



**Murdoch**  
UNIVERSITY

## MURDOCH RESEARCH REPOSITORY

*This is the author's final version of the work, as accepted for publication following peer review but without the publisher's layout or pagination.*

*The definitive version is available at*

<http://dx.doi.org/10.1109/ICONN.2008.4639235>

**Cornish, J.C.L. and Abdelaal, R. (2008) *Modification of the density of crystallites in silicon nano-crystalline thin films by substrate profiling*. In: International Conference on Nanoscience and Nanotechnology, ICONN 2008, 25 - 29 February, Melbourne, Australia.**

<http://researchrepository.murdoch.edu.au/8359/>

Copyright © 2008 IEEE

Personal use of this material is permitted. However, permission to reprint/republish this material for advertising or promotional purposes or for creating new collective works for resale or redistribution to servers or lists, or to reuse any copyrighted component of this work in other works must be obtained from the IEEE.

# Modification of the Density of Crystallites in Silicon Nano-crystalline Thin Films by Substrate Profiling

John C.L. Cornish and Reem Abdelaal

Physics and Energy Studies  
Murdoch University, Murdoch, WA 6150, Australia

Email: [J.Cornish@murdoch.edu.au](mailto:J.Cornish@murdoch.edu.au)

Telephone: (61-8) 9360 2433, Fax: (61-8) 9360 6183

**Abstract--** In this paper we describe the production of nano-crystallites of silicon embedded in an amorphous silicon matrix by Hot Wire CVD. Prior modification of the substrate results in a procedure for increasing the volume fraction and density of the nano-crystallites relative to the other phases. A macroscopic process, random linear grooving, applied to the substrates has been shown to have a significant affect on the structure of the thin film nano-crystalline silicon subsequently grown on these profiled substrates. This has been found to occur for samples produced under different temperature regimes resulting in crystalline fractions in the range of 10% to 80%. Analysis of the RAMAN spectra for these samples shows a reduction in the amorphous fraction while the fractions of both the crystalline material and the intermediate phase increase. Electron micrographs show increased crystallite size. The films on the modified substrates appear to be denser than the films on the smooth substrates.

**Keywords:** silicon, thin films, Hot Wire CVD, amorphous, nano-crystallites, nano-structures, crystalline fraction, intermediate fraction, substrate.

## I. INTRODUCTION

The unique properties of silicon recommend it as a material to play a substantial role in new devices based on nanotechnology. Thin films of silicon containing nanostructures are finding increased application in devices such as photovoltaic solar cells [1, 2, 3]. The films can be analysed with Raman spectroscopy and consist of three phases: crystalline material in the form of nano-crystallites, a matrix of amorphous silicon and a "mixed" or "intermediate" phase thought to consist predominantly of grain boundaries. The nano-crystallites within these films have different optical properties to either amorphous or single crystal material. We have previously reported a procedure for increasing the ratio of the crystalline phase in relation to the other two phases [4].

Small crystals of silicon, in the range of 2 to 10 nanometres, are termed proto-crystals, nano-crystals or quantum dots, larger crystals 10 to 20 nanometres are micro-crystals [5]. Small crystallites have different electronic, optical and thermal properties from the bulk material. As more atoms are added to the nano-crystal particles and as they grow in size, the properties of these crystallites eventually approach the bulk values. In particular, the band gap that defines the optical and electronic properties of these nano-crystals varies with their size. As a result, silicon nano-crystals exhibit a significant blue shift in optical properties from the bulk infrared band gap

energy to the visible range [6]. The contribution of the nano-crystals to the amorphous silicon film depends on their size, shape, orientation, distribution and volume fraction. These are properties that we are investigating and trying to control.

In this paper we describe the prior modification of the substrate by a procedure which results in an increase in the volume fraction and density of the nano-crystallites relative to the other phases.

## II. EXPERIMENTAL DETAILS

Thin films of silicon ranging from fully amorphous to polycrystalline were deposited by the Hot Wire method in which pure silane was passed over a hot tantalum filament and the resultant interaction of the ions and radicals with the growing surface formed a thin film [7]. The deposition was carried out in a purpose built chamber with an airlock and transport system. The effect of deposition conditions: filament temperature, substrate temperature, gas flow rate, gas pressure and deposition time have been investigated enabling the conditions, under which nano-crystallites embedded in an amorphous matrix are formed, to be mapped.

