

**Microcrystalline Silicon Thin Films Prepared
by Hot-Wire Chemical Vapour Deposition**

Eman Mohamed
(B.Sc., Post. Grad. Diploma, MPhil., Egypt)

This thesis is presented for the degree of Doctor of Philosophy,

Murdoch University, Western Australia

2004

*I declare that this thesis is my own account
of my research and contains as its main
content work, which has not previously been
submitted for a degree at any tertiary
educational institution.*

Eman Mohamed

ABSTRACT

Silicon is widely used in optoelectronic devices, including solar cells. In recent years new forms of silicon have become available, including amorphous, microcrystalline and nano-crystalline material. These new forms have great promise for low cost, thin film solar cells and the purpose of this work is to investigate their preparation and properties with a view to their future use in solar cells.

A Hot Wire-Deposition Chemical Vapour Deposition CVD (HW-CVD) system was constructed to create a multi-chamber high vacuum system in combination with an existing Plasma Enhanced Chemical Vapour Deposition (PECVD) system; to study the amorphous to crystalline transition in silicon thin films. As the two chambers were linked by a common airlock, it was essential to construct a transfer mechanism to allow the transfer of the sample holder between the two systems. This was accomplished by the incorporation of two gate valves between the two chambers and the common airlock as well as a rail system and a magnetic drive that were designed to support the weight of, and to guide the sample holder through the system.

The effect of different deposition conditions on the properties and structure of the material deposited in the combined HW-CVD:PECVD system were investigated. The conditions needed to obtain a range of materials, including amorphous, nano- and microcrystalline silicon films were determined and then successfully replicated.

The structure of each material was analysed using Transmission Electron Microscopy (TEM). The presence of crystallites in the material was confirmed and the structure of the material detected by TEM was compared to the results obtained by Raman spectroscopy. The Raman spectrum of each sample was decoupled into three components representing the amorphous, intermediate and crystalline phases. The Raman analysis revealed that the amorphous silicon thin film had a dominant amorphous phase with smaller contribution from the intermediate and crystalline phase. This result supported the findings of the TEM studies which showed some medium range order. Analysis of the Raman spectrum for samples deposited at increasing filament temperatures showed that the degree of order within the samples

increased, with the evolution of the crystalline phase and decline of the amorphous phase. The Selected Area Diffraction (SAD) patterns obtained from the TEM were analysed to gain qualitative information regarding the change in crystallite size. These findings have been confirmed by the TEM micrograph measurements.

The deposition regime where the transition from amorphous to microcrystalline silicon took place was examined by varying the deposition parameters of filament temperature, total pressure in the chamber, gas flow rate, deposition time and substrate temperature.

The IR absorption spectrum for $\mu\text{c-Si}$ showed the typical peaks at 2100cm^{-1} and 626cm^{-1} , of the stretching and wagging modes, respectively. The increase in the crystallinity of the thin films was consistent with the evolution of the 2100cm^{-1} band in IR, and the decreasing hydrogen content, as well as the shift of the wagging mode to lower wavenumber. IR spectroscopy has proven to be a sensitive technique for detecting the crystalline phase in the deposited material.

Several devices were also constructed by depositing the $\mu\text{c-Si}$ thin films as the intrinsic layer in a solar cell, to obtain information on their characteristics. The p-layer (amorphous silicon) was deposited in the PECVD chamber, and the sample was then transferred under vacuum using the transport system to the HW-CVD chamber where the i-layer (microcrystalline silicon) was deposited. The sample holder was transferred back to the PECVD chamber where the n-layer (amorphous silicon) was deposited.

The research presented in this thesis represents a preliminary investigation of the properties of $\mu\text{c-Si}$ thin films. Once the properties and optimum deposition characteristics for thin films are established, this research can form the basis for the optimization of a solar cell consisting of the most efficient combination of amorphous, nano- and microcrystalline materials.

