Towards high-efficiency thin-film silicon solar cells with the "micromorph" concept

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Abstract

Tandem solar cells with a microcrystalline silicon bottom cell (1 eV gap) and an amorphous-silicon top cell (1.7 eV gap) have recently been introduced by the authors; they were designated as "micromorph" tandem cells. As of now, stabilised efficiencies of 11.2% have been achieved for micromorph tandem cells, whereas a 10.7% cell is confirmed by ISE Freiburg. Micromorph cells show a rather low relative temperature coefficient of 0.27%/K. Applying the grain-boundary trapping model so far developed for CVD polysilicon to hydrogenated microcrystalline silicon deposited by VHF plasma, an upper limit for the average defect density of around $2 \times 10^{16}/cm^3$ could be deduced; this fact suggests a rather effective hydrogen passivation of the grain-boundaries. First TEM investigations on μc-Si : H p–i–n cells support earlier findings of a pronounced columnar grain structure. Using Ar dilution, deposition rates of up to 9 Å/s for microcrystalline silicon could be achieved.

Keywords: Hydrogenated microcrystalline silicon; Tandem solar cell; Thin-film crystalline silicon; Very high frequency glow-discharge; Micromorph concept

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1. Introduction

The world-wide challenge to improve the efficiency of the thin-film solar cell device motivated our group to investigate intrinsic hydrogenated microcrystalline silicon (μc-Si : H) as a possible new absorber material [1]. Our μc-Si : H is deposited by the very high frequency glow-discharge (VHF-GD) process [2] at plasma excitation frequencies of 70 and 110 MHz; this process enhances the quality of μc-Si : H as compared to materials deposited by standard RF glow discharge at 13.56 MHz or by some other more "conventional" techniques [3–6]. The very high average defect density found in earlier studies of μc-Si : H was generally taken as an argument for its poor quality as semiconductor. This attitude hindered a detailed exploitation of this material with respect to photovoltaic energy conversion. In contrast to this, our work has shown that intrinsic microcrystalline silicon can constitute a promising new form of thin-film crystalline silicon; furthermore, this material can be directly, in one step, deposited as a p–i–n cell at low temperatures (200°C) on glass substrates.

In contrast to all previous work performed on μc-Si : H, a more pronounced absorption edge is observed for μc-Si : H deposited by VHF-GD [1]. Due to this fact, the energy gap could be deduced for the first time to be as low as approx. 1 eV [7]. The most striking feature in the absorption behaviour of μc-Si : H, compared to a-Si : H, is the shift of the absorption edge to the infrared. Compared to c-Si, the overall absorption of μc-Si : H when deposited by VHF-GD at 200°C is, on the other hand, increased over the whole range used for photovoltaic energy conversion.

It was shown by different groups that the n-type character of as-grown undoped μc-Si : H could be compensated by adding small traces of diborane to the feed gas during deposition. Thus, "midgap" material was established by this so-called "microdoping" approach (see also Fig. 2); the use of such "midgap" material as an i-layer is the key for the preparation of μc-Si : H p–i–n solar cells. Recently, our group has introduced a new way to obtain "midgap" μc-Si : H by the application of a gas purifier [8, 9]. Such a gas purifier allows for a reduction of the oxygen content in the feed gas and thus, one is able to deposit "truly intrinsic" μc-Si : H. The use of such "purified" i-layers in the p–i–n structure lead so far to the best μc-Si : H cell efficiency of 7.7%. As is predicted from the absorption behaviour, μc-Si : H cells show an enhanced infrared spectral response when compared to a-Si : H cells. Light-soaking experiments, even under intense illumination (10 suns), do not affect the stability of μc-Si : H solar cells [8, 9].

This new low-band-gap thin-film semiconductor based on silicon alone opens new ways to improve the efficiency of thin-film solar cells, especially in combination with amorphous silicon, leading to the so-called "micromorph" tandem cells introduced by our group [9, 10]. μc-Si : H has furthermore a basic potential for producing low-cost cells, since the deposition technology is similar to that for a-Si : H.

