Limited influence of grain boundary defects in hot-wire CVD polysilicon films on solar cell performance

J.K. Rath *, A. Barbon, R.E.I. Schropp

Utrecht Uni(ersity, Debye Institute, P.O. Box 80000, 3508 TA Utrecht, Netherlands

Corresponding author. Fax: q31-30 254 3165: e-mail: j.k.rath@fys.ruu.nl.

Abstract

Grain boundary defects in poly-Si:H films have been analysed by infrared spectroscopy, photothermal deflection spectroscopy, dual beam photoconductivity and electron spin resonance techniques. Complete absence of 2100 cmy1 mode in infrared spectrum is observed in a material with a low defect concentration. The dangling bond resonance line at *g*s2.0055 showed narrowing_temperature-independent.with increasing defect density in the material. The narrowing is attributed to Heisenberg exchange at clustered defects. The transport path in a cell is through the grains and the carrier transport bypasses these grain boundary defects. This bypass explains why our n–i–p cell incorporating a 1.5-mm poly-Si:H i-layer generates a current of 18.2 mA cmy2 even though the defect density is 7.8=1016 cmy3. q1998 Elsevier Science B.V. All rights reserved.

Keywords: Grain boundary defects; Poly-Si:H films; Solar cell

1. Introduction

For thin film polycrystalline silicon devices, a one-step production process is desirable which yields films with a low density of grain boundary defects, without using any post-deposition hydrogen treatment. At present there are two approaches to reach this target: (1). High temperature processing to get thick poly-Si films with a larger grain sizes, _2. lower temperature processing, such as very high frequency plasma enhanced chemical vapor deposition_(VHF PECVD) .and hot-wire chemical vapour deposition, where the grain sizes are typically <100 nm. A process that can deliver poly-Si at lower process temperatures at a relatively fast rate without too many grain boundary defects is essential. This paper shows how this has been achieved with hot wire chemical vapour deposition (HWCVD).process. As we have reported earlier, purely intrinsic poly-Si:H has been achieved without incorporation of boron microdoping or using a gas purifier w1x. Preliminary n–i–p cells incorporating this poly-Si:H resulted in 3.15% efficiency w2x. Though the rough surface texture_as observed by AFM.and a larger absorption compared to c-Si effectively explains the current generation in a thin film w3x, the adverse effect of still a high grain boundary defect density which is not well understood. It is our purpose to study the properties of the grain boundary defects and their role in the electronic transport.

2. Experimental

Poly-silicon films were deposited on 10 cm x 10 cm glass_Corning 7059.and c-Si wafer substrates by HWCVD in one of the chambers of an ultra high vacuum multichamber system_PASTA.. Details of the hot wire-set up and deposition process have been described elsewhere w4x. The thickness of the films was measured with a profilometer_Dektak.and with reflectionrtransmission measurements. Samples were characterised by X-ray diffraction_XRD., Raman spectroscopy, Fourier transform infrared (FTIR). spectroscopy, atomic force microscopy (AFM), photothermal deflection spectroscopy (PDS), dual beam photoconductivity_(DBP), electron spin resonance_(ESR)., steady state photo-carrier grating technique_(SSPG), Hall mobility measurement and electrical conductivity in the dark and in white light.

ESR spectra were recorded with a spectrometer in X-band_Bruker ESP 300.. Clear field cross sectional transmission electron micrographs_XTEM.were made with an electron microscope_Phillips CM30T. working at 300 kV. High resolution electron micrographs_HREM.of the material were made to detect crystallinity, especially near the interfaces. The resolution of magnetic field in ESR is 0.001 mT. Relative errors in the estimation of defect density by ESR is "10%.

An n–i–p cell was made in the configuration nqc-Sirpoly-Si:H _HWCVD.rp-m c-Si:H (PECVD/ITO). Highly doped nqc-Si_0.01 V cm. wafers served as substrates as well as the n-layer of the cell. The cells were characterised by light *I–V* measurements at AM 1.5 illumination.

