



# Sub-Microsecond Pulsed Plasma Surface Modification as a Combinational, all Atmospheric Pressure Approach to Nano-structured Thin Film Production

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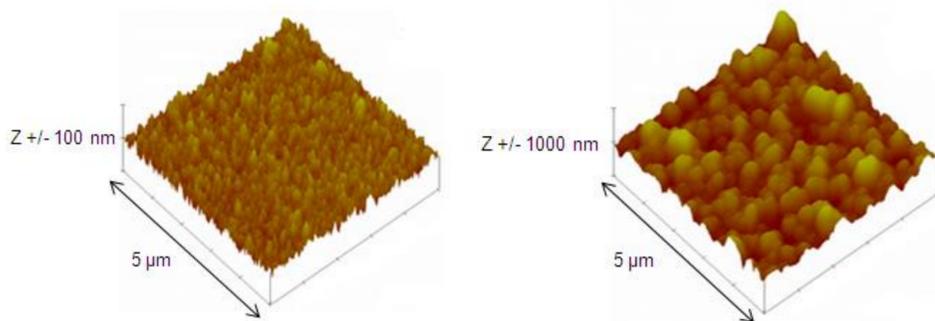
## Abstract

Atmospheric pressure (AP) CVD systems have significant advantages over vacuum based processes for large area, low cost substrates such as glass. The ability to control the surfaces texture is also of considerable advantage for many thin film structures. The nano-scale features may be further optimised via post growth etching, by, for example, to round from sharp vertices or induce or exaggerate texture in a film material that is intrinsically smooth. This is normally achieved via low pressure plasma treatments or wet chemical processes, hence the presented AP plasma approach offers reduced capital costs combined with ease of scalability and process integration. In this work we demonstrate the new capability offered by our sub-microsecond pulsed plasma system for the activation of AP film growth and control of structure. Further modification is shown by the application of the plasma to a post growth etching process.

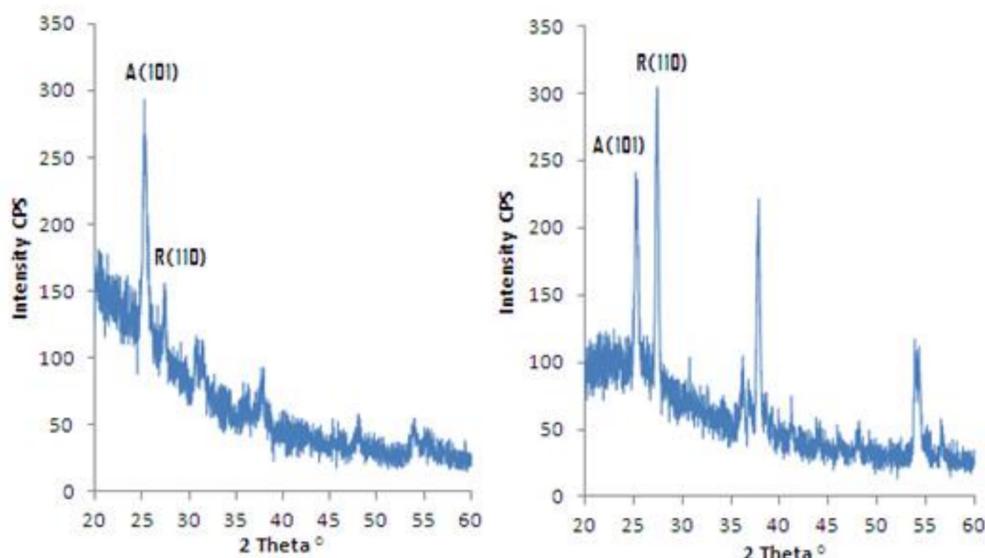
## Example 1: Control of film growth

A bespoke unit capable of delivering sub-µsecond voltage pulses was integrated with an AP PECVD system with a view to assessing any influence over the deposition of titania films as a model thin film system.

Previous work had shown that conventional thermally driven APCVD requires a substrate temperature over 450 °C to produce the anatase structure with rutile phase requiring higher temperatures in excess of 550 °C. It was postulated that the higher level of activation provided by the short pulse plasma might enable the controlled deposition of a more crystalline material at significantly reduced substrate temperatures.



**Fig 1.1:** 5 µm AFM images showing the surface topography of the samples produced using pulse repetition rates of (a) 20 kHz, (z +/- 100nm), (b) 90 kHz, (z +/- 1000nm) at a surface temperature of 275 °C

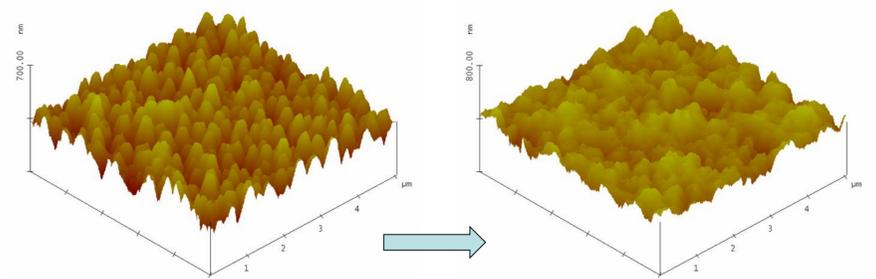


**Fig 1.2:** X-ray diffraction patterns for the titania films grown using pulse repetition rate of 5 kHz (a) and right 70 kHz (b) at a surface temperature of 420 °C. Note anatase /rutile weight fraction reduced from 91 to 36%.

