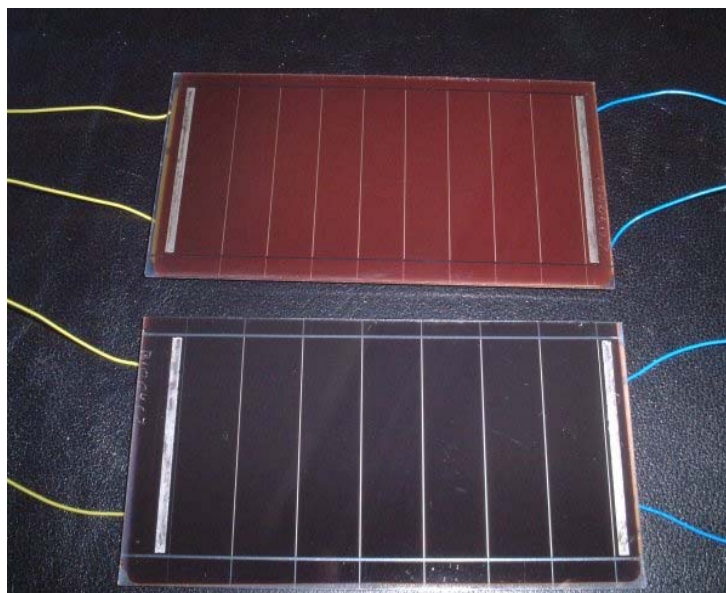Schlussbericht PV Forschung, DIS 36487 / 59014, Juni 2003

Technologische Weiterentwicklung der mikromorphen Solarzellen
basierend auf amorphem und mikrokristallinem Silizium

ausgearbeitet durch:
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Summary

The three-year project (2000-2002) described in this report was concerned with specific issues that have to be addressed in order to ensure Industrialization of the "micromorph" (microcrystalline/amorphous) thin-film silicon solar cell concept introduced in 1994 by IMT Neuchâtel:

1) Increase of microcrystalline silicon deposition rate, with corresponding fabrication of entire solar cells; here, novel compact VHF (Very High Frequency), electrodes were introduced in a part of our deposition systems, ensuring, thereby, higher deposition rates, as well as greater compatibility with the "plasmabox"-type electrodes used in the KAI-type industrial production systems of UNAXIS; furthermore, first results were obtained on high-rate deposition in the so-called HPD (high-pressure depletion) regime.

2) Improvement of the performances of nip-type single-junction microcrystalline silicon solar cells; a record (stable) efficiency value of 9.2 % could be obtained for such a small-size solar cell.

3) Investigation of the microstructure of microcrystalline silicon solar cells; establishment of a relationship between cell microstructure, as seen by TEM (transmission electron microscopy) and, also, by Raman spectroscopy, on one hand and the open-circuit voltage value of entire solar cells, on the other hand. This relationship is valid for both nip-type and pin-type solar cells. Furthermore, insight was gained into the complex growth mechanisms of microcrystalline layers and cells on various substrates.

4) Improvement of pin- and nip-type amorphous silicon solar cells.
   Here, pin-type single-junction amorphous silicon solar cells with a stabilised efficiency of over 9% could be obtained, thanks to the excellent light trapping obtained with our in-house LP-CVD (low-pressure chemical vapour deposition) zinc oxide.
   In the case of nip-type solar cells, the accent has been on 2 separate issues:
   a) Improvement of stabilized efficiency AND of optical absorption thanks to the use of "moderately high temperatures" (300 to 350 degrees) for the plasma deposition of the intrinsic layer;
   b) Deposition of amorphous silicon layers at lower temperatures (190 degrees) on very low-cost substrates, like PET.
   These particular investigations on nip-solar cells are not yet completed.

5) Specific studies on transparent conductive oxides (TCOs), and on light trapping (solar cell current enhancement) obtained with various TCOs and, in general with various types of back reflectors and various substrate materials. Here, the main accent has been on the development of LP-CVD ZnO on transparent glass substrates, for pin-type solar cells, and on the preparation of a larger area (30cm x 30cm) deposition system for the same. A further accent was on the development of rough silver layers, useable as textured back reflectors, on opaque substrates, in the case of nip-type solar cells.

6) Basic considerations on the necessary spectral ranges for light trapping, both for amorphous silicon and for microcrystalline silicon solar cells of typical thickness were carried out. It was shown that the spectral ranges involved in the 2 cases are far from being the same.

7) Implementation of entire micromorph tandem solar cells, both in the pin- and in the nip-configuration, as well as realization of pin-type micromorph minimodules with monolithic series connections. Schemes to improve the efficiency, such as the use of an intermediate reflector between the top cell and the bottom cell were studied. The problem of current matching of micromorph tandem solar cells was addressed.

A considerable part (20 to 30%) of IMT's project resources was invested, during the project period 2000-2002, in improving the infrastructure base (equipment/set-ups) of the thin-film solar cell laboratory: in materials and cell characterization, in laser scribing and, specially, in plasma-assisted deposition. This was absolutely necessary because we at IMT Neuchâtel do not have the financial resources for purchasing expensive commercial equipment, as our main competitors in Japan and Germany do.

Finally, let us also mention that IMT Neuchâtel has now established a close collaboration with two Industrial firms:

a) UNAXIS A.G., Balzers (FL), and

b) VHF-Technologies, Le Locle.

The collaboration involves extensive license agreements, based on intellectual property (IP) obtained by IMT Neuchâtel within the whole series of its research projects financed by the Swiss Office of Energy.

These newly established Industrial collaborations should lead within the next few years to

a) availability of professional mass production equipment from a Swiss manufacturer for the production of very low-cost thin-film silicon modules on glass substrates,

b) low-cost flexible PV modules on plastic substrates based on amorphous silicon and produced in the Neuchâtel region (Le Locle, Yverdon).

A substantial part of IMT's efforts during the project period 2000-2002 was, therefore, devoted to building up these collaborations and to giving direct support to the firms involved. Investment from the Private (Industrial) sector) is, on the other hand, also very substantial; the following figures are being mentioned:

a) a sum of the order of 15 to 20 Million Swiss Francs is envisaged (including investments already consented/planned) for during the period 2003-2005,

b) a sum of approx 3 Million Swiss Francs has up to now already been invested, for the period 2000-2002 and corresponding additional amounts (of the same order of magnitude) are planned for the next few years, i.e. for the period 2003-2005.

Zusammenfassung

Das Dreijahresprojekt (2000-2002) war auf ganz spezifische Probleme im Hinblick auf eine Industrialisierung von "Mikromorph"-Solarzellen (Tandemsolarzellen aus mikrokristallinem und amorphem Silizium, 1994 vom IMT Neuchâtel eingeführt) ausgerichtet:

1) Die Erhöhung der Abscheiderate für intrinsische mikrokristalline Siliziumschichten und deren Einbau in ganze Solarzellen. Mit den neu eingeführten kompakten VHF-Elektroden in einem Teil unserer Abscheidesysteme wurden nicht nur die Abscheideraten erhöht, sondern auch eine bessere Kompatibilität mit den industriellen Produktionssystemen vom Typ KAI der Firma UNAXIS erreicht. Zudem wurden erste Resultate im sogenannten "High Pressure Depletion" (HPD) - Regime der Plasmaabscheidung erhalten, welches gestattet, noch höhere Abscheideraten zu erreichen.

2) Die Verbesserung der nip-Einfachzelle aus mikrokristallinem Silizium; hier konnte ein Rekordwert für den stabilisierten Wirkungsgrad von 9,2% erzielt werden.

3) Untersuchungen über die Mikrostruktur innerhalb von Solarzellen aus mikrokristallinem Silizium. Eine einfache Korrelation wurde gefunden zwischen der Mikrostruktur (wie aus TEM-Bildern ersichtlich) und der Kristallinität (wie mit Ramanspektroskopie gemessen) einerseits, und der Leerlaufspannung V_{oc} von ganzen Solarzellen anderseits, welche sowohl für pin- wie auch für nip-Solarzellen Gültigkeit hat. Ferner war es möglich, mehr Einsicht in die komplexen Wachstumsmechanismen des mikrokristallinen Siliziums auf verschieden-artigen Substratmaterialien zu bekommen.

4) Die Verbesserung der Einfachzellen aus amorphem Silizium, sowohl für die pin-, wie auch für die nip-Konfiguration. Hier konnten pin-Einfachzellen aus amorphem Silizium mit über 9% stabilsiertem Wirkungsgrad erhalten werden, dank den hervorragenden optischen Eigenschaften unserer hauseigenen Zinkoxydschichten, welche mit dem LP-CVD (low pressure chemical vapour deposition) -Verfahren hergestellt wurden. Diese Schichten gewährleisten eine starke Lichtstreuung und damit eine hohe effektive optische Absorption innerhalb der relativ dünnen Zelle.
Bei den nip-Zellen lag der Akzent auf 2 verschiedenen Aspekten:
   a) Gleichzeitige Verbesserung des stabilsierten Wirkungsgrads UND des optischen Absorptionskoeffizienten dank der Abscheidungvon der intrinsische Schicht bei « mässig » hohen Temperaturen (300 bis 350 °C);
   b) Abscheidung von amorphen Schichten bei tieferen Temperaturen (190 °C) auf billigen Substraten wie PET.
Die Untersuchungen bei den nip-Solarzellen sind noch nicht abgeschlossen.

5) Gezielte Studien über durschsichtige Kontaktschichten, sog. TCOs (Transparent conductive oxides), und über den Lichteinfang in der Solarzelle mit Hilfe von texturierten (rauhen) TCO-Schichten und metallischen Reflektorschichten. Der Hauptakzent lag auf der Entwicklung von transparenten Frontkontaktschichten aus Zinkoxyd (ZnO) auf Glas für pin-Solarzellen und auf der Konstruktion eines grossflächigen (30 x 30 cm) Depositionssystems für diese ZnO-Schichten, basierend auf dem LP-CVD-Verfahren. Eine zweite Entwicklung betraf die Abscheidung von rauhen Silberschichten auf undurchsichtigen Substraten (Metall, Kunststoff) als rückseitige Reflektoren für nip-Solarzellen.

6) Grundsätzliche Ueberlegungen zum Spektralbereich, wo der Lichteinfang wirksam sein muss um die optische Gesamtabsorption in der Solarzelle zu erhöhen, und zwar sowohl für amorphe wie auch für mikrokristalline Solarzellen. Die betroffenen Spektralbereiche sind in beiden Fällen stark verschieden.

7) Die Fabrikation von ganzen mikromorphen Tandemzellen, sowohl in der pin- wie auch in der nip-Konfiguration, sowie Realisierung von mikromorphen pin-Minimodulen mit monolithischer Serieverschaltung der Einzelzellen. Weiter wurden Konzepte studiert, um grunsätzlich den Wirkungsgrad zu erhöhen, z.B. die Verwendung eines Zwischenreflektors (aus ZnO) zwischen der oberen amorphenTeilzelle und der unteren mikrokristallinen Teilzelle. Das Problem der Stromanpssung zwischen oberer und unterer Teilzelle wurde angegangen.

Ein beträchtlicher Anteil unsererer Projektmittel und unserer Arbeitszeit (20 bis 30%) wurde während der Projektperiode 2000-2002 dazu verwendet, die apparative Infrastruktur unseres Laboratoriums zu konsolidieren und zu verbessern: Charakterisierung von Materialien und von ganzen Solarzellen, Laserverfahren zur Zellstrukturierung und zur Modulfabrikation und besonders unsere VHF-Plasmareaktoren für die Fabrikation von Dünnschicht-Solarzellen. Dies war deshalb nötig, weil das IMT Neuchâtel nicht über grosse Gerätekredite verfügt (wie sie andere Labors in Deutschland und Japan haben), um kommerzielle Apparaturen zu kaufen.

Abschliessend soll erwähnt werden, dass das IMT Neuchâtel in der Berichtsperiode 2000-2002 eine enge Zusammenarbeit mit zwei Firmen aufgebaut hat:

a) UNAXIS AG, Balzers (FL)
b) VHF Technologies S.A., Le Locle

Die Zusammenarbeit beinhaltet auch Lizenzabkommen über Patente und Know-How, welche das IMT Neuchâtel während den langjährigen BFE-Projekten erworben hat.

Diese neu etablierten Zusammenarbeiten mit den 2 erwähnten Industrien sollen dazu führen, innerhalb von wenigen Jahren verfügbarzu machen:

a) Produktionsmaschinen für eine kostengünstige Massenproduktion von Solarmodulen auf Glassubstraten; dabei würden die Maschinen in der Schweiz (Truebbach SG) hergestellt und an Modulfabrikanten in der ganzen Welt verkauft.
b) Billige flexible amorphe Solarmodule auf Plastiksusbtraten, die in der Region Neuenburg (Le Locle, Yverdon) hergestellt werden.

Ein beträchtlicher Teil der Anstrengungen des IMT war deshalb dem Aufbau dieser beiden Kollaborationen und der direkten technisch-wissenschaftlichen Unterstützung der beiden Firmen gewidmet.
Die Investitionen aus dem Privatsektor sind aber auch beträchtlich. Man redet von folgenden Grössenordnungen:

a) bei UNAXIS ist ein Betrag von 15 bis 20 Millionen Franken im Zeitraum 2003-2005 reserviert für den Aufbau einer Photovoltaikaktivität und für die Entwicklung der ersten verkaufbaren Produktionsmaschinen.
b) bei VHF ist seit 2000 ein Betrag von 3 Millionen Franken bereits investiert worden; ein vergleichbarer Betrag soll nun in der Periode 2003-2005 weiter investiert werden.

Résumé

Le projet de trois ans (2000-2002), décrit dans ce rapport, concernait des points spécifiques qui devaient être abordés pour assurer l'industrialisation des cellules solaires « micromorphes » (déposées en couches minces de silicium microcristallin et amorphe), dont le concept a été introduit en 1994 par l'IMT de Neuchâtel :

1) L'augmentation du taux de dépôt du silicium microcristallin ainsi que la fabrication des cellules entières correspondantes : Pour ceci, un nouveau type d'électrode VHF (Very High Frequency) compacte a été installé dans certains de nos systèmes de dépôt, permettant d'obtenir des taux de dépôt plus hauts ainsi qu'une meilleure compatibilité avec les électrodes type « plasmabox » utilisées dans le système KAI de production industriel de UNAXIS. De plus, des premiers résultats concernant de plus hauts taux de dépôt ont pu être obtenus dans le régime appelé de « déplétion haute pression » ou HPD (High-Pressure Depletion).

2) L'amélioration des performances des cellules solaires à jonction simple en silicium microcristallin ; une efficacité (stable) record de 9.2% a pu être obtenue pour de telles cellules solaires de petite taille.

3) L'étude de la microstructure des cellules solaires en silicium microcristallin; Une relation entre la microstructure des cellules, déjà observée par MEB (Microscopie Electronique à Balayage) et par spectrométrie Raman, et la valeur de la tension en circuit ouvert (V_{oc}) des cellules solaires entières a été établie. Cette relation est valable pour les deux types nip et pin de cellules solaires. De plus, un aperçu des mécanismes complexes de croissance des couches et des cellules microcristallines sur divers substrats a pu être obtenu.

4) L'amélioration des performances des cellules solaires nip et pin en silicium amorphe. Des cellules types pin, simples jonctions, en silicium amorphe, avec des efficacités stabilisées supérieures à 9%, ont pu être obtenues grâce à l'excellent piégeage de la lumière généré par notre Oxyde de zinc fabriqué et optimisé en interne par LP-CVD (Low-Pressure Chemical Vapour Deposition).
   Dans le cas des cellules solaires nip, l'accent a été porté sur deux points différents :
   a) L'amélioration de l'efficacité (état stable) ET de l'absorption optique grâce à l'utilisation de couches intrinsèques déposées à des températures modérément hautes (300 à 350 degrés) pour les techniques de dépôt assistées d'un plasma.
   b) Dépôt de couches de silicium amorphe à plus basse température (190 degrés) sur des substrats bon-marché comme le PET.
   Ces recherches sur les cellules nip ne sont actuellement pas terminées.