3. Results

Poly-Si:H films were made by HWCVD by a systematic variation of substrate temperature _*T*., s chamber pressure_*P*., SiH4/H_2 flow rate, and wire r 4 2 temperature _*T* .. Details of optimisation procedure w have been described elsewhere w3x. The ESR spectrum of the poly-Si:H films showed a line at *g*s 2.0055"0.0005, characteristic of dangling bonds _db., from which defect density was calculated. Variation of the wire temperature _*T* . from 19008C to w 17008C at the chamber pressure of 0.1 mbar shows

that the defect density in the poly-Si:H film reaches a minimum_Fig. 1a.of 7.8=10_{16} cm_{y3} at T of $_{w}$ 18008C. At this temperature, the IR spectrum shows complete absence of the 2100-cm_{y1} band _attributed to Si–H bonds on grain boundaries., which is strongly observed at T of 19008C_Fig. 1b.. We attribute this $_{w}$ absence to very thin grain boundary regions in the optimised material_T s18008C.facilitating recon- $_{w}$ struction of the grain boundary defects. The optimised material shows a very small barrier to electron transport_E s0.012 eV., as determined from tem- $_{a}$ perature-dependent Hall mobility measurements. This suggests negligible trapping of carriers in the defects at the grain boundaries. In contrast to this, a film made at 19008C but at a high chamber pressure of 0.3 mbar had a defect density of 3.4=10_{18} cm_{y3} while the intensity of the 2100 cm_{y1} mode was still small. This is attributed to the lack of passivation in the thicker grain boundary regions created at high wire temperature and pressure. At a high chamber

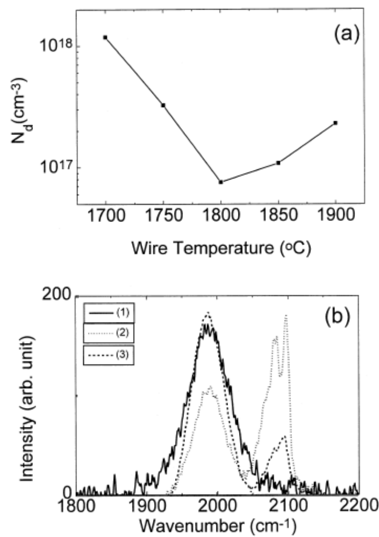

Fig. 1. _a. Dangling bond density _N_{d}. of poly-Si:H films at different wire temperatureT_{w}_P_{r}s0.1 mbar.. _b. Infrared spectra of poly-Si:H films deposited: _1. T_{w}s18008C, P_{r}s0.1 mbar, _2. T_{w}s19008C, P_{r}s0.1 mbar, _3. T_{w}s19008C, P_{r}s0.3 mbar.

pressure much of the hydrogen may be consumed in the gas phase reaction w5x, and less hydrogen will reach the growing surface for hydrogen passivation. The ESR spectra of these films show only a single line at gs2.0055"0.0005 _db.. No line at gs 1.998 _the so called CESR line corresponding to free electrons as observed in PECVD films w6x. was observed even at temperatures down to 10 K w7x. This absence is attributed to the intrinsic property of the film. The ESR peak to peak line width_DH .of $_{pp}$ the db_dangling bond.line of our optimised film _N s7.8=10_{16} cm_{y3}. is 0.76 mT. The line width $_{d}$ is invariant to defect densities of F2.3=10_{17} cm_{y3}. However, for films with a larger defect density, the line width decreases. Fig. 2 shows the integrated ESR spectrum of the db line of two films of two different defect concentrations. The intensities of the two lines have been normalised. At the defect density of 3.4=10_{18} cm_{y3}, the line width narrows down to 0.56 mT. An increase of the defect density is achieved by increasing the deposition chamber pressures from 0.1 mbar to 0.3 mbar. The structural studies of the poly-Si:H films made at different chamber pressures show same orientation of grains, i.e, they have identical XRD spectra showing only a _220.orientation. The Raman spectra were also similar and the crystalline volume fraction marginally reduces from 95% at 0.1 mbar to 89.6% at 0.3 mbar. The XTEM picture also reveals similar columnar growth. DH showed a monotonic decrease with $_{pp}$ increasing defect density _increasing chamber pressure. and a good correlation of narrowing of line width with defect density is obtained. We studied the temperature dependence of the line width. The temperature at the site of the sample was carefully