In the following we will present new aspects of our μc-Si : H material as deposited by VHF-GD: these aspects concern its structure as well as first improvements in the deposition rate; we will also report on the stabilised efficiencies obtained for our recent micromorph tandems.

2. New results

2.1. Transmission electron microscopy (TEM) on μc-Si : H p–i–n cells

Previously reported structural investigations on our microcrystalline silicon material by X-ray diffraction (XRD) showed a preferential growth in the (2 2 0) direction. The average grain size was hereby determined by Scherrer's equation to be around 16–17 nm [9]. Scanning electron microscopy (SEM) of a cross-section of a μc-Si : H film can observe a columnar structure which supports the XRD data [9]. However, no direct proof of the crystallinity of this structure could so far be found. In order to get more details on the crystallinity, Transmission Electron Microscopy (TEM) was carried out. Entirely μc-Si : H solar cell samples were prepared for TEM analysis in such a way as to display the structure of the grains in the direction of the current transport of the device. Fig. 1 shows the cross-section of the interface between a μc-Si : H p–i–n solar cell and the SnO_2 window contact deposited on the substrate (black part on the right).

In the brighter left part one can clearly observe the crystalline structure of the grains. The white line marks a grain that shows a pronounced columnar shape. In contrast with the values obtained by XRD for the grain size, the TEM micrograph in Fig. 1 proves that we do have in VHF-GD μc-Si : H much larger grains (> 200 nm), especially in the direction of the electronic transport of a solar cell device. The existence of such columnar crystallites supports our earlier suggestion that the current transport probably takes part preferentially within hydrogen-passivated crystallites

