Table of Contents

Abstract (in Chinese)……..I
Abstract (in English)……III
Acknowledgements……...V
Table of Contents……VI
List of Tables……..……IX
List of Figures……...X

Chapter1 Intorduction 1
1.1 Background……1
1.1.1 Planar organic materials……2
1.1.1.1 Coronene……3
1.1.1.2 Copper phthalocyanine (CuPc)……..……3
1.1.1.3 Perylene tetracarboxylic dianhydride (PTCDA)..……..…4
1.1.2 Molecular Electronic Devices……4
1.1.2.1 Organic Thin Film Transistors (OTFTs)..……..…4
1.1.2.2 Organic Light Emitting Diodes (OLEDs) ……6
1.1.2.3 Photovoltaic Devices……...……..…7
1.1.3 One Dimensional Nanostructures……..……7
1.2 Aims of this Thesis……8
1.3 Outline of this Thesis……..9

Chapter2 Literature Review 11
2.1 Thin Film Growth……11
2.2 Surface Energy…….……15
2.2.1 Definition of Surface Energy……..…….……15
2.2.2 Wetting……...…….……16
2.2.3 Contact Angle and surface energy……...…...…….……17
2.2.3.1 The ZISMAN method…….……..…18
2.2.3.2 Equation of State…….……..…19
2.2.3.3 The FOWKES method……..…20
2.2.3.4 The OWENS, WENDT, RABEL and KAELBLE method……..22

2.2.3.5 The WU method……..23
2.3 Intermolecular Forces……..…25
2.3.1 Interaction between dipolar molecules…….…….…….…..…26
2.3.2 Dipole-induced dipole interactions…….…….…….……..….27
2.3.3 Dispersion forces……..…..…….……..…28
2.3.4 Repulsive forces…….…29
2.4 One Dimensional Organic Nanostructures…….…….……..…30
2.4.1 AlQ_3 nanowires……..…….……..…30
2.4.2 Anthracene (AN) nanowires and perylene (PY) nanorods……..…31
2.4.3 AgTCNQ and CuTCNQ nanowires……..…….…….……..…33
2.5 Field Emission Theory……...…….…….……..…34

Chapter 3 Self-assembled Nanofibers of Polycyclic Aromatic Hydrocarbon 37
3.1 Introduction……...……...…….……..……37
3.2 Experimental Section……...…….……..……38
3.3 Results and Discussion……..…….……..…..…39
3.3.1 Factors that influence film morphology…..…….……..…..…40
3.3.1.1 Deposition time……...…40
3.3.1.2 Deposition rate……...…41
3.3.1.3 Substrate Temperature…..……...….42
3.3.1.4 Substrate Effect (Surface Energy)……...43
3.3.2 HRTEM…..……..…….……..…..…43
3.3.3 Thermal Stability……..…….……..…..…45
3.3.4 Field Emission of CNFs film……..…….……..…..…46
3.3.5 Field Emission of single individual CNF……..…….…….……..…..…48
3.3.6 Application as a pillar template…..…….……...…..……..…..…50
3.4 Conclusions……....…….……..…..…51

Chapter 4 Self-assembled Nanofibers of Copper Phthalocyanine 52
4.1 Introduction……...……...…….……..……52
4.2 Experimental Section……...…….……..……53
4.3 Results and Discussion……...…….……..……54
4.3.1 Film morphology……...…….……..……54

4.3.2 Surface energy……56
4.3.3 Crystal phase indentified by GIXRD……57
4.3.4 Crystal phase indentified by Raman spectrometer……59
4.3.5 HRTEM……61
4.3.6 Field emission of CuPc nanofibers film……63
4.4 Conclusions……65

Chapter 5 Self-assembled nanofibers of perylene derivative molecules 66
5.1 Introduction……66
5.2 Experimental Section……67
5.3 Results and Discussion……68
5.3.1 Film morphology……69
5.3.2 Subatrate effect……71
5.3.2.1 Topography of substrate……71
5.3.2.2 Reactive sites of substrate……73
5.3.3 HRTEM……73
5.3.4 Exterior of PTCDA nanofibers……75
5.3.5 Field emission of PTCDA nanofibers film……76
5.3.6 Field emission of single PTCDA nanofiber……78
5.4 Conclusions……81

Chapter 6 Conclusions……82
Chapter 7 Future works……86
References…… 88
List of Publication……100

List of Tables

Table 4-1 Raman peak parameters of α- and β-phase CuPc thin film. The corresponding interpretation is also listed in the table [149]……..……....60

Table 5-1 The concentration of trace elements on Ti-CVD substrate and Ti-PVD substrate. ……..……...……....73

List of Figures

Figure 1-1 Self-assembly of plannar molecules resulted in π–stacked columnar aggregates. The vertical arrow indicated the one-dimensional charge transport pathway along the columnar stacks.……..……....2

