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Semiconductor Nanostructures: Fabrication, Characterization and Application
半導體納米結構：合成，表徵和應用

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Abstract

Nowadays, fabrication, characterization and application of semiconductor nanostructures progress rapidly. Controlled synthesis of one-dimensional nanostructures and controlled assembling of nanoparticles into superstructures are two key topics in materials science and technology for their important application in nano-electronics and nano-optoelectronics.

The objective of the thesis is to design and construct a MOCVD (Metalorganic chemical vapor deposition) system for preparing one dimensional semiconductor nanostructure for nano-device application. So the first part of thesis is the instrument building for nanowire synthesis; Simultaneously, ZnO as a semiconductor material system is chosen as an example to be studied involving the growth mechanism of VS growth of ZnO nanowire and self-assembly mechanism of ZnO mesocrystals which demonstrate in the second and third parts of the work.

MOCVD, a complementary deposition technique to molecular beam epitaxy (MBE), enables growing device-quality semiconducting materials including single-crystal films. With the emergence of the bottom-up approach for device

fabrication, this technique has been implemented for controlled growth of nanomaterials too. The first part of this thesis discusses the construction of a recently built MOCVD system at COSDAF, principle of its operation and use for synthesis of nanomaterials. In particular, the system was tested and used to synthesize ZnSe nanowires with a small diameter of about 20 nm.

Zinc oxide (ZnO) nanowire synthesized from direct Zinc (Zn) vapor transport in O_2 environment has been studied in the second part of this work. The results show that the first step is the formation of a ZnO film on the substrate. Then an anisotropic abnormal grain growth in the form of ZnO platelets takes place. Subsequently, single crystalline ZnO platelets grow in [0001] direction to form whiskers. During whisker growth, transformation from layer-by-layer growth to simultaneous multilayer growth occurs when the two-dimensional (2D) Ehrlich-Schwoebel (ES) barrier at the ZnO island edge is sufficiently large and the monolayer island diameter is smaller than the island spacing. As multilayered islands grow far away from the base, isotropic mass diffusion (spherical diffusion) will gradually displace anisotropic diffusion (linear diffusion), which contributes to the formation of a pyramid on the top plane of the whisker. Once the pyramid contains enough atomic layers, the 2-dimensional ES barrier transits to 3-dimensional ES barrier which leads to repeated nucleation and growth of multilayered islands or pyramids on the existing pyramids. The pyramids play a critical role to taper the whisker to nanorod with a diameter less than 100 nm. The nanorod then grows to nanowire via repeated growth of epitaxial hexagonal-pyramid shape-like islands on the (0001)-plane with $\{11\bar{2}3\}$ facets as the slope planes. During coarsening, the breakage of step motion of $\{11\bar{2}3\}$ facets and the appearance of $\{11\bar{2}0\}$ facets on the base of pyramids may result from the step bunching of {0001} facets, which is consistent with the existence of “2D” Ehrlich-Schwoebel barrier on the edge of (0001) facets.

Alignment of nanoparticle building blocks into ordered superstructures by the bottom-up approach has been studied in the third part of this work. Self-organization of ZnO nanoparticles into various superstructures (sheet, platelet, ring, dumbbell-shaped tube and rod) has been achieved with the assistance of micelles formed by surfactant cetyltrimethylammonium bromide (CTAB) under one-pot condition. The CTAB-modified zinc hydroxy double salt (Zn-HDS) mesocrystals act as intermediates to form ZnO hexagonal superstructures at temperatures as low as 50 °C. The thermal decomposition temperature of Zn-HDS mesocrystals is much lower than that of the corresponding bulk for that the organic additive CTAB effectively decreases the degree of crystallinity. Taking advantage of temperature-induced phase transformation of micelles, two-stage self-organization can form ZnO platelet mesocrystals. The structural transformation of micelles to shape templates can offer a potential new route for

self-assembly of non-spherical colloids as building blocks into three-dimensional photonic crystals. The influence of continuous nucleation and ion-by-ion attachment on mesocrystals formation has been systematically studied, and the findings demonstrate they not only facilitate modification of orientation of nanocrystals, but also enhance the elimination of defects and organics leading to more perfect single crystals.

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hindered by the ES barrier at the edge of {0001} facets, which contribute to step bunching and formation of a hexagonal prism with six sidewall facets $\{11\bar{2}0\}$ (Fig. 3-6d, 3-6e) or a dodecagonal prism bounded by $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ (Fig. 3-6f).

Fig. 4-1 (a) XRD results on the products by injecting ammonia solution into $Zn(NO_3)_2 \cdot 6H_2O$ and CTAB solution at 25°C , 50 °C, and 100°C respectively; (b) XRD results on the products by injecting ammonia solution into $Zn(NO_3)_2 \cdot 6H_2O$ solution at 25°C, 50 °C, or 100°C respectively.

Fig. 4-2 (a) FE-SEM and (b) HRTEM image analysis for the product prepared by just mixing ammonia solution with $Zn(NO_3)_2 \cdot 6H_2O$ solution at 25°C;(c) FE-SEM image for the product prepared by mixing ammonia solution with $Zn(NO_3)_2 \cdot 6H_2O$ solution at 50°C; (d) FE-SEM image for product prepared by just mixing ammonia solution with $Zn(NO_3)_2 \cdot 6H_2O$ solution at 100°C. Without CTAB, the products prepared at 25 ^{o}C (Fig. 4-2a); 50 ^{o}C (Fig. 4-2c); and 100 ^{o}C (Fig. 4-2d) have the same sheet morphology. The HRTEM image (Fig. 4-2b) demonstrates that the sheet is formed by aggregated growth of nanoparticles without inter-crystalline free spacing, different from the sheets prepared with CTAB.