TABLE OF CONTENTS

	Page No.
ABSTRACT	<i>i</i>
TABLE OF CONTENTS	<i>iii</i>
ACKNOWLEDGEMENTS	<i>vii</i>
PUBLICATIONS	<i>ix</i>
CHAPTER 1. INTRODUCTION	
1.1 Motivation	1
1.2 Thin Films	2
1.3 Deposition Technique	4
1.4 Silicon thin films	5
1.5 Aims	7
1.6 Thesis Overview	8
CHAPTER 2. GENERAL REVIEW	9
2.1 Introduction	9
2.2 Hot Wire Chemical Vapour Deposition technique (HW-CVD)	9
2.2.1 Technique	9
2.2.2 Silane Reactions	11
2.2.3 Filament Effects	14
2.3 Plasma Enhanced Chemical Vapour Deposition technique (PECVD)	18
2.4 Advantages of the HW-CVD technique	22
2.5 Solar Cells	23
2.6 Silicon (Si)	28
2.6.1 Crystalline Silicon	28
2.6.2 Hydrogenated Amorphous Silicon	29
2.6.3 Polycrystalline Silicon	31
2.6.4 Proto-crystalline Silicon	31
2.6.5 Polymorphous Silicon	32
2.6.6 Nanocrystalline and Microcrystalline Silicon	32

2.6.7 Microcrystalline Silicon	32
CHAPTER 3. EXPERIMENTAL	39
3.1 Introduction	39
3.2 Pre-existing PECVD	39
3.3 Design, Modification and Construction	40
3.3.1 High Vacuum (HV) Chambers	40
3.3.2 High Vacuum Sample Holder	43
3.3.3 Transfer Mechanism (Rail System and Transfer swing)	45
3.3.3.1 Rail System	45
3.3.3.2 Transfer Swing	46
3.3.4 Magnetic Drive	48
3.4 Hot Wire Chemical Vapour Deposition (HW-CVD)	53
3.4.1 Deposition Chamber	53
3.4.2 Filament	54
3.4.3 Measurement Instrumentation	55
3.4.4 Substrate Heater, Shutter and Temperature Measurement	55
3.5 Plasma Enhanced Chemical Vapour Deposition (PECVD)	56
3.6 Pumping and Gas Handling System	57
3.7 Operation of the System	60
3.8 Deposition of Aluminium Contacts	61
3.9 Sample Preparation	62
3.9.1 Transmission Electron Microscopy (TEM) technique	63
3.9.1.1 Planar View Inspection	63
3.9.1.2 Cross-sectional Inspection	63
3.9.2 X-ray Photoelectron Spectroscopy (XPS)	65
CHAPTER 4. CHARACTERIZATION TECHNIQUES	68
4.1 Introduction	68
4.2 Material Characterization	68
4.2.1 Fourier Transform-Infrared Spectroscopy (FTIR)	68
4.2.2 Ultraviolet-visible Spectroscopy	74

4.2.3 Transmission Electron Microscopy (TEM)	78
4.2.4 Raman Spectroscopy	87
4.2.5 X-ray Photoelectron Spectroscopy (XPS)	90
4.3 Device Characterization	94
4.3.1 Current-Voltage (I-V) Characteristics	94
4.3.2 Spectral Photoresponse	95
4.4 Data Analysis	97
4.4.1 Decoupling the Raman Spectrum	97
4.4.2 FTIR spectrum Analysis	100
4.4.3 Optical Band Gap	103
4.4.4 Transmission Electron Microscopy (TEM)	103
CHAPTER 5. RESULTS AND DISCUSSION	105
5.1 Introduction	105
5.2 Filament Temperature	107
5.2.1 Results	107
5.2.2 Discussion	125
5.2.3 Conclusions	136
5.3 Deposition Time	138
5.3.1 Results	138
5.3.2 Discussion	147
5.3.3 Conclusions	150
5.4 Silane Flow Rate	151
5.4.1 Results	151
5.4.2 Discussion	158
5.4.3 Conclusions	161
5.5 Substrate Temperature	163
5.5.1 Introduction	163
5.5.2 Results	163
5.5.3 Subsidiary Result	173
5.5.4 Discussion	174
5.5.5 Conclusions	177

