

Microcrystalline silicon and the impact on micromorph tandem solar cells

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Abstract

Intrinsic microcrystalline silicon opens up new ways for silicon thin-film multi-junction solar cells, the most promising being the “micromorph” tandem concept. The microstructure of entirely microcrystalline p-i-n solar cells is investigated by transmission electron microscopy. By applying low pressure chemical vapor deposition ZnO as front TCO in p-i-n configured micromorph tandems, a remarkable reduction of the microcrystalline bottom cell thickness is achieved. Micromorph tandem cells with high open circuit voltages of 1.413 V could be accomplished. A stabilized efficiency of around 11% is estimated for micromorph tandems consisting of 2 μm thick bottom cells. Applying the monolithic series connection, a micromorph module (23.3 cm²) of 9.1% stabilized efficiency could be obtained.

Keywords: Hydrogenated microcrystalline silicon; Thin-film silicon; VHF-GD; LP-CVD ZnO; Light-trapping

1. Introduction

In 1994, our group at Institute of Microtechnology (IMT) Neuchâtel succeeded in the preparation of a fully microcrystalline (μc-Si:H) silicon p-i-n single-junction solar cell with new striking advantages compared to amorphous silicon (a-Si:H) [1]: This new photovoltaic absorber material shows no light-induced degradation unlike a-Si:H, and has a lower band gap than a-Si:H, i.e. a higher current potential for solar cells. In the same year, IMT also presented the “micromorph” concept consisting of

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an amorphous silicon top cell and a microcrystalline silicon bottom cell [2]. This original work was pioneered from the beginning in the “superstrate configuration”, e.g. p-i-n/p-i-n tandem cells were deposited on a glass substrate coated with transparent conductive oxide (TCO). With this new concept, stabilized cell efficiencies in the range of 11–12% have been achieved [3–7]. This type of thin-film solar cell, based on silicon alone, is today considered to be one of the most promising cell concepts with respect to cost reduction with simultaneous efficiency enhancement, availability of raw materials and technological feasibility of up-scaling to large-area modules. For the deposition of microcrystalline silicon, the same deposition equipment can, in principle, be used as in the case of amorphous silicon. The latter is at present the only thin-film solar cell that has established itself for MW-scale manufacturing. Recently, Kaneka Corp. changed their strategy by adopting IMT’s original concept of a superstrate micromorph tandem configuration deposited on glass (called “hybrid” solar cells by them) and visibly substantially reducing their deposition temperature. Thereby, they were able to fabricate large-area PV “micromorph” or “hybrid” modules of 0.4 m² size [8], that have since been introduced into the European market. These modules show initial efficiencies close to 10%, which are well above those that are currently obtained for commercially mass-produced amorphous silicon-based solar modules. Thus, one can say that micromorph tandems open up a new efficiency segment range for thin-film solar cells; indeed, they have the potential for overlapping with the region of wafer-based solar cells, especially when taking the better temperature coefficient of micromorph tandems into account and considering solar module performance under real outdoor working conditions [4,8].

As crystalline silicon is a material with an indirect band gap, the optical absorption coefficient for photon energies just over the band gap is relatively low. This means that in a micromorph tandem, the microcrystalline bottom cell will have to be thicker than the amorphous top cell in order to obtain current matching conditions. The challenge of making micromorph cells economically viable is given therefore not only by the question of obtaining higher efficiencies, but by the technological aspect of achieving high deposition rates and the further aspect of optimizing the light-trapping for the thin-film cell. A highly efficient light-trapping allows for the reduction of the thickness of the $\mu\text{-Si:H}$ bottom cell, and a high deposition rate allows for a high throughput. Both are important factors for the economical manufacturing of micromorph tandems. The key question is to what extent the $\mu\text{-Si:H}$ cell thickness can be reduced while still achieving optimal efficiency potential for micromorph modules.

2. Results and discussion

2.1. Microcrystalline silicon p-i-n cells

As microcrystalline silicon cells do not show any light-induced degradation effect, this material can be considered to be an interesting substitute for low-band gap

amorphous silicon–germanium alloys based on the use of germane (an expensive source gas). For this reason, broad research has been started by different groups on microcrystalline silicon solar cells.