Fig. 4-3 (a) FE-SEM image and (b) TEM image of the sheets obtained in the typical synthesis using CTAB as organic additive and ammonia as reaction precursor at 25^0C; (c) SAED pattern consists of two dimensional elongated but individual diffraction spots corresponding to Zn-HDS; (d) HRTEM image of the central part of the sheet. The crystals 1, 2, 3 and 4 are assembled with space (arrow) separating them.

Fig. 4-4 (a) FE-SEM images of sheets obtained in the typical synthesis using CTAB as additive and ammonia as reaction precursor at 50^0C. (b) Some sheets are not in perfect hexagonal shape with equal sizes. Images in (b) and (c) show the sheets are usually composed of several layers (arrow). Hexagonal rings composed of large nanocrystals can be observed in (c) and enlarged image in (d).

Fig. 4-5 (a) TEM image of sheets; (b) HRTEM image of one side of the sheet shows good crystalline structure. (c) Fourier transform; and (d) enlarged image of the square region in (b) demonstrates the subunits share a single crystallographic orientation with edge dislocations between them.

Fig. 4-6 (a) XRD, (b) FE-SEM and (c) HRTEM analysis for the products, which were prepared by reacting $Zn(NO_3)_2{\cdot}6H_2O$ and CTAB solution with ammonia solution at 25 ^{o}C, then gradually heating to 100 ^{o}C at 2 ^{o}C /min and maintained at 100 ^{o}C for 5 mins.

Fig. 4-7 (a, b) FE-SEM images of platelets and rings obtained in a typical synthesis using CTAB as organic additive and ammonia as reaction precursor at 100^0C; (c) A pentagon ring is rare but does exist; (d) The sides of platelet are unequal with the core showing some holes among loosely-aligned ellipsoidal ZnO nanostructures; (e) The cross-section of a platelet shows that it is composed of two layers of ellipsoidal structures; (f) The large, free ellipsoidal nanostructures are composed of smaller nanocrystals.

Fig. 4-8 (a) TEM image of the complex platelet and (b) the corresponding electron diffraction pattern of (a); (c) Enlarged TEM image suggests that complex hexagon sheets are composed of many ZnO nanocrystals following (0001) direction; (d) The HRTEM image and (e) Fourier transform confirm that particles are aggregated to share a single crystallographic orientation; (f) Cross-section of ZnO complex platelets shows they are composed of two layers of rod-like structure (single rod: width: 40 nm, height: 80 nm); (h) HRTEM image and (g) Fourier transformation demonstrate that the rod is composed of smaller prismatic ZnO nanocrystals (width: about 10 nm) observed along $[10\bar{1}0]$ direction; (i) TEM image of ellipsoidal mesocrystals and (j) the enlarged image of the top demonstrate that they are also assembled from smaller nanocrystals. The elongated but individual spots in the corresponding SEAD (k) further support the assembly of nanocrystals.

Fig. 4-9 A two-step oriented attachment proposed for the formation of ZnO platelet mesocrystals.

Fig. 4-10 (a) FE-SEM image of sheets obtained in a typical synthesis with HMT as the reaction precursor at 60^{o}C; (b) TEM image of sheet shows an elongated hexagonal morphology; (b1) The spots of the corresponding SAED confirm the self-assembled structure; (b2) The four sides making two 60 ° angles show “hair-like” structures; (c) The enlarged TEM image clearly shows that the sheet is composed of small nanocrystals; (d) The HRTEM image of the tip and (e) center of the sheet demonstrate that it is also assembled from many nanocrystals following $[10\bar{1}0]$ direction; (f) Fourier transformation demonstrates that the assembled structure has a near-perfect single-crystal orientation.

Fig. 4-11 (a) TEM image of the sheet structure; (b) Enlarged TEM image of the hair-like structures at the ends of the sheet structure; (c) The HRTEM images of the top and (d) the side of the rod show the hairs are due to aggregation of nanocrystals.

Fig. 4-12 Schematic demonstrates the oriented attachment process leading to the formation of a sheet prepared with HMT as the precursor at 60°C.

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List of Acronyms

NWs	nanowires
LEDs	light emitting diodes
APDs	avalanche photodiodes
VLS	vapour–liquid–solid
SLS	solid–liquid–solid
VS	vapor-solid
CVD	chemical vapour deposition
MBE	molecular beam epitaxy
MOCVD	metalorganic chemical vapor deposition
OMCVD	organometallic chemical vapor deposition
MOVPE	metalorganic vapor phase epitaxy
OMVPE	organometallic vapor phase epitaxy
VPE	vapor epitaxy
OMs	metalorganics
EP	electropolish
ML	monolayer
UHV	ultra high vacuum
GSMBE	gas source molecular beam epitaxy
CBE	chemical beam epitaxy

OAG	oxide-assisted growth
SEM	scanning electron microscopy
TEM	transmission electron microscopy
HRTEM	high-resolution transmission electron microscopy
XRD	X-ray diffraction
PL	photoluminescence spectra
CL	cathodoluminescence spectra
ES barrier	Ehrilich-Schwoebel barriers
2D ES barrier	two dimensional Ehrilich-Schwoebel barriers
3D ES barrier	three dimensional Ehrilich-Schwoebel barriers
CTAB	cetyltrimethylammonium bromide
Cmc	critical micelle concentration
HMT	hexamethylenetetramine
Zn-HDS	zinc hydroxy double salt
SAED	selective area diffraction