Complete microcrystalline *p-i-n* solar cell—Crystalline or amorphous cell behavior?

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Complete μc-Si:H *p-i-n* solar cells have been prepared by the very high frequency glow discharge method. Up to now, intrinsic μc-Si:H has never attracted much attention as a photovoltaic active material. However, an efficiency of 4.6% and remarkably high short circuit current densities of up to 21.9 mA/cm^2 due to an enhanced absorption in the near-infrared could be obtained. First light-soaking experiments indicate no degradation for the entirely μc-Si:H cells. Voltage-dependent spectral response measurements suggest that the carrier transport in complete μc-Si:H *p-i-n* cells may possibly be cosupported by diffusion (in addition to drift).

Microcrystalline silicon (μc-Si:H) consists of small crystalline grains (10–500 Å) embedded in an amorphous silicon matrix. The deposition of μc-Si:H can be generally implemented through strong hydrogen dilution of the silane gas in a rf glow discharge plasma at temperatures around 200–300 °C and at high power densities. Depending on the deposition conditions, the crystalline fraction of the material can be varied up to 80%–90%.

Doping experiments have shown μc-Si:H to be an excellent material for both $\langle n \rangle$- and $\langle p \rangle$-type contacts and barrier layers in semiconductor devices such as solar cells. Compared to doped amorphous silicon or amorphous silicon alloys, higher conductivities are achievable for μc-Si:H, thanks to the more efficient doping of the crystalline phase.[1-4]

The aim of the present study is to show that undoped or slightly compensated μc-Si:H has the potential to be a very interesting new photovoltaic thin film material, and that in contrast with the established general viewpoint.

Different characterization methods as electron spin resonance (ESR),[5,6] field effect measurements,[7] and others[8,9] suggest for the μc-Si:H a defect-rich region at the grain boundaries or amorphous zones, with defect densities in the order of 10^{17}–5×10^{18} cm^{-3}, distributed energy-wise over the whole energy gap. These high defect densities probably hindered up to now the use of undoped μc-Si:H material for solar cell applications. Very little work has been done concerning undoped μc-Si:H in *p-i-n* cells.[3,10-12] However, investigations on films led to the general recognition of the fact that undoped or compensated μc-Si:H is more stable under light exposure than a-Si:H.[3,5,13,14]

For the deposition of all types of μc-Si:H ($\langle n \rangle$, $\langle p \rangle$, and $\langle i \rangle$ layers) we used a capacitively coupled very high frequency glow discharge (VHF-GD) plasma reactor at an excitation frequency of 70 MHz, as described elsewhere.[15] Compared to conventional 13.56 MHz plasma excitation, the VHF technique allows higher deposition rates for both a-Si:H and μc-Si:H. Thus, typical deposition rates of 1 Å/s were obtained for the μc-Si:H $\langle i \rangle$ layer at a plasma power density of 60 mW/cm^2.

As-grown undoped μc-Si:H shows a rather $\langle n \rangle$-type character, probably due to oxygen and other contaminants and possibly, also due to structural effects. In previous studies[3,14] we have presented results on the properties of compensated μc-Si:H material, as obtained by adding small traces of boron in the ppm range into the gas phase. Similar results have been published by another group.[10] These results were used for the deposition of the $\langle i \rangle$ layer in the cells. Recently developed $\langle p \rangle$-window layers,[3,4] less critical $\langle n \rangle$ μc-Si:H back contacts,[1,2] together with compensated $\langle i \rangle$ layers have all been applied in the cell. For the transparent conduction oxide (TCO)-coated glass substrate we used both SnO$_2$ and ZnO. The deposition temperatures for the layers were 170 °C for the $\langle p \rangle$ and 220 °C for the $\langle i \rangle$ and $\langle n \rangle$ layers, respectively. The thicknesses were 150 Å for the $\langle p \rangle$ layer, 1.7 μm for the $\langle i \rangle$ layer, and 400 Å for the $\langle n \rangle$-layer.