5) Les études spécifiques concernant, d'une part, les oxydes transparents conducteurs (TCOs), et d'autre part, le piégeage de la lumière (augmentation du courant des cellules solaires) obtenu avec différents TCOs, différents types de réflecteurs arrières et différents matériaux pour les substrats.
   L'accent a été mis, principalement, sur le développement du ZnO déposé par LP-CVD sur verre (substrat transparent) pour des cellules pin ainsi que sur la préparation d'un système de dépôt plus grande surface (30cm×30cm) pour la réalisation d'échantillons équivalents. Un accent supplémentaire a été porté sur le développement de couches d'argent texturées utilisables en tant que réflecteur arrière texturé sur substrat opaque pour des cellules solaires nip.

6) Les considérations élémentaires qui ont été conduites sur la gamme des longueurs d'onde qu'il est nécessaire de piéger dans les cellules en silicium amorphe et microcristallin d'épaisseur donnée. Il a été montré que la gamme de longueurs d'onde impliquée est de très loin différente selon le cas.

7) La réalisation de cellules solaires tandem « micromorphes » dans les deux configurations pin et nip ainsi que de mini modules micromorphes types pin avec des connections monolithiques en série. Des moyens pour améliorer l'efficacité, tels que l'utilisation d'un réflecteur intermédiaire entre les cellules avant et arrière, ont été étudiés. Le problème de l'adaptation du courant pour les cellules solaires tandem micromorphes a été abordé.

Une part considérable (20 à 30%) des ressources relatives aux projets de l'IMT a été investie pendant la période 2000-2002 afin d'améliorer l'infrastructure (équipements, installations) du laboratoire pour la caractérisation des matériaux et cellules, pour la structuration par laser et plus particulièrement pour les systèmes de dépôt assistés par plasma. Ceci était absolument nécessaire car, contrairement à nos principaux concurrents japonais ou allemands, nous n'avons pas, à l'IMT de Neuchâtel, les ressources financières nécessaires à l'achat d'équipements industriels coûteux.

Pour finir, il est important de mentionner que l'IMT de Neuchâtel a maintenant mis en place une collaboration étroite avec deux firmes industrielles:

a) UNAXIS A.G., Balzers (FL),

b) VHF-Technologies, Le Locle.

Ces collaborations impliquent de nombreux accords concernant les licences basées sur la propriété intellectuelle (PI) obtenue par l'IMT de Neuchâtel au cours de tous ses projets financés par l'Office Fédéral de l'Energie.

Ces collaborations nouvellement établies avec l'industrie devraient mener dans ces quelques prochaines années à :

a) La mise sur le marché, par un industriel suisse, d'équipement professionnel de production de masse pour la fabrication, sur du verre et à bas prix, de modules en couches minces de silicium.

b) La fabrication de modules photovoltaïques bon-marché en silicium amorphe sur substrats plastiques dans la région de Neuchâtel (Le Locle, Yverdon).

Une part importante des efforts de l'IMT pendant la période 2000-2002 a été consacrée à mettre en place ces collaborations ainsi qu'à assurer un support direct aux entreprises engagées. D'autre part, les investissements de la part du secteur privé (industriel) sont également considérables. Les chiffres suivants ont été mentionnés :

a) Un montant de l'ordre de 15 à 20 millions de Francs suisses est prévu par UNAXIS (prenant en compte les investissements déjà planifiés) pour la période 2003-2005,

b) Un montant d'approximativement 3 millions de Francs suisses a déjà été investi par VHF-Technologies pour la période 2000-2002 et des sommes supplémentaires du même ordre de grandeur sont prévues pour la période 2003-2005.

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1 Starting-point and goals

Thanks to the pioneering work of the IMT on microcrystalline silicon (μc-Si:H), the micromorph concept is internationally considered today (2003) as one of the most promising future thin-film solar cell concepts.

In 1999, a study had been completed for BFE/PSEL, (the so-called "Micromorph feasibility study"); this study treated the aspects of mass production (industrialization) and the upscaling of micromorph cells to large-area modules. The main result of this study is that modules based on micromorph tandem cells are very attractive from the manufacturing point of view and should be able to secure a good market position. Therefore, the 3-year project described here, and extending over the period 2000-2002, was oriented towards improving and further developing IMT's micromorph lab technology with the goal to simplify and develop processes and obtaining thereby an industrially relevant approach.

A key issue for all thin-film solar cells is the TCO (transparent conductive oxide). From the above mentioned feasibility study one can draw the conclusion that an in-house TCO with excellent light-scattering properties should be developed for achieving the full efficiency potential for micromorph modules. Therefore, one of the main focus points of this project period was the development of an in-house low-cost ZnO, including the development of corresponding cell fabrication "know-how".

The project goals also include microcrystalline and amorphous cell developments. In fact, a high-quality amorphous silicon top solar cell is the base for a high-efficiency micromorph solar cell device. This is true for the p-i-n (superstrate) and the n-i-p (substrate) configuration, which are both included in the project. Depending upon the specific application and on the substrate material used, one prefers either the p-i-n or the n-i-p configuration. Furthermore, one can learn a lot about the limitations and the potential of micromorph cells by comparing both configurations.

The specific goals of this project, described in detail in the project proposal, are summarized in short below. An overview of the achieved results during this project period is given in the Appendix.

The overall goal was the achievement of a stable tandem cell efficiency of 12 %. The steps envisaged to reach this overall goal were:

a) Optimization of microcrystalline silicon solar cells with respect to micromorph tandem cells:

- Open circuit voltage > 530 mV with FF $\geq$ 68 % and a short-circuit current potential for wavelength >550 nm of $\geq$13.5 mA/cm2 (optimisation with respect to micromorph tandems).
- Above goals with a deposition rate for μc-Si:H cells with 10 Å/sec and a cell thickness of $\leq$ 2 μm.

b) Optimisation of light-trapping

- Reduction of ZnO layer thickness from 2.6 μm to 1 to 1.5 μm for the front TCO at improved surface texture (RMS-value of surface roughness > 100 nm).
- Improvement of the back reflectors.
- Study of stability of different fabricated ZnO layers.
- Buildup and process development of large area LP-CVD ZnO system (30x30 cm).

c) Optimisation of amorphous top cells

- For a-Si:H p-i-n: stable J_{sc} of 13.5 mA/cm^2 with FF = 68% and V_{oc} = 880 mV.

d) Cell structuring and cell calibration

- Certification of test cells (in collaboration e.g. Freiburg or NREL).
- Structuring of test cells (laser and/or tampography).
- Control and service of in-house cell efficiency measurements.

e) Preparation of large-area deposition (30x30cm)

- First micromorph tandem cells
- µc-Si:H bottom cells with 12 mA/cm2 for λ >550nm
- µc-Si:H deposition rates for layers $\geq$ 7Å/sec

2 Main results

2.1 Introduction

The present project deals with micromorph (microcrystalline/ amorphous) tandem thin-film silicon solar cells.

Such cells consist of 3 essential components:

a) microcrystalline bottom cell, b) an amorphous top cell, c) transparent conductive oxide (TCO) layers and other contact/reflector layers.

a) Hydrogenated microcrystalline silicon (μc-Si:H), deposited by plasma-enhanced chemical vapour deposition (PE-CVD) can be readily used within pin- and nip-type solar cells, as photovoltaic converter material. In most cases, it hardly suffers from light-induced degradation (Staebler-Wronski effect). The best μc-Si:H cells produced so far have stable single-junction efficiencies that are slightly over 9%. Here IMT's results of around 9 % for both pin- and nip-type solar cells are in the world's leading category. Whereas IMT was the only lab to produce such excellent cells some years ago, there are now more than half a dozen other labs (from J, D, USA, Thailand) obtaining similar results. It seems that it may only be possible to reach significantly higher values with more sophisticated light-trapping techniques that increase the effective optical absorption within the microcrystalline silicon absorber layer (i-layer). This is so because μc-Si:H is physically a material with an indirect band gap, i.e. with an exceedingly low absorption coefficient. To reach high enough values of photo-induced current (i.e. a high enough absorbed photon flux), one therefore certainly also needs reasonably thick layers (d_i = 1.5 to 2 μm in μc-Si:H as compared to d_i = 0.2 to 0.3 μm in a-Si:H). Achieving a high deposition rate without sacrificing layer/cell quality is therefore a key question for future economical production of μc-Si:H modules. IMT has during this project period obtained deposition rates for individual intrinsic μc-Si:H layers with high quality that are well over 10 R/sec. However could sofar <u>not</u> yet be incorporated into full pin- or nip-type μc-Si:H solar cells.

b) Hydrogenated amorphous silicon (a-Si:H) is already well known, since over 2 decades, as low-cost thin-film solar cell material. In the context of micromorph tandem cells the amorphous silicon top cell has to fulfil particular conditions (so as to be able to be compatible with the rest of the tandem): high optical absorption coefficient (obtainable through a lowering of the gap by the use of somewhat higher deposition temperatures), reduced cell degradation (obtainable through the use of thinner i-layers). These effects are now well mastered at IMT Neuchâtel. And one of the world's so far best a-Si:H single-junction solar cells has been realised here: it has a stabilized efficiency of 9.5%

c) Transparent conductive oxides (TCOs) and other contact and reflector layer materials constitute a major part of all thin-film silicon solar cells. IMT has made significant progress in this field – both with its in-house LPCVD (low pressure chemical vapour deposition) zinc oxide layers (with as-grown rough, textured surfaces), that is readily used for pin-type solar cells (on glass substrates), and also for opaque back reflectors with random texturing; the latter being used for nip-type solar cells. Whereas results achieved in this sector are already quite noteworthy, significant further progress is still to be achieved – it can, in fact, be theoretically shown that contact/reflector layers with less optical absorption and more pronounced light scattering properties could substantially further improve the solar cell efficiency.

2.2 Microcrystalline silicon (µc-Si:H)

2.2.1 Introduction of novel "compact VHF electrodes", increase of µc-Si:H deposition rate

In order to improve our VHF-GD (Very High Frequency Glow Discharge) deposition process, as used in our small-area (8x8 cm) systems, we developed a new and more compact design for our electrodes. The aim of this new design was to confine the plasma in a better way and to increase the deposition rate. In this context, we also had to fully reestablish all the deposition parameters for these modified deposition chambers. By introducing a shower head for gas input through the cathode, we also hope to improve the homogeneity of the layers deposited in the system. A first step here was undertaken by a new Ph.D. student, Urs Graf, who joined our group in November 2000. First results obtained are given in Fig. 1: by increasing the VHF-power and the silane concentration, an increase of layer deposition rate over the 10 Å/s mark could be obtained for individual i-layers (but sofar not for entire pin-cells). These experiments were sofar executed at a pressure of 0.3 mbar. Recent work of Japanese groups has, on the other hand, shown that a drastical improvement of the deposition rate can be obtained in the so-called HPD (high pressure depletion) regime: this regime allows (in combination with VHF plasma excitation) for deposition rates up to 60 Å/s. (Problems with powder formation, layer inhomogenity and exorbitantly high gas usage are expected in this regime.) In order to experiment with this regime, our VHF electrodes had, however, to be modified further.
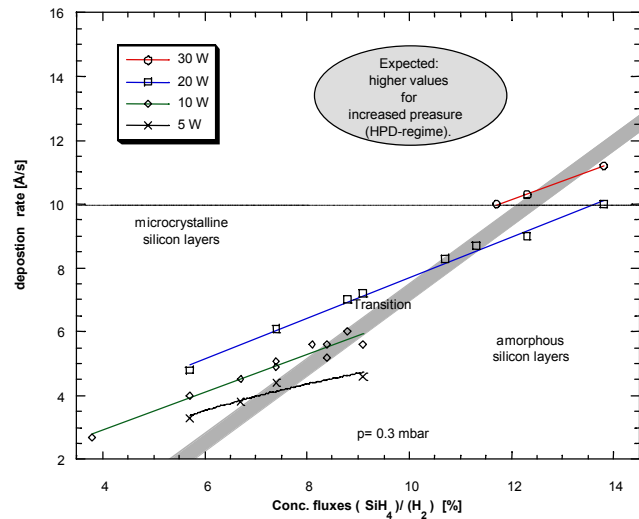

Fig 1: Deposition rate [Å/s] in function of silane concentration and VHF-power. Note, that by increasing the pressure above the "conventional" deposition pressure values of 1 mbar and, thus, entering the so-called HPD (High-Pressure-Depletion) regime, the deposition rate can be further increased. (see Fig. 2)

2.2.2 Microcrystalline silicon, deposited at high rates by VHF-GD at high pressure

We therefore subsequently investigated the adaptation of a "simple" VHF-GD reactor to the deposition of microcrystalline silicon in the high pressure regime (>1mbar). The aim of this study is to exploit the possibilities of an extended parameter range for high-rate deposition of microcrystalline silicon. With a further revised electrode design and thanks to systematic variation of deposition parameters (pressure, total gas flux, power), we achieved deposition rates of around 25 Å/s (Fig. 2a) at the vicinity of the microcrystalline / amorphous transition (Fig. 2b). These results were obtained using low gas flows of only ~100 sccm (total flux) at 3 mbar pressure with VHF-powers up to 120 W at 70 MHz .

Thus, using the VHF-GD technique at high pressure, high deposition rates of up to ~25 Å/sec for individual µc-Si:H i-layers even at low total feedstock gas flows of around 100 sccm (for an electrode size of 8×8 cm). The incorporation of these i-layers into entire pin-type µc-Si:H solar cells has, however, led to unexpected problems for us at IMT, and it is currently under investigation.
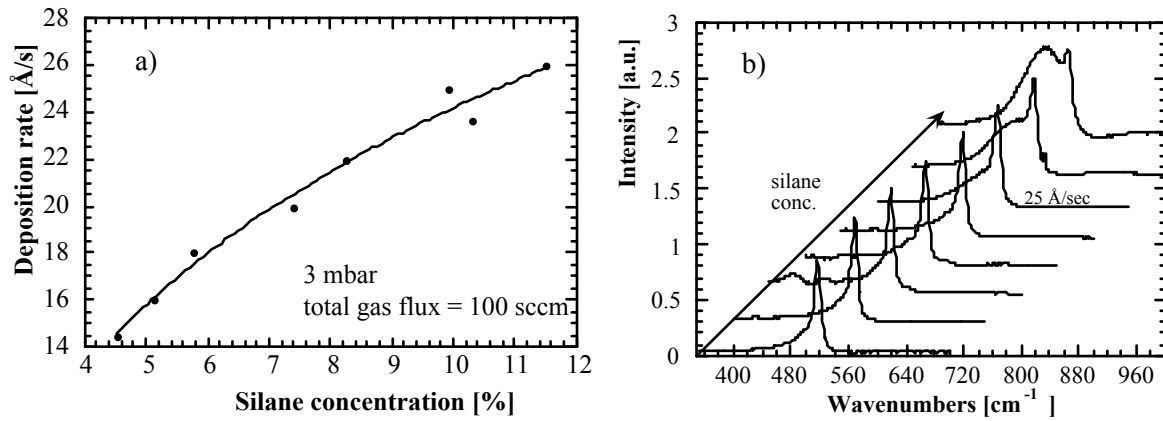
Fig. 2a) The deposition rate vs. SiH$_4$ concentration for c-Si films, for VHF-GD deposition at high pressures, b) corresponding series of Raman spectra, for increasing values of the silane concentration, measured on the film side with a He/Ne laser (633 nm).

2.2.3 VHF deposition of microcrystalline silicon with assistance of a remote microwave plasma

We have investigated the additional introduction of a remote microwave plasma into a 70 MHz VHF plasma reactor, and its effect on microcrystalline silicon growth. For this purpose, a 4.15 GHz microwave generator was used to generate a H$_2$/Ar plasma in a quartz tube with a diameter of 20 mm and a length of 500 mm. Excited gas from this plasma entered the VHF deposition zone from the outlet of the quartz tube. In the deposition zone silane, and, optionally, additional hydrogen was entered too. In order to obtain a homogeneous distribution of the excited gas in the deposition zone, a ring-shaped gas shower made of quartz was constructed.

