ELECTRON BEAM MICROANALYSIS OF CRYSTALLINE SILICON FILMS GROWN ON FOREIGN SUBSTRATES FOR SOLAR CELLS

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ABSTRACT: Electron backscattering pattern analysis is a powerful, relatively new scanning electron microscope technique that can rapidly determine the degree of crystallinity e.g. the size and orientation of large numbers of grains and the presence or absence of elastic strain in polycrystalline thin films. By measuring the electron beam induced current in a solar cell for a range of beam energies, the value of the minority carrier diffusion length at the point of beam impact can be determined. These techniques were used to characterise thin crystalline silicon films and solar cells formed by electron cyclotron resonance – plasma assisted chemical vapour deposition on a variety of foreign substrates.
Keywords: characterization, CVD deposition, microcrystalline Si

1. INTRODUCTION

Thin film crystalline silicon solar cells on foreign substrates are attracting considerable interest for high performance, low cost and stable photovoltaic devices [1,2]. Structural and electronic characterisation of the grown films and solar cells is a key requirement. Two powerful scanning electron microscope (SEM) techniques for the study of polycrystalline silicon films and solar cells are electron backscattering patterns (EBSPs) [3] and minority carrier diffusion length determinations [4,5], the latter so far only applied to monocrystalline solar cells.

This paper reports the results of applying these SEM techniques to silicon films deposited by ECR-PACVD (electron cyclotron resonance - plasma assisted chemical vapour deposition) on Corning glass and on oxidised silicon wafers and crystallised using aluminium-induced and excimer laser crystallisation.

2. EXPERIMENTAL

The silicon films were all grown at South Bank University by ECR-PACVD as described elsewhere [6,7]. Silane was used as the feedstock and hydrogen as the plasma cavity gas. Corning 1737 glass and SiO_2-coated Si wafers have been used as substrates in this work. The as-grown films ranged from amorphous to microcrystalline with varying crystal fractions, as indicated by Rahman and X-ray studies, depending on deposition conditions. Following growth the samples were crystallised by aluminium-induced crystallisation (AIC) or by excimer laser crystallisation (ELC). Growth and processing temperatures were kept below 700 °C. The ELC experiments were carried out using a KrF laser, with the samples in an Ar atmosphere at room temperature. Details of the crystallization procedures will be given elsewhere [8,9]. X-ray diffraction (XRD) and Raman spectroscopy measurements were carried out to determine film structure at South Bank using a Philips X'Pert system and a Renishaw Ramascope 2000 instrument, respectively. The grain size was estimated from the XRD spectra using the well known Debye-Scherrer method. In the case of Raman spectroscopy, the Si phonon band at 520 cm^{-1} was monitored and the film crystalline fraction estimated using the method described by Kaneko et. al. [10].

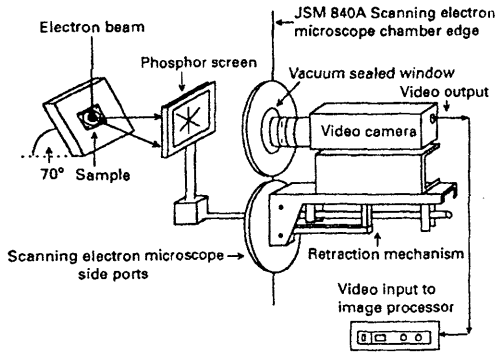

Figure 1. Experimental arrangement for EBSP (electron back scattering pattern) analyses.

The SEM studies were carried out at Imperial College on a JEOL JSM-840A SEM fitted with an EBSP system by HKL Ltd. and a Matelect ISM–5 EBIC system. For EBSP the equipment shown in Figure 1 was used with a beam accelerating voltage of 20 kV, with typical beam currents of 5 to 20 nA. The specimen was tilted 70° towards the screen where the patterns were formed and imaged with a CCD camera. Provided the grain size is ≥ the volume excited by the electron beam (~ 1 μm^3) Kikuchi lines will appear. Software can then index the diffraction patterns, if sufficiently sharp, as in the example if Figure 2, to determine the crystallographic orientation at the points of beam impact of the scanning electron

microscope (SEM) beam [3].

The instrument could be set to automatically determine the orientations at a set of points forming a square array at a chosen spacing. Software then produces both a stereographic plot of the grain orientations and an

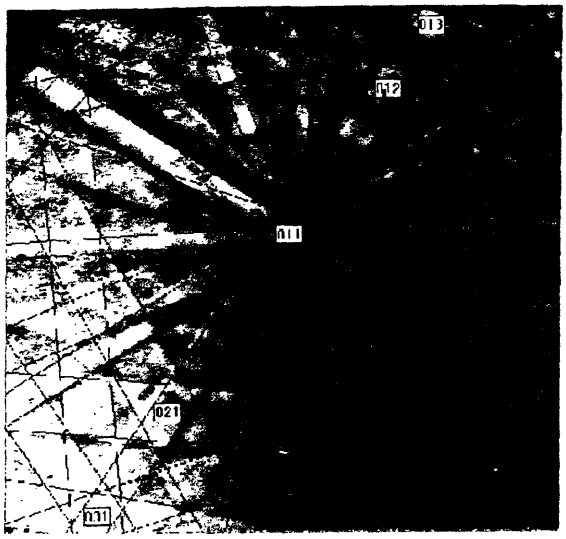

Figure 2. An indexed electron backscattered pattern (EBSP) i.e. Kikuchi pattern. The sharpness of the pattern lines is an indicator of crystalline perfection. Elastic strains e.g. due to crystallographic defects, blur these lines and if the pattern is too blurred it becomes unindexable.

image of the scanned area with the grains colour coded according to orientation. For each grain boundary (GB) the software gives the axis and angle of misorientation. From tables, in many cases, the Σ (Friedel index) value for the GB can be found.

By using Monte Carlo electron trajectory simulation programs as a basis it is possible to calculate the EBIC (electron beam induced current: I_{cc}) collected by the solar cell junction. Plotting such EBIC values versus the electron beam accelerating voltage (V_b) gives simulated curves for a range of assumed values of the minority carrier diffusion length (L). Fittting the experimental data points to simulated $I_{cc}(V_b)$ curves enables L to be determined [4,5]. The cells were produced in the p-i-n configuration by depositing p- and i-type layers on SiO_2 coated n-type substrates. The i-layer thicknesses were in the range 1-2 μm.

3. RESULTS

3.1 EBSP Studies

It was found that several levels of crystallinity could be recognized in the ECR-PACVD films from their EBSPs. In order of improving crystallinity (see Table I, column 1) (i) no EBSPs could be detected at all, (ii) EBSPs could be seen but were too blurred for any of them to be indexed (i.e. have the hkl values for pairs of the lines (bands) identified), (iii) EBSPs occurred of which a minority only could be indexed and (iv) EBSPs were observed essentially all of which could be indexed. The complete absence of EBSPs is indicative of very small grain sizes (nanocrystallinity) so that a multitude of orientations occurred in the volume of the order of a μm^3 excited by the electron beam. The appearance of EBSPs occurs for grain sizes ≥ 1 μm and indexability is indicative

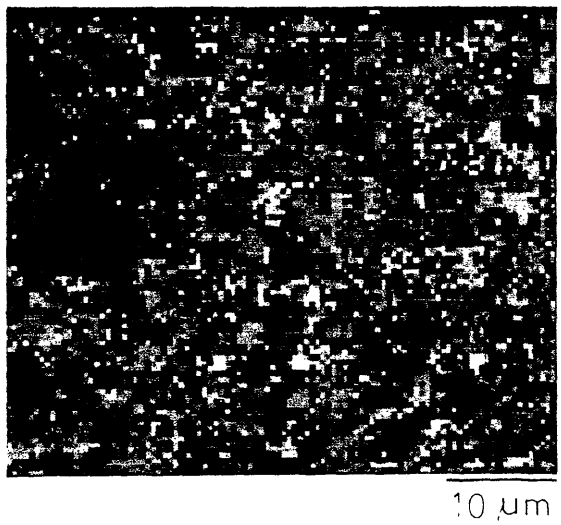

Figure 3. Image of an area of an ECR-PACVD grown polycrystalline film (#4) after Al induced crystallization. Each grain is colour coded (reproduced here as grey scales) to indicate its orientation. The black areas are Si free.

of a high degree of elastic strain-free perfection.

In case (iv), the grain orientations and the grain boundary geometries [1] are determined. Figure 3 is a map of the grains in specimen #4 greyscale-coded as to orientation for a grid of 100 x 100 points with a separation of 0.5 μm. The black areas correspond to no Si coverage after Al induced recrystallization. The stereographic plot of the grains showed random orientations i.e. no preferred orientation or texture was present. Histograms showed a relatively uniform distribution of grain boundary misorientations but with maxima for 60° (corresponding to coherent first-order Σ = 3 twin boundaries) and 36° (corresponding to second-order twin boundaries).

Some details of the crystallization treatment of the samples are summarised in Table 1. For the Al induced crystallization studies, all the as-grown films were microcrystalline with thicknesses < 1μm. XRD showed they were randomly orientated with grain sizes <100 nm. No EBSPs were seen from these films. After crystallization, the samples show EBSPs of varying perfection indicating grain growth to ≥ 1μm dimensions. The EBSP observations are consistent with the XRD and Raman data. The samples which exhibit fully indexable patterns were processed at the highest temperature (~680° C). However the films were not fully continuous. By modifying the crystallization treatment, continuous films were realised (e.g. Seed 16) at temperatures <500° C but with a loss of crystalline perfection. The samples for ELC were also microcrystalline in the as-grown condition. After ELC, a significant improvement in crystalline quality was observed by XRD and Raman measurements [9]. However, (Table 1) no EBSPs were observed. This is indicative of sub-micron grain sizes and/or high levels of elastic strain in the grains for these samples as discussed

previously.

