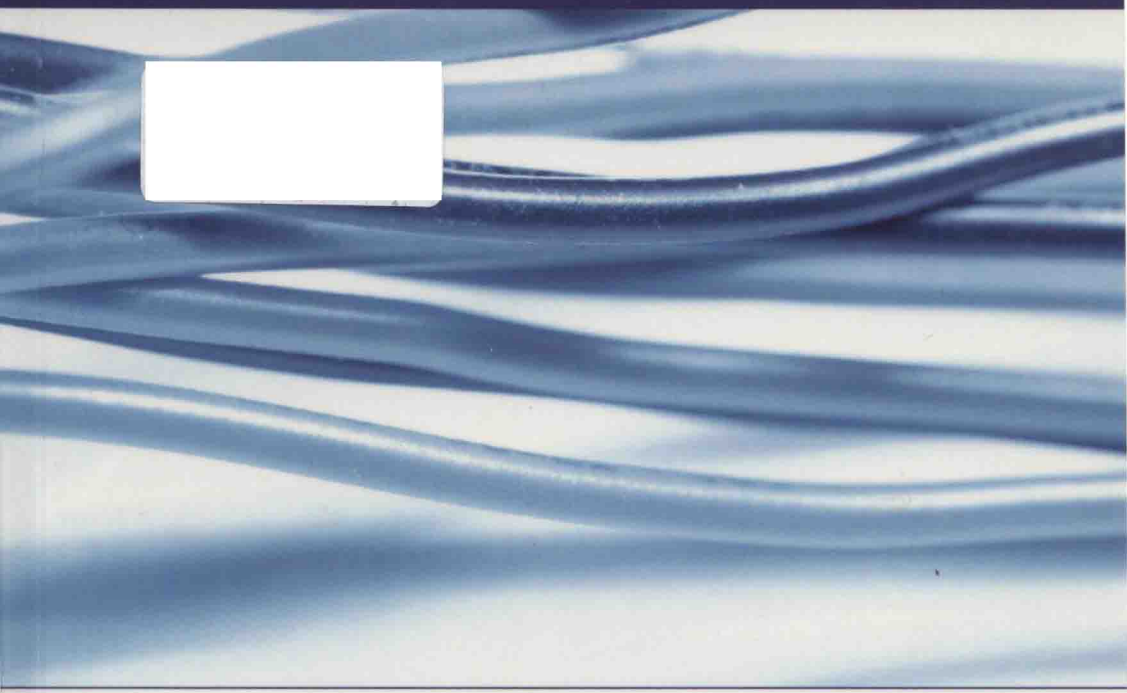

Marianna Perdiki

# Synthesis And Characterization Of Copper Oxide Nanowires

## CuO Nanowires as Semiconductors

LAP LAMBERT Academic Publishing

Marianna Perdiki

# Synthesis And Characterization Of Copper Oxide Nanowires

## CuO Nanowires as Semiconductors



LAP LAMBERT Academic Publishing

**Impressum / Imprint**
Bibliografische Information der Deutschen Nationalbibliothek: Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.d-nb.de abrufbar.


Bibliographic information published by the Deutsche Nationalbibliothek: The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.


Coverbild / Cover image: www.ingimage.com

Verlag / Publisher:
LAP LAMBERT Academic Publishing
ist ein Imprint der / is a trademark of
AV Akademikerverlag GmbH & Co. KG
Heinrich-Böcking-Str. 6-8, 66121 Saarbrücken, Deutschland / Germany
Email: info@lap-publishing.com

Herstellung: siehe letzte Seite /
Printed at: see last page
**ISBN: 978-3-659-31145-1**

Zugl. / Approved by: Nicosia, University of Cyprus, 2011

Marianna Perdiki

# Synthesis And Characterization Of Copper Oxide Nanowires

**Acknowledgements**

First and foremost I want to thank my supervisor Dr. Andreas Othonos, for his guidance during my research and study at the University of Cyprus. I appreciate his crucial contributions of time, ideas, and support without which this project would not have been completed or written. I gratefully thank Dr Mathew Zervos from the department of Mechanical and Manufacturing Engineering and Polina Papageorgiou for helping me learn SEM imaging and encouraging me during this project. I wish to thank all my family members for supporting and encouraging me to pursue this degree. Finally, I would like to thank my parents who raised me with a love for science and supported me in all my pursuits.

