Characterisation of PECVD silicon films deposited at 162MHz, using a large area, scalable, multi-tile-electrode plasma source

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Abstract

Thin film, hydrogenated silicon deposited by PECVD in both amorphous (a-Si:H) and microcrystalline (μc-Si:H) phases are commonly used in the manufacture of solar panels. Here we present a scalable, multi-tile electrode topology, large area (600×720mm) plasma source capable of producing depositions of μc-Si:H at high deposition rates. Depositions of μc-Si:H with SiH_4 concentrations of 20% at rates of up to 10Å/s are achieved. Here we present a characterisation of the film properties seen in these depositions. The behaviour of the crystalline fraction, χ_c is observed using Raman spectroscopy, x-ray diffractometry, and dark/light-conductivity measurements. A qualitative interpretation of these results is also presented, relating them to SiH_4 gas phase depletion [4] within the plasma.

Introduction

Thin film deposition of silicon by PECVD is widely used in the manufacture of solar panels. The vast majority of Panels produced now consist of amorphous material. The use of microcrystalline layers as a bottom junction in tandem cells has been shown to increase efficiency of the panel through the absorption of longer wavelength light due to its lower band-gap. However the deposition of high quality, uniform microcrystalline material has been limited by slow deposition rate. VHF-PECVD (30-300MHz) has been shown to produce suitable material at high deposition rates without compromising material quality [1, 2]. This method until recently has been limited to small scale depositions as wavelength dependant in-homogeneities appear at larger dimensions [3]. By segmenting the electrode and powering

the tiles in push pull pairs it is possible to achieve uniform large area plasmas with high excitation frequencies.

Experiment

The following experiments are preformed with a multi-tile source. Pairs of tiles are powered at 162 MHz in a push-pull configuration (180 degrees out of phase with their neighbours). Both the vacuum enclosure and the substrate heater are grounded. The total electrode area is 600mm×720mm [5]. Power was delivered by an AE Ovation 35-162 Generator and split using a Phive Plasma Tech. Power Splitter (PSTLD) [6]. Gases are premixed in a single feed line then delivered to the individual tiles through a showerhead configuration for even gas distribution across the source and pumped out through the sides.

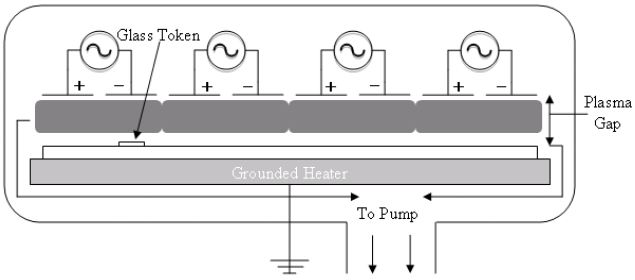

Figure 1: *The Segmented electrode source used operates in a push-pull configuration with power divided between each pair of tiles. The substrate is held on a grounded movable heater and exhaust is pumped from both ends.*

To test film quality 1 inch square tokens are placed at repeatable positions on the substrate. The tokens are 1mm thick display glass with pre-sputtered metallic contacts for conductivity measurements. After deposition each token is tested for dark/light-conductivity to obtain an estimate of crystallinity. A constant voltage (~90V) is placed across the metallic contacts in (a dark) vacuum and the current is measured as the sample is put through a temperature cycle. The resistance is calculated and the activation energy (E_a) is determined from $E_a = \frac{k_b T}{Ln(R)}$. When the sample returns to room temperature (~20C) the current is noted for both dark and light conditions to find the conductivity ratio A; High conductivity ratio (>1000) and E_a (>0.5eV) are taken to indicate amorphous material alternatively samples are said to be crystalline. Select samples are further tested using raman spectroscopy [7] and x-ray diffractometry [8]. The LO-TO Peak of the Raman Spectra was analysed by fitting 3 Gaussian/Lorentzian peaks, allowed to vary around 480cm^{-1} 500cm^{-1} and 520cm^{-1} using a least squares technique. The crystallinity is calculated by comparing the integrated areas under the peaks, $\chi_c = \frac{I_c}{I_c + \gamma I_a}$, where I_a and I_c are the amorphous and crystalline areas respectively and γ is the ratio of the material cross sections. Using x-ray diffractogrames, the relative size of the crystalline peaks is compared to further substantiate the crystallinity behaviour. The fraction of material in each orientation is also determined by

comparing the integrated area of each peak in a given scan.

Results

It was found that (with the exception of infrequent outliers) dark/light-conductivity ratio and activation energy reliably reflect the crystalline fraction (figure 2). Furthermore the dark/light-conductivity changes by multiple orders of magnitude from ~10^5 for a-Si:H to ~10^2 for μc-Si:H. This makes it easy to distinguish highly crystalline material from highly amorphous but difficult to predict the exact crystalline fraction. The shift was primarily due to the increase in dark current as the photoconductivity remained relatively static. As mentioned above one of the advantages of VHF-PECVD is the ability to produce high quality microcrystalline material at higher deposition rates than conventional PECVD. This can be explained by more efficient depletion of silane in the plasma. In effect for capacitively coupled plasma (CCP), as the frequency increases, the sheath impendence of the plasma drops $Z = \frac{1}{j\omega C}$. This allows for greater power dissipation in the plasma ($I_pR_p^2$), where I_p and R_p are the plasma current and resistance respectively and more efficient dissociation of silane and less power dissipated in the sheath (I_pZ). The activated silane has a high sticking probability, thus in VHF operation the silane partial pressure is reduced despite higher total flow or gas flow concentration; this effect can be seen in figures 3 and 4. As the silane flow concentration is increased the crystalline fraction as determined by 633nm Raman spectroscopy is reduced. Interestingly the crystallinity as observed by shorter wavelengths, 488nm/514nm does not reflect the same trends. Initially this was not understood until the thickness of each sample was examined. The sample deposited at 20% concentration is 500Å