In the early phase of pioneering microcrystalline silicon as PV material, single-junction devices showed rather low open circuit voltages (V_{oc}) of barely 400 mV [1]. In the meantime, remarkably high V_{oc} -values of between 520 and 550 mV could be obtained by different groups [5,9–12]. Fig. 1 gives the I - V characteristics for a corresponding $\mu\text{c-Si:H}$ p-i-n cell fabricated at IMT.

In our effort to further understand $\mu\text{c-Si:H}$ solar cells, our group has been analyzing the internal microstructure of $\mu\text{c-Si:H}$ single-junction cells by transmission electron microscopy (TEM) [13,14].

The cells that we have investigated here were deposited on low pressure chemical vapor deposition (LP-CVD) ZnO, and only the deposition conditions for the intrinsic $\mu\text{c-Si:H}$ absorber layer were slightly varied. The corresponding microstructure as observed by TEM is shown in Figs. 2 and 3. The i-layer consists of an agglomeration of small crystallites (dark spots in Fig. 2 and bright ones in Fig. 3) with a diameter of a few tens of nm, while their length depends on their location within the cell. Indeed, close to the ZnO interface they grow perpendicular to the ZnO facets; their length is of the order of several tens of nm. However, further away, they grow perpendicular to the average substrate plane and their length can reach several μm . Small crystallites aggregate into a larger microstructure with a diameter of several hundreds of nanometers—microstructure that runs across the whole thickness of the device. Therefore, we call these microstructures “columns”. Close to the substrate, the columns are loosely packed, resulting in visible cracks. Such cracks may consist of an amorphous tissue, or may just be voids. Towards the top of the cell, the microstructure becomes denser. The boundaries between the columns boundaries are systematically observed to originate at the bottom of the ZnO valleys.

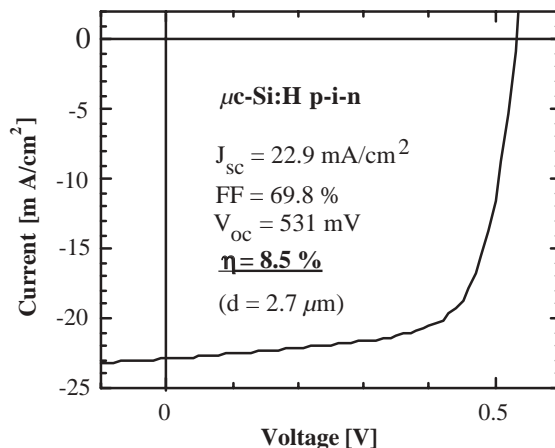


Fig. 1. I - V characteristics of a $\mu\text{c-Si:H}$ p-i-n solar cell under AM1.5 illumination.

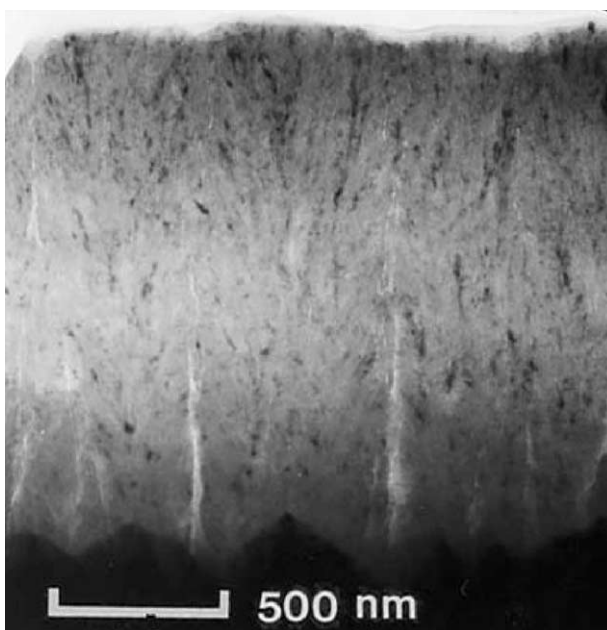


Fig. 2. Bright field cross section micrograph of cell A ($V_{oc} = 530$ mV, FF=68%) [13]. Voids and cracks appear brighter at the ZnO/p-i-n cell interface (bottom of the figure).

