

# 介相材料建構奈米光電元件特性之研究

研究生:林永昌

指導教授: 郭浩中教授

國立交通大學光電工程研究所碩士班

## 摘要

在本論文中，我們利用離子佈植、高密度電漿及脈衝式高密度電漿等三種不同的方法將矽量子點摻雜至奈米介孔洞二氧化矽中，形成許多矽量子點/二氧化矽的表面態，而發出有效率的光激發螢光(PL)，其波長範圍為 410 nm ~ 580 nm。高密度電漿由於具有高擴散率及高解離率的特性，使得矽量子點能有效率地沈積在孔壁上，其密度可高達  $1 \times 10^{18}/\text{cm}^3$ 。相對應地，其主要波長(460 nm)峰值強度也較離子佈植的方法強上四倍以上。脈衝式高密度電漿的方法可更增加矽量子點在奈米介孔洞二氧化矽中的密度，其值高達  $8 \times 10^{18}/\text{cm}^3$ ，同樣地，其主要波長的光激發螢光強度也較純高密度電漿的方法強上二倍以上。

根據光激發螢光光譜，證明矽量子點/二氧化矽的表面態可當作有效率的藍光奈米材料，因此可用來做為紫外光至藍光範圍的光偵測器。此元件傾向利用電子傳輸為主，在 3V 時，其暗電流為  $2.3 \times 10^{-5} \text{ A/cm}^2$ ，主要偵測波長在 370 nm，在 3V 時，此波長下的光電轉換效率為 0.77 A/W，而此元件在 10 分鐘的可靠度量測中，也具有穩定的特性。

Study of Mesostructural Materials Constructed  
Nano-optoelectronics

Student: Yung-Chang Lin

Advisor: Prof. Hao-Chung Kuo

Institute of Electro-Optical Engineering  
National Chiao Tung University

**Abstract**

In this thesis, we employed ion implantation, high-density plasma, and pulse high-density plasma methods to dope three-dimensional Si nanocrystals (NCs) within the nanopores of mesoporous silica films. Surface states of the resulting Si NCs/silica arrays initiate blue-white photoluminescence (PL). ICP makes reactive species highly mobile and enables deposited NCs bonded with pore-wall well, therefore, efficiently constructing photoemission arrays. The mean density of HDP-synthesized semiconducting NCs is as high as  $1 \times 10^{18}/\text{cm}^3$ . Accordingly, blue-PL of arrays obtained with HDP is 4 times stronger than those obtained with ion implantation.

Besides, the mean density of Pulse ICPCVD-based semiconducting NCs is as high as  $8 \times 10^{18}/\text{cm}^3$ . Accordingly, blue-PL of arrays obtained with Pulse ICP is 2 times stronger than those obtained with HDP.

According to photoluminescence spectra, this constructed enormous Si NCs/silica arrays has been demonstrated as an efficient blue-luminescent nanomaterial. By this characteristic, we also fabricate an UV to blue light photodetector using this nanomaterial. This photodetector tends to be electron-transport-dominated and the dark current is about  $2.3 \times 10^{-5} \text{ A/cm}^2$  at 3V reverse bias. The main detected wavelength is 370 nm, and the responsivity is about 0.77 A/W at 3V reverse bias. As for reliability, this device is stable under ten minute's measurement.

## 誌謝

回首這兩年的研究生涯，首先感謝王興宗教授與郭浩中教授在研究方面諄諄教誨，讓我學習到研究應有的態度及方法，使我獲益良多。另外，特別感謝國家奈米元件實驗室謝嘉民博士，在我研究生涯這段日子裡，指點我許多研究方向。指導我的學長：奈米元件實驗室工程師賴一凡及卓恩宗學長，感謝這兩年來在實驗上的教導及提供寶貴的意見，給予我在實驗思考上許多的協助。學弟志堯協助我順利完成實驗；感謝實驗室各位學長姊在實驗上的協助；裕鈞、文燈、蕙婷、敏瑛、瑞溢、國峰、傳煜等碩二同學，因為你們，讓我的碩士生活更加有趣，還有其他碩一的學弟妹們，謝謝你們的幫忙。另外，也要感謝好友筱瑩，室友堯俊、東龍、兆輝等人，謝謝你們陪我度過兩年的時光。