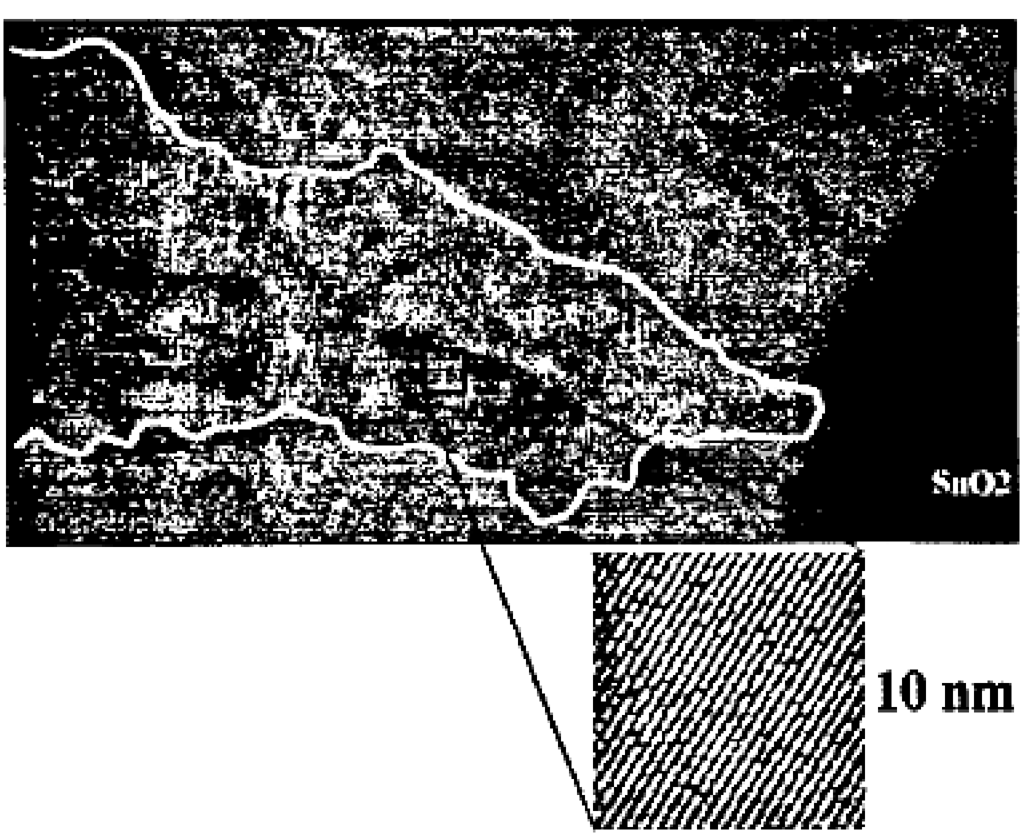

Fig. 1. TEM micrograph of the cross-section of the SnO_2/μc-Si : H p–i–n cell interface. The darker part represents the SnO_2, while the brighter part shows the μc-Si : H cell. To guide the eye the shape of a columnar crystallite is marked.

[9] ranging through the whole cell thickness. However, further detailed investigation are yet to be done to obtain more information on the crystallite dimensions and especially also on the nature of the grain boundaries.

2.2. Grain-boundary trapping model applied to μc-Si : H

In order to characterise the equilibrium transport and the effect of doping in polysilicon, the so-called grain-boundary trapping (GBT) model has been developed by Seto [11] and other workers in the 1970s. This model has also been applied to the interpretation of dark conductivity and Hall-mobility measurements in early work [12] on doped layers of hydrogenated μc-Si : H, deposited by the 13.56 MHz GD process. The basic idea of the GBT model is that the grain boundaries in polysilicon constitute "defects" or "traps" that capture the excess free carriers introduced by doping. Thereby, a depletion zone is built up in the grains. The potential barrier (VB) thus created can be evaluated by the Poisson equation. For a given grain-boundary trap (surface) density Q_t, there exists a corresponding critical doping density $N_{crit} = Q_t/L$ such that doping can supply sufficient carriers to saturate all grain-boundary traps (here L is the width of the grain). For $N > N_{crit}$, only a part of the crystallite will be depleted and the barrier height V_B drops [11].

The GBT-model [11] predicts the following cases which can be observed as function of the doping concentration N:

1. For $N < N_{crit}$, the barrier height VB increases and the dark conductivity of the grains increases as well. In total, one observes a *moderate increase of the dark conductivity*.
2. For $N > N_{crit}$, the barrier height VB decreases and the dark conductivity of the grains goes on to increase. In total, the *dark conductivity shoots up*.

Note, that in the basic work of the GBT-model (e.g. Ref. [11]) the calculation of electrical transport over the grain boundary was based on thermionic emission, whereas in later papers other concepts were also introduced. Experimental data on doping series of polysilicon generally confirm this model. As a function of doping, σ_{dark} at first hardly increases, then, after a certain critical level, it suddenly shoots up. Corresponding to the behaviour of σ_{dark}, the Hall mobility of polysilicon decreases to a minimum at a certain doping level $N = N_{crit}$ and thereafter increases for $N > N_{crit}$ again, to reach similar high values of mobility as for single-crystalline silicon. For polysilicon layers deposited by thermal CVD at 650°C with grain sizes around 200 Å the value of N_{crit} is reported to be around $2 \times 10^{18}/\mathrm{cm}^3$ (see Ref. [11]). Note that layers deposited at such high temperatures have almost certainly no hydrogen passivation of their grain boundaries.

If we now go over to hydrogenated μc-Si : H deposited by plasma-CVD at low temperatures, we may basically adopt the same model. However, we should expect that due to hydrogenation of our μc-Si : H layers (especially in the case of μc-Si : H deposited by VHF-GD) a reduced (internal) surface density of unpassivated defects at the grain boundaries should be present; we may assume the average defect density to be reduced by a factor of about 1000 with respect to unhydrogenated polysilicon produced by thermal CVD; this means that, for similar grain sizes as reported above, the value of N_{crit} will also be reduced by a factor 1000 to around $10^{15}/cm^3$; we have thereby taken the factor 1000 by rough extrapolation from results on the defect densities of a-Si : H when compared to unhydrogenated a-Si. (Note, that in μc-Si : H layers of "reduced" quality; as often produced, e.g., at 13.56 MHz, the total unpassivated dangling-bond density may be considerably higher than in our VHF-GD layers, because of a higher fraction of the amorphous matrix.)