Main results of these experiments (see Fig. 3) are that:

1) the growth rate can be relatively enhanced by applying a remote microwave plasma by about 15% (albeit still at rather low absolute values),

2) a remote Ar plasma is more effective for growth rate enhancement than a mixed plasma consisting of H$_2$ and Ar,

3) optical emission spectroscopy shows that the formation of SiH* radicals in the VHF plasma is suppressed by applying a remote microwave plasma: that means the remote plasma on one hand increases the deposition rate and but at the same time it suppresses the SiH* concentration. This is an indication that the mixture of radicals (SiH, SiH$_2$, SiH$_3$) prevailing in the growth zone is altered by the remote microwave plasma, probably resulting in a higher relative concentration of SiH$_3$. This would imply that higher VHF power densities
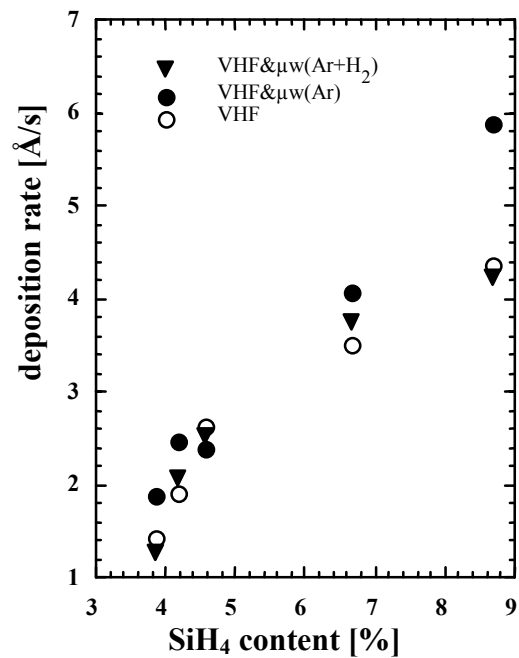

Fig. 3: VHF deposition combined with remote microwave plasma: Deposition rate as a function of the silane flow, for a typical set of deposition conditions (p=0.8 Torr, P=10 W, T=200 ºC, Ar flow = 50 sccm, H$_2$ flow=50 sccm).

could be used in combination with the microwave remote plasma, without the risk of powder formation, and that, thus, an additional enhancement of the growth rate could potentially be obtained.

These experiments have to be considered as preliminary, exploratory work and need to be taken up again, if manpower permits, in a later project.

2.2.4 Microstructure of microcrystalline solar cells

The development of microcrystalline silicon solar cells is still in the early stage (just 10 years have past since their first successful introduction by IMT Neuchâtel). Therefore basic studies on growth and performance of microcrystalline silicon cells are still very much called for. We have indeed obtained several interesting results in this field during the present project period. Some typical results will be described hereunder.

While, since a few years already, more detailed characteristics of microcrystalline silicon material were available in terms of absorption behavior, transport properties, device performance and stability, only relatively little was known about the internal crystalline microstructure of this material. Therefore, we have undertaken the study of μc-Si:H microstructure with transmission electron microscopy (TEM). We had observed previously with TEM that undoped microcrystalline silicon deposited on glass substrate shows a large variation of internal microstructures (see our 1999 annual report). In particular, we found that the microstructure is strongly dependent on the hydrogen to silane dilution ratio used during deposition. On the other hand, it is known that the microstructure is critically substrate-dependent, at least during the early stage of growth. In case of entirely microcrystalline p-i-n devices, not only the microstructure but also the electrical contact is essential for obtaining satisfactory solar cell performance. Especially, the initial crystalline growth of the p-i interface on the TCO is critical for obtaining satisfactory device performance.

In one of our experiments, we have studied two microcrystalline single-junction solar cells named hereunder cell A and cell B. A fully microcrystalline p-i-n structure was grown by VHF-GD on a rough LP-CVD ZnO layer deposited by us on a glass substrate. In this superstrate configuration, the critical p-i interface is formed at the beginning of microcrystalline deposition. In this

cell parameter	cell A	cell B
V_{oc} [mV]	530	486
J_{sc} [mA/cm^2]	16.6	22.5
FF [%]	68	64
<i> layer thickness [μm]	1.4	5.4
deposition rate [Å/s]	5.2	4.6

Table. I: Parameters of solar cells investigated by TEM w.r.t. medium scale

case, the condition of the substrate is certainly decisive for obtaining an optimally grown p-i interface. The p-doped layers of both cells were deposited using the same deposition parameters. Both <i> layers were deposited under similar conditions, except for the silane concentration, which is 5.6% for cell A and 5% for cell B. Even if these cells were not optimized with respect to obtaining an ultra-thin p-window or a high reflectivity of the back reflector, they still have quite reasonable conversion efficiencies between 6 and 7%. Table I shows the electrical properties of these 2 cells.

The microstructure as observed by TEM is shown in Figs. 4 and 5. At the bottom of each figure, we can observe the teeth-shaped zinc oxide substrate on which our cells were deposited in the upwards direction. On the top of each figure, we can see the as-deposited roughness of our cells. It seems that it is not much affected by the roughness of the substrate.

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The microstructure of the <i>-layer consists of an agglomerate of small crystallites (dark spots in Fig. 4). These small crystallites have a diameter of a few tens of nanometer, 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 nanometers. However, further away, they grow perpendicular to the average substrate plane and their length can reach several micrometers. The agglomerate of small crystallites have a diameter of several hundreds of nanometers and run across the whole thickness of the device. Therefore, we can call them "columns". Close to the substrate, the columns are loosely packed, resulting in visible cracks. These cracks may consist of an amorphous tissue, or may just be voids. Towards the top of the cell, the microstructure becomes denser. The column size is determined in both cells by the surface geometry. Indeed, column boundaries are systematically observed at the bottom of the ZnO valleys.

As the cells have quite different thickness, the electrical characteristics can be compared only with respect to V_{oc} and FF. Surprisingly, the V_{oc} is higher for cell A, which exhibits voids at the ZnO p-i interface. This suggests that a high V_{oc} is due to features at lower scale such as the quality of the p-i interface, the impurity contamination, and the passivation of grain boundaries. Such features cannot be observed on our medium-resolution micrographs. Nevertheless, these micrographs permit the observation of the microstructural variations of the material (at the micrometer scale); such variations are observed even for small changes in the deposition parameters as well as for a variation in cell thickness.
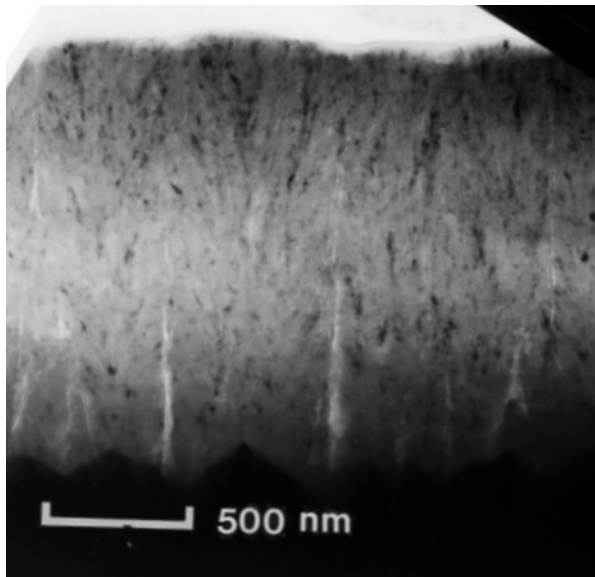

Fig. 4: Bright Field cross-section micrograph of cell A. Voids and cracks appear brighter at the ZnO/p-i-n cell interface (bottom of the figure).
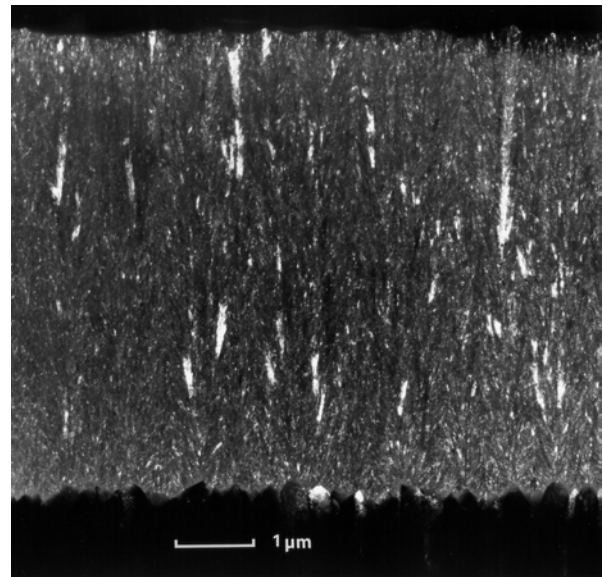
Fig. 5: TEM dark field micrograph of cell B. The crystallites best satisfying diffraction conditions appear bright. Note how their length depends on the position within the layer.

2.2.5 Growth mechanisms and device properties of microcrystalline silicon

A few years ago, our group pioneered the study of the microstructure of microcrystalline silicon within complete p-i-n and n-i-p solar cells by Transmission Electron Microscopy (TEM). These studies revealed the complexity of the material when incorporated into devices. Microcrystalline silicon consists of conical conglomerates of nanocrystals of a few tens of nanometer in diameter. Between the conglomerates, amorphous tissue passivates the surface of the conglomerates. Apart from these general observations, TEM studies principally

revealed that the microstructure of the doped and undoped layers vary over the micrometer scale in such devices, depending on the deposition conditions used for the fabrication of the doped and intrinsic layers. Currently, TEM investigations are used to compare the microstructure of high open-circuit voltage (V_{oc}), high efficiency microcrystalline silicon solar cells to ones showing particular failures such as low fill-factors or low V_{oc}. Our current expertise suggests that microstructure variation over the micrometer scale is usually responsible for the observed deficiencies in the electrical performances of the device. At present, there is no other means for identifying problems in poorly performing devices. The problem with TEM investigations is that the sample preparation is destructive, lengthy, and cumbersome. Thus, in parallel to TEM experiments, Raman spectroscopy has been introduced as a non-destructive tool for the characterization of the crystallinity of the various n, i and p layers.

In the Raman spectra, the signature of the presence of amorphous material is a broad peak centered at 480 cm^{-1}, whereas a narrow peak at 520 cm^{-1} indicates the presence of microcrystalline material. The ratio of the microcrystalline peak intensity over the total Raman scattered intensity yields what will be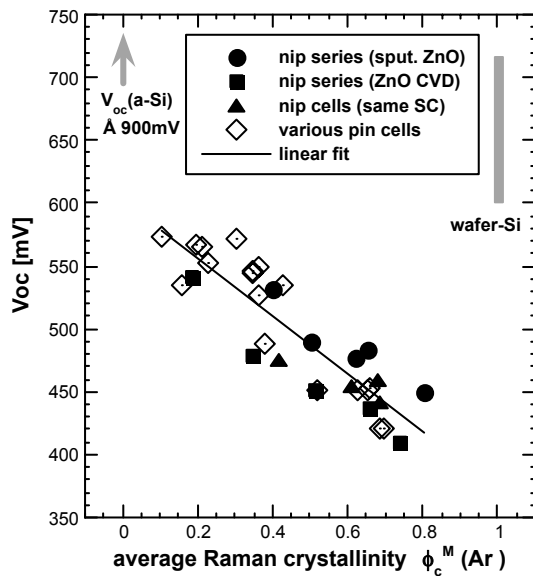 called thereafter the Raman crystallinity. It has been possible to perform Raman experiments by exciting light entering devices either from the top (growing surface), or from the bottom (substrate/device side) on solar cells deposited onto TCO covered glass. Such bifacial Raman measurements allow the evaluation of crystallinity of the material at the top and, respectively, at the bottom of the device. It was then possible to establish the relationship between material crystallinity and open circuit voltage (V_{oc}) in both nip and pin solar cells. The result is quite convincing as it shows that the Voc decreases linearly with the average crystallinity of the top and bottom part of the solar cell (see Fig. 6).

Fig. 6: Relationship between average Raman crystallinity and open circuit voltage V_{oc} on various pin and nip solar cells. The V_{oc} decreases linearly with increasing average crystallinity (top crystallinity + bottom crystallinity/2).

Hitherto, such a direct and simple link between material microstructure and device performance was lacking. Our work demonstrates that Raman spectroscopy is an efficient, non destructive tool for the evaluation of the crystallinity of the various layers incorporated into a microcrystalline silicon solar cell. Nevertheless, further work is needed before a simple physical picture relating the crystallinity and the V_{oc} can be devised.

2.2.6 Microcrystalline n-i-p solar cells

One of the advantages of solar cells in the n-i-p configuration (compared to cells in the p-i-n configuration) is the possibility to use cheap and flexible (but non-transparent) substrates in the place of glass substrates. (for non-transparent substrates, the use of the n-i-p configuration is so far considered mandatory because one generally is able to fabricate better thin-film

silicon solar cells[1], if the light enters the solar cell from the p layer). One of the main goals of our BFE project was therefore to investigate the more fundamental research aspects for thin-film silicon solar cells on cheap and flexible substrates.

<u>a) Substrates</u>

We mainly used 3 kinds of flexible substrates:
- SS (Stainless steel):with SS substrates, it is possible to deposit solar cells at temperatures higher than 200°C and thereby obtain good performances.
- PI (polyimide) : this plastic is stable at 200-300°C, but a bit expensive.
- PET, PEN, PC…: these plastics are very cheap but are not so stable at temperatures higher than 150°C.

These substrates are far from being equal w.r.t. "stress resistance". Indeed, when the layer thickness deposited on the substrate is more than 500 nm, and especially if the layer consists of microcrystalline silicon, the layer can peal off or the substrate can bend under the effect of stress. This is specially the case for plastic substrates. It is for this reason that Stainless Steel (SS) was chosen for the initial optimisation of our µc-Si solar cells. SS has also been chosen as substrate material by USSC which fabricate triple- junction a-Si solar modules for building applications. Note that USSC hold the world record for the highest efficiency of thin-film silicon solar cells (13% on a small surface area) but one must realise that triple junctions are very difficult to fabricate. Therefore, USSC themselves are looking at nip-type micromorph tandem solar cells.

<u>b) Back contacts and back reflectors</u>

One of the most important parts of a thin-film silicon solar cell is the back reflector. This is so, because e.g. only 47% of the AM1.5 solar spectrum can be absorbed after one passage through a 2µm thick microcrystalline silicon solar cell, compared to 76% for a thick monocrystalline silicon solar cell. Therefore, it is primordial to trap the light in a thin film silicon solar cell. It is in this context that the back reflector/back contact layer plays a key role for nip-type thin-film silicon solar cells.

Let us look at the **light trapping problem in general**: the light must be trapped into the i layer, so, first, the light must enter into the solar cell (necessity to have an anti-reflective layer). Then, if the photons are not absorbed after the first passage through the solar cell, the light must be reflected by the back contact, preferably in an angle which allows further subsequent reflections in the front silicon/TCO interface and, thus, can lead to many further passage through the absorber layer (i-layer).

The ideal concept is to fabricate a wave-guide to give to the light all the chance to be trapped. With this aim solar cells on different textures on glass and SS were studied. Glass was used to compare textured surfaces with perfect flat surfaces.

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[1] This is particularly true for amorphous silicon cells and, thus, also for micromorph tandem cells, whereas the situation is not clear for microcrystalline silicon cells. Some other groups like the Juelich group have indeed made excellent microcrystalline silicon solar cells where the light enters from the n-side. As we (at IMT) are not interested in single-junction microcrystalline cells per se but ultimately only in micromorph tandem cells, we have not pursued this avenue further but only looked at cells where the light enters from the p-side.

Fig. 7 shows the spectral range of photons for which back reflectors must reflect and diffuse light in amorphous and microcrystalline solar cells.