最後，我要感謝叔叔和哥哥，因為你們的支持，讓我也能夠順利完成學業，謝謝你們！

## Contents

<b>摘要.....</b>	i
<b>Abstract.....</b>	ii
<b>誌謝.....</b>	iii
<b>Contents.....</b>	iv
<b>List of Tables.....</b>	viii
<b>List of Figures.....</b>	ix

### **Chapter 1 Introduction**

1-1. Applications of Si-based nanomaterials.....	1
1-2. Properties of semiconducting nanomaterials.....	1
1-3. Research of low dimensional Si-based materials.....	2
1-4. Motivation.....	3



### **Chapter 2 Optical measurement theory and instrument**

2-1. Photoluminescence (PL).....	5
2-1.1 Theory of photoluminescence.....	5
2-1.2 Photoluminescence measurement system.....	8
2-2. Photoluminescence Excitation (PLE).....	9
2-2.1 Theory of photoluminescence excitation.....	9
2-2.2 Photoluminescence excitation measurement system.....	9

### **Chapter 3 Mesoporous silica (MS) films**

3-1. Fabrication of MS films.....	11
3-2. Material analysis of MS films.....	11
3-2.1 TEM image of MS films.....	11
3-2.2 Kr absorption/desorption isotherms of MS films.....	12
3-2.3 X-ray diffraction patterns of MS films.....	12
3-2.4 Measurements of different calcination processes.....	12

3-3. Room-temperature PL spectra of MS films.....	14
3-3.1 PL spectra of MS films.....	14
3-3.2 PL-related bonds of MS films and silylation reaction.....	14
3-3.3 FTIR and TDS spectra of MS films.....	16
3-3.4 PL spectra for MS with different pore-size and pore-wall.....	18
3-4. Conclusion.....	21

## **Chapter 4 3-D Si Nano-dots/SiO<sub>2</sub> arrays: Fabricated By Ion Implantation**

4-1. Introduction.....	22
4-2. Ion implantation process.....	22
4-2.1 Spatial dimension of pore nature of MS films.....	22
4-2.2 Si implantation with different dosages and energies.....	23
4-3. Room-temperature PL spectra of SiO <sub>2</sub> :Si <sup>+</sup> and MS:Si <sup>+</sup> .....	23
4-3.1 PL spectra of implantation samples.....	23
4-3.2 Discussion of PL spectra of implantation samples.....	24
4-3.3 The best condition of implantation samples.....	25
4-4. Conclusion.....	26

## **Chapter 5 3-D Si Nano-dots/SiO<sub>2</sub> arrays: Fabricated By ICP-CVD**

5-1. Introduction.....	27
5-2. ICP-CVD process.....	27
5-2.1 Fabrication of MS <sub>as</sub> films.....	27
5-2.2 Comparison of different doping methods.....	28
5-2.3 Analysis of those samples.....	29
5-3. Room-temperature PL spectra and other material analysis.....	29
5-3.1 PL spectra of those samples.....	29
5-3.2 Examining existence of nanocrystals.....	29
5-3.3 Hydrogen-elimination reaction.....	32

5-3.4 Analysis of Ge-related SIMS spectra .....	34
5-3.5 Analysis of FTIR spectra.....	34
5-3.6 Discussion of PL spectra.....	35
5-4. Conclusion.....	36

## **Chapter 6 3-D Si Nano-dots/SiO<sub>2</sub> arrays: Fabricated By Pulse ICP-CVD**

6-1. Introduction.....	37
6-2. Pulse ICP-CVD process.....	37
6-2.1 Fabrication of MS <sub>as</sub> films.....	37
6-2.2 TEM image and Ge-related SIMS spectra.....	37
6-3. Mechanism of Pulse ICPCVD-based 3-D NCs-synthesis.....	40
6-3.1 Mechanism of 3-D NCs-synthesis.....	40
6-3.2 XPS spectra of Ge NCs/Silica arrays.....	41
6-4. RT PL spectra with different pore size and thickness.....	41
6-4.1 PL spectra with different pore size,.....	41
6-4.2 PL spectra with different thickness.....	43
6-5. Conclusion.....	44