**Abstract**

Copper oxide nanowires are source of a great interest in the scientific community due to numerous properties and the wide range of possible applications of this nanoscale material. In this project, CuO nanowire growth was achieved using an atmospheric pressure chemical vapor deposition (APCVD) reactor via dry oxidation at various temperatures and gas flow rates. CuO nanowire synthesis was studied on a variety of different substrates, such as 50 nm Cu/$p^+$Si, 100 nm Cu/$p^+$Si, thin copper foil (0.12 mm thickness) and thick copper foil (1mm thickness). The growth of nanowires was successful, when the substrate was a thin copper foil. In particular, CuO nanowires were fabricated at temperatures between 400 °C and 700 °C. The growth lasted one hour using oxygen flow rate of 100 standard cubic centimeters per minute (sccm). In our experiments, copper oxide nanowires formed at 600 °C with ramp rate = 30 $^0$C/min. They have 2.5 - 9.0 μm length and diameters smaller than 200 nm. Afterwards, transport of nanowires on $p^+$Si(001) was studied using an ultrasonicator. The copper oxided layers were ultrasonicated with isopropanol at various times in order to have only nanowires without pieces of oxide layer on silicon substrate. The best results of transfer were found when the ultrasonication lasted twenty seconds. In this case, 1.82 ml of solution with nanowires was dropped on the surface of silicon, which was successfully covered with copper oxide nanowires. The photoluminescence (PL) spectrum at 300 K consisted of a broad peak centered at 419 nm. Moreover, time correlated single photon counting (TCSPC) PL measurements were taken at room temperature (RT) for 400 nm emission wavelength over a time span of 50 ns. These measurements show that the PL decay can be well described by a linear combination of three exponentials suggesting a complex energy level scheme structure for the CuO NWs.