Raman spectroscopy and scanning electron microscopy were used to characterise the nanostructured silicon films. For this purpose, the films were grown on polished stainless steel substrates. The top dashed curve in Fig. 1 shows a typical Raman spectrum when all the three phases are present.

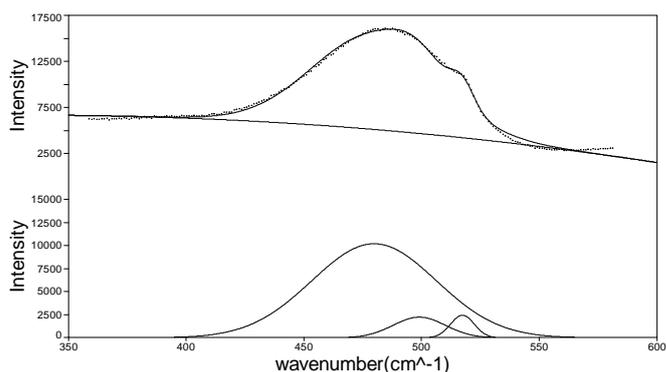


Figure 1. Raman spectrum for thin film nano-crystalline silicon on a stainless steel substrate. Decoupling of the spectrum shows the contribution of each of the three phases. The amorphous silicon phase has a large intensity; centred at  $480\text{ cm}^{-1}$ , the intermediate peak a slightly lower intensity; centred at  $510\text{ cm}^{-1}$  and the low intensity crystalline silicon phase is at  $520\text{ cm}^{-1}$ .

The spectrum was decoupled using commercial software [8] to display the individual contributions of the three phases. The spectrum after it was decoupled using Peakfit is shown at the bottom of Fig. 1. At the top of Fig. 1, the continuous curve is an indication of the goodness of fit of the decoupling process.

The first peak at  $480\text{ cm}^{-1}$  is the amorphous component, the third small peak at  $520\text{ cm}^{-1}$  is the crystalline component. The second, intermediate peak centred at  $510\text{ cm}^{-1}$  is generally referred to as arising due to grain boundaries. It should be noted that the latter two centre frequencies are not fixed but are a function of the size of the nano-crystallites.

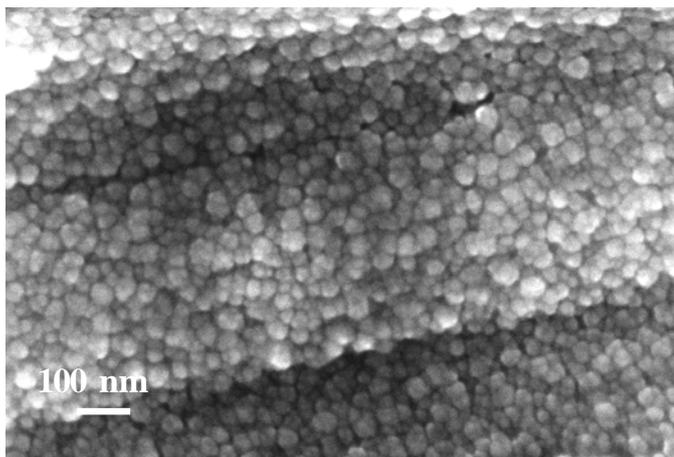
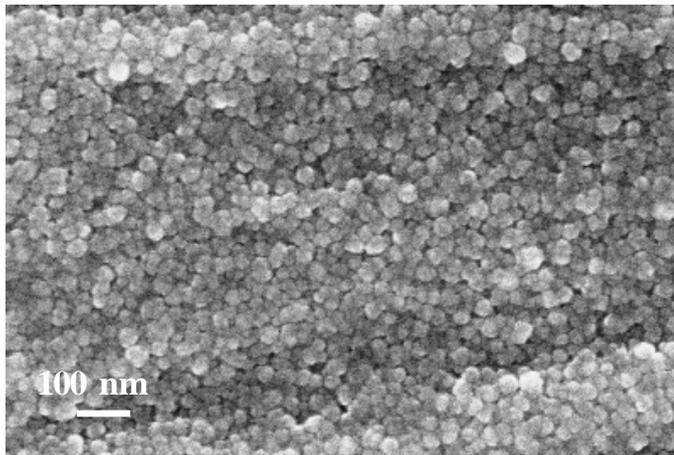


Figure 2. Electron micrographs of samples deposited on polished substrate (top), and on profiled substrate (bottom).