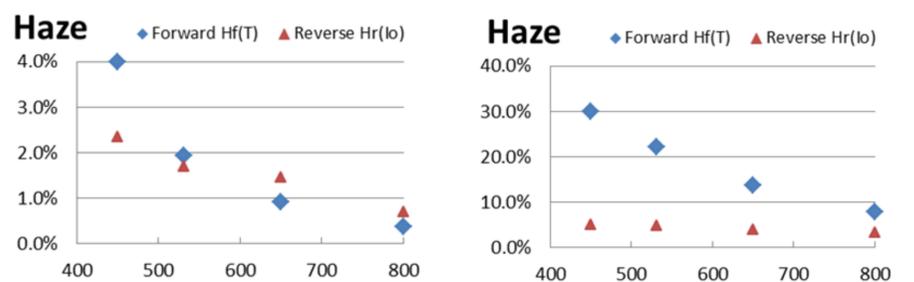
## Example 2: Post Growth Surface Modification

In this example we show the manipulation of an APCVD Al:ZnO surface for optimum performance in Si micromorph solar cells via the application of an atmospheric pressure plasma etch system. The objective is to facilitate the trade off between transparency, light scattering and electrical conductivity whilst providing a suitable surface for stable Si growth.

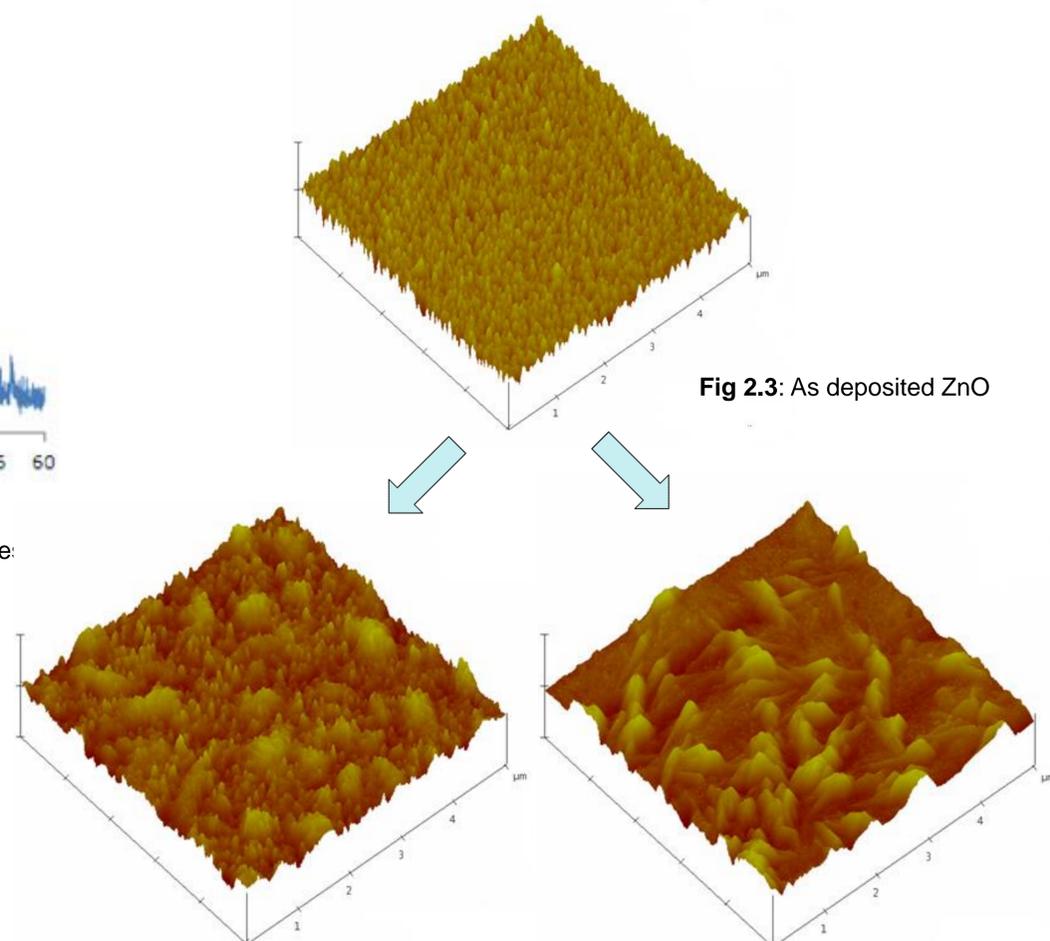
The use of the sub-microsecond pulse plasma in this application provides significant modification of the ZnO surface. A key advantage over the audio frequency plasma is the ability to vary the effect via the pulse repetition rate.



**Fig 2.1:** AFM showing the reduction in aspect ratio and increased feature size achieved by audio frequency plasma etch (RMS 48.4 → 41.8nm)



**Fig 2.2:** APCVD Al:ZnO Measured haze as deposited left and following AP plasma etching right



**Fig 2.3:** As deposited ZnO

**Fig 2.4:** Following pulse plasma etch applied at 20 kHz repetition

**Fig 2.5:** Following pulse plasma etch applied at 50 kHz repetition