As is well known, microcrystalline silicon shows a weaker absorption for the short wavelengths than amorphous silicon; however, in the near infrared it has an enhanced absorption, as represented in the photothermal deflection spectroscopy (PDS) spectra of Fig. 1. Similar absorption spectra for μc-Si:H have been published by other groups.[16,10] We
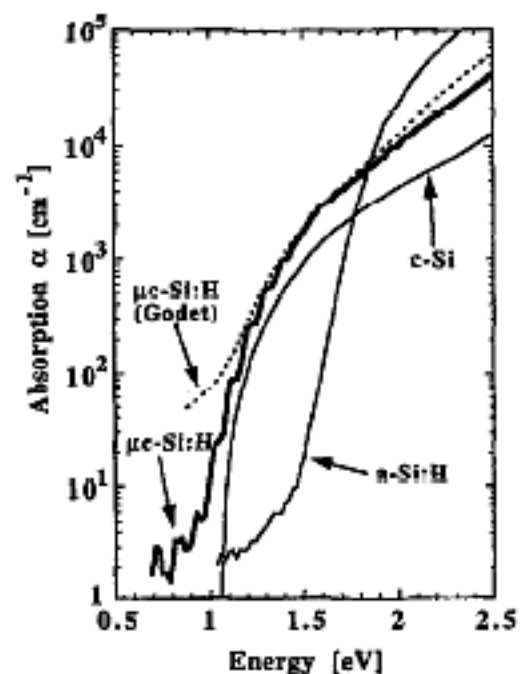

FIG. 1. Absorption spectra by PDS and transmission spectroscopy of a compensated 1.8-μm-thick μc-Si:H film in comparison with the absorption of crystalline and amorphous silicon. Also added are μc-Si:H absorption data obtained by another group (Ref. 16).
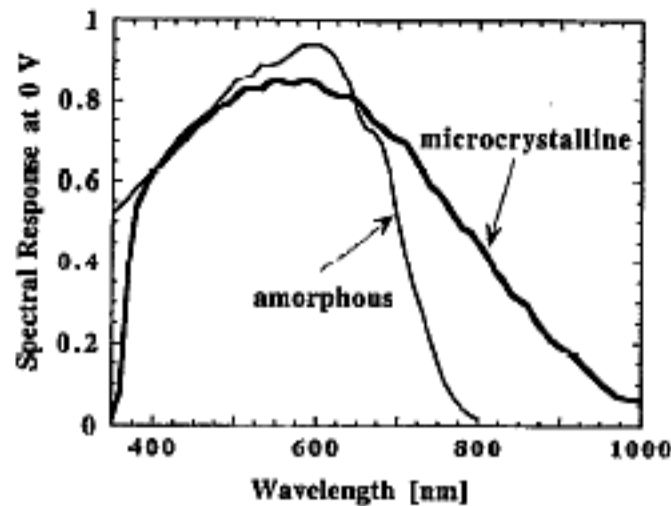
FIG. 2. Spectral response of a 1.7-μm-thick entirely μc-Si:H p-i-n solar cell in comparison with an a-Si:H cell. The integration for AM1.5 conditions (100 mW/cm^2) leads to a short circuit current density of 21.9 mA/cm^2. (The μc-Si:H cell is deposited on ZnO coated, the a-Si:H on SnO$_2$ coated glass).

FIG. 3. Stability behavior of an all μc-Si:H p-i-n solar cell under long-term light exposure (~90 mW/cm^2 AM1.5, $T=47\pm2$ °C). For comparison, typical results of degraded a-Si:H single p-i-n cells (>10% efficiency) obtained by the same degradation light source are also plotted.

found (see Fig. 1) a significantly lower subgap absorption for our material as compared to that found by other groups. The subgap absorption of the μc-Si:H reaches the one obtained for good amorphous material in the annealed state.

Compared to a-Si:H, the μc-Si:H absorption opens a potential of additionally making use of the suns spectrum of the near infrared to a higher extent and, thus, increasing the short circuit (J_{sc}); however, to this end, the $\langle i \rangle$-layer thickness has to be increased or more sophisticated light trapping has to be applied as usual. Indeed, spectral response (SR) measurements in Fig. 2 of our μc-Si:H p-i-n cells confirm clearly higher infrared absorption. As a surprising fact, we found that also in cells with thicknesses as high as 1.7 μm, practically all photogenerated carriers can be collected, which is in contrary not the case for a similar thick amorphous p-i-n cell. For AM1.5 conditions, we obtained a short curcuit current density of 21.9 mA/cm^2 which is significantly higher than the highest value ever reported for amorphous silicon solar cells and which fulfills the prediction of the absorption spectra (Fig. 1). The good collection saturation at zero bias for the 1.7-μm-thick cell let us conclude that the short curcuit current can be further increased by increasing the $\langle i \rangle$-layer thickness. The best cells (1.7 μm) showed an efficiency of 4.6% (active area 5 mm^2), whereas the obtained open circuit voltages (V_{oc}) were between 340 and 389 mV and the fill factors (FF) between 40% and 60%. The potential in further increasing the efficiency lies in the optimization of the p-i interface for achieving higher V_{oc} values. We have previously shown[3] in a different study that V_{oc} values as high as 600 mV are feasible by introducing a-Si:H buffer layers.