Fig. 2 shows the result of low-level boron doping on μc-Si : H layers produced by VHF-GD [13]. The layers were deposited without a gas purifier, and therefore contain about $2 \times 10^{19}/cm^3$ of oxygen: this fact accounts for the n-type character of the as-grown layers. This means there is a significant offset of the x-abscissa due to the oxygen contamination; this offset requires a compensation by about $2.5 \times 10^{16}/cm^3$ of boron in order to obtain midgap layers. We note from Fig. 2 that N_{crit} is approximately around $10^{16}/cm^3$ for our GD μc-Si : H and, thus, two orders of magnitude lower than the value that one observes for polysilicon deposited by thermal CVD. The rough prediction of $N_{crit} \approx 10^{15}/cm^3$ suggested above seems to be about a factor 10 too low; however, we do have to take into account the large amount of the n-type impurities present in the case of Fig. 2. These certainly affect the shift of the compensation region to higher boron doping concentrations and thus reduce the possibility for doing proper predictions. Further work, using our purifier technique combined with a full microdoping series is now required to confirm the above considerations and to obtain more precise data on the factor of grain-boundary defect density due to hydrogen passivation.

Because of experimental difficulties, our midgap layers could so far not be evaluated with respect to Hall mobility. However, earlier work done with our n-type μc-Si : H

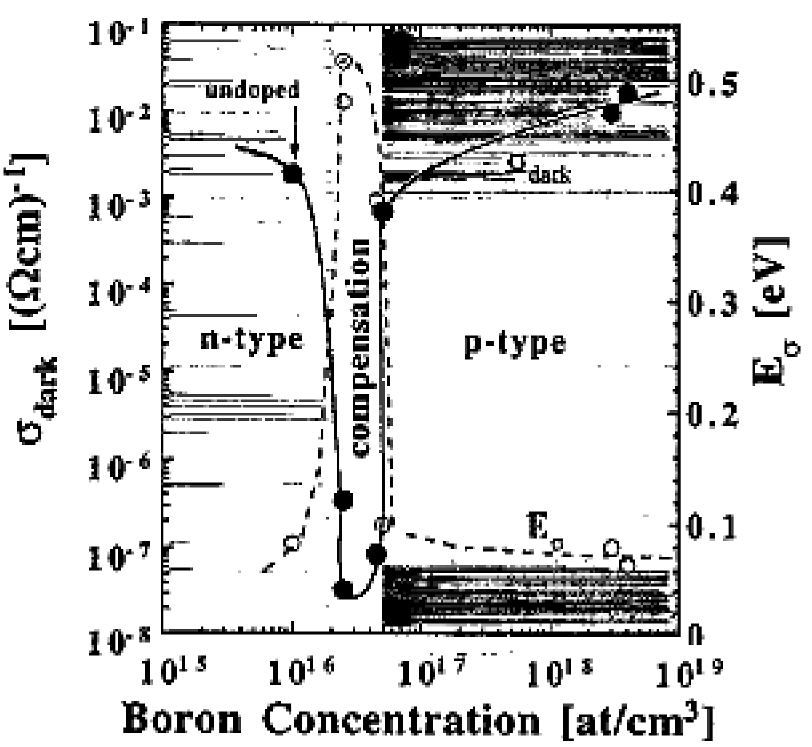

Fig. 2. Dark conductivity (σ_{dark}) and corresponding activation energy (E_σ) of μc-Si : H layers deposited by VHF-GD in function of the microdoping with boron [13]. The boron concentrations were measured by SIMS.

layers has rendered Hall mobilities μH < 10 cm^2/Vs [14]. This indicates, according to the model, lower potential barriers V_B than in polysilicon and, thus, once again lower trap or defect densities at the grain boundaries.