Finally it is significant that the relatively thick, as-grown sample SBU-4BB exhibits EBSPs. This shows the direct growth of large grain size material at 530° C onto a glass-like surface by the ECR technique. However the EBSP and XRD data indicate that the film contained a mixture of crystal sizes from the μm to the 10s of nm scale, with a crystal fraction < 100%. It is likely that the crystal size increased with film thickness as thinner films did not exhibit EBSPs

3.2 Minority Carrier Diffusion Length Studies

Figure 4 shows experimental curves of EBIC gain, the ratio of the charge collection current I_{cc} to the beam current I_b, versus beam accelerating voltage (i.e. the beam penetration range in silicon) V_b. The upper three curves, for different values of I_b, were recorded with the beam incident between the metallization fingers and the lower three curves with the beam incident on the metallization. The shift to higher beam voltages of the EBIC curves for the beam incident on the metal is due to the absorption of some beam energy by the metallization. This does not contribute to the electron voltaic effect, of course. With the beam incident between the metal fingers, Monte Carlo electron trajectory simulations showed that the beam energy was dissipated in producing hole-electron pairs entirely within the n- and i-layers up to V_b = 10 keV. It can be seen from the experimental data that almost no EBIC gain was detectable. This showed that the charge collection efficiency of the layers, i.e. the value of L, was negligible compared to that in the substrate whose large value of L dominates the charge collection behaviour at higher beam voltages. This was an initial attempt to test the utility of the method for the ECR-PACVD solar cells. In later cells, made entirely of deposited material, this behaviour will not occur and a value for L should be obtainable by detecting smaller EBIC gains, using more sensitive settings of the detecting amplifier.

It was observed that I_{cc}, for any given value of V_b, did not vary laterally from point to point over the solar cell i.e. there was little contrast in EBIC plan view images of the solar cells. A scattering of small black dots (regions of low charge collection) occurred, however. Thus the technique gives a rapid indication of the uniformity of L even for fine grained polycrystalline material.

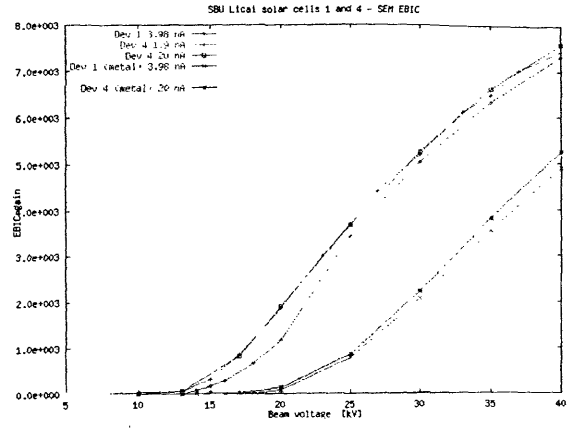

Figure 4. Experimental curves of EBIC gain = I_{cc}/I_b vs V_b for a solar cell of 0.65 μm of Ag-Al on a silicon 0.35 μm n-layer and a 0.83 μm i-layer deposited on a p-type substrate. The upper curves for 3 values of beam current were for the beam incident between the metallization fingers. The lower 3 curves had the beam incident on the contact metal.

DISCUSSION

The EBSP and L determination methods have not previously been applied to such relatively small grain size and strained material as that studied here.

The SEM-EBSP technique proved valuable for the characterization of the ECR-PACVD polycrystalline photovoltaic material. The information on the crystallinity produced can help optimise the growth technique to produce efficient solar cells. The inability to obtain backscattered Kikuchi patterns for grains smaller than 1 μm is due to the spreading of the electrons of the incident high energy beam in the sample.

The L determination method is expected to be more useful for later solar cells consisting entirely of ECR-PACVD material and, particularly, once the structure is relatively large grained and strain-free, when L will be larger.

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Table 1. EBSP Results on the Crystallinity of ECR-PACVD Si Films.

Crystallinity	Sample	Crystallization treatment
(i) no EBSPs i.e. grain size (GS) is sub μm	SP111-448[+] (120nm on CG1737) II-18 (15) (190nm on SiO_2/Si) VAL2 (270 nm on Al on CG1737)	ELC 448 $mJcm^{-2}$ (1 shot) 500 $mJcm^{-2}$ (128 shots) 270 $mJcm^{-2}$ (3 shots)
(ii) EBSPs present but unindexable i.e. GS ≥ 1μm, considerable strain	Seed 16 0.4μm thick Si film on CG1737	AIC 520°C, 50 mins
(iii) EBSPs present and a few indexable i.e. GS ≥ μm, less strain	SBU-4BB 2.4 μm thick Si film on SiO_2/Si	None – as grown film
(iv) EBSPs present and all indexable i.e. GS ≥ 1μm, little strain	#4 (0.9 μm thick Si film on SiO_2/Si) #6 (0.7 μm thick Si film on SiO_2/Si)	AIC 630 °C, 40 mins 680 °C, 30 mins

[+]sputtered film; CG=Corning Glass

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