively. d and e are the Fourier filtered lattice images of the areas b and c in a. To study the relative orientation relationship between In₂O₃ and Si, we performed the simulation of electron diffraction patterns along the [110] directions of In₂O₃ (Sys: Cubic, S. G.: Ia3(206)) (f) and Si (g), both of them have been rotated so that they fit the patterns in b and c exactly. The surface normal of the Si (001) substrate is defined by the arrow in g. We moved the arrow to f and found that the In₂O₃ (222) plane has almost the same direction as the surface normal direction of Si, which indicates that the In₂O₃ (222) plane is parallel to the Si (002) plane. Therefore, the relative orientation relationship between In₂O₃ and Si was identified as In₂O₃(222)[110]//Si(002)[110]. The white parallels lines at the bottom right corner in d and e are the In₂O₃ (222) and Si (002) planes, respectively. There is about 13 lattice distances for In₂O₃ (222) plane and about 14 lattice distances for Si (002) plane along the surface normal direction in d and e. Thus the lattice distance ratio of In₂O₃ (222) to Si (002) is about 1.077 (14:13), which is in good agreement with the standard value of 1.074 (2.92:2.72).