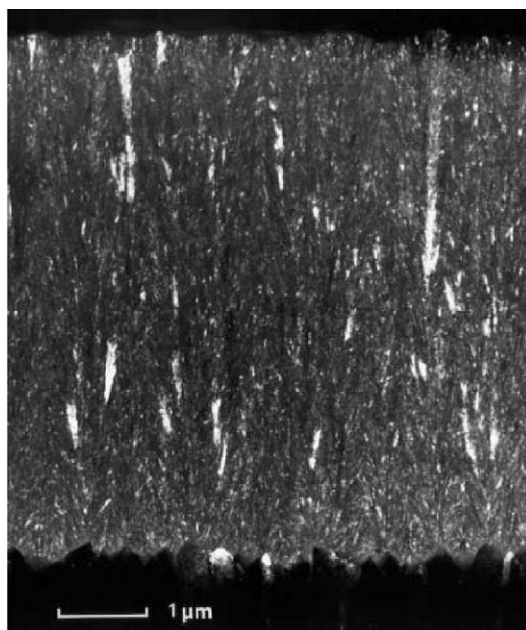


Fig. 3. TEM dark field micrograph of cell B ($V_{oc} = 486$ mV, FF=64%) [13]. The crystallites best satisfying diffraction conditions appear bright. Note how their length depends on the position within the layer.

As the cells have quite different thicknesses, the electrical characteristics can be compared only with respect to their V_{oc} - and FF-values. Surprisingly, the V_{oc} - and FF-values are higher for the cell in Fig. 2 (than for the cell in Fig. 3), i.e. higher for that cell that exhibits voids at the ZnO p-i interface, as these voids are considered to be responsible for shunting the solar cell. In order to get more insight into the relationship between device characteristics and microstructure, more systematic TEM investigations have to be done [15].

2.2. Light-trapping

In thin-film silicon solar cells, light-trapping is a key issue for two reasons: (1) both for realizing the full efficiency potential, and (2) for reducing the absorber thickness and, thus, the fabrication time. Light-trapping, therefore, contributes much to reduce the cost per W_{peak} . To improve light-trapping, IMT has developed its own in-house TCO, namely zinc oxide prepared by LP-CVD [16]. The typical surface morphology of such a ZnO layer is shown in Fig. 4 by means of a SEM micrograph and is compared with the best commercially available (but expensive) TCO, as can be found on SnO₂-coated glass substrates from Asahi (type U). In the present paper, recent results w.r.t. its use in micromorph tandem solar cells will be extended.

The LP-CVD ZnO developed by IMT has already proven its effectiveness in achieving a considerable improvement of the performance for single-junction amorphous silicon (a-Si:H) solar cells (see Fig. 5) as compared to SnO₂ (type U) [17]. Our amorphous silicon p-i-n solar cells on LP-CVD ZnO TCO have independently

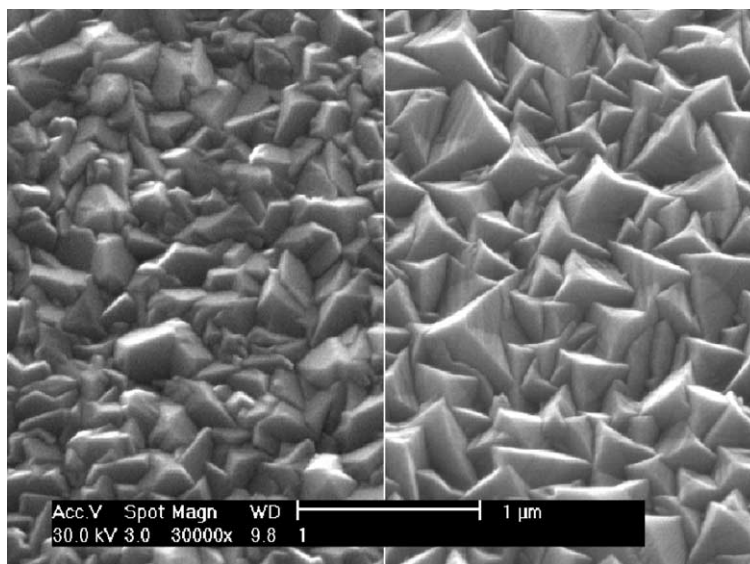


Fig. 4. SEM micrographs of a SnO₂ Asahi type U substrate (left) and of a typical as-grown LP-CVD ZnO layer (right) used for p-i-n configured solar cells.

University of Neuchatel (Switzerland)
a-Si Cell

Device ID: C200700 IIC2 Device Temperature: $25.0 \pm 1 \text{ }^\circ\text{C}$
 Aug 29, 2000 2:12 PM Device Area: 0.9965 cm^2
 Reporting Spectrum: Global AM1.5 Irradiance: 1000.0 W/m^2

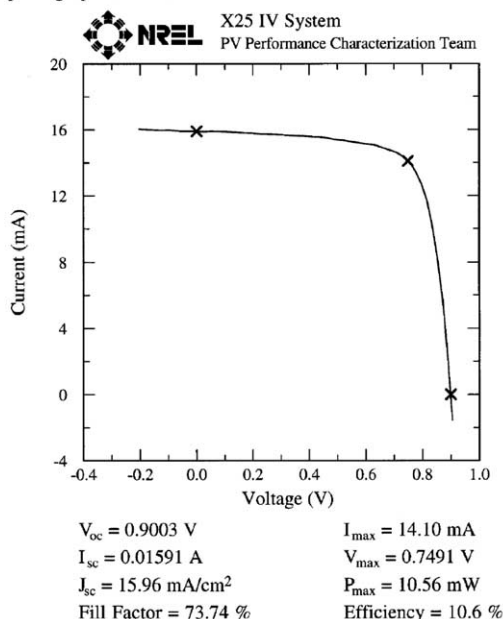


Fig. 5. Independently confirmed initial cell efficiency of an amorphous silicon p-i-n solar cell deposited at IMT on LP-CVD ZnO. The i-layer thickness has a thickness of only $0.25 \mu\text{m}$.

been confirmed by NREL with an initial efficiency of 10.6% (1 cm^2) and a high open circuit voltage of 900 mV. Notably, the absorber of this cell is only $0.25 \mu\text{m}$ thick which leads to a stable efficiency potential of 9% for IMT's single-junction a-Si:H p-i-n device technology [17].

In order to compare the effect of light confinement at the corresponding intended wavelength the two different front TCOs (IMT's LP-CVD ZnO and Asahi's U-type SnO_2) were tested within the micromorph tandem cell configuration. First, the amorphous top cells were deposited on the TCO-coated glass; here the thickness of the p-type window layer was adjusted, so as to optically suit the corresponding TCO but the intrinsic absorber layer was exactly the same (same deposition conditions, same thickness). Thereafter, the $\mu\text{c-Si:H}$ bottom cell was deposited in a simultaneous deposition cycle for both TCO substrates. The two TCOs exhibit quite different behavior with respect to their optical and electrooptical properties. In Fig. 6 we show the typical spectral transmittance and reflection characteristics of the two TCO layers alone, as well as of the glass/TCO/tandem cell system. Due to its larger energy band gap, SnO_2 possesses a higher transmission in the short wavelength range,

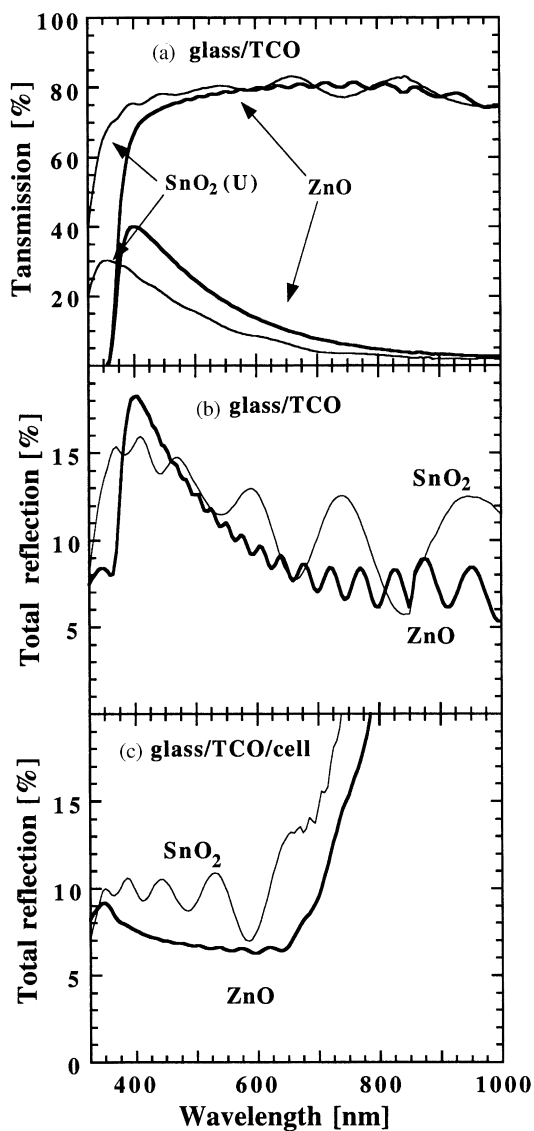


Fig. 6. (a) Total and diffuse spectral transmittance of glass/SnO₂ and glass/LP-CVD ZnO; (b) total reflection of SnO₂- and LP-CVD ZnO-covered glass substrates; (c) total reflection of micromorph p-i-n/p-i-n tandem cells deposited on SnO₂ and ZnO; the SnO₂-covered glass substrates are U-type substrates from Asahi Glass Corp.

whereas in the region above 550 nm both TCOs behave similarly (Fig. 6a). Regarding the diffused part of the optical transmittance, one observes, however, a remarkable enhancement for ZnO in the important absorption region of 500–1000 nm wavelength. In addition, the measurements in Fig. 6c clearly reveal

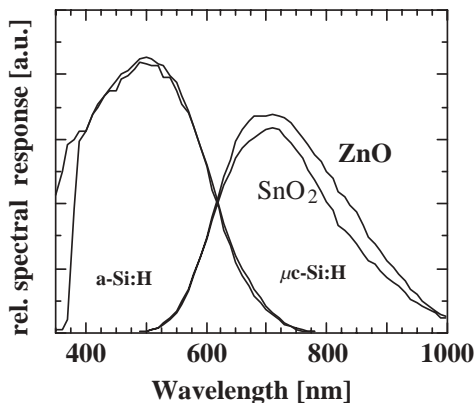


Fig. 7. Relative spectral response of a micromorph tandem cell on SnO_2 - (Ashai U type) and LP-CVD ZnO-coated glass substrate. Note, the amorphous and microcrystalline absorber have the same thicknesses and the cells the identical back reflector.

that in case of the cells on ZnO a reduced reflection is present compared to SnO_2 coated glass substrates. This may be explained by the greater roughness of the ZnO, and further, by a better matched refraction index between the glass and the silicon absorber. The difference in the reflection characteristics of the two TCOs (Fig. 6c) is supported by the naked eye in a simple manner: in the case of LP-CVD ZnO, the micromorph tandem cell appears as black, whereas in the case of SnO_2 the micromorph tandem cell appears to have a brighter color.

Relative spectral response measurements on the two micromorph tandem cells (Fig. 7) confirm that light-trapping is distinctly better in case of LP-CVD ZnO. While both top cells behave quite similarly, the enhanced scattering capability of the ZnO substrate has a remarkable effect in the longer wavelength range on the current generation as given here by the bottom cell (Note: this behavior has been already observed in case of single-junction a-Si:H p-i-n cells for wavelength above ~ 500 nm [17]). Indeed, if one uses SnO_2 -clad glass substrates (Asahi type U) for micromorph tandem cells, the bottom cell thickness must be approximately $1\ \mu\text{m}$ (or more) thicker, in order to generate the same current density as is generated by its counterpart deposited on LP-CVD ZnO.

2.3. Recent micromorph tandem cells

The objective here was to combine both our high quality amorphous p-i-n solar cells, as exemplified by the results shown in Fig. 5, with the high V_{oc} , high efficient microcrystalline p-i-n cells, as shown in Fig. 1, and to prepare thus, high- V_{oc} micromorph tandem devices. Hereupon, IMT has to implement all its technological knowledge starting from the glass cleaning to the cell fabrication. The employment of LP-CVD ZnO allows for the reduction of the microcrystalline bottom cell

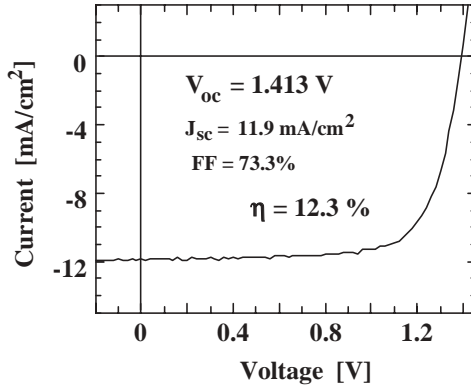


Fig. 8. Recent micromorph p-i-n/p-i-n tandem cell obtained by using LP-CVD ZnO and applying a $\mu\text{c-Si:H}$ bottom cell of $2\ \mu\text{m}$ thickness.

thickness. By combining both individual cell preparation techniques with the LP-CVD front TCO we have now succeeded in improving the open circuit voltage of our micromorph tandem cell to over 1.4 V (a-Si:H top 890–900 mV and $\mu\text{c-Si:H}$ bottom 530–540 mV). This has been realized by improving and controlling each interface in the whole cell structure. Thanks to the high haze factor (see Fig. 6a) of our LP-CVD ZnO, we were able to reduce the bottom cell thickness to $2\ \mu\text{m}$. A current balance between the a-Si:H top and the $\mu\text{c-Si:H}$ bottom cell, each $11.9\ \text{mA/cm}^2$, could be attained. Fig. 8 shows that a high fill factor (FF) of over 73% and a high V_{oc} -value of 1.413 V resulted, thereby, giving an initial micromorph cell efficiency of 12.3%. Experience has shown us that such micromorph tandems should lead to a stabilized efficiency of around 11% (10% relative degradation).

As already mentioned, maintaining high efficiency and keeping the $\mu\text{c-Si:H}$ cell as thin as possible is a primary factor for the economic success of the micromorph tandem solar cell as it shortens the deposition time and therefore minimizes the fabrication cost per W_{peak} .

2.4. Micromorph modules

In this part, the feasibility of an integrated series connection technique [18] has to be proven in order to show the potential of a production technology for entire large-area ($1\ \text{m}^2$) modules. Hereby, we applied the laser scribing technique to the thicker micromorph tandem cells and our in-house ZnO deposited by LP-CVD [19,20]. Using our small size VHF-GD reactor ($8 \times 8\ \text{cm}^2$ electrode area) small modules of an active area of $23.3\ \text{cm}^2$, and with a configuration of 6 segments, have been fabricated. The I - V characteristics of our best module in the stabilized state is given in Fig. 9. So far, an aperture efficiency of 9.1% has been achieved [20].

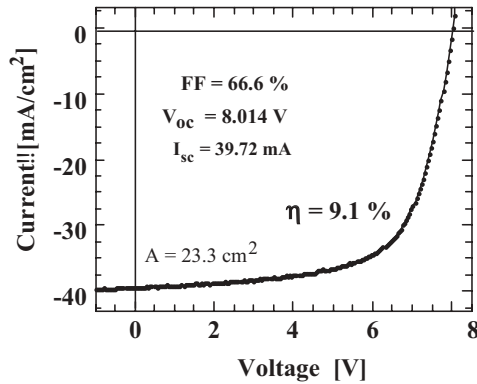


Fig. 9. I - V characteristics of a micromorph module with 9.1% stabilized efficiency [19].

3. Conclusions

Microcrystalline silicon is not just an individual new absorber material for solar cells, it contains a large morphological variety. As can be seen from our first, preliminary TEM investigations on entire $\mu\text{-Si:H}$ solar cells, the microstructure leading to cells with high V_{oc} and FF is fairly complex and its role is not at present understood.

To exploit the low-cost potential of future high-efficient thin-film solar cells, IMT has taken up its own in-house TCO activities. The choice of LP-CVD ZnO as TCO by IMT has been made for its significant economic potential based on the simplicity of the corresponding deposition process and on the abundance of required raw materials. For the micromorph tandem cell the introduction of LP-CVD ZnO has lead to optimized efficient light-trapping, permitting a considerable reduction of the microcrystalline bottom cell as compared to the best commercially available TCO (Ashai U-type SnO_2). Keeping the bottom cell thickness at $2\ \mu\text{m}$, our micromorph tandem cells on LP-CVD ZnO are estimated to have reached a stabilized efficiency of around 11%. Furthermore, high open circuit voltage values for the micromorph tandem cells of over 1.4 V have been realized by combining both high-quality a-Si:H top and $\mu\text{-Si:H}$ bottom cells as well as improved interfaces.