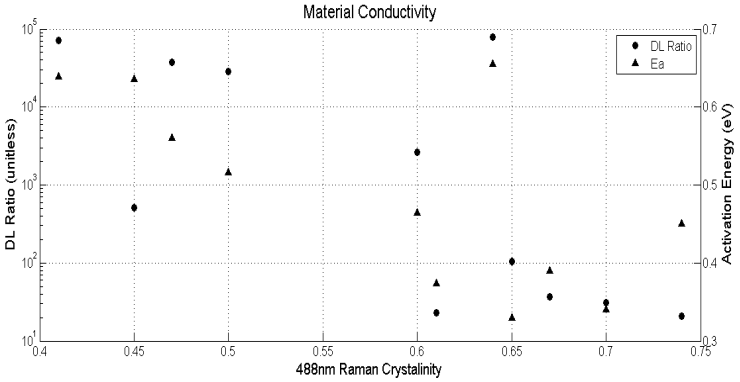

Figure 2: *Behaviour of activation energy and dark-photoconductivity ratio as a function of Raman crystalline fraction*

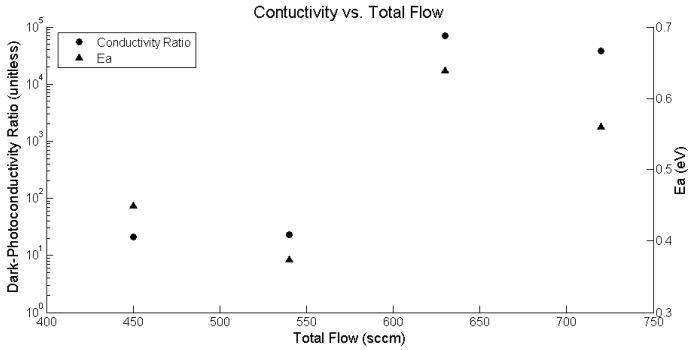

Figure 3: *Behaviour of Dark-Photo conductivity ration as a Function of total flow. Power and Silane Flow Concentration are held constant at 2400W and 0.2 respectively*

thicker than the others. It is well documented that the crystalline fraction of μc-Si:H increases dramatically as a function of thickness thus shorter wavelength Raman which only samples

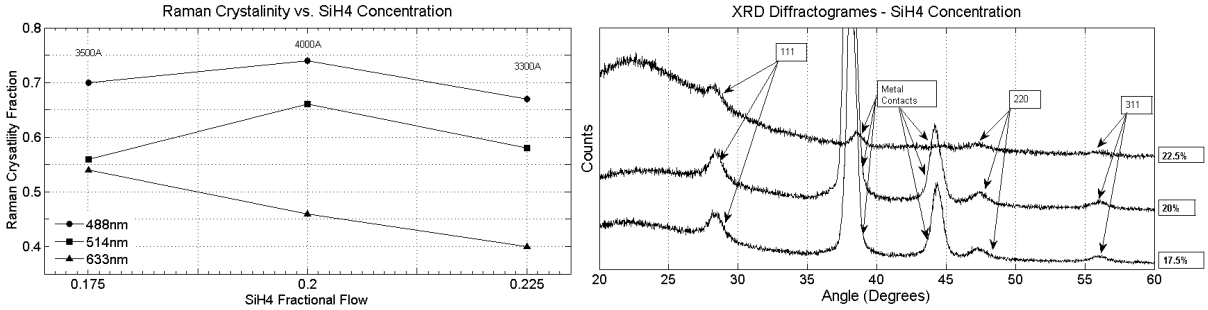

Figure 4: Transition from micro-crystalline to amorphous silicon behaviour with increasing silane partial flow. Left is Raman analysis at wavelengths of 488nm, 514nm and 633nm. Right are 3 X-ray diffractogrames of the same 3 samples. Area Comparison of the crystalline peaks estimates the orientation is 60% [111], 30% [220], 10% [311].

the surface of the layer is extremely sensitive to thickness. Also given that the layers we have grown are <5000Å and that absorption layers in solar cells are typically three times this. It could be expected that material grown to this thickness would be highly crystalline.

Conclusions

Multi-tile electrodes allow for the utilisation of higher RF frequencies in the production of amorphous and microcrystalline material for manufacture of solar panels and are scalable to large areas where wavelength effects would usually dominate. Dark/light-conductivity ration and activation energy have shown to be an effective diagnostic in the determination of material crystallinity. Multi wavelength Raman analysis has shown to be an effective analysis of depth dependent crystalline as well as a prediction of the crystallinity of thicker films. X-ray diffractogrames confirm behaviour of the raman crystallinity

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