5.6 Pressure	179
5.6.1 Results	179
5.6.2 Discussion	184
5.6.3 Conclusions	187
5.7 Applications	188
5.7.1 X-ray Photoelectron Spectroscopy (XPS) Line Shape Analysis	188
5.7.1.1 Introduction	188
5.7.1.2 Results	188
5.7.1.3 Discussion	191
5.7.1.4 Conclusions	192
5.7.2 Devices Based on Microcrystalline silicon	193
5.7.2.1 Introduction	193
5.7.2.2 Results	193
5.7.2.3 Discussion	199
5.7.2.4 Conclusions	201
CHAPTER 6. CONCLUSIONS AND FURTHER WORK	203
6.1 Conclusions	203
6.2 Recommendations for Further Work	209
REFERENCES	211

ACKNOWLEDGEMENTS

The work presented in this thesis was carried out under the supervision of Dr. J.C.L. Cornish and Professor P.J. Jennings, to whom I extend my gratitude for their valuable and friendly guidance, encouragement and helpful suggestions throughout the progress of the research and in the preparation of this thesis.

I would like to extend my special thanks to the members of the Amorphous Silicon Research Group, DJ Santjojo for his ideas, discussions and assistance during the development of the Hot-Wire Chemical Vapor Deposition system. Dr. Kazmierz Luczak for his patient instructions and assistance in using the Plasma Enhanced Chemical Vapor Deposition system, and useful discussions. Dr Elaine Walker for allowing me to use her software *PeakFit v.4*, and friendship throughout this work. Dr. Chris Lund for his valuable discussions during this study, Rick Hughes for providing me with useful advice and suggestions when using the transfer vessel for XPS analysis. My gratitude to Reem Abdelaal, for her support and assistance and for being more like a sister than only a friend.

My gratitude and heartfelt thanks to Karin Strehlow and Anthony Horton, for their support, friendship, help and encouragement, God Bless.

My thanks to Dr Rob Hart, Curtin University, for his patience and help in operating the Transmission Electron Microscope. Mr. Peter Chapman, Curtin University, for the Raman Spectroscopy training sessions and assistance.

I also would like to express my indebtedness to the staff of the central mechanical workshop, for their high quality work, which made it possible to construct the multi-chamber high vacuum system, Ernie Etherington, Kleber Claux, Murray Lindau, and Fritz Wagner. My gratitude to John Orton for his administrative and technical assistance through out this research. My thanks also to the technical staff, Will Stirling, Ted Lamont, Tom Osborne, John Snowball and Justin Jordan for their friendly and useful help through out this study.

My deepest thanks to Maria Kempf for her support and friendship. Thanks also to June Burnett, Kat Lyon, Sue Taylor, Vic Clare, Dianne, Kath, Christine Creagh, Lian Chan and so many others for their help and making me feel welcome, Thank You. Thanks also to all friends for their help and those have made my stay in Australia a memorable experience.

I would like to thank the Ministry of Higher Education in Egypt for granting the scholarship award that has allowed me to pursue a higher degree at Murdoch University.

Finally, my thanks and gratitude go to my husband, Tarek and daughter, Amira who have been understanding, patient, supportive and making *duaa* for the success of my study. Thank you also to my parents, sister and brothers for their encouragement and support during my stay in Australia.

PUBLICATIONS

Mohamed, E., Cornish, J.C.L. and Santjojo, D.J., 2004, *A versatile transfer mechanism of a sample holder in a high vacuum chamber*. Review of Scientific Instruments, to be published.

Cornish, J.C.L., Mohamed, E. and Abdelaal, R., 2004, *Nanocrystalline Engineering*, Proceedings of the Pacific Rim Conference in Nanoscience, Molecular Simulation, published.

Cornish, J.C.L., Mohamed, E., 2002, *Deposition of Amorphous Silicon*, XXIII Conference on Solid State Science & Workshop on Physics and Application Potential of Functional Ceramic Thin Films, Egyptian Society of Solid State Science and Applications (ESSSA), Sharm Al-Shiekh - Sinai – Egypt, unpublished.

Cornish, J.C.L., Mohamed, E., Abdelaal, R. and Hart, R., 2004, *A Novel Procedure for the Semi-quantitative Analysis of Selected Area Diffraction (SAD) Patterns*, to be published.