Figure 1-2 Plannar molecule studied in this thesis: (a) coronene, (b) perylene tetracarboxylic dianhydride, and (c) copper phthalocyanine…….……....3

Figure 1-3 Two kinds of scheme of organic thin film transistor: (a) bottom contact mode, and (b) top contact mode…….……...……....5

Figure 1-4 The scheme of (a) organic light emitting diode, and (b) photovoltaic device…….……6

Figure 2-1 (a) Elementary processes during MBE growth. Atoms from the gas phase adsorb on the surface. There, the monomers diffuse on terraces, incorporate in step edges, form two dimensional and three-dimensional clusters or desorb again into the gas phase. The arrows indicate a selection of possible processes during the deposition. (b) Energy of a system which changes from state *a* to state *b*. The energy barriers E_{ab} for the transition *a* → *b* and E_{ba} for the transition *b* → *a* are indicated, together with the energy E^* of the most unfavored transition state. ……..…12

Figure 2-2 Schematic of the Ehrlich-Schwoebel barrier. (a) Adatoms diffusing from the lower layer to the step edge. (b) Adatoms diffusing from the upper layer to the step edge…….……..…12

Figure 2-3 Different types of epitaxial relationships between the two-dimensional lattices of the substrate surface (lattice vectors a_1 and a_2) and an adsorbate layer (lattice vectors b_1 and b_2). (a) Commensurate structure, (b) coincident structure, and (c) incommensurate structure. …….. 13

Figure 2-4 Schematic of the basic growth modes: (a) layer-by-layer growth, (b) island growth, and (c) Stransky-Krastanov growth…… 15

Figure 2-5 Contact angle of a liquid on a solid surface. The symbols σs and σl describe the surface tension components of the two phases; symbol γsl represents the interfacial tension between the two phases…….…..… 18

Figure 2-6 Schematic diagram of the way to determine the critical surface tension according the ZISMAN method…….…..… 19

Figure 2-7 Schematic diagram of the way to determine (a) the disperse fraction of surface energy and (b) the polar fraction of surface energy according the FOWKES method……21

Figure 2-8 Schematic diagram of the way to determine the disperse and polar fraction of surface energy of a solid according the RABEL method……23

Figure 2-9 Dipoles in radom orientations specified by polar coordinatesθ_1 , ϕ_1 and θ_2 , ϕ_2, respectively [15]……..……26

Figure 2-10 TEM images of the AlQ_3 nanostructures, (a) TEM image of the AlQ_3 nanowires with a diameter of about 30-50 nm. (b) HRTEM image of a typical AlQ_3 nanowire. (c) TEM image of the AlQ3 nanobelts with a width of about 40–60 nm. (d) An AlQ_3 nanobelt rolls up along the axial direction after irradiated by the electron beam in TEM. The rolling angle increase as the current density increases. [97] ……...…. 31

Figure 2-11 (a) SEM image of the AN nanostructures, (b) SEM image of typical single AN nanowire, (c) Low magnification TEM image of the AN nanostructures, and (d) TEM image of typical AN nanowires. [98]……...……. 32

Figure 2-12 (a) SEM image of the perylene nanostructures, (b) SEM image of perylene nanorods, (c) Low magnification TEM image of the perylene nanorods, and (d) TEM image of a typical perylene nanorod. [98]……...…. 32

Figure 2-13 (a) SEM image of the AgTCNQ nanowires. The inset is its higher magnification image. (b) SEM image of the CuTCNQ nanowires. The inset is its higher magnification image. [99]……..……...…. 34

Figure 3-1 (a) Cross-sectional SEM image of PAH-CNFs deposited by vacuum sublimation for 90 minutes. (b) Illustration of the way to caculated the features of PAH-CNFs. ……39

Figure 3-2 Histograms of (a) tip radius, (b) fiber diameter and (c) fiber length of PAH-CNFs……..……..…. 39

Figure 3-3 SEM images of PAH-CNFs deposited by vacuum sublimation for (a) 1 minute, (b) 2 minutes, and (c) 15 minutes, respectively……...…. 41

Figure 3-4 (a) Side-view SEM images and (b) top-view SEM images of PAH-CNFs deposited by vacuum sublimation for 120 minutes……....…… 41

Figure 3-5 Side-view SEM images of PAH-CNFs deposited on gold substrate with rates of (a) 0.1 Å/sec and (b) 8 Å/sec……..…… 42