2.3. Improvement of deposition rate of μc-Si : H

The deposition rates of our intrinsic μc-Si : H absorber material incorporated so far in the p–i–n devices are around 1–2 Å/s and are therefore at present far too low for economical use in solar cells. Hot-wire deposition of μc-Si : H from silane show rates as high as 20 Å/s; thus, one can conclude that the limiting factor is not the depletion of the gas, but its dissociation. In order to decrease the deposition time for μc-Si : H we investigated the possibility of introducing argon into the plasma phase. Ar has a similar mass as the silane molecule and has the potential for thermalizing the high-energy Si ions in the sheath. Furthermore, it has the property of creating metastable states of high energy by plasma excitation. These metastable states contribute to enhance the dissociation of the silane molecule and, thus, may possibly increase the concentration of precursors that are responsible for the growth of μc-Si : H [15]. In earlier work [16], the deposition rate for μc-Si : H could be correlated with the H_α-intensity (656 nm) of the plasma phase. In order to characterise our Ar dilution experiments we have also performed optical emission spectroscopy (OES) of the H_α-line. Fig. 3 shows the deposition rate and the intensity of the H_α-line as a function of the Ar dilution. As suggested by our considerations given above, one can clearly observe an increase of the deposition rate and of the corresponding H_α-intensity when adding Ar into the gas phase. By using Ar dilution, it is possible to

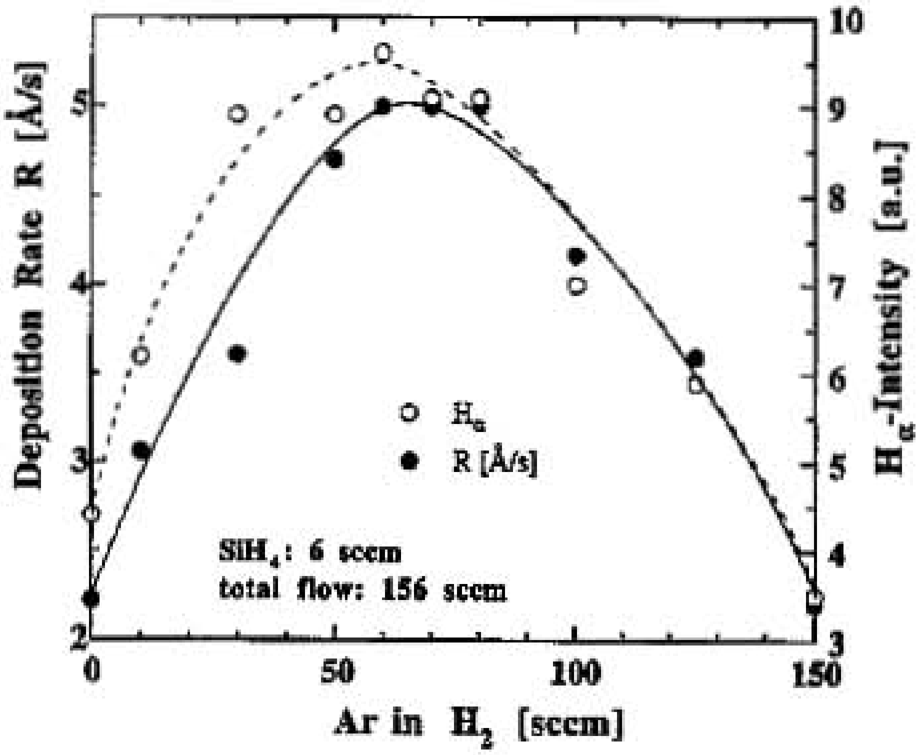

Fig. 3. Deposition rate of μc-Si : H and corresponding optical emission intensity of the H_α-line at 656 nm in function of the amount of argon dilution for deposition by VHF-GD at 220°C [15]. All films were deposited at 70 MHz excitation frequency and were checked for crystallinity.

more than double the deposition rate up to close to 5 Å/s. In a further experiment we then varied the silane concentration at the parameters given by the maximum of the deposition rate in Fig. 3. Thereby we achieved deposition rates of up 9.4 Å/s. All films were identified to be microcrystalline, more details are described in Ref. [15]. In very preliminary experiment we incorporated such a high-rate i-layer deposited at 8.7 Å/s into a n–i–p device and obtained an efficiency of 3% [15, 17, 18].

These Ar dilution experiments have shown that it is in principle possible to enhance the deposition rate for μc-Si : H using the GD technique. As far as we can see today, there seems to be no basic physical bottleneck which hinders a fast construction of the crystalline network of the silicon grains.

2.4. Concept of "micromorph" tandem cells

As is well-known, tandem cells that consist of semiconductors with different optical gap energies can make better use of the solar spectrum. Thus, tandem cells principally bear the potential for higher efficiencies than each single junction cell alone. With the development of intrinsic μc-Si : H as thin-film silicon, a new low-bandgap base material is now at hand. The combination of a-Si : H as high-bandgap material ($E_g \approx 1.7$ eV) and μc-Si : H as a low-bandgap material ($E_g \approx 1$ eV) leads to a "real" tandem cell structure. In earlier work we have designated this structure as the "micromorph" cell [9, 10]. Micromorph tandem cells make a better use of the sun's spectrum in contrast to conventional double-stacked a-Si : H/a-Si : H tandems.

Light-soaking experiments on micromorph tandem cells were performed under spectral conditions close to AM1.5 at 50°C over 1000 h. Fig. 4 shows the *I–V* characteristics of two micromorph cells in the stabilised state: Tandem A contains a hydrogen diluted [19], high-voltage amorphous top cell (0.21 μm) and cell

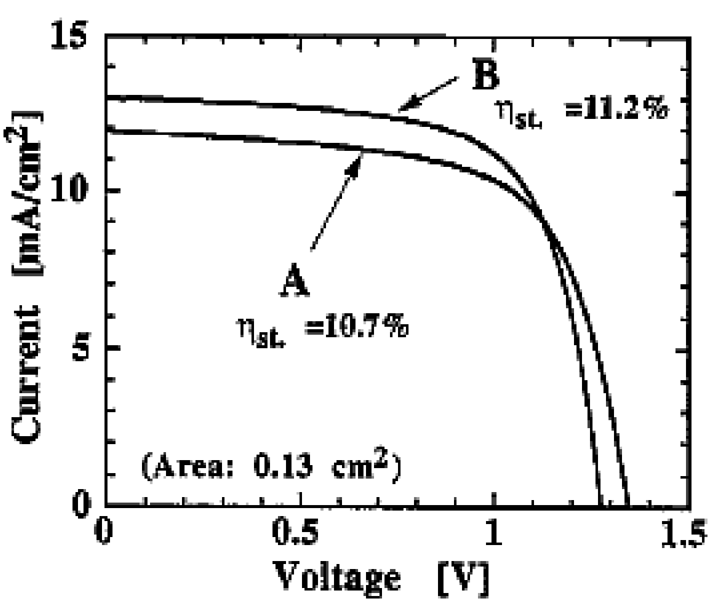

Fig. 4. *I–V* characteristics of two different micromorph tandem cells. Cell A contains a hydrogen diluted, low-temperature (180°C) amorphous-silicon top cell, while for tandem B an undiluted a-Si : H top cell (220°C) was incorporated. The efficiency of cell A has been confirmed by ISE Freiburg [20].