The advantage of the nip structure is that it is possible here to change the substrate surface shape which will also change the surface shapes of all the interfaces (because layers are deposited on the substrate), without deteriorating the solar cell. To do this, is much less obvious in the pin-structure because there the texture must be fabricated on a transparent layer (on glass or on TCO, for instance) whereas in nip-structures the texture is fabricated on non-transparent layers: it is therefore possible to use here e.g. optical glue whilst fabricating the back reflector. (In the pin-structure, the role of light scattering is taken over by the front TCO, see section 3.3.1 and 3.5.1 of this report)
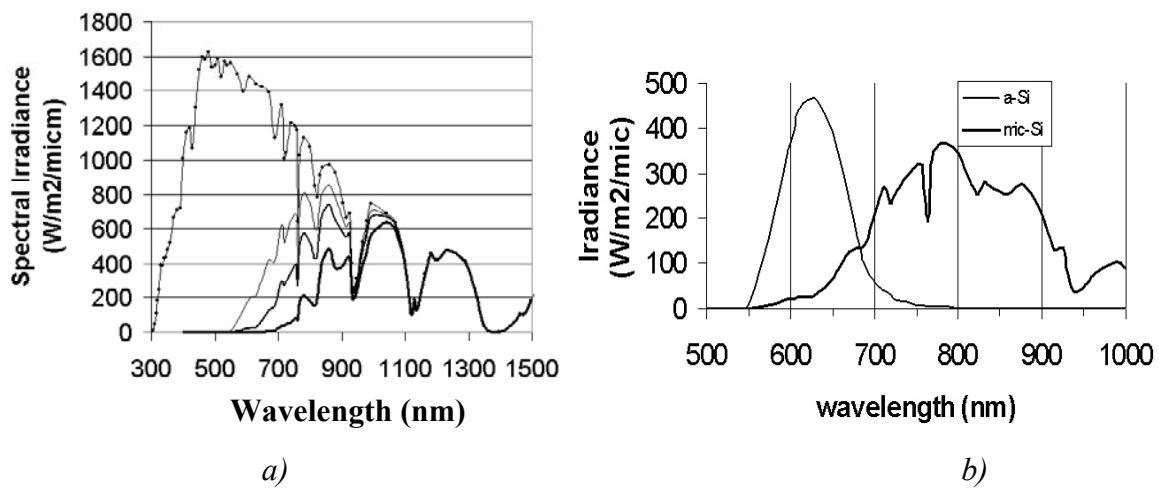
a)   *b)*

Fig. 7:
a) Spectral irradiance of the sun (AM1.5) (dotted line), after one passage (thin line), 2 passages (midium thickness line), 5 passages (thick line) through a 2μm thick μc-Si layer.
b) Absorption gain between a mirror (2 passages) and a light diffusing reflector (5 passages) for an a-Si layer (0.3μm thick, thin line) and a μc-Si layer (2μm thick, thick line). One can see that the surface must in particular scatter or diffract photons in a spectral range between 550 and 700nm for a-Si solar cells and 700 and 900nm for μc-Si solar cells.
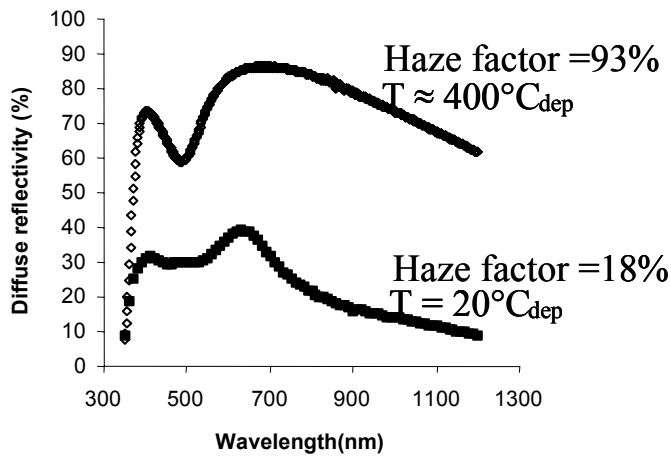
Fig. 8: Diffuse reflectivity of reflectors made from SS/as grown textured Ag/ZnO:Al deposited at the ambient temperature and at 400°C. (Bumps of the curves are due to optical interferences).

With the goal of **fabricating suitable back contacts** (back reflectors), studies on the **surface texturing of ZnO:Al as well as on the deposition of as-grown textured Ag** were performed. ZnO:Al was textured with a chemical etch and the optimal etch time was determined. see [L. Feitknecht, O. Kluth, Y. Ziegler, X. Niquille, P. Torres, J. Meier, N. Wyrsch, A. Shah, "Microcrystalline NIP Solar Cells Deposited at 10 Å/sec by VHF-GD", Solar Energy Materials& Solar Cells, presented at PVSEC-11, Sapporo, 20-24 September 1999, Vol. 66 (2001) pp. 397-403].

Concerning the as-grown textured Ag back reflectors deposited by a magnetron sputtering process, several parameters were varied to determine the most influential one. It was found that the parameter, which has the highest influence on the surface roughness and, thus, also on the diffuse reflectivity in the red, is the deposition temperature. Fig 8 illustrates this result by showing the diffuse reflectivity of reflectors made from "as-grown textured Ag + ZnO:Al" deposited at ambient temperature and at around 400°C.

c) Silane concentration for deposition of i-layer:

Fine-tuning of the silane concentration (SC) in the silane + hydrogen source gas used for deposition of the intrinsic <i> absorber layer was studied.

The silane concentration (SC) was chosen as such a way as to obtain intrinsic films close to the amorphous/micro-crystalline transition. As Fig. 9 shows, films deposited at SC=6% are in-between the two phases (amorphous and crystalline), whereas, films deposited at SC=7% are entirely amorphous. As expected, the best solar cell is obtained with SC near the transition (but still giving optically fully microcrystalline layers); this means here: SC=5%.
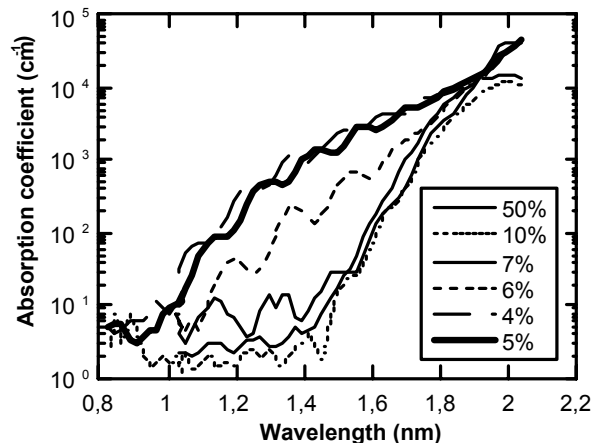

Fig. 9: Absorption coefficient of absorber layers deposited at different silicon concentration (SC).

d) Solar cells

Fig 10 shows the substantial increase of current in the red light range for solar cells deposited on textured Ag reflectors and with a silane concentration equal to 5%, as compared to solar cells deposited with a lower silane concentration, on a "poor" reflector made on approximately flat SS and. With SC=3%, more photons are absorbed between 600 and 1000nm when the solar cell is deposited on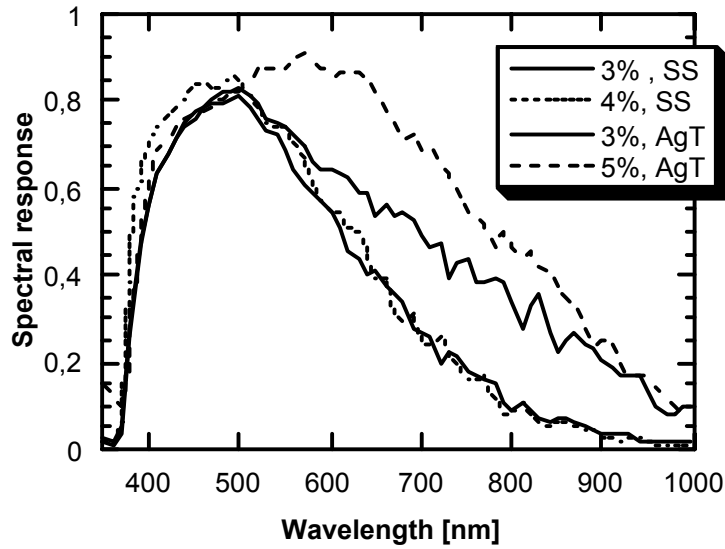 textured Ag, as compared to solar cells deposited on stainless steel (SS) substrates. It is clear also that the performance of the solar cells is improved if the intrinsic layer is deposited close to the transition a-Si/μc-Si (SC=5%). By combining both advantages, i.e. an optically well-performing back reflector and an optimally deposited intrinsic layer, it is possible to increase drastically the current of the solar cell compared to the current obtained with a "poor" reflector such as approximately flat SS (13.3mA/cm^2 to 22.8 mA/cm^2).

Fig. 10 : Spectral response of μc-Si:H solar cells deposited with different SC values and on different substrates.

Table II summarizes solar cell results obtained with different substrates and at different silane concentrations.

SC	V_{oc} SS	V_{oc} AgT	FF SS	FFAgT	J_{sc} SS	J_{sc} AgT	η SS	η AgT
%	mV	mV	%	%	mA/cm^2	mA/cm^2	%	%
3	411	444	733	745	13.37	18.36	4.03	6.07
4	459		736		14		4.73	
5		**520**		**730**		**24.2**		**9.19**
6	556	577	724	703	13.22	14.23	5.32	5.77

Table II: Summary of solar cell results for single junction μc-Si:H nip-type solar cells. SC: Silane concentration, AgT : Ag as-grown textured, SS: Stainless steel, V_{oc}: Open circuit voltage, J_{sc}: Short-circuit current, FF : Fill factor, η : conversion efficiency.

Fig. 11 a) shows that V_{oc} increase quite regularly between SC=3% and 6%. This may possible be explained by the fact that in the transition phase, a combination of both materials (with 2 different gap energies) exists, i.e. a combination of a-Si and μc-Si. Fig. 11 b) illustrates the current increase, taking place especially when the silane concentration, used for deposition of the intrinsic (i) absorber layer, is optimal.
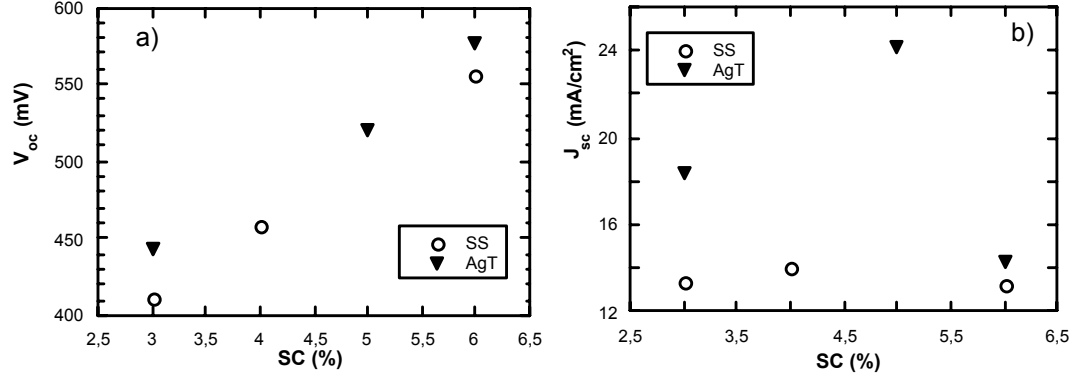
Fig. 11 shows V_{oc} and J_{sc} variations in function of SC. One can observe a quite linear variation of V_{oc} versus SC.

We can report here on the successful realisation of a single-junction microcrystalline silicon n-i-p solar cell which has a conversion efficiency exceeding 9% (V_{oc} =520mV, FF=73%, J_{SC}=24.2mA/cm^2). This result is one of the best results in the world, in the field of nip-type μc-Si solar cells.

2.3 Amorphous silicon (a-Si:H)

The main challenge during this period was the incorporation of our in-house LP-CVD ZnO in the amorphous silicon single-junction and micromorph (a-Si:H/µc-Si:H) tandem solar cells. In order to develop high efficient cells the reliability of the ZnO layers with respect to the daily reproducibility of the deposition process was an important issue.

2.3.1 Amorphous silicon p-i-n solar cells

a) Comparison of LP-CVD ZnO with SnO$_2$ from Asahi (U-type)

Amorphous p-i-n solar cells deposited on self-developed LP-CVD ZnO were compared with today's best (but expensive) commercially available TCO, of SnO$_2$-coated glass substrates from Asahi (type U2).

Case of "thick" a-Si:H p-i-n solar cells: In first experiments, a-Si:H p-i-n cells with an absorber thickness of ~0.35 µm have been deposited on two types of TCO substrates. Whereas fill factors of 72- 74 % and V$_{oc}$-values in the range of 860 - 900 mV can be achieved on both TCO's, there is a net gain in the short circuit current for cells deposited on LP-CVD ZnO. This fact is illustrated in Fig. 12 by the I-V characteristics (obtained for AM1.5 illumination) on both types of cells. Whereas on SnO$_2$, typical short circuit current densities J$_{sc}$ of around 16.2 mA/cm^2 can be achieved, the same cells on LP-CVD ZnO have J$_{sc}$-values exceeding 17.5 mA/cm^2, leading thereby to (initial) efficiencies above 11 %.

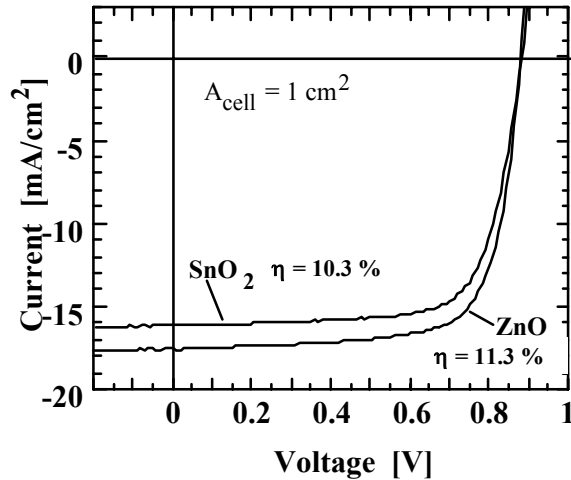

Fig. 12: Initial I-V characteristics under AM1.5 illumination of 0.35 µm thick a-Si:H p-i-n test cells deposited on glass substrates clad with SnO$_2$ (U-type) and with LP-CVD ZnO.
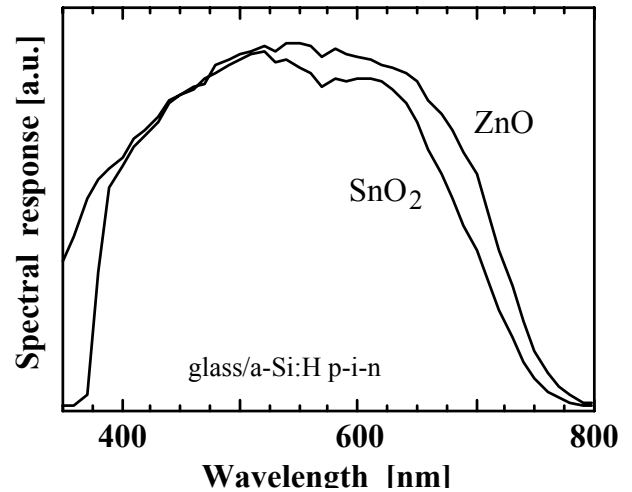
Fig. 13: Comparison of the relative spectral response of 0.35 µm thick a-Si:H p-i-n cells deposited on glass substrates covered with LP-CVD ZnO and SnO$_2$.

As the spectral response measurements shown in Fig. 13 reveal, the current enhancement is obtained especially in the wavelength range above 500 nm where obviously a more efficient light-trapping takes place thanks to the LP-CVD ZnO layer. This improvement is attributed partially to the increased diffused transmission for ZnO, as illustrated in Fig. 14a).

The analysis of the spectral reflection behavior of entire cells as shown in Fig. 14b) indicates, furthermore, a reduction of the optical reflection for cells deposited on LP-CVD ZnO. In the case of ZnO one observes lower values (< 7 %) and smoother reflection characteristics than in the case of SnO$_2$, where remarkable amplitudes of the interference

fringes are present in the relevant part of the spectrum. We suggest that the difference in the amplitude of the interference fringes are linked to the differences in the surface topology of the TCO layer. The overall reduced reflection of the LP-CVD ZnO cell system (Fig. 14b) is certainly one of the reasons for the higher photocurrent obtained in the corresponding solar cells, as here more light is entering the cell.

b) p-i-n cells with high stable efficiencies

Case of "thin" a-Si:H p-i-n solar cells: As "thick" cells, as described above, still degrade substantially under light-soaking, thinner a-Si:H p-i-n cells (with a thickness of 0.25 μm) have been optimized on LP-CVD ZnO substrates. Such a cell has been sent to NREL. Fig. 15 shows the initial cell efficiency under AM1.5 illumination measured by NREL. This cell has a thickness of the intrinsic absorber of only 0.25 μm. The area of this cell has been defined by our laser-scribing equipment and is 1 cm^2.

Fig. 16 gives the AM1.5 characteristics of a similar cell after light-soaking in the stabilized state. The cell has a high stable efficiency of 9 %, which proves the high quality of both the LP-CVD ZnO as front TCO and IMT's high quality a-Si:H p-i-n solar cell deposited by the VHF-GD technology.

On another device which was light-soaked, however, with only 0.75 sun intensity and over a light-soaking period of 700 h, NREL was able to measure the quantum efficiency which is given in Fig. 17. This cell has again a cell thickness of 0.25 μm and shows an efficiency of 9.5 % (AM1.5 measured by NREL) due to the excellent QE curve. This result reveals the interesting potential for amorphous single-junction p-i-n cells in combination with a high-quality TCO. It reveals also that research on the development of TCO's with high optical and electrical quality is as important as improvements on the cell side. IMT's LP-CVD ZnO turns out to be one of the best candidates that can reduce cost and improve performances of amorphous silicon modules.

The 9 % cell relating to Fig. 16 demonstrates that one is indeed able, with a combination of a high-quality front TCO and an adequate cell design, to obtain remarkable values for the stabilized efficiency, even for simple single-junction p-i-n solar cells. It is surprising that based on this simple concept of a single-junction, entirely amorphous solar cell with such high stabilized cell efficiencies can be obtained. Note, however, that it had already been pointed out in 1993 by the Siemens group that an upscaling to 1ft^2 of the single-junction cell concept, in combination with the integrated series connection, has the possibility to lead to
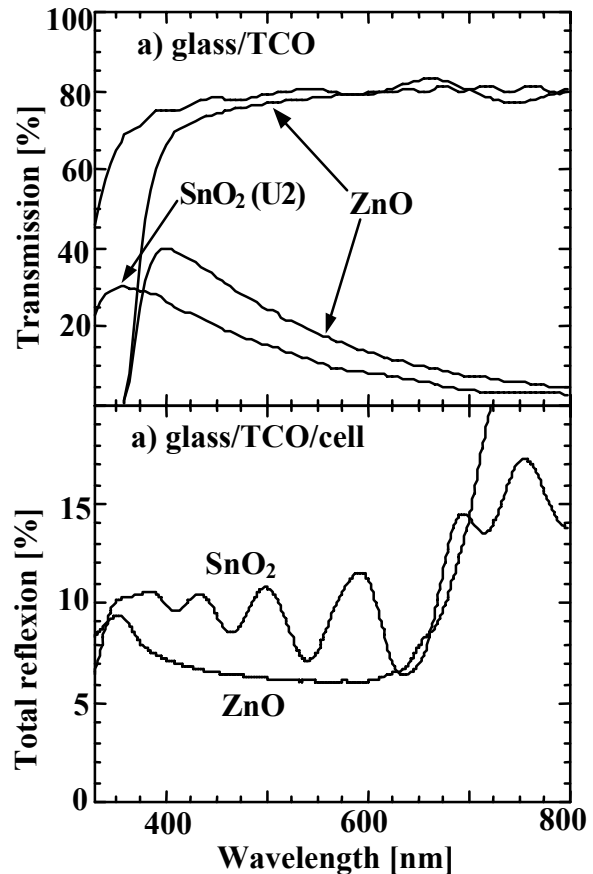

Fig. 14:
a) Total and diffuse spectral transmittance of glass/SnO$_2$ and glass/LP-CVD ZnO;
b) total reflection of a-Si:H p-i-n cells deposited on SnO$_2$ and ZnO; the SnO$_2$-covered
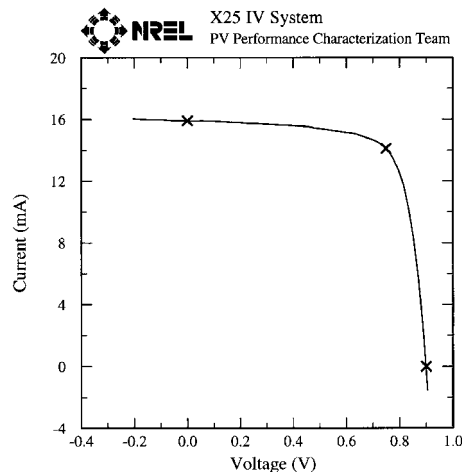
stable module efficiencies of 9 %. In this context, the plans for the 20 MW manufacturing unit of Kaneka Corporation, with a goal of producing 8 % stable single-junction p-i-n a-Si:H modules, appear to be fairly realistic. This technology is proven for mass production, reliable and simple.

Compared to today's commercially available modules, based on tandem and triple-junction a-Si:H/a-SiGe:H solar cells (with efficiencies in the range of 5 to 7 %), such a single-junction cell technology possesses, beside its potential for relatively high efficiency values, some other striking advantages, like an easier control of the cell deposition process (no precise control of sub-cells is needed), a cost reduction by avoiding expensive germane, and finally a better performance of single-junction modules under realistic outdoor conditions (reduced losses when compared to stacked junctions w.r.t. spectral sharing between sub-cells).

Application prospects: Such single-junction amorphous silicon cells with high efficiencies could lead, if fabricated with our VHF fast deposition method, to competitive and relatively efficient amorphous silicon solar modules.

Fig. 16: AM1.5 I-V characteristics of a stabilized a-Si:H p-i-n solar cell (thickness 0.25 µm), deposited on IMT's in-house LP-CVD ZnO, as measured after light-soaking (1000h 50°C, AM1.5).

University of Neuchatel (Switzerland)
a-Si Cell

Device ID: C200700 lIC2
Aug 29, 2000 2:12 PM
Reporting Spectrum: Global AM1.5

Device Temperature: 25.0 ± 1 °C
Device Area: 0.9965 cm²
Irradiance: 1000.0 W/m²

X25 IV System
PV Performance Characterization Team

V_{oc} = 0.9003 V
I_{sc} = 0.01591 A
J_{sc} = 15.96 mA/cm²
Fill Factor = 73.74 %

I_{max} = 14.10 mA
V_{max} = 0.7491 V
P_{max} = 10.56 mW
Efficiency = 10.6 %

Fig. 15: Independently confirmed initial cell efficiency of an amorphous silicon p-i-n solar cell deposited at IMT on in-house LP-CVD ZnO. The i-layer has a thickness of only 0.25 µm.

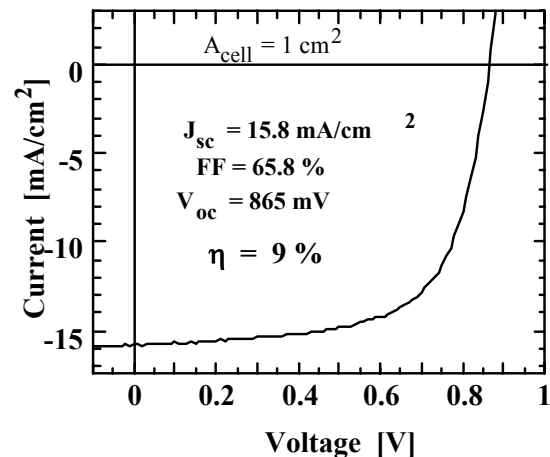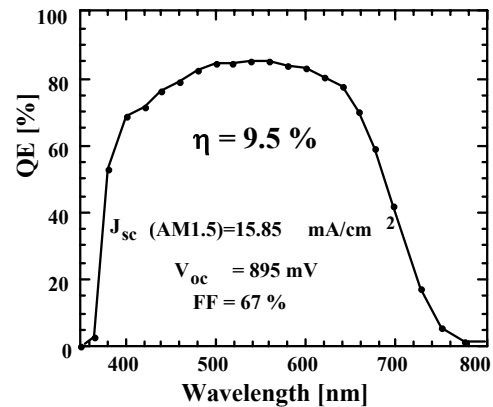Fig. 17: Typical shape of the external quantum efficiency of an amorphous p-i-n solar cell of 0.25 µm thickness on LP-CVD ZnO. The QE-values are deduced from a NREL QE-measurement of this cell. The indicated cell performance of 9.5 % after degradation was evaluated by NREL.

2.3.2 Amorphous silicon n-i-p solar cells

The key advantage of nip-type amorphous silicon solar cells (i.e. of single-junction amorphous silicon cells that are not integrated into a micromorph tandem solar cell), is (as already mentioned) the possibility to deposit such a cell on cheap and flexible plastic substrates- like PET, PEN or PI. In these cases the substrate temperature must be maintained under 200°C. As it is possible to deposit solar cell with satisfactory performances on such plastic materials, it is also possible to use gratings (embossed on plastic), in order to increase light trapping. A feasibility project (Top Nano 21 project) on this subject was executed: it demonstrated the great potential of this concept. (An "Integrated Project" will now be submitted to CTI, together with VHF-Technologies, OVD Kinegram, PSI and IMT's optical team, in June 2003).

Depositing a-Si amorphous silicon solar cells on textured plastic substrates at low temperatures has therefore been one of the important variants studied in this project.

One of the major drawbacks of all amorphous silicon solar cells is their degradation under light soaking. Therefore a comprehensive study was carried out on amorphous silicon solar cell stability. Mainly two deposition parameters were varied to increase stability : substrate temperature and silane dilution in hydrogen (A substantial part of this work was initially done within a "parallel" research project financed by the Japanese New Energy Development Organization NEDO).

a) Substrate temperature :

n-i-p solar cells with intrinsic layers deposited both at standard temperature (200°C) and at moderately high temperature (350°C) have been studied and compared: it had been established in a collaboration project with the Japanese NEDO (New Energy Development Organization) that intrinsic layers deposited at higher temperatures have both better stability and higher optical absorption. It was therefore our goal to see the effect of these improvements on complete n-i-p solar cells. The deposition parameters for the solar cells are listed in Table III.

	n-type layer	i-type layer	p-type layer
Standard temperature	350°C	200°C	170°C
Moderately high temperature	350°C	**350°C**	170°C

Table III: Deposition temperatures of the doped and intrinsic layers of the n-i-p single-junction a-Si:H cells.

The n-type layers used in both cells have been deposited at 350°C, in order to render these layers more dense and, thus, to limit the diffusion of phosphor from these layers into the intrinsic layers (deposited either at 200°C or 350°C).

The spectral response (SR) of both cells are compared after a light-soaking of 500 hours (see Fig. 18). The observed behavior fulfills our prediction that incorporating a more absorbent and more stable intrinsic layer, produced at moderately high temperatures (350 °C), results in a photocurrent gain in the long wavelength range.
Note that the short circuit currents (J_{sc}) [obtained as integral over the spectral response (SR) curves] are relatively low in both cases because of the use of a smooth substrate without any back reflector.

The open circuit voltages (V_{oc}) measured on cells deposited at 350°C and at 200°C are roughly the same.
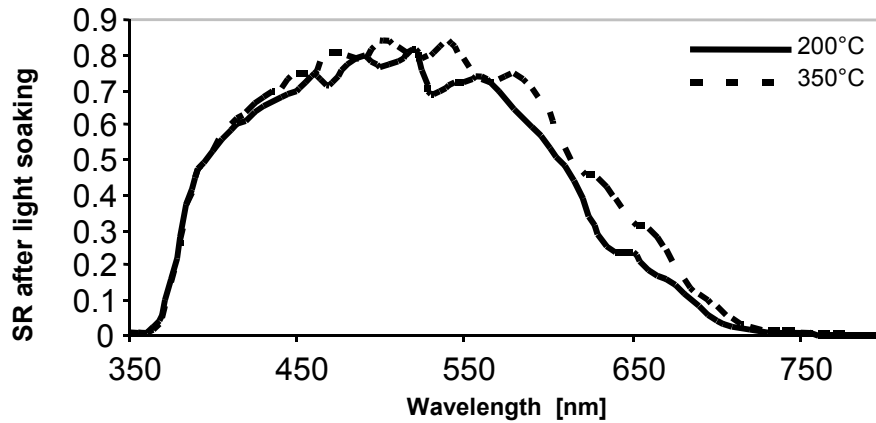

Fig. 18: Spectral response curves measured after 500 hours of light-soaking on cells with intrinsic layers deposited at 350 °C and 200 °C.

Concerning the fill factor (FF), the cell deposited at 350°C is less affected by light soaking than the cell deposited at 200°C. Moreover, the stabilized FF of the cell deposited at 350°C is slightly higher than that of the cell deposited at 200°C (65% compared with 64.3%).

Intrinsic layer	FF (%)	V_{oc} (V)	J_{sc} (mA/cm²)	Efficiency (%)
200°C	64.3	0.880	10.28	5.81
350°C	65.0	0.876	10.77	6.13

Tab. IV: Characteristics of single-junction a-Si:H nip-type cells incorporating intrinsic layers deposited at 200°C and 350°C after light-soaking (1000 hours); The cells are deposited on smooth substratse and without a back reflector.

Finally, the efficiencies of the cells have been compared in the degraded state (Table IV). The overall performance of the cells studied here remains relatively poor, because of the use of smooth back contacts and because of the lack of a suitable back reflector. In this particular experiment, one can, however, see that the cell deposited at 350°C already has a higher stabilized efficiency than the cell deposited at 200°C. These promising results are explained by an increase in the stabilized values of J_{sc} and FF (fig. 19). With the help of fine-tuning of all the layers involved, further improvement should be possible, for such cells deposited at moderately high temperatures. One must immediately remark, however, that such "moderately high temperatures" of around 350° <u>cannot</u> be used in connection with present-day plastic substrates. In the latter case one has, in fact, to use substrate temperatures below 190°C, especially with very low cost substrates, such as PET.
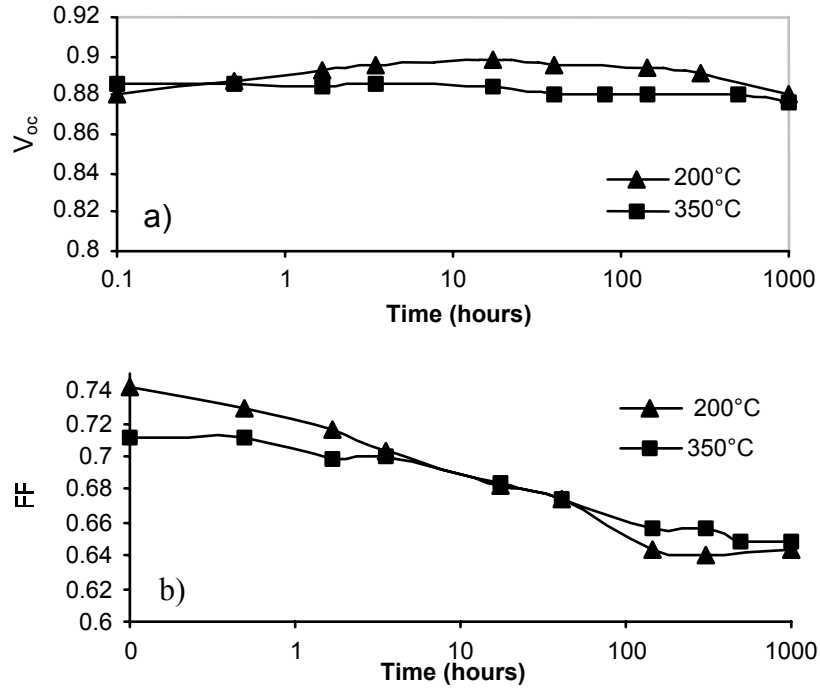
Fig. 19: Comparison of the values of V_{oc} (a) and of FF (b) for cells incorporating intrinsic layers deposited at 200 °C and 350 °C, as measured during light-soaking.

b) Silane dilution

Solar cells deposited in this series had an intrinsic layer thickness of 250-300nm (optimum thickness for a-Si solar cell). The dilution ratio (Hydrogen flux/silane flux) was varied here between 0 and 9. These amorphous silicon solar cells were degraded by light soaking of 1000h at 50°C.

a)   *b)*
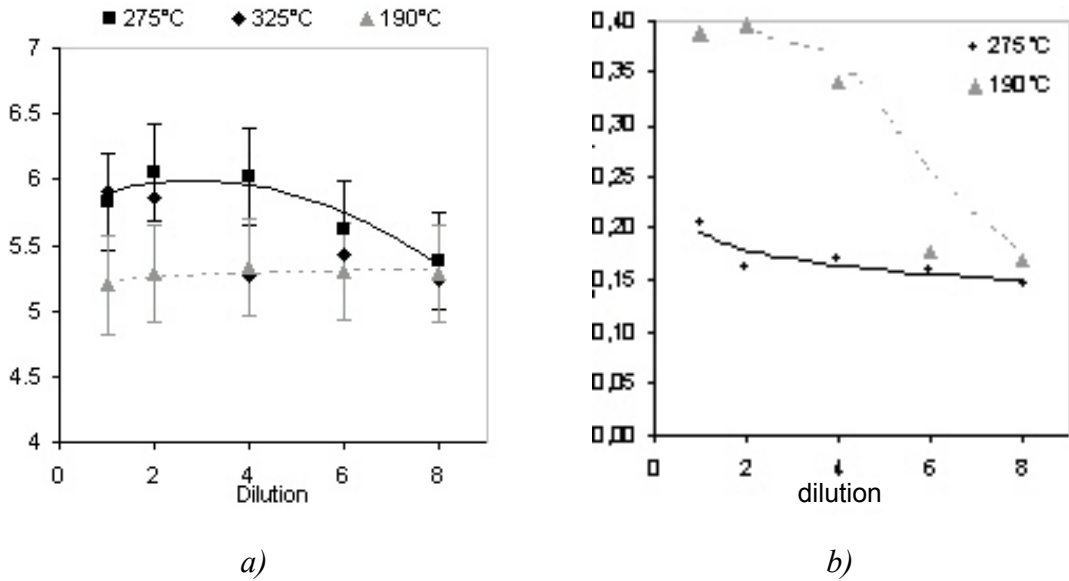
Fig. 20: Efficiencies (a) and Degradation (b) of amorphous silicon performances after light soaking. (For dilution=2 performance degradation can reach 40%)

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Fig. 20 shows that solar cells deposited at 190°C degrade drastically (more than 35%) if the dilution ratio is inferior to 6. Therefore, if amorphous silicon solar cells are deposited on plastics at low substrate temperatures it is necessary to deposit the "i" layer with dilution ratios higher than 6. Note, however, that on the other hand, a definite advantage of using lower dilution ratios is the higher deposition rate (5 Å/s at Dilution=2 and 3.5 Å/s at Dilution=8 for Ts=275°C) for comparable solar cell performances.

2.4 Transparent conductive oxides (TCO)

2.4.1 TCO technology development in our laboratory: ZnO by LP-CVD

As mentioned above, one of the main focus points of the first project year, was the development of improved TCO (transparent conductive oxide) layers. In our case, we have mainly worked on ZnO layers deposited by LP-CVD (low pressure chemical vapor deposition). These layers have been successfully used in our pin-type solar cells. Thereby they are deposited on glass substrates and constitute here the underlying layer on which all subsequent thin-film silicon deposition takes place. LP-CVD ZnO is also used, in our laboratory, for both pin-type and nip-type solar cells as "top" TCO layer.

Concerning the characterization of our ZnO layers, several additional methods other than the usual transparency and conductivity measurements have been explored by us. Optical reflection followed by a determination of the plasma frequency, and Hall effect measurements allow to decompose the conductivity into its two components: the carrier concentration and their mobility. First measurements of our standard ZnO layers show a higher carrier concentration compared to literature, but with mobility values approaching rather the lowest values given in literature. This indicates that the relatively good conductivity of our layer is basically due to a good doping efficiency. X-Ray measurements now allow us to observe the crystalline texture of our ZnO films. Measurements on our standard ZnO layers show a high preferential orientation along the (110) axis. A temperature series has been deposited and characterized. An increase of the deposition temperature up to 250°C reveals a significant drop of the conductivity due to a drop of the mobility, while the free-carrier concentration seems to remain constant. The X-Ray measurements show that at 250°C, the preferential growth orientation observed at our standard growth condition is no more present. The drop in the free carrier mobility is probably due to a reduction in grain size and more grain boundaries.

During the first year, a new large-area MOCVD deposition system was developed by us and put into operation. After optimization, 30x30cm^2 ZnO layers were obtained, having good TCO properties, similar to the ZnO layers deposited in the small area system: i.e. a resistivity of 14×10^{-4} Ωcm, a haze factor of 22 % at 600 nm, and an optical transmittance of more than 80% at 600 nm. The layer transparency is, thus, even slightly better than that of layers prepared in the small-
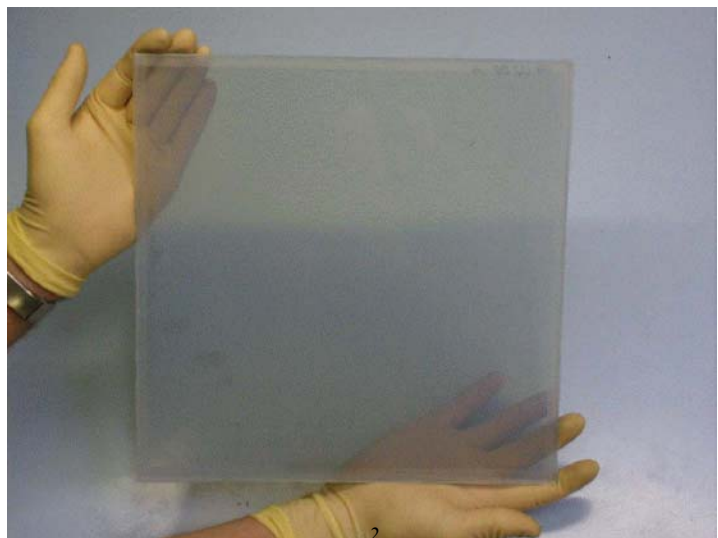

Fig. 21: Large-area (30x30 cm^2) deposition of LP-CVD ZnO on glass.

area system, due to a thinner thickness of the layer (2 μm while the ZnO layers of the small area system have a thickness of 2.6 μm). Sofar, a deposition rate of 8.3 Å/s was obtained for these large-area high-quality ZnO layers. The ZnO layer thickness varies by about 10% for a surface of 25x25 cm^2, this means that our deposition process has a relatively good homogeneity.

Further studies were conducted with the goal of clearly defining the process conditions for ZnO layers that are suitable for use within thin-film silicon solar cells in the substrate temperature range from 150°C to 200°C. A morphological transition has been observed around 170°C. Analysis by X-Ray spectroscopy detects a change of the preferential growth orientation, from the (002) to the (110) crystallographic direction. The morphological transition has a strong effect on the surface texture of the ZnO layers, as seen in images obtained by Scanning Electron Microscopy (SEM). Indeed, at 150°C, flat layers are deposited, whereas at higher temperatures one obtains strongly textured surface topography consisting of regular pyramids: a topography which is known to be very efficient for scattering the light inside the solar cell. It has to be noted that these pyramids are monocrystalline ZnO grains. Additionally, the morphological transition is accompanied by a strong variation of the resistivity, which drops almost two orders of magnitude to values of about 1.10^{-3} Ωcm just after the transition, i.e. for
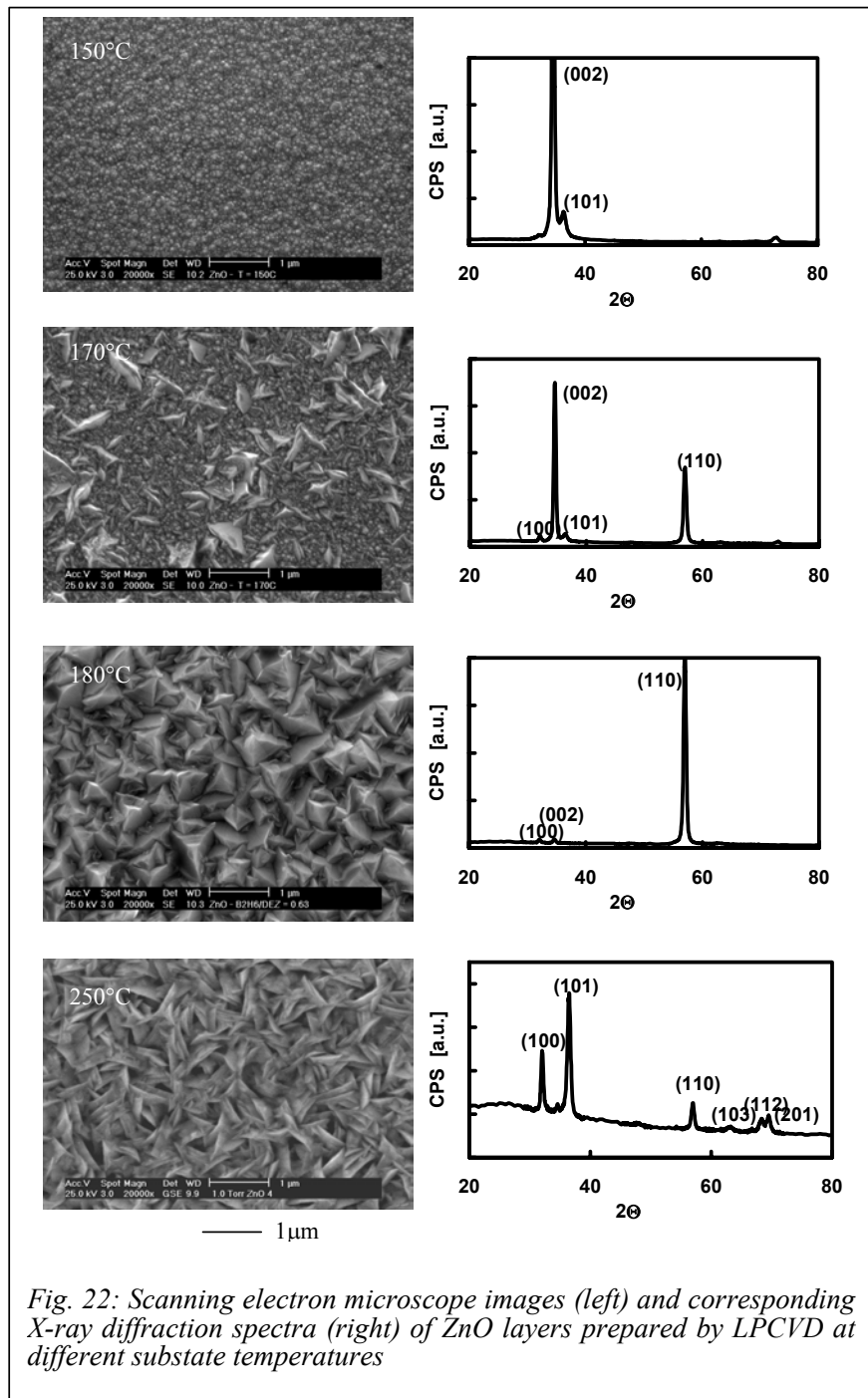

Fig. 22: Scanning electron microscope images (left) and corresponding X-ray diffraction spectra (right) of ZnO layers prepared by LPCVD at different substate temperatures

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precisely those temperatures for which a rough surface is observed. At 250°C, a new transition into randomly-oriented growth occurs. High deposition rates are still obtained, together with a rough surface, but the resistivity now becomes almost two orders of magnitude higher. This means that, there is only a small process window, between 180°C and 200°C, for which ZnO samples that are suitable as TCO for thin-film solar cells can be deposited. However, a higher deposition temperature could lead to a better material stability. Therefore, it is important to further explore this area of deposition parameters in order to try to find new regimes for the deposition of high quality ZnO.

2.4.2   Use of other TCO's

nip-type solar cells could sofar not be successfully deposited, with best efficiency results, on LP-CVD ZnO. We have therefore used for nip-type solar cells sputtered ZnO, deposited at IMT according to "standard, non-optimized" deposition procedures, as the underlying TCO layer. For comparison purposes, IMT has used commercial glass substrates covered with SnO2 layers. Finally, IMT also has "standard" ITO (indium tin oxyde) deposition technology (by sputtering); these ITO layers can be used as top TCO layers on solar cells. (Their use as underlying TCO layers must be avoided for thin-film solar cells, because of Indium diffusion/contamination during subsequent plasma deposition of thin-film silicon). Because of the relatively high cost of indium, ITO layers have not been used as top layers for our regular solar cell work, although they have been (and still are) used for specific applications (solar cells for watches, detectors, etc.).

2.5 Micromorph tandem cells

2.5.1 Micromorph tandem cells in p-i-n configuration

<u>a) Light-trapping issues of p-i-n/p-i-n Micromorph tandem cells</u>

One of the main tasks in this project is to achieve efficient light-trapping within the micromorph tandem cells. We first compared our LP-CVD ZnO with the best commercially available (but expensive) SnO_2 substrates from Asahi (type U), and found that our LP-CVD ZnO has a superior capacity for light-trapping. This is shown in Fig. 23 where the relative spectral response curves are given for two tandem cells, one on LP-CVD ZnO and one on Asahi SnO_2. While both top cells behave quite similarly, the enhanced scattering capability of the ZnO substrate has a remarkable effect in the longer wavelength range; it increases current generation substantially in the μc-Si:H bottom cell (This behaviour had already been observed in case of single-junction a-Si:H p-i-n cells for light wavelengths above ~500 nm, see Fig. 13). Indeed, if one uses SnO_2-clad glass substrates (Asahi type U) for micromorph tandem cells, the bottom cell thickness must be approximately 1 μm more, in order to generate the same current density as is generated by its counterpart deposited on IMT's in-house LP-CVD ZnO. This is an important result: it shows that it is absolutely necessary to have an efficient light-trapping in the infrared, this being

Fig. 23: Relative spectral response curves for 2 micromorph tandem solar cells: one on commercially available SnO_2 (Asahi U-type) and the other one on our in-house LP-CVD ZnO coated glass substrate. Note, that the amorphous and microcrystalline absorber layers have the same thicknesses in both cases and that the two cells possess identical back reflectors.

even more crucial for the micromorph tandem cell than for the single-junction amorphous cell. The practical benefit is a considerable reduction of the μc-Si:H cell thickness, a fact that heavily counts for, in the reduction of production time and costs.

In Fig. 24 we show the typical spectral reflection characteristics of the two corresponding glass/TCO/tandem cell systems. The measurements clearly reveal that in the case of p-i-n solar cells on ZnO a reduced reflection is present as compared to that which is measured for SnO_2-coated glass substrates; this can probably be explained by the greater roughness of the ZnO. The difference in the reflection characteristics of the two TCO's can be observed by the naked eye in a simple manner: In the case of LP-CVD ZnO, the micromorph tandem cell

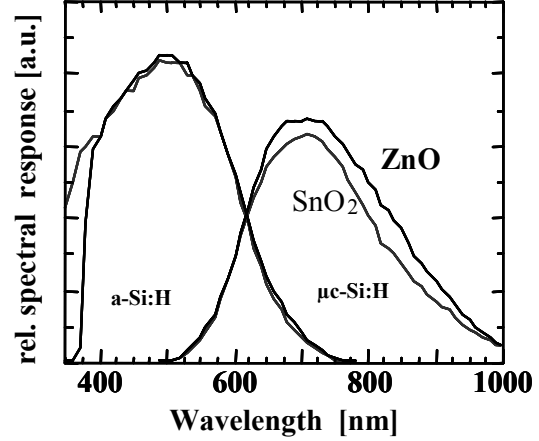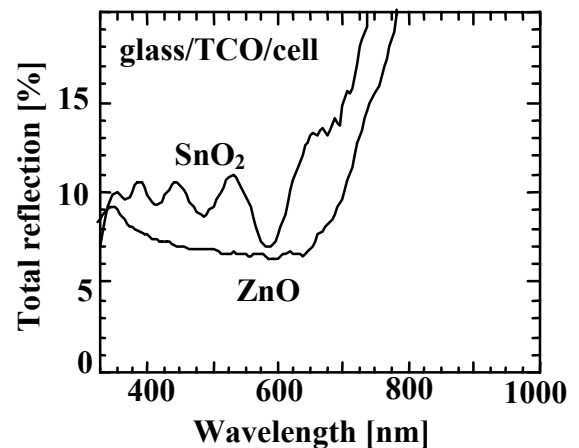*Fig. 24: Complete ("total") reflection characteristics of micromorph p-i-n/p-i-n tandem cells deposited on SnO_2 and on ZnO; the SnO_2-covered glass substrates are U-type substrates from Asahi Glass Corp.; the ZnO was deposited at IMT by LP-CVD.*

appears as black; in the case of SnO$_2$, the micromorph tandem cell appears to have a brighter colour. On the other hand: if we compare IMT's micromorph tandem cells, as deposited on ZnO layers with Kaneka's "hybrid" modules we can see that IMT's micromorph cells are darker; this corresponds to a higher absorption potential due to a better light-trapping in the solar cell design implemented by IMT.