Figure 3-6 Side-view SEM images of PAH-CNFs deposited at (a) 40 °C, (b) 60 °C and (c) 100 °C, respectively……...…… 42
Figure 3-7 Top-view SEM images of PAH-CNFs deposited on (a) gold substrate and (b) silicon dioxide substrate……..… 43
Figure 3-8 (a) HRTEM image of a single PAH-CNF (diameter: 51 nm). Inset: the corresponding electron diffraction pattern. (b) Magnified image of this nanofiber. (c) HRTEM image of a hollow PAH-CNF (diameter: 420 nm). Inset: the corresponding electron diffraction pattern. (d) Magnified image of this hollow nanofiber along the edge……..…..… 44
Figure 3-9 Thermal desorption curve of (a) CO_2 (m/z = 44) and (b) C_6H_6 (m/z = 78) for both CNTs and PAH-CN……...…….……. 45
Figure 3-10 *J–E* curve of PAH-CNFs. Inset: corresponding Fowler-Nordheim plot.…. 46
Figure 3-11 Emission current stability of the PAH-CNFs at constant voltage…..…..… 47
Figure 3-12 SEM image of a tungsten probe kept at a distance of 200 nm above a one-micrometer-long PAH-CNF……..… 48
Figure 3-13 The field emission performance of the single individual PAH-CNF. The inset reveals J-E characteristics for PAH-CNFs followed Fowler Nordheim behavior…...49
Figure 3-14 (a) side-view and (b) top-view SEM images of PAH-CNFs capped with silicon dioxide by PECVD process. (c) side-view and (d) top-view SEM images of PAH-CNFs capped with silicon nitride by PECVD process……..…….…… 50

Figure 4-1 Top-view SEM images of CuPc layers deposited at room temperature on (a) SiO_2 and (b) Au and at 100 °C on (c) SiO_2 and (d) Au…… 55
Figure 4-2 Top-view SEM images of CuPc layers deposited on Au substrates at (a) room temperature and at (b) 100, (c) 150, and (d) 200 °C……..…… 56
Figure 4-3 XRD spectra of CuPc layers deposited on Au substrates at (a) room temperature and (b) 150 °C……..… 58
Figure 4-4 The molecular structure and atomic notation of CuPc molecule [148]...… 60
Figure 4-5 The Raman spectra of CuPc films deposited at 25 °C, 100 °C and 150 °C, respectively……...… 61
Figure 4-6 (a) HRTEM image of a single CuPc nanofiber (diameter: 16 nm). (b) Magnified image of this nanofiber, which has been over-contrasted to intensify the fringes, and the corresponding profile analyzed using Fuji Imagegauge software. (c) Schematic

illustration of CuPc molecules stacked at different inclination angles (φ)……..… 62

Figure 4-7 Field emission *J–E* curve of the CuPc nanofibers. Inset: Corresponding FN plot……...… 64

Figure 4-8 Emission current stability of the CuPc nanofibers at constant voltage..… 64

Figure 5-1 Top-view SEM images of PTCDA layers deposited on an Au substrate at values of T_{sub} of (a) 25, (b) 80, (c) 100, and (d) 120 °C and on a Ti substrate at values of T_{sub} of (e) 25, (f) 80, (g) 100, and (h) 120 °C. To discern the subtle difference between samples deposited at room temperature, the images of Figures 5-1 (a) and (e) have been magnified by 70,000 times, whereas the others have been magnified only 10,000 times..……... 70

Figure 5-2 Top-view SEM images of PTCDA layers deposited on (a) Ti-CVD and (b) Ti-PVD at values of T_{sub} of 100 °C……..… 72

Figure 5-3 AFM images of the (a) Ti-CVD (image area: 5 × 5 μm^2; height: 200 nm) and (b) Ti-PVD (image area: 2 × 2 μm^2; height: 34.77 nm) substrates……...… 72

Figure 5-4 (a) HRTEM image of a single PTCDA nanofiber formed on the Ti-CVD substrate at a value of T_{sub} of 100 °C. Inset: The corresponding electron diffraction pattern. (b) A magnified image of the nanofiber in (a), displaying its amorphous structure. (c) HRTEM image of a single Ti-included PTCDA nanofiber (diameter: 12 nm). The corresponding electron diffraction pattern in the inset displays Ti atoms within the fiber. (d) Magnified image of the nanofiber in (c), highlighting the heterogeneous region, which exhibits a crystallized structure……...… 74

Figure 5-5 Side-view SEM images of PTCDA nanofibers deposited on the Ti-CVD substrate at a value of T_{sub} of 100 °C……...… 75

Figure 5-6 Field emission *J–E* curve of the PTCDA nanofibers. Inset: Corresponding FN plot……..……...… 77

Figure 5-7 Emission current of the PTCDA nanofibers plotted at a constant voltage……..… 78

Figure 5-8 SEM image of a tungsten probe kept at a distance of 200 nm above a one-micrometer-long PAH-CNF……...… 79

Figure 5-9 Field emission *J–E* curve of the PTCDA nanofibers. Inset: Corresponding FN plot…… 79

E
S
A
1896