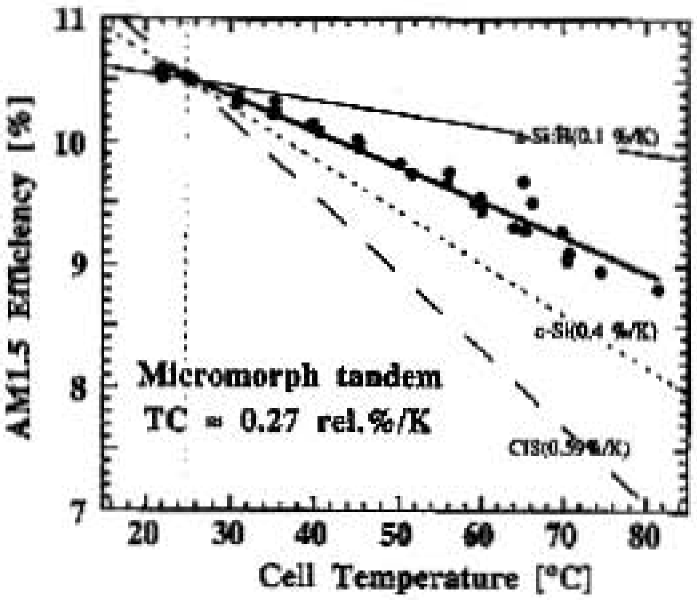

Fig. 5. Temperature dependence of a stabilised micromorph tandem cell efficiency. The relative temperature coefficient (TC) for our tandem is 0.27%/K; for comparison typical temperature behaviour of a-Si : H, c-Si and CIS cells is given [21].

B (0.35 μm) an undiluted standard a-Si : H top cell. For cell B, a new generation of top cells, the junction between both cells was further optimised to lead to better stabilised fill factors. The stabilised cell A has an efficiency of 10.7% as was recently confirmed by ISE Freiburg [20]; cell B has a higher stabilised efficiency of 11.2% (not yet confirmed). Further detailed degradation experiments on different amorphous top-cell thicknesses have to be performed in order to obtain an optimum for the stabilised micromorph tandem cell efficiency. The stabilised efficiencies in Fig. 4 show, however, that micromorph tandem cells indeed bear the potential for a high-efficiency thin-film solar cell based on silicon alone (i.e. not containing germanium, as in a-Si : Ge : H alloys!). In a future paper of our group, we will report on the use of the "inverse" (n–i–p) structure for micromorph tandems deposited on flat aluminium substrates [18].

An important factor for every type of solar cell is the temperature dependence of its efficiency. Entirely amorphous silicon cells have an advantageously low relative temperature coefficient (TC) of 0.1%/K, whereas crystalline silicon cells show 0.4%/K and CIS cells 0.59%/K [21]. In Fig. 5 the data are presented for micromorph cells: we obtain a TC of about 0.27%/K for a 10.5% stabilised tandem, which is definitively lower than those that are observed for c-Si or CIS.

3. Summary

Intrinsic hydrogenated microcrystalline silicon (μc-Si : H) deposited by the VHF-GD process represents a new form of thin-film crystalline silicon that can be deposited at low temperatures. Looking at the structural properties of μc-Si : H with its many grain boundaries one would not expect good PV properties, according to the past general experience with polycrystalline silicon. By applying the grain-boundary trapping model to the VHF-GD μc-Si : H an average defect density in the range of $1 \times 10^{16}/cm^3$ is estimated, this is some two orders of magnitude lower than that observed in polysilicon deposited by thermal CVD. We assume, therefore, that with the VHF-GD process a very efficient grain-boundary passivation by hydrogen takes place during the growth of the columnar microcrystalline material at low temperatures around 200°C. Our first TEM investigations of entirely microcrystalline solar cells show the existence of columnar grains (> 200 nm) with columns having the same orientation as the electronic transport path of the device. We therefore suggest that the carrier transport takes part preferentially within the well-passivated grains that have a tendency to range throughout the whole cell.

For our so far best stabilised micromorph tandem cell an efficiency of 11.2% could be achieved; an efficiency of a prior deposited micromorph cell of 10.7% was confirmed by ISE Freiburg [20]. Furthermore, a relative temperature coefficient of 0.27%/K could be found for the stabilised micromorph tandem cells. The micromorph concept has, thus, not only the basic potential for obtaining thin-film silicon solar cells with a relatively high efficiency, but also leads to a reasonably good temperature performance, the latter being a very important point for the efficiency of the cells under real working conditions.