This result proves once more that it was absolutely necessary for us at IMT to develop our own TCO-activity to demonstrate the full potential of our novel micromorph tandem cell concept and to remain competitive with Japanese R&D groups. Considering the reduction of production costs in future mass production of modules, it is obvious that plasma deposition of the silicon layers is only one aspect, the other important aspect is indeed light-trapping (which, in its turn, is, in the case of the p-i-n cell configuration, mainly determined by the front TCO, i.e. by the underlying layer on which all thin-film silicon layers are deposited).

b) Current balancing between top and bottom cell

The "micromorph feasibility study" had demonstrated that the microcrystalline absorber layer should not be thicker than 2 µm if a cost target of 2.54 SFr/W$_p$ is to be obtained. We, therefore, improved the micromorph cell with respect to top and bottom current balance while maintaining a µc-Si:H bottom cell thickness of 2 µm. Microcrystalline bottom cells of around 530 to 540 mV open circuit voltage (V$_{oc}$) were combined with amorphous top cells optimized and deposited around 200 ºC. These a-Si:H top cells have, at these relatively low deposition temperatures, a higher bandgap; this leads to typical V$_{oc}$-values of 880 to 900 mV. The results are given in Fig. 25. A full current balance between the a-Si:H top and the µc-Si:H bottom cell, each having 11.9 mA/cm^2, could be attained. Fig. 25 shows that high initial values of fill factor (over 73 %) and of V$_{oc}$ (1.413 V) were obtained for this tandem cell, yielding an initial cell efficiency of 12.3 %.
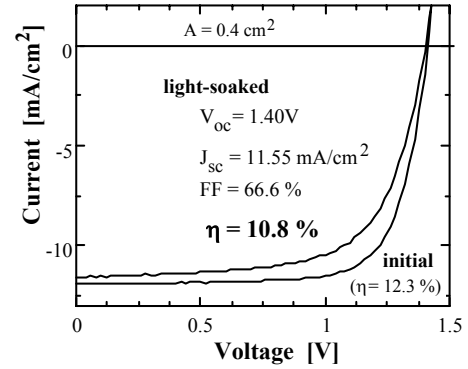
Fig. 25: AM1.5 I-V characteristics of a micromorph tandem test cell on LP-CVD ZnO in the initial state and after light-soaking (1000h @ 1 sun and 50ºC). The µc-Si:H bottom cell has a thickness of 2 µm.

In collaboration with Solaronix SA IMT had access to a reliable degradation system which allows us now to check in detail the stability of our solar cells. These light-soaking tests have been performed on our micromorph tandem cells yielding to a stabilized efficiency of 10.8 %.

c) Micromorph tandem cells with intermediate TCO layer

The high photocurrent potential of microcrystalline silicon solar cells can be optimally utilized with the application of an intermediate reflector between the amorphous silicon (a-Si:H) top and the microcrystalline silicon (µc-Si:H) bottom cell. This concept, introduced by IMT in 1996, permits an increase of the a-Si:H top cell current, as well as a reduction of the top a-Si:H cell thickness (the latter measure permits one to improve the stability of the tandem cell). By applying this intermediate TCO reflector

cell state	V$_{oc}$ (V)	FF (%)	J$_{sc}$ (mA/cm^2)	η (%)
initial	1.378	73.6	10.5	10.65
light-soaked	1.418	72.1	10.5	**10.73**

Table V: Micromorph tandem cell with an intermediate ZnO layer in the initial state and after 1300 h of light-soaking.

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concept, Kaneka Corp. (Japan) has recently demonstrated an initial cell efficiency of 14.5 %. We at IMT have recently again taken up research on this concept. Hereby it turns out that the structuring of well-defined cell areas by laser-scribing is a particularly difficult task, for these tandem cells with a conductive intermediate TCO layer. Nevertheless we obtained such "modified micromorph" tandem cells with an initial efficiency of sofar 10.65%. Examination, under prolonged light-soaking, of such tandem cells reveals a surprisingly high stability: As Table II reflects, there is no significant change in I-V characteristics after a period of over 1300 h.

Explanation: The tandem cell in Table III consists of a very thin a-Si:H top cell (<0.2 µm), which combined with a µc-Si:H bottom cell of only 1.8 µm thickness, leads to a large mismatch of the AM1.5 photocurrent (> 1 mA/cm^2). The fill factor is principally affected by the stable µc-Si:H bottom cell and less influenced by small alterations (by light-induced degradation) in the thin a-Si:H top cell.

d) Fabrication of amorphous single-junction and micromorph tandem mini-modules

Laser-patterned LP-CVD ZnO glass substrates have been used for the deposition of amorphous single-junction cells for the fabrication of "entirely" amorphous (p-i-n single-junction) and micromorph tandem (p-i-n/p-i-n) mini-modules, with integrated monolithic series connection. Both type of cells were deposited in a laboratory size reactor of the dimension 8x8 cm^2 and the laser-patterning has been carried out on our self-build laser-scribing equipment (see section 3.7).

Fig. 26 shows the AM1.5 I-V characteristics of a 12-segmented amorphous module and Fig. 27 the one of a 9-segmented micromorph tandem cell module, both in the initial and stabilized states (1000 h of light-soaking). These high values for the initial, but especially for the stabilized efficiencies, reveal that IMT has successfully managed to fabricate modules incorporating electrical series interconnection by laser-scribing, as well as use of IMT's own in-house LP-CVD ZnO technology.

Fig. 26: AM1.5 I-V characteristics of a 12-segmented a-Si:H single-junction module based on LP-CVD ZnO as front TCO. The module was light-soaked for 1000 h (1 sun @ 50 °C).

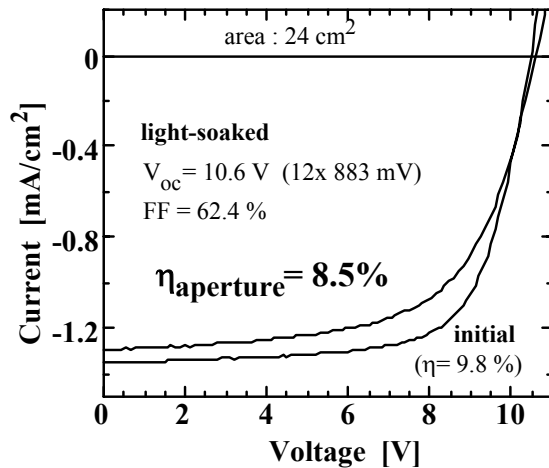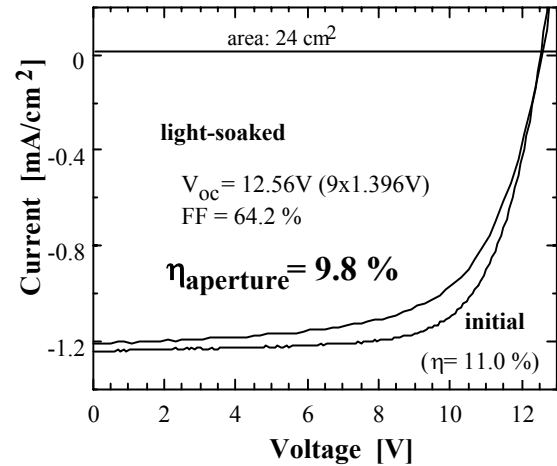*Fig. 27: AM1.5 I-V characteristics of a micromorph tandem cell module fabricated on LP-CVD ZnO-coated glass in the initial and light-soaked state. The µc-Si:H bottom cell has a thickness of 2 µm.*

Thanks to the improved light-trapping of our ZnO very high stabilized aperture module efficiencies of 8.5 % for the simple amorphous single-junction cell could be obtained. Taking the scribe loss area and slight inhomogeneities of the cell deposition into account these mini-modules confirm the high efficiency potential of our amorphous silicon single-junction solar cells (9 % stabilized, see section 3.3).

The micromorph tandem module shows initially an efficiency of 11 %, a fact that confirms the high quality of the electrical series interconnection that we have developed. After light-soaking a stabilized aperture efficiency of 9.8 % could be obtained. To mention is that the μc-Si:H bottom cell consists of a thickness of only 2 μm. With some further improvements in the amorphous top cell (e.g. higher deposition temperature) and by further optimising the electrical interconnection pattern obtained by laser-scribing (reduction of scribe-area related losses), stable module efficiencies above 10 % should be achievable.

The 9.8 % stable efficiency of the micromorph mini-module (with a 2 μm thick μc-Si:H bottom cell applied) corroborates the target of 9 % module efficiency for industrial production as assumed in the BFE/PSEL study of 1999.

2.5.2   Micromorph n-i-p tandem solar cells

Micromorph tandem solar cells, with following initial values were obtained:
V_{oc}=1.365V
FF=70.1%
J_{sc}(a-Si)=12.4mA/cm^2
J_{sc}(μc-Si)=11mA/cm^2
(η=10.5%)
As the Fig. 28 shows, the currents are not yet balanced which means there is still a good margin for further progress. This solar cell was deposited on as grown textured Ag.

Fig.28 Spectral response of nip/nip solar cell.

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2.6 Laboratory infrastructure

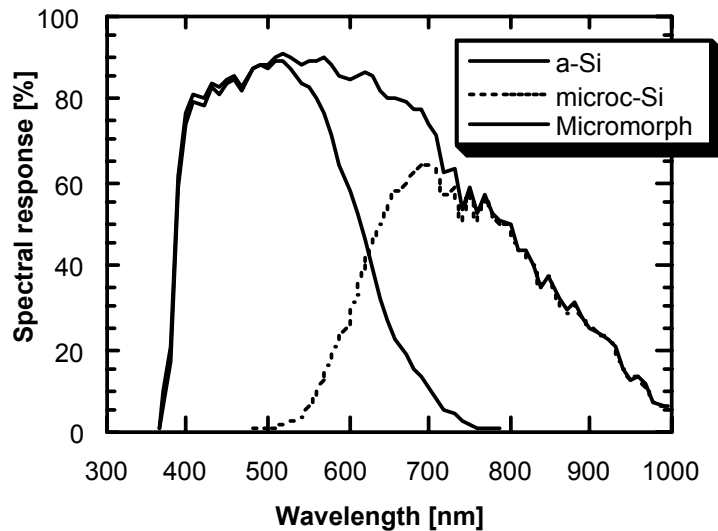### 2.6.1 Deposition equipment

A. *Plasma (PECVD) deposition systems*

1. Small substrate area (8 x 8 cm^2) systems
Several of the 7 deposition systems, built earlier by IMT were to a large extent modified during the project period 2000-02 (table IV).

System	Modification during 2000-2002	Present use
A	System entirely rebuilt Integrated VHF-electrode, load lock and gas purifier added	HPD (High Pressure Depletion) deposition of μc-Si layers and pin-type solar cells
B	2nd deposition chamber added	Deposition of μc-Si pin-type solar cells
C	None	Deposition of a-Si pin-type solar cells
D	System rebuilt	Deposition of thick a-Si nip-type detectors/solar cells
E	Load lock and integrated VHF-electrode added	Deposition of a-Si nip-type solar cells
F	None	Deposition of a-Si nip-type detectors/solar cells
G	The entirely rebuilt system contains: 2 new deposition chambers with integrated VHF-electrodes, load lock and gas purifier	Deposition of μc-Si nip-type solar cells

Table VI : Modifications and present use of small substrate area PECVD deposition

2. Large substrate area (30 x 30 cm^2) systems
2 large area systems were designed and built by IMT during the project period, using vacuum chambers and components (pumps, valves etc.) from a previous PECVD laboratory production equipment donated by Balzers AG.

Two-chamber system XL
A second chamber with gate valve was added to the initial single chamber system deposition system for amorphous silicon solar cells, thus enabling the fabrication of microcrystalline (and later entire micromorph) solar cells. The system features are:
- 1st chamber: load-lock and deposition of doped layers
- 2nd chamber: deposition of intrinsic layers
- both chambers are equipped with integrated VHF-electrodes (designed by IMT)
- automatized transport of substrate between chambers
- gas purifier for deposition of intrinsic microcrystalline layers
- substrate temperature: up to 250°C

Single-chamber system KAI^{TM}-S
The direct loading system is equipped with a Plasmabox-type electrode, adapted to VHF frequencies up to 40 MHz. The system is able to produce high quality amorphous silicon solar cells in a single reactor (project CTI-UNAXIS).

B. LP-CVD (low pressure chemical vapor deposition) of ZnO

An old large-area LP-CVD deposition chamber, donated by Siemens Solar, was modified and adapted to the IMT process for deposition of ZnO. The entire ZnO deposition system was rebuilt and consists now of 2 deposition chambers which can be operated alternatively

- a large area 30 x 30 cm^2 LP-CVD deposition chamber for standard ZnO deposition
- a small area 8 x 8 cm^2 LP-CVD deposition chamber for special/research on ZnO deposition
- a common thermal evaporation and gas flow control unit
- a common low-pressure control and pumping unit

C. Sputtering systems

The large area (MRC, 30 x 30 cm^2) and small area (Leybold, 5 x 5 cm^2) systems (acquired as second-hand systems already 8 years ago), were both partly revised and further improved for sputtering of metals (Ag, Al) and ITO (Indium Tin Oxyde).

D. Thermal evaporation systems

The now 15 years old Leybold thermal evaporation system needs regular maintenance and components replacement (turbo molecular pump crashed etc.) but still gives good service.

E. Plasma etching system

This is a very frequently used system which still gives excellent services after more than ten years of operation.

2.6.2 Laser structuring

Based on a special grant of 145 kCHF, allotted by the University of Neuchâtel in December 1999, our group was able to purchase 2 new lasers: i.e. a Nd:YAG (wavelength of 1064 nm, pulse frequency 1-100 kHz with max. average power of 10 W and max. pulse energy of 2 mJ in a 2 ns pulse) diode laser and a Nd:YVO$_4$ (wavelength of 532 nm, pulse frequency 1-100 kHz with max. average power of 3W and max. pulse energy 1mJ in a 2ns) diode laser. The lasers have been mounted onto an old laser scribing system we had obtained a few years ago, as a donation, from RWE-Schott Solar (Munich). This "old laser scribing system" has been suitably modified during 2000 by improving both hardware and software aspects. The new diode lasers that have been filled into our laser scribing system are very compact (see left-side photo) and allowed us to construct a suitable optical setup, so that we

can now use directly (without changing hardware), either the infrared or the green laser, as selected by computer control (Fig. 29).

The infrared laser is used to scribe the front ZnO contact, while the green laser is used for scribing the cell. The layout of the scribing system is foreseen for module fabrication (patterning with 3 scribe steps), for test cell patterning (patterning with one scribe step) and allows us now to work on a total area of 30x30 cm^2. The high pulse frequency enables us to scribe much faster and more precisely than with our previous 20 Hz laser, that had been purchased originally for degradation studies. A typical scribe experiment which took us before several hours is now completed within a few minutes.

Fig. 29: IMT's updated "old" laser scribing system (originally donated by Industry), containing now the two new diode lasers ($\lambda = 1064$ nm & 564 nm).

Even though this set-up certainly allows for scribing of test cells on large substrates (30 x 30 cm^2) there are still a number of major problems to be solved for reproducible structuring of <u>entire</u> amorphous and microcrystalline <u>modules</u>. IMT presently lacks the personnel for making further improvements in this sector. It has also no process backup from an experienced specialized industry. One has also to keep in mind that a commercial module structuring system cost around 500 kCHF and includes process backup, whereas IMT only had a grant of 145 kCHF for this sector and had to develop all scribing process sofar without any external help.

2.6.3 Characterization infrastructure

a) TEM and Raman

The study by Transmission Electron Microscopy (TEM) of the microstructure of microcrystalline silicon (µc-Si:H) conducted in our group has revealed that this material, when incorporated in standard microcrystalline solar cells, is a complex mixture of (nano)-crystalline phase, amorphous phase, grain boundaries and voids. A typical microstructure consists of conical conglomerates that are made up of nanocrystallites, merging, after having reached the so-called "coalescence threshold", into columns. As TEM is a destructive technique, a further original approach introduced by us here has been to apply Raman spectroscopy for the monitoring of the

Fig.30: MicroRaman set-up now available at IMT

cristallinity of entire solar cells in a non-destructive manner. Raman spectroscopy is a fast and non-destructive tool that can be used to analyse the crystalline fraction in µc-Si:H layers on glass. Typically, a Raman spectrum consists of peaks at different wave numbers that are assignated to three phases: amorphous silicon, crystalline silicon and defective silicon (grain boundaries). The investigation of crystalline fraction measurements of i-layers incorporated into solar cells was executed with a Micro-Raman set-up available at the Centre Suisse d'Electronique et de Microtechnique (CSEM) that has been lent to our group, and refurbished by us. (see Fig.30).