**Table of Contents**

**ACKNOWLEDGEMENTS** ..... **1**

**ABSTRACT** ..... **2**

**TABLE OF CONTENTS** ..... **3**

**LIST OF FIGURES** ..... **7**

**LIST OF TABLES** ..... **15**

**INTRODUCTION** ..... **17**

1.1 WHAT IS NANOTECHNOLOGY? ..... 17

1.2 APPLICATIONS OF NANOTECHNOLOGY ..... 19

1.3 PROGRESS IN NANOTECHNOLOGY ..... 20

1.4 PROPERTIES AND APPLICATIONS OF ONE-DIMENSIONAL METAL OXIDE NANOSTRUCTURES ..... 20

1.5 SYNTHESIS OF ONE-DIMENSIONAL NANOSTRUCTURES ..... 21

1.6 NANOWIRES ..... 23

1.7 COPPER OXIDE NANOWIRES ..... 25

1.8 OUTLINE OF THE PROJECT ..... 27

**LITERATURE REVIEW** ..... **29**

**EXPERIMENTAL METHODS AND THEORY** ..... **32**

3.1 INTRODUCTION ..... 32

3.2 EXPERIMENTAL PROCEDURE FOR NANOWIRE GROWTH ..... 32

*3.2.1 Copper* ..... *33*

*3.2.2 Cleaning procedure of copper before growth* ..... *34*

*3.2.3 Procedure of growth of copper oxide nanowires* ..... *34*

3.3 SAMPLE PREPARATION FOR NANOWIRE TRANSFER ..... 39

3.4 ULTRASONICATION ..... 40

*3.4.1 Temperature controller* ..... *44*

3.5 CHEMICAL VAPOR DEPOSITION (CVD) ..... 46
*3.5.1 Fundamental Principles* ..... *47*
3.5.1.1 Kinetics and Transport ..... 47
3.5.1.2 Thermodynamics ..... 48
*3.5.2 Atmospheric pressure chemical vapor deposition (APCVD) -The atmospheric pressure chemical vapor deposition reactor of atomate* ..... *50*
3.6 CHARACTERIZATION TECHNIQUES ..... 52
*3.6.1 Structural analysis* ..... *53*
3.6.1.1 Scanning Electron Microscope ..... 53
**3.6.1.1.1 Why is scanning electron microscope used?** ..... 56
**3.6.1.1.2 Filament** ..... 57
**3.6.1.1.3 Electron Velocities** ..... 57
**3.6.1.1.4 Electron Lenses** ..... 58
**3.6.1.1.5 Types of Electrons** ..... 60
**3.6.1.1.6 Detection of secondary electrons** ..... 61
**3.6.1.1.7 Detection of backscattered electrons** ..... 62
3.6.1.2 X-Ray Diffractometer ..... 63
**3.6.1.2.1** Explanation of X-ray Diffraction ..... 66
3.7 OPTICAL CHARACTERIZATION ..... 70
*3.7.1 Photoluminescence* ..... *70*
*3.7.2 Time-Correlated Single Photon Counting* ..... *74*
3.7.2.1 Data Analysis ..... 78
**GROWTH OF COPPER OXIDE NANOWIRES ..... 81**
4.1 INTRODUCTION ..... 81
4 .2 EXPERIMENTAL PROCEDURE ..... 81
4.3 RESULTS AFTER THERMAL OXIDATION OF 100 NM CU/$P^+$ SI (001) FOR ONE HOUR 87
4.4 RESULTS AFTER THERMAL OXIDATION OF A THICK COPPER FOIL FOR ONE HOUR AT DIFFERENT TEMPERATURES ..... 88

*4.4.1 Conclusions about thermal oxidation between 400 and 700 °C of thick copper foil* ..... *92*
4.5 RESULTS OF EFFECT OF RAMP RATES IN THE FORMATION OF CuO NANOWIRES AFTER THERMAL OXIDATION OF THICK COPPER FOIL FOR ONE HOUR AT 600 °C ..... 93
*4.5.1 Conclusions about thermal oxidation of thick copper foil in different ramp rates* ..... *95*
4.6 RESULTS AFTER THERMAL OXIDATION OF THIN COPPER STRIPE FOR ONE HOUR AT DIFFERENT TEMPERATURES ..... 95
*4.6.1 Conclusions about thermal oxidation between 400 and 700 °C of thin copper stripes* ..... *98*
4.7 RESULTS OF EFFECT OF RAMP RATES IN THE FORMATION OF CuO NANOWIRES AFTER THERMAL OXIDATION OF THIN COPPER STRIPES FOR ONE HOUR AT 600 °C ..... 99
*4.7.1 Conclusions about the thermal oxidation of thin copper stripes in different ramp rates* ..... *101*
4.8 RESULTS AFTER THERMAL OXIDATION OF THIN COPPER FOIL FOR ONE HOUR AT DIFFERENT TEMPERATURES ..... 102
*4.8.1 Conclusions about thermal oxidation between 400 and 700 °C of thin copper foils* ..... *108*
4.9 RESULTS OF EFFECT OF RAMP RATES IN THE FORMATION OF CuO NANOWIRES AFTER THERMAL OXIDATION OF THIN COPPER FOILS FOR ONE HOUR AT 600 °C ..... 108
*4.9.1 Conclusions about thermal oxidation of thin copper foils in different ramp rates* ..... *111*
4.10 THE GROWTH MECHANISM OF THE CuO NANOWIRES ..... 111
*4.10.1 VLS mechanism is not responsible for CuO nanowire growth* ..... *111*
*4.10.2 VS mechanism is not valid for CuO nanowire growth* ..... *113*
*4.10.3 Rapid, short-circuit diffusion is responsible for synthesis of CuO nanowires* ..... *114*
**TRANSFER COPPER OXIDE NANOWIRES TO SILICON ..... 117**

5.1 INTRODUCTION ..... 117
5.2 TRANSFER CuO NANOWIRES BY SCRATCHING THE CuO SAMPLE INTO SILICON SUBSTRATE ..... 117
5.3 TRANSFER CuO NANOWIRES VIA SONICATION TECHNIQUE ..... 118
*5.3.1 Experimental procedure ..... 118*
*5.3.2 Experimental Results ..... 120*
*5.3.3 Conclusions ..... 133*
**OPTICAL MEASUREMENTS ..... 134**
6.1 PHOTOLUMINESCENCE (PL) ..... 134
6.2 TIME-CORRELATED SINGLE PHOTON COUNTING (TCSPC) ..... 137
**CONCLUSION ..... 140**
**REFERENCES ..... 142**
**APPENDIXES ..... 151**
APPENDIX I: STARTING AND STOPPING PROCEDURE FOR SEM ..... 151
APPENDIX II-STARTING& STOPPING PROCEDURE FOR XRD-6000 ..... 153