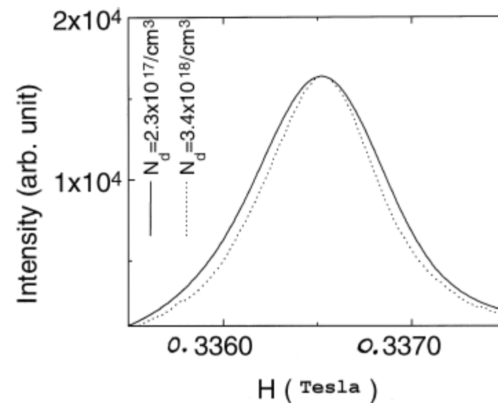

Fig. 2. The ESR spectra of the poly-Si:H films of different dangling bond concentrations.

measured by a thermocouple. Line width did not show any noticeable change for all the samples from 290 K to 550 K. Moreover, for the sample with line width of 0.56 mT, decreasing the temperature to 10 K did not change the line width.

A preliminary n–i–p cell made in the configuration n_{q}c-Sirpoly-Si:H_HWCVD.rp-mc-Si:HrITO had an efficiency of 3.15% with a V_{oc} of 0.45 V, J_{sc} of 18.2 mA cm_{y2} and FF of 0.38. The surface roughness of ;150 nm _as estimated from AFM

and XTEM pictures. has contributed significantly to achieve such large currents in only a 1.5-mm thick i-layer. The reflectance of the film is considerably less than that of a c-Si wafer w7x. However it is still surprising that the cells work so well whereas the defect density is still too high _7.8=10$_{16}$ cm$_{y3}$. for carrier collection. Fig. 3 shows the optical absorption spectrum of the poly-Si:H film on glass measured by photothermal deflection spectroscopy _PDS.. The spectrum has a considerable absorption in the low energy region which is characteristic of absorption by grain boundary defects. This absorption is consistent with the ESR results. The contribution from the substrate, the surface or the interface absorption is

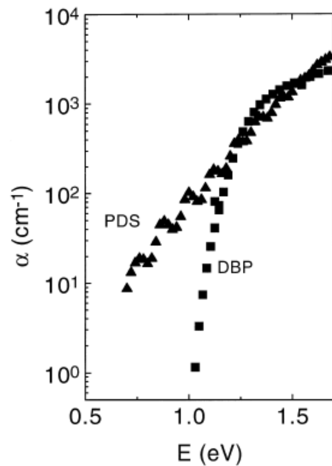

Fig. 3. The optical absorption spectrum of poly-Si:H as a layer on glass, measured by PDS, and in the cell configuration, measured by DBP.

considered to be negligible because the PDS absorption in Fig. 3 is much higher than the PDS detection limit imposed by such absorptions for a 1.5-mm film w8x. However, the absorption spectrum measured by dual beam photoconductivity _DBP. of the same material incorporated in a cell configuration has similar characteristics to c-Si, i.e., the spectrum has an absorption edge at 1.1 eV. Details of the DBP technique and its validity to measure the subgap optical absorption of a material in the cell structure has been reported earlier w9x. A similar photoconductivity
experiment, i.e., CPM has been used to measure the optical absorption of cells w10x.

4. Discussion

We will discuss three possible causes for the narrowing of the ESR line at the larger defect densities and determine the most probable mechanism.

_1. Structural order: The ESR line width of the polycrystalline films is caused by the distribution of spin orientations due to random size and orientations of the grains. The orientations of the grains and columns pose constraints on the orientations of the spins and thus any change of the orientations of grains can change the line width due to a different distribution of spin orientations. However all the structural properties_XRD, XTEM, Raman.suggest that at least there is no improvement of structural order going from 0.1 mbar to 0.3 mbar. This lack of change rules out the possibility of narrowing due to structural order.

_2. Motional narrowing: If the defects are predominantly situated at the grain boundaries, the hop-
ping frequency _n . of the electrons through these H defects can be given by the relation n H s n_y2 *RrR* y*ErkT*., where, *R* is the distance 0 db and *E* is the energy difference between two sites w11x. *R* is the localisation length of the Si dangling db bond_*R* f0.3 nm.. The line width D*H* is then db pp obtained by the relation D*H* sD*H* r_1qn *T*., pp 0 H 1 where *T* is the saturation life time. At the larger 1 defect densities, increase of n H due to reduced *R* can decrease the line width. However, in this process, the line width will change with temperature due to variation of hopping frequency. In our experiments the db line in the ESR spectra of our poly-Si:H films shows no change of line width with temperature. We conclude that hopping of spins at the grain boundary is not fast enough for any motional narrowing.