With solar cells fabricated in both the nip- and the pin- configurations on transparent substrates, it has been observed that neither the glass, nor the TCO layer hinder the Raman scattering from silicon-based material. Thus it is possible to deduce material crystallinity from both the front and back sides of the solar cell; in general these crystallinities are not equal, according to our TEM observations. This approach has been extremely successful, since a linear relationship between the solar cell open-circuit voltage (V_{oc}) and the average Raman-crystallinity of the material averaged over both the p-i and n-i interfaces could be observed, for a large set of solar cells representative of our in-house VHF-GD technology for nip and pin solar cells (see Fig. 6). This is the first time, in the field of microcrystalline solar cells, that such a simple relationship between material microstructure and device characteristics has been reported. The corresponding paper, presented by our Ph.D. student, Corinne Droz, received the "Young Researcher Award" for the field of thin-film silicon at the 3rd World PV Confrerence held in Osaka in May 2003.

Systems	Field	Analysed properties	Brand	Remarks
Steady-State-Photocarrier-Grating (SSPG)	L	Ambipolar diffusion length $\mu^0 \tau^0$ product	IMT-built	HeNe laser, low light intensity
SSPG	L	Ambipolar diffusion length $\mu^0 \tau^0$ product	IMT-built	Kr laser, 500 mW
Time-Of-Flight (TOF)	L	Carrier $\mu\tau$ product, drift mobilities	IMT-built	pumped Dye Laser, 400-700 nm
Dark-/Photo-conductivity	L	Conductivity, activation energy	IMT-built	300-600 K
Photothermal Deflection Spectroscopy (PDS) /Absolute Constant Photocurrent Measurement (A-CPM)	L	Sub bandgap optical Absorption, defect density	IMT-built	500-1800 nm
Diffusion length setup	L	Diffusion length	IMT-built	
UV/VIS/IR spectrometer Lambda 900	L	Optical absorption, energy gap	Perkin-Elmer	
FTIR Spectrometer 1720x	L	Optical absorption, hydrogen bonding/content	Perkin-Elmer	
Optical Spectrometer	O	Light spectra	Ocean Optics	250-1000 nm
Profiler Alpha-step 200	L/C	Thickness profiles	Tencor	
AFM/STM microscope VISTA 100	L/C	Surface morphology	Burleigh	7 and 180 mm scanners, 15x15 cm samples
Optical microscope	L/C	Surface morphology	Leitz	
Light degradation setup	C/L	Light induced degradation	Solaronix	1000 Wm^2, 50 °C
Solar simulator	C	I(V) characteristics	Wacom	2 light sources
Variable Intensity Measurement (VIM)	C	Shunt resistance, material quality ($\mu^0 \tau^0$ product)	IMT-built	
Spectral response (SR)	C	Collection efficiency	IMT-built	300-1000 nm
Spectral response (SR)	C	Collection efficiency	IMT-built	400-1100 nm
Light-Beam Induced Current (LBIC)	C	Current collection map	IMT-built	15x15 mm scan
LBIC	C	Current collection map	IMT-built	30x30 cm scans

Tab. VI: Overview of the now available characterization systems at IMT. Field indication refers to cells (C), layers (L) or other (O).

3 Conclusions and Perspectives

The main goal for our OFEN project 2000-2002, 12 % stabilized efficiency for p-i-n and n-i-p micromorph tandem cells for the microcrystalline absorber layer, could indeed not yet be reached. In fact sofar, we have "only" obtained 10.8 % stabilized efficiency for micromorph p-i-n tandem cells and 10.5% initial efficiency for micromorph n-i-p tandem cells. However, a number of **industrially relevant results have been achieved,** namely:

For **glass superstrate/p-i-n type cells** and modules in combination with IMT's LP-CVD ZnO technology we have obtained:
- laser-scribing of mini-modules for both amorphous single-junction and micromorph tandems on 8x8 cm^2 lab size substrates with stabilized efficiencies of 8.5 % respectively 9.8 %.
- first micromorph test cells with implemented intermediate reflector of 10. 7 % stable efficiency

Our collaboration together with Unaxis AG Balzers showed that these results already form the basis for an economically advantageous mass production of amorphous silicon modules on modern (KAI-type) production equipment for thin-film silicon layer. The mass production of micromorph tandem modules requires dedicated further research in close collaboration between industry and IMT.

For **substrate/n-i-p type cells** we have obtained
- Amorphous silicon single-junction cells were fabricated on flexible substrates with short-circuit currents of 14.4 mA/cm^2 on PET and 15.3 mA/cm^2 on glass substrates
- Single-junction microcrystalline silicon solar cells with a conversion efficiency of 9.2%
- Micromorph tandem solar cells were deposited with an initial conversion efficiency of 10.5 %

Intensive collaboration with "our" start-up firm, VHF-Technologies SA Le Locle, has been re-initiated; we have tuned ourselves to their immediate requirements, which are related to roll-to-roll production of single-junction amorphous silicon cells on cheap plastics.

In the coming years, our work will have to develop under 2 aspects:
- Intensified collaboration with "our" associated Industrial firms, i.e. with Unaxis AG Balzers (for the glass/p-i-n configuration) and VHF-Technologies SA LeLocle (for the substrate /n-i-p configuration). Our programme here will depend on their specific requirements.
- Innovation on the basic research front, to provide results based on new methods that will be of interest to Industry only 3 to 5 years from now.

It is thereby clear that we have to be less ambitious and more focused on specific partial goals, in order to be successful. We are, after all in company with much larger groups in Japan (Kaneka Corp., Canon, MHI, Sharp, AIST Tsukuba, many other labs), in Germany (Jülich) and in the USA (ECD, Unisolar, other labs) that also have solid experience and can in most cases base their work on an equipment park that has easily cost 5 to 10 times what has been invested in IMT.

Still, there is absolutely no doubt that IMT Neuchâtel continuous, in spite of this increasingly stiff competition, to be world-wide one of the leaders in the field of thin-film silicon solar cells and modules.

Thanks to the newly established collaboration with Unaxis Solar, IMT is now entering a totally different phase. So far, all thin-film photovoltaic module manufacturers have built their own in-house equipment. This is comparable to the situation up to the 19th century where every printing company/book publishing house had to assemble its own, individual printing press: naturally, this led to expensive books. At a given moment (around 1900) commercial rotary presses became available from professional manufacturers of printing equipment. Immediately, printing press output was tremendously increased and prices were cut, ensuring rapid overall dissemination of printed books.

Transferred to the PV field, this is exactly what Unaxis Solar is planning to do in the next few years, in close collaboration with IMT Neuchâtel: make available professional high-throughput production equipment. There is absolutely no doubt that this approach, if successful, will lead to a drastic decrease in PV module price. **In order for the Unaxis Solar approach to be successful, continued, targeted scientific and technical backup by IMT Neuchâtel is absolutely essential during the next few years.**

4 Collaboration with other research groups and with industries

National:

EPF Lausanne (Dr. Ch. Hollenstein, Dr. A.A. Howling, L. Sansonnens)	:	High-rate deposition of microcrystalline silicon, large-area deposition, VHF plasma diagnostics
Institut de Physique, Université de Neuchâtel	:	XRD (X-ray diffraction)
Unaxis (A. Büchel)	:	large-area and high-rate deposition of a-Si:H p-i-n solar cells on glass substrates
VHF-Technologies S.A., Le Locle (Dr. D. Fischer)	:	deposition of n-i-p a-Si:H solar cells on plastic substrates
PSI Villigen (Dr. R. Morf)	:	light-trapping

International:

Forschungsanstalt Jülich (Dr. B. Rech and collaborators)	:	Micromorph cells, RF deposition (E.U. project "DOIT")
Academy of Sciences Prag (Dr. M. Vanecek)	:	Optical characterisation, light-trapping (E.U. project "DOIT")
NREL (National Renewable Energy Laboratory, Dr. K. Emery)	:	Certification of test cells
Fraunhofer Institut Freiburg (Drs. S. Brachmann, W. Warta)	:	Calibration of solar simulator and reference cells, certification of cells
RWE-Schott Solar (Putzbrunn, Drs H.Schade and P. Lechner)	:	Donation of Laser scribing system, "Micromorph feasibility Study", collaboration within E.U. project "DOIT"
Siemens-Solar GmbH (Dr. K. Ufert)	:	light-trapping
Uni-Solar (Dr. S. Guha, Detroit USA)	:	µc-Si:H bottom cells for triple-junction devices including a-SiGe:H middle cell
		(sofar not successful, because of transport problems: cells do not withstand transport by airmail packets, before full completion of multi-junction device)
TSI St. Etienne (F) (Dr. O. Parriaux)	:	light-trapping

Tab. XI: Overview of national and international groups having some form of collaboration with the IMT.

5   List of symbols

a-Si:H	: hydrogenated amorphous silicon
μc-Si:H	: hydrogenated microcrystalline silicon
V_{oc}	: Open circuit voltage [V]
J_{sc}	: short-circuit current density [mA/cm^2]
FF	: Fill factor
η	: Solar cell efficiency [%]
VHF	: Very High Frequency
GD	: Glow discharge
CVD	: Chemical vapour deposition
LP-CVD	: Low pressure chemical vapour deposition
HW	: Hot wire
σ_{photo}	: photoconductivity [Ω^{-1}cm^{-1}]
L_{amb}	: ambipolar diffusion length [cm]
SSPG	: steady-state photocarrier grating
$\mu\tau$-product	: mobility ∞ lifetime product [cm^2/V]
$\mu^0\tau^0$-product	: normalised mobility ∞ lifetime product [cm^2/V]
E_{gap}	: Energy bandgap of a semiconductor [eV]
E_F	: Fermi level
PDS	: Photothermal Deflection Spectroscopy
CPM	: Constant Photocurrent Method
TOF	: Time of Flight
VIM	: Variable Intensity Measurement
R_{SC}	: short circuit resistance [Ω]
R_S	: series resistance [Ω]
R_P	: parallel resistance (shunts) [Ω]
$V_{Collection}$	: collection voltage [V]
d	: intrinsic layer thickness [μm]
T_s	: substrate temperature [ºC]
TEM	: Transmission Electron Microscopy
AFM	: Atomic Force Microscopy
SEM	: Scanning Electron Microscopy
AES	: Auger Electron Spectroscopy
TC	: relative temperature coefficient

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7 Appendix : Comparison of project goals and results

7.1 Comparison of project goals and results obtained of p-i-n configurated solar cells & modules, LP-CVD ZnO and laser scribing

Goals of the project	Achieved results
Microcrystalline silicon p-i-n solar cells:	**Microcrystalline silicon p-i-n solar cells**
V_{oc} >530mV	Microcrystalline p-i-n cells were directly obtimised on amorphous top cells, hereby the V_{oc}-values of these bottom cells are in the range of 520 to 540 mV, leading to V_{oc}-values of 1.40 to 1.420V for the tandems
FF >68%	In the micromorph tandem cells fill factors of up to 75 % could be prepared
J_{sc}>13.5 pour λ>550 at thickness $\leq 2\mu$m	Light-trapping was obtimised for μc-Si:H bottom cells of 2 μm thickness; the total current potential of the a-Si:H top and μc-Si:H bottom cell together is about 24 to 25 mA/cm^2 for these kind of bottom cells
rate=10 A/s	All μc-Si:H bottom cells were deposited at a rate of ~ 5 Å/sec. In addition we were able to deposit μc-Si:H films at rates up to 25 Å/sec
Amorphous silicon p-i-n solar cell	**Amorphous silicon p-i-n solar cell**
V_{oc} = 880mV (stabilized)	<u>initial</u> p-i-n cell of 0.25 μm thickness on LP-CVD ZnO confirmed by NREL with an <u>efficiency of 10.6%</u> (V_{oc} = 900 mV, FF = 73.74 %, J_{sc} = 15.96 mA/cm^2)
	<u>light-soaked</u> (700h under 0.75 sun and 50 ºC) p-i-n cell of 0.25 μm thickness on LP-CVD ZnO confirmed by NREL with an efficiency of <u>9.51 %</u> (V_{oc} = 895 mV, FF = 67.04 %, J_{sc} = 15.85 mA/cm^2)
FF = 68% (stabilized in tandem)	FF of 66.6% could be obtained in micromorph tandems after degradation (initial 74-75 %)
J_{sc}=13.5 mA/cm^2 (stabilized in tandem)	Sofar a J_{sc}-value of about 11.6 mA/cm^2 after degradation could be obtained within the tandem cell. The problem of the low current is due to the low current generated in the a-Si:H top cell and not due to the μc-Si:H bottom cell.
Micromorph p-i-n/p-i-n tandem cells	**Micromorph p-i-n/p-i-n tandem cells**
η = 12 % at 2 μm bottom cell thickness	η = 10.8 % at 2 μm bottom cell thickness on LP-CVD ZnO (V_{oc} = 1.40 V, FF = 66.6 %, J_{sc} = 11.55 mA/cm^2)

Structuration of test cells	Monolithic series interconnection by laser-scribing for module fabrication
	12-segmented a-Si:H p-i-n modules on LP-CVD ZnO with a stabilized efficiency of 8.5 % could be fabricated (12x883 mV (V_{oc}=10.6V), FF = 62.4% on 24 cm^2)
	9-segmented (p-i-n/p-i-n) micromorph tandem modules on LP-CVD ZnO with a stabilized efficiency of 9.8 % could be obtained (9x1.396 V (V_{oc}=12.56V), FF = 64.2 % on 24 cm^2); the μc-Si:H bottom cell has a thickness of 2 μm.
Optimisation of light-trapping	**Optimisation of light-trapping**
Reduction of LP-CVD ZnO thickness of 2.6 μm to 1 to 1.5 μm for glass/front TCO	Improved Haze at ZnO thicknesses of ~2.2 μm
Check of stability of LP-CVD ZnO	deposition temperatures for LP-CVD ZnO over 400 ºC have been studied, however these films show higher resistivities
buildup of large area LP-CVD deposition system (30x30 cm^2) and optimisation of ZnO films	homogeneous ZnO films over 30x30 cm^2 could be prepared. No problem occurred in the transfer from the small reactor (10x10 cm^2) to the large system
Large-area PECVD deposition (30x30cm^2)	**Large-area PECVD deposition (30x30 cm^2)**
first micromorph tandem test cells	work on large-area a-Si:H top cell deposition has not been started
μc-Si:H bottom cells with 12 mA/cm2 for λ>550 nm	first μc-Si:H p-i-n cells have been fabricated
μc-Si:H deposition rates for films at ≥ 7 Å/sec	Within DOIT project rates for μc-Si:H films of 4 to 10 Å/sec could be achieved

7.2 Comparison of project goals and achieved results of n-i-p configurated solar cells

Goals of the project	Achieved results
Amorphous silicon n-i-p solar cell	**Amorphous silicon n-i-p solar cell**
V_{oc} = 950mV	V_{oc1} =893mV (initial), V_{oc1} = 887mV (estimated after degradation)
	V_{oc2} = 0.845 mV
FF = 68%	FF_1 = 71.8% (initial), FF_1=68.3% (estimated after degradation)
	FF_2 = 62%
	I_{sc1} = 13.2mA/cm^2 (initial), I_{sc1}=12.4 (estimated after degradation) I_{scmax}=15.3 mA/cm^2 (initial with reflector)
	I_{sc2} = 11.5 mA/cm^2
	Remarks : - Index 1 refers to optimized solar cells, that were, however not measured in the degraded state, but where the degradation was only estimated (at 15% of the initial efficiency value). - Index 2 refers to results obtained with solar cells that are not fully optimized but are measured after a real degradation (which turned out to be 15%)
Microcrystalline silicon n-i-p solar cell	**Microcrystalline silicon n-i-p solar cell**
Voc >530mV	Voc=520mV
FF >68%	FF=73%
Isc>13.5 pour λ>550	$I_{sc\,tot}$=24.2 mA/cm2, I_{sc} λ>550=16 mA/cm^2
Thickness <2μm, Deposition rate=10 Å/s	Thickness =2.6μm, Deposition rate=2.4 Å/s
Micromorph tandem n-i-p solar cell	**Micromorph tandem n-i-p solar cell**
	Voc=1.365V
	FF=70.1%
I_{sc} >12.3mA/cm^2	I_{sc} (a-Si) =12.4mA/cm^2 , (I_{sc} (μc-Si) =11mA/cm^2)
η=12% stabilized	η=10.5% initial