Confining the $\mu\text{-Si:H}$ cell thickness to $2\ \mu\text{m}$ or less, while simultaneously sustaining a high efficiency, is essential for the production of a commercially superior PV module, as the short deposition time results in a greater profit margin. Low-cost micromorph manufacturing at a stabilized module efficiency of above 10% is a realistic objective, particularly when taking our LP-CVD ZnO into account. One can argue that the micromorph tandem cell concept is rapidly becoming the most favorable concept for the next generation of thin-film solar cells, especially in view of its potential for high efficiency and low cost. The micromorph cell fulfills the requirements for a high process reliability, a reduced process energy and a flow of materials which all are highly abundant.

Acknowledgements

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References

- [1] J. Meier, R. Flückiger, H. Keppner, A. Shah, *Appl. Phys. Lett.* 65 (1994) 860.
- [2] J. Meier, S. Dubail, R. Flückiger, D. Fischer, H. Keppner, A. Shah, *Proceedings of the First WCPEC*, 1994, p. 409.
- [3] J. Meier, S. Dubail, J. Cuperus, U. Kroll, R. Platz, P. Torres, J.A. Anna Selvan, P. Pernet, N. Beck, Pellaton, N. Vaucher, Ch. Hof, D. Fischer, H. Keppner, A. Shah, *J. Non-Cryst. Solids* 227–230 (1998) 1250.
- [4] H. Keppner, J. Meier, P. Torres, D. Fischer, A. Shah, *Appl. Phys. A* 69 (1999) 169–177.
- [5] K. Yamamoto, et al., *J. Non-Cryst. Solids* 266–269 (1–3) (2000) 1082–1087.
- [6] K. Saito, M. Sano, K. Matuda, T. Kondo, T. Nishimoto, K. Ogawa, I. Kajita, *Proceedings of the Second WCPEC*, 1998, p. 351.
- [7] K. Yamamoto, T. Suzuki, M. Yoshimi, A. Nakajima, *Proceedings of the 14th EU PVSEC*, 1997, p. 1018.
- [8] K. Yamamoto, M. Yoshimi, T. Suzuki, T. Nakata, T. Sawada, A. Nakajima, K. Hayashi, *Proceedings of the 28th IEEE PVSC*, 2000, p. 1428.
- [9] K. Yamamoto, M. Yoshimi, T. Suzuki, Y. Tawada, Y. Okamoto, A. Nakajima, *Proceedings of the Second WCPEC*, 1998, p. 1284.
- [10] O. Vetterl, et al. *Proc. Mater. Res. Soc. Symp.* 609 (2000) A15.2.1; www.mrs.org
- [11] Y. Nasuno, M. Kondo, A. Matsuda, *Proceedings of the 28th IEEE PVSC*, 2000, p. 142.
- [12] S.J. Jones, R. Crucet, M. Izu, *Proceedings of the 28th IEEE PVSC*, 2000, p. 134.
- [13] J. Dubail, et al. *Proc. Mater. Res. Soc. Symp.* 609 (2000) A13.6.1; www.mrs.org.
- [14] E. Vallat-Sauvain, U. Kroll, J. Meier, A. Shah, J. Pohl, *J. Appl. Phys.* 87 (2000) 3137.
- [15] J. Bailat, E. Vallat-Sauvain, L. Feitknecht, A. Shah, *J. Non-Cryst. Solids* 299–302 (2001) 1219.
- [16] S. Faÿ, S. Dubail, U. Kroll, J. Meier, Y. Ziegler, A. Shah, *Proceedings of the 16th EU PVSEC*, 2000, p. 361.
- [17] J. Meier, U. Kroll, S. Dubail, S. Golay, S. Faÿ, J. Dubail, A. Shah, *Proceedings of the 28th IEEE PVSC*, 2000, p. 746.
- [18] D. Carlson, et al. *Proceedings of the 25th IEEE PVSC*, 1996, p. 1023.
- [19] S. Golay, J. Meier, S. Dubail, U. Kroll, A. Shah, *Proceedings of the 16th EU EPVSEC*, 2000, p. 494.
- [20] S. Golay, J. Meier, S. Dubail, S. Faÿ, U. Kroll, A. Shah, *Proceedings of the 28th IEEE PVSC*, 2000, p. 1456.