Electron microscopy has been used to provide images of the structure of the thin film and enabled the sizes of nano-crystallites to be measured. Typical Electron micrographs are shown in Fig. 2. These show the surfaces of the samples for which the Raman spectrums are shown in Figs. 1 and 4.

The profiling of the substrate was achieved by a simple mechanical process. First, the stainless steel substrate was first highly polished, finishing with fine silicon carbide abrasive paper. The substrate was then rubbed in a single direction with similar abrasive paper but two grades coarser than this. The resulting surface consisted of closely spaced random linear

grooves cut into the polished material. An example of this surface can be seen in Fig. 3.

### III. RESULTS

Thin film nanocrystalline films were deposited on both polished and grooved substrates using hot wire CVD. The Raman spectrum for one of these films on the polished surface is shown in Fig. 1 while the spectrum for a similar film deposited simultaneously on a grooved substrate is shown in Fig. 4 below. Electron micrographs of the surfaces of the samples of Figs.1 and 4 are shown in Fig. 2.

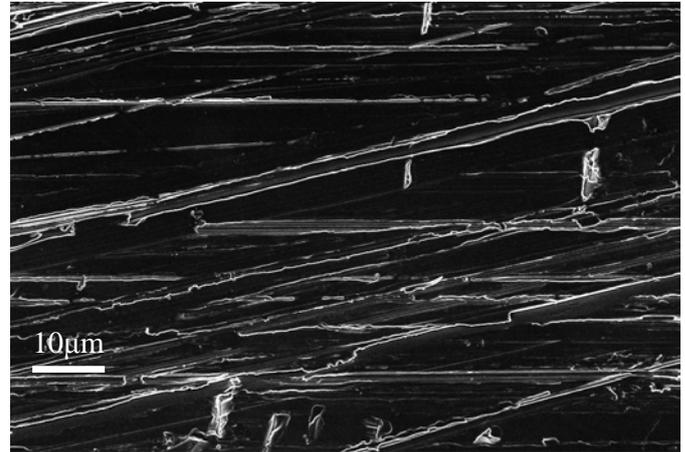


Figure 3. Electron microscope picture of the linear random grooved surface.

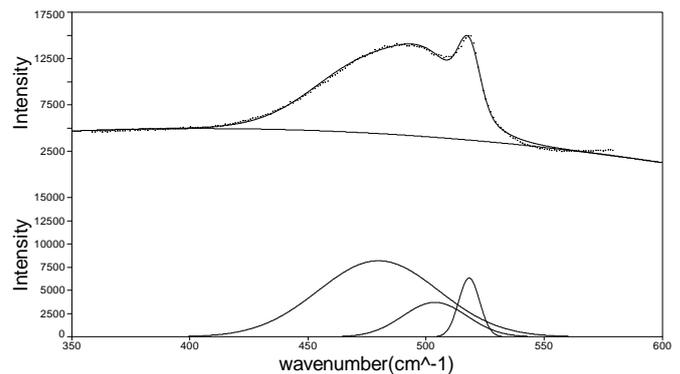


Figure 4. Raman spectrum for thin film nano-crystalline silicon on randomly linearly grooved stainless steel substrate. This was deposited simultaneously with the sample shown in Fig. 1.

To compare the effect of the substrate surface modification, quantitative data have been extracted from the decoupled spectra for a number of samples deposited under different temperature regimes and exhibiting a range of crystalline fractions. These are shown in Table 1. The polished and profiled forms of samples 2 are the ones illustrated by the spectra and electron micrographs shown in the figures above. For these it can be seen that the percentage area of the amorphous peak has decreased from 88% to 73% as a result of profiling the substrate. The intermediate peak shows an increase from 10% to 17% while the crystalline peak has increased to 10% from 2%. Similar changes are shown for the other three pairs of samples.