**List Of Figures**

Figure 1.1: Nanostructures and their assemblies and dimensions. ..... 18
Figure 1.2: Four generations of nanotechnology development . ..... 19
Figure 1.3: ZnO nanowires are used in applications such as Light Emitting Diodes (LEDs), Solar Cells and Cosmetics . ..... 21
Figure 1.4: Schematic presentation of different types of one dimensional nanostructures. (a) Nanowires and nanorods; (b) core–shell structures with metallic core, semiconductor or metal-oxide shell; (c) nanotubes/nanopipes and hollow nanorods; (d) segmented heterostructures; (e) nanobelts/nanoribbons; (f) nanotapes; (g) dendrites; (h) hierarchical nanostructures; (i) nanosphere assembly; (j) nanosprings . ..... 23
Figure 1.5: SEM image of copper oxide nanowires obtained from the samples electrochemically deposited . ..... 24
Figure 1.6: CuO nanowires were grown on a copper plate in ambient atmosphere .. 26
Figure 1.7: The schematic device diagram of a CuO nanowire field effect transistor.27
Figure 3.1: (a) Thin foil of copper with 0.12 mm thickness, (b) thick foil of copper with1mm thickness. ..... 34
Figure 3.2: A typical process sheet completed..... 38
Figure 3.3: A silicon wafer before cutting ..... 39
Figure 3.4: A schematic showing the steps of the substrate preparation process: (a) Si(001) wafer scribed with a straight line on its back side,(b) wafer separated in two semicircles, (c) the two semicircles separated in four quarter-pieces, (d) square and rectangular pieces..... 40
Figure 3.5: A sonicator was used to remove the CuO nanowires from the copper oxide layer. ..... 41
Figure 3.6: Small glassy tubes in which a substrate of copper oxide NWs and one milliliter of isopropanol were placed. ..... 42
Figure 3.7: A pipette for transfer nanowires from glassy tube to silicon substrate. ... 42

Figure 3.8: A volumetric tube was used for measurement of milliliters of isopropanol.....43
Figure 3.9: The procedure of sonication of copper oxide nanowires and transfer on silicon substrate.....44
Figure 3.10: The temperature controller which was used to evaporate isopropanol from $p^+$ silicon.....45
Figure 3.11: The experimental setout for drying the $p^+Si$.....45
Figure 3.12: Processes taking place in a typical CVD reactor.....48
Figure 3.13: The furnace system of APCVD reactor.....50
Figure 3.14: APCVD reactor system.....51
Figure 3.15: Schematic Diagram of the APCVD system by Atomate describing its various components including the (a) furnace (b) 1" quartz tube (c) gas cylinders and ¼ " stainless steel tube connection to MFC's (d)MFC's and (e) control unit .....52
Figure 3.16: A photograph of the TESCAN SEM used for imaging of the surfaces of the specimens.....54
Figure 3.17: The travel of electrons from the electron gun to the specimen.....55
Figure 3.18: Al stubs were used to place the samples inside the SEM.....55
Figure 3.19: An image showing CuO nanowires grown on copper.....56
Figure 3.20: Cross sections of a generic electron lens. a) The rotation of the beam as it passes through the lens. b) The electron path through the lens is helical. Electrons further from the optic axis undergo greater deflection. Individual lenses vary widely in shape and power.....58
Figure 3.21: Scanning coils in the objective (final) lens of an SEM enable the electron beam tobe rastered across the sample.....60
Figure 3.22: The BSE strike the chamber walls, where they create secondary electrons. These SE are collected by the E—T detector with high efficiency.....62
Figure 3.23: A Shimadzu X-Ray diffractometer.....63
Figure 3.24: An aluminum sample holder.....64