_3. Heisenberg exchange narrowing: To explain a temperature independent narrowing of lines, the Heisenberg exchange interaction is an appropriate answer. Such an interaction can be given by the relation, *E* sy*J*_*S*P*S*., where *S* and *S* are true ex *i j i j i j* spins and *J* is the exchange integral causing the *i j* interaction to be short range with nearest or next nearest neighbour atomsw12x. In our highly defective sample, if we assume that defects are mostly in the non-crystalline region, i.e., 10.4% volume fraction, then the defect density in this region will be ;3= 10$_{19}$ cm$_{y3}$, which gives an average distance between defects to be ;03.1 nm. This distance is much larger than the average distance between Si atoms and cannot account for Heisenberg exchange. We propose that there are regions at the grain boundary where the defects are clustered in which defects are spaced close enough for exchange interaction. The reason why the Heisenberg exchange is not observed in case of a-Si:H is that the dangling bonds are spatially distributed in a random way and they can be considered isolated from each other w13x. However, in poly-Si:H films the defects have to be accommodated in the smaller regions between columns, thus creating clusters of defects.

In the DBP measurement of the cell, the photoconductivity

transport path is in the vertical direction.
As the crystalline growth is columnar, as is inferred from the_220.preferential orientation_from XRD. of grains, the transport path in the cell is along the length of the columnar grains, thus bypassing the clustered defects between the columns. This model of the structure is indeed confirmed by cross-sectional TEM where a columnar growth of the grains on the substrate is observed. The absence of any defect absorption in the DBP of the cell also indicates there is no significant defect density within the grains, the type of which is observed in the low temperature furnace-annealed poly-Si filmsw14x. The diffusion length of the minority carrier _568 nm from SSPG. measured in the planar configuration is limited by the width of the grains whereas in the cell configuration the carriers can diffuse along the length

of the columns _extending over the thickness of the i-layer. without encountering defects.

5. Conclusion

The optimised poly-Si:H film by HWCVD shows complete absence of 2100 cmy1 mode in IR spectrum. An Heisenberg exchange interaction between the defects are observed. Clustering of the defects is proposed for the close interaction. The transport path in an n–i–p solar cell incorporating poly-Si:H i-layer is through the columnar grains and electron transport bypasses the grain boundary defects.

Acknowledgements

The authors thank D. Ruff and Dr. H. Mell, Phillips Univ. Marburg for PDS and Hall measurements and useful discussion. This research was partially funded by NOVEM _Netherlands Organisation for Energy and Environment. and is part of a film-Si project co-ordinated by ECN, Petten.

References

w1x J.K. Rath, D. Ruff, H. Meiling, R.E.I. Schropp, Mater. Res. Soc. Symp. Proc. 452_1996.977.
w2x J.K. Rath et al., Tech. Digest Int. PVSEC-9, Miyazaki, Japan, 1996, p. 227.
w3x J.K. Rath, H. Meiling, R.E.I. Schropp, Sol. Energy Mater. Sol. Cells 48_1997.269.
w4x R.E.I. Schropp, K.F. Feenstra, E.C. Molenbroek, H. Meiling, J.K. Rath, Philos. Mag. B 76_1997.309.
w5x R. Doyle, R. Robertson, G.H. Lin, M.Z. He, A. Gallagher, J. Appl. Phys. 64_1988.3215.
w6x F. Finger, C. Malten, P. Hapke, R. Carius, R. Fluckiger, H. Wagner, Philos. Mag. Lett. 70_1994.247.
w7x J.K. Rath, M.W.M. van Cleef, R.E.I. Schropp, Proc. 14th ECPVSEC, Barcelona, 1997, in print.
w8x N. Beck et al., Mater. Res. Soc. Symp. Proc. 452_1996.761.
w9x J.K. Rath, U.K. Das, P. Choudhuri, Proc. 13th EPVSEC, Nice, 1995, p. 280.
w10x P. St'ahel, P. Sla´dek, Proc. 13th EPVSEC, Nice, 1995, p. 214.
w11x N.H. Nickel, E.A. Schiff, Mater. Res. Soc. Symp. Proc. 452 _1996.1019.
w12x Abragam, Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.
w13x S. Yamasaki, J. Isoya, J. Non-Cryst. Solids 164–166_1993. 169.
w14x K. Choi, M. Han, J. Appl. Phys. 80_1996.1883.