TABLE I. ANALYSIS OF THE DECOUPLED PEAKS FROM THE RAMAN SPECTRA SHOWN IN FIGS. 1 AND 4 AND OTHERS.

(a) Polished substrates

Sample #		1		2		3		4	
Peak type	Centre	FWHM	% Area						
Amorphous	480	65	89	62	88	52	60	42	28
Intermediate	~510	36	10	32	10	28	22	27	41
Crystalline	~520	10	1	10	2	9.5	18	9	31

(b) Random linear grooved substrates

Sample #		1		2		3		4	
Peak type	Centre	FWHM	% Area						
Amorphous	480	62	84	60	73	46	53	35	21
Intermediate	~510	28	10	32	17	27	27	28	46
Crystalline	~520	12	6	10.5	10	9.5	20	9	33

It is clear that the modification of the substrate has resulted in a measurable increase in the proportion of crystalline material that has been deposited in each case. This increase appears to result from a greater density of crystallites within the film.

IV. DISCUSSION

A macroscopic process, random linear grooving, applied to the substrates has been shown to have a significant affect on the structure of the thin film nanocrystalline silicon subsequently grown on the profiled substrates. Analysis of the RAMAN spectra obtained shows a reduction in the amorphous fraction while the fractions of both the crystalline material and the intermediate phase both increase. Electron micrographs show increased crystallite size. The films on the grooved substrates are denser than the films on the smooth substrates. This has been found to occur for samples produced under different temperature regimes resulting in crystalline fractions in the range of approximately 10% up to 80%.

ACKNOWLEDGMENTS

The authors wish to acknowledge support from the Murdoch University research funding scheme which made this work possible. David Parlevliet of Murdoch University produced the electron micrographs.

REFERENCES

- [1] Baojie Yan, Guozhen Yue, and Subhenda Guha, "Status of nc-Si:H solar cells at United Solar and roadmap for manufacturing a-Si:H and nc-Si:H based solar panels," in *Amorphous and Polycrystalline Thin-Film Silicon Science and Technology—2007*, edited by V. Chu, S. Miyazaki, A. Nathan, J. Yang, H.W. Zan (Mater Res. Soc. Symp., Proc. Vol. 989) (2007), A15-01
- [2] Ruud E.I. Schropp, Hongbo Li, Ronald H.J. Franken, Jatindra K. Rath, Karine van der Werf, Jan Willem Schüttauf, Robert L. Stolk, "Triple junction n-i-p solar cells with hot-wire deposited protocrystalline and microcrystalline silicon," in *Amorphous and Polycrystalline Thin-Film Silicon Science and Technology—2007*, edited by V. Chu, S. Miyazaki, A. Nathan, J. Yang, H.W. Zan (Mater Res.Soc. Symp, Proc. Vol. 989) (2007) A15-03
- [3] Xinmin Cao, Wenhui Du, Y. Ishikawa, Xianbo Liao, Robert W. Collins, Xunming Deng, "Fabrication and optimization of a-Si:H n-i-p single-junction solar cells with 8 Å/s intrinsic layers of protocrystalline Si:H materials," in *Amorphous and Polycrystalline Thin-Film Silicon Science and Technology—2007*, edited by V. Chu, S. Miyazaki, A. Nathan, J. Yang, H.W. Zan (Mater. Res. Soc. Symp. Proc. Volume 989), (2007), A15-05
- [4] John CL Cornish, Eman Mohamed and Reem Abdelaal, "Engineering nanocrystals of silicon," *Molecular Simulation*, Vol. 31, No 6, (2004) 405-410.
- [5] Cabarrocas, P. Roca. I., *Phys. Stat. Sol. (c)*, 1, NO. 5, (2004) 1115-1130.
- [6] Shah, A. V., Meier, J., Vallat-Sauvain, E., Wyrsh, N., Kroll, U., Droz, C. and Graf, U. *Solar Energy Materials & Solar Cells*, 78, (2003) 469-491.
- [7] Shropp, R.E.I. and Zeman, M., "Amorphous and microcrystalline silicon solar cells, modeling," in *Materials and Device Technology*, Kluwer Academic Press, Massachusetts 1998.
- [8] Jandel, Peakfit, San Rafael, California, Jandel Scientific Software, 1995.