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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<sub>2</sub> 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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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°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.

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Fig. 4-14 (a) TEM image of dumbbell-shaped tube and (b) the corresponding electron diffraction image; HRTEM images showing the outside part of one side (c) and one corner (d) of the nanotube, and the inside part of the corresponding side (e) and the corner (f) of the nanotube demonstrate that the tube is assembled from nanocrystals; (g) TEM image of the tube viewed from the side and (h) the corresponding electron diffraction demonstrate that the tube has a single-crystal structure; (i) The HRTEM image at the waist positions of the tube shows no twin structure.

Fig. 4-15 (a, b) FE-SEM images of the sample obtained when the reaction time was extended to half an hour; (c) FE-SEM image demonstrates that the dumbbell-shaped tube begins to grow inward at the waist; (d) FE-SEM image demonstrates that the center of the dumbbell-shaped rod usually has some holes.

Fig. 4-16 Growth process of the dumbbell-shaped tube and rod.



# List of Tables

Table 2-1 A list of differences between MOCVD and MBE.

# 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	Ehrlich-Schwoebel barriers
2D ES barrier	two dimensional Ehrlich-Schwoebel barriers
3D ES barrier	three dimensional Ehrlich-Schwoebel barriers
CTAB	cetyltrimethylammonium bromide
Cmc	critical micelle concentration
HMT	hexamethylenetetramine
Zn-HDS	zinc hydroxy double salt
SAED	selective area diffraction