## **Chapter 7 An UV to blue light detector constructed by 3-D Si Nano-dots/SiO<sub>2</sub> arrays**

7-1. Introduction.....	45
7-2. Fabrication of the photodetector.....	45
7-3. Properties of the photodetector.....	46
7-3.1 I-V characteristics.....	46
7-3.2 Response versus wavelength.....	47
7-3.3 Comparison with other researches.....	48
7-3.4 Reliability.....	48
7-4. Conclusion.....	49

## **Chapter 8 Conclusions and Future works**

8-1. Conclusions.....	50
8-2. Future works.....	50
References.....	51



## **List of Tables**

Table I : Summarizes the parameters associated with those NC-synthesis methods..	28
Table II: The comparison with other researches about UV photodetectors.....	48



## List of Figures

<b>Fig. 1-1:</b> Relationship of dimension and density of state.....	2
<b>Fig. 2-1:</b> Diagram of photoluminescence measurement system.....	8
<b>Fig. 2-2:</b> Diagram of photoluminescence excitation measurement system.....	9
<b>Fig. 3-1:</b> (a): Kr absorption/desorption isotherms with various templates.....	12
<b>Fig. 3-1:</b> (b): X-ray diffraction patterns with various organic templates.....	13
<b>Fig. 3-1:</b> (c): Kr absorption/desorption spectra with calcination processes.....	13
<b>Fig. 3-1:</b> (d): X-ray diffraction patterns undergoing calcination processes.....	14
<b>Fig. 3-2:</b> PL spectra of MS and $MS_{HMDS}$ .....	15
<b>Fig. 3-3:</b> (a): FTIR spectra of $MS_{as}$ , MS and $MS_{HMDS}$ .....	17
<b>Fig. 3-3:</b> (b): $H_2O$ -related and $CH_4$ -related TDS for MS and $MS_{HMDS}$ .....	18
<b>Fig. 3-4:</b> (a): Surface areas of porechannels versus pore-size and pore-wall.....	19
<b>Fig. 3-4:</b> (b): PL spectra for MS with different pore-sizes.....	20
<b>Fig. 3-4:</b> (c): PL spectra for MS with various pore-walls.....	20
<b>Fig. 4-1:</b> Spatial dimension of pore nature of MS films.....	23
<b>Fig. 4-2:</b> PL spectra of MS and $SiO_2$ film doping by ion implantation.....	25
<b>Fig. 4-3:</b> PL peak intensity with different dosages and energies.....	26
<b>Fig. 5-1:</b> PL spectra of various mesostructured materials.....	30
<b>Fig. 5-2:</b> Cross-sectional STEM images.....	31
<b>Fig. 5-3:</b> SIMS spectra.....	32
<b>Fig. 5-4:</b> Schematic representation.....	33
<b>Fig. 5-5:</b> FTIR spectra.....	35
<b>Fig. 6-1:</b> (a): SIMS depth profiles.....	38
<b>Fig. 6-1:</b> (b): Cross-sectional TEM image.....	38

<b>Fig. 6-2:</b> (a): PL spectra by high-density ICP and Pulse-ICP process.....	39
<b>Fig. 6-2:</b> (b): Picture of naked-eye visible blue-white PL.....	39
<b>Fig. 6-3:</b> Schematic mechanism of 3D Si nanodots by Pulse-ICP process.....	40
<b>Fig. 6-4:</b> X-ray photoelectron spectroscopy.....	41
<b>Fig. 6-5:</b> Room-temperature PL spectra with difference pore.....	42
<b>Fig. 6-6:</b> Room-temperature PL spectra with difference thickness.....	43
<b>Fig. 7-1:</b> Schematic of the photodiode.....	45
<b>Fig. 7-2:</b> I-V characteristics of a typical diode.....	46
<b>Fig. 7-3:</b> I-V characteristics under different illuminated powers.....	47
<b>Fig. 7-4:</b> Response versus wavelength.....	47
<b>Fig. 7-5:</b> Reliability of the photodetector.....	49