Using Ar/H_2 dilution and the VHF-GD technique we have shown that microcrystalline silicon could be basically deposited at rates as high as 9 Å/s; this possibility improves the cost reduction potential for high-efficiency thin-film silicon micromorph cells.

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References

[1] J. Meier, R. Flückiger, H. Keppner, A. Shah, Appl. Phys. Lett. 65 (1994) 860.
[2] H. Curtins, N. Wyrsch, A. Shah, Electron. Lett. 23 (1987) 228.
[3] F. Finger, P. Hapke, M. Luysberg, R. Carius, H. Wagner, Appl. Phys. Lett. 65 (1994) 2588.
[4] R. Flückiger, J. Meier, G. Crovini, F. Demichelis, F. Giorgis, C.F. Pirri, E. Tresso, J. Pohl, V. Rigato, S. Zandolin, F. Caccavale, Mater. Res. Soc. Symp. Proc. 358 (1995) 751.
[5] C. Wang, G. Lucowsky, 21st IEEE (1990), p. 1614.
[6] M.J. Williams, C. Wang, G. Lucovsky, J. Non-Cryst. Solids 137, 138 (1991) 737.
[7] N. Beck, J. Meier, J. Fric, Z. Remes, A. Poruba, R. Flückiger, J. Pohl, A. Shah, M. Vanecek, J. Non-Cryst. Solids 198–200 (1996) 903.
[8] P. Torres, J. Meier, R. Flückiger, U. Kroll, J.A. Anna Selvan, H. Keppner, A. Shah, S.D. Littlewood, I.E. Kelly, P. Giannoulès, Appl. Phys. Lett. 69 (1996) 1373.
[9] J. Meier, P. Torres, R. Platz, S. Dubail, U. Kroll, J.A. Anna Selvan, N. Pellaton Vaucher, Ch. Hof, D. Fischer, H. Keppner, A. Shah., K.-D. Ufert, P. Giannoulès, J. Koehler, Mater. Res. Soc. Symp. Proc. 420 (1996) p. 3.
[10] J. Meier, S. Dubail, R. Flückiger, D. Fischer, H. Keppner, A. Shah, Proc. 1st WCPEC, 1994, p. 409.
[11] J.Y.W. Seto, J. Appl. Phys. 46 (1975) 5247.
[12] G. Willeke, PhD Thesis, University of Dundee, 1983.

[13] R. Flückiger, J. Meier, M. Goetz, A. Shah, J. Appl. Phys. 77 (1995) 712.
[14] J.M. Dubois, G. Willeke, K. Prasad, O. Blenk, A. Shah, E. Bucher, 11th EC PVSEC (1992) p. 718.
[15] H. Keppner, P. Torres, J. Meier, R. Platz, D. Fischer, U. Kroll, S. Dubail, J.A. Anna Selvan, N. Pellaton Vaucher, Y. Ziegler, R. Tscharner, Ch. Hof, N. Beck, M. Goetz, P. Pernet, M. Goerlitzer, N. Wyrsch, J. Veuille, J. Cuperus, A. Shah and J. Pohl, Mater. Res. Soc. Symp. Proc. 452 (1996) 865.
[16] A. Matsuda, J. Non-Cryst. Solids 59, 60 (1983) 767.
[17] P. Torres, J. Meier, M. Goetz, N. Beck, U. Kroll, H. Keppner, A. Shah, Mat. Res. Soc. Symp. Proc. 452 (1996) 883.
[18] M. Goetz, P. Torres, P. Pernet, J. Meier, D. Fischer, H. Keppner, A. Shah, Mater. Res. Soc. Symp. Proc. 452 (1996) 877.
[19] R. Platz, D. Fischer, C. Hof, S. Dubail, U. Kroll, J. Meier, A. Shah, Mater. Res. Soc. Symp. Proc. 420 (1996) 51.
[20] The Fraunhofer ISE PV-Charts, ed. 8, November 1996.
[21] K. Bücher, Proc. 13th EPVSEC, Nice, 1995, p. 2097.