Figure 3.25: Geometric derivation of Bragg's law: Constructive interference occurs when the delay between waves scattered from adjacent lattice planes given by $a_1 + a_2$ is an integer multiple of the wavelength λ.....66
Figure 3.26: Constructive and destructive interference.....67
Figure 3.27: Crystal lattice.....67
Figure 3.28: Miller indices.....69
Figure 3.29: The x-ray diffraction pattern from a thick copper foil.....70
Figure 3.30: Photoluminescence schematic. (a) An electron absorbs a photon and is promoted from the valence band to the conduction band. (b) The electrons cools down to the bottom of the conduction band. (c) The electron recombines with the hole resulting in the emission of light with energy hv.....72
Figure 3.31: The experimental setup used to measure photoluminescence from CuO NWs.....73
Figure 3.32: Schematic diagram of the reverse single photon counting method. The blue lines represent the probability of detecting a single emitted photon, the red bar represents the detection of a photon and the "start" signal and the yellow peak represents the trigger signal from the laser and the "stop" signal. It is referred to as the reverse single photon counting method because typical TCSPC systems have the trigger as the start and detection as the stop signal.....74
Figure 3.33: Simulated pulse excitation followed by single exponential fluorescence decay.....75
Figure 3.34: Time-resolved photoluminescence measurement system by using time-correlated single photon counting.....77
Figure 3.35: Exponential decay.....79

Figure 4.1: SEM images of CVD 989, showing the surface morphology of the sample of 100 nm Cu/$p^+$ Si (001) after thermal oxidation, (a) at 700 $^0$C (CVD 989),(b) at 500 $^0$C (CVD 990). ..... 87

Figure 4.2: SEM images of CVD 988, showing nanowires after thermal oxidation at 600 $^0$C using a thick copper foil: (a) low magnification image, (b) high magnification image. ..... 88
Figure 4.3: SEM images of CVD 989, showing CuO nanowires after thermal oxidation at 700 $^0$C using a thick copper foil in 100 sccm's of $O_2$: (a) low magnification image, (b) high magnification image. ..... 89
Figure 4.4: SEM image (CVD 989) of the copper oxide flake removed from an oxided thick copper foil after thermal oxidation at 700 $^0$C..... 90
Figure 4.5: SEM images of CVD 990, showing the surface of the thick copper foil annealed thermally at 500 $^0$C in 100 sccm's of $O_2$: (a) low magnification image, (b) high magnification image. ..... 91
Figure 4.6: SEM images of CVD 991, showing the surface morphology evolution of the thick Cu foil after thermal oxidation at 400 $^0$C: (a) low magnification image, (b) high magnification image. ..... 91
Figure 4.7: Top view SEM images of CVD 992, showing the surface morphology of thick copper foil, which was thermally oxidized at 800 $^0$C. ..... 92
Figure 4.8: SEM image of CVD 993, showing the surface morphology of thick Cu foil after thermal oxidation with ramp rate = 30 $^0$C/min. ..... 93
Figure 4.9: SEM images of CVD 994, showing the surface morphology of thick copper foil after thermal oxidation with ramp rate = 5 $^0$C/min..... 94
Figure 4.10: Copper oxide nanowires were formed on thick Cu foil thermally annealed at 600 $^0$C under oxygen flow, with : (a) ramp rate = 30 $^0$C/min , (b) ramp rate = 10 $^0$C/min, (c) ramp rate = 5 $^0$C/min. ..... 94
Figure 4.11: SEM images of CVD 988, showing CuO NWs after the Cu stripe annealed at 600 $^0$C in 100 sccm's of $O_2$..... 95
Figure 4.12: SEM images of CVD 991, showing the surface of thin copper stripe after thermal oxidation at 400 $^0$C: (a) low magnification image, (b) high magnification image. ..... 96

Figure 4.13: SEM images of CVD 992, showing the morphology of a thin copper stripe after heating in oxygen flow at 800 $^0$C..... 96
Figure 4.14: XRD pattern of CuO microstructures that were formed on thin copper stripe annealed thermally at 800 °C in oxygen flow with 10 °C/min, for one hour.... 97
Figure 4.15: An image of a thin copper stripe after thermal oxidation at 800 $^0$C (CVD 992)..... 98
Figure 4.16 : Top view SEM images of CVD 993, showing the surface morphology evolution of thin copper stripe after thermal oxidation with ramp rate = 30 $^0$C/min.99
Figure 4.17: SEM images of CVD 994, showing the surface of thin Cu stripe after thermal oxidation with ramp rate = 5 $^0$C/min: (a) low magnification image, (b) high magnification image..... 99
Figure 4.18: XRD pattern of CuO nanowires that were grown on thin Cu stripe at 600 °C annealed thermally with 5 °C/min in oxygen flow for one hour..... 100
Figure 4.19: CuO nanowires were grown on thin Cu stripe after thermal oxidation at 600 ° C with: (a) ramp rate = 30 $^0$C/min (CVD993), (b) ramp rate = 5 $^0$C/min(CVD 994)..... 101
Figure 4.20: Top view SEM images of CVD 988, showing the surface of thin copper foil after thermal oxidation at 600 $^0$C: (a) low magnification image, (b) high magnification image..... 102
Figure 4.21: SEM images of CVD 989, showing the morphology of the nanowires, which were formed on the surface of the thin Cu foil heated in oxygen flow at 700 $^0$C : (a) low magnification image, (b) high magnification image. ..... 10102
Figure 4.22: XRD pattern of CuO nanowires prepared by thermal oxidation of Cu foil at 700 °C with 10 °C/min, for one hour.....103
Figure 4.23: Top view SEM images of CVD 990, showing the surface morphology of thin Cu foil after thermal oxidation at 500 $^0$: (a) low magnification image, (b) high magnification image..... 104
Figure 4.24: XRD pattern of copper oxide nanowires that were grown on thin copper foil heated in oxygen flow at 500 °C with 10 °C/min, for one hour..... 105

Figure 4.25: SEM images of CVD 991, showing the morphology of thin copper foil annealed thermally at 400 $^0$C in 100 sccm's: (a) low magnification image, (b) high magnification image. ..... 105
Figure 4.26: SEM images of CuO nanowires obtained by heating thin copper foils in oxygen flow at (a) 400°C,(b) 500°C, (c)600°C and (d)700 °C for 1 h. ..... 106
Figure 4.27: XRD patterns of the copper foil and the copper foils annealed in oxygen flow for one hour at 500 and 700 °C. ..... 107
Figure 4.28: SEM images of CVD 993, showing the surface of thin copper foil annealed thermally in 100 sccm' $O_2$ with ramp rate = 30 $^0$C/min: (a) low magnification image, (b) ..... 108
Figure 4.29: SEM images of CVD 994, showing CuO nanowires were grown on thin copper foil annealed thermally in 100 sccm's of $O_2$ with ramp rate = 5 $^0$C/min. ..... 109
Figure 4.30: XRD pattern of CuO nanowires prepared by thermal oxidation of thin Cu foil at 600 °C with 5 °C/min, for one hour. ..... 110
Figure 4.31: SEM images showing CuO nanowires formed on thin copper foil heated in oxygen flow with: (a) ramp rate = 30 $^0$C/min(CVD993), (b) ramp rate = 10 $^0$C/min(CVD988),(c) ramp rate = 5 $^0$C/min(CVD994). ..... 110
Figure 4.32: SEM images of CuO nanowires prepared at 600 $^0$C, with ramp rate 30 $^0$C/min (CVD 993). The left picture shows the nanowires grown on thin copper foil. The right picture shows the nanowires grown on thin, copper stripe. ..... 112
Figure 4.33: (a) Initial growth of CuO NWs on the outer surface of CuO grains; (b) growth of the CuO substrate gradually buries the root of the NWs; (c) continued decomposition of the CuO layer at the CuO/$Cu_2O$ interface leading to the direct contact between the NW roots and the $Cu_2O$ layer; (d) an experimental cross-sectional SEM image from the oxidation of Cu at 600 °C for 4 h, showing that CuO whiskers are buried by the CuO layer and their roots have direct contact with the $Cu_2O$ layer ..... 115
Figure 4.34: (Color online) Scheme of proposed model for the growth of CuO NWs by thermal oxidation (right). Cross-sectional view of an oxide layer (grown at 400