In the following, the important problem of *stability* under long-term light-soaking conditions was tested for our new cell. The degradation procedure was taken out as it is recommended from the National Renewable Energy Laboratory (NREL, USA) for amorphous silicon solar cells (100 mW/cm^2 AM1.5, 1000 h, 50 °C).[17] The microcrystalline cells were exposed to an AM1.5 light source of 90 mW/cm^2 (an array of 5 Philips PL-L 24 W/95/4P lamps) over more than 640 h. The temperature was kept constant at 47 ± 2 °C. The

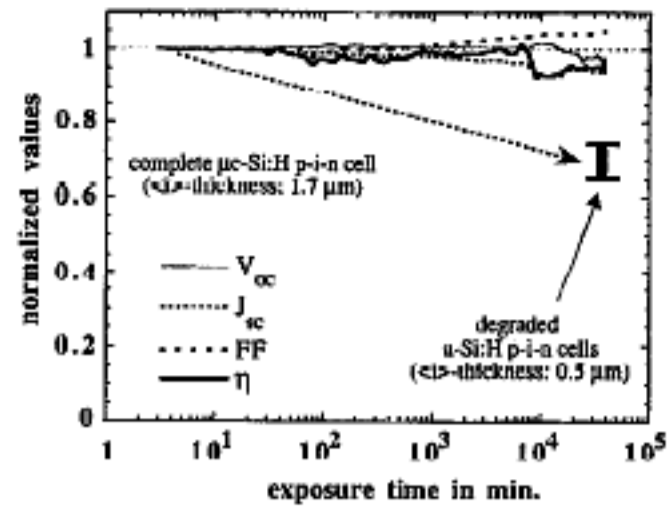surprising result is given in Fig. 3, where the normalized values of J_{sc}, V_{oc}, FF, and η are plotted over the exposure time and compared with our typical standard amorphous p-i-n solar cells of >10% efficiencies ($\langle i \rangle$-layer thickness ~0.5 μm). The precise characterization by SR and standard current voltage (I-V) measurements of the microcrystalline cells before and immediately after the degradation (without an annealing) results in the following changes (including fluctuations of the apparatus): $\Delta V_{oc} < 2\%$, $\Delta J_{sc} < 1\%$, ΔFF $<2\%$. Compared to the high efficiency amorphous cells, there seems to be no destructive light-soaking effect present in the μc-Si:H solar cell devices. The stability of μc-Si:H against light soaking has already been found from film degradation studies. This comparison, however, might yet not be deemed to be representative, as we only have a cell with 4.6% conversion efficiency, and as it is known, a-Si:H cells with, i.e., 5% efficiencies are less affected by light soaking as high efficiency cells (>10%). On the other hand, one has to note that both the FF and the high value of J_{sc} are *not* affected by light soaking, whereas the limiting factor for our cells is only the low V_{oc} value.

A closer look to the spectral response measurements gives more insight in the transport mechanism of entirely microcrystalline cells. While, for a-Si:H cells drift collection is the predominated transport mechanism, carrier diffusion is the governing mechanism in crystalline silicon cells. The two cases are represented in Fig. 4(b) for the normalized voltages and currents. However, the μc-Si:H p-i-n cell in Fig. 4(a) shows a carrier collection behavior which seems to lie between a-Si:H and c-Si. At bias voltages still far above the V_{oc} value for AM1.5, a positive SR signal can be measured which should correspond, according to a general rule, to a partly diffusion-supported carrier collection. The SR(V) collection data have been obtained by the integration of the SR at a given voltage and the sun spectrum AM1.5. One more indication for transport supported by carrier diffusion could be deduced from the strong peripheral effect observed in the μc-Si:H cells, which has to be carefully taken into account for efficiency measurements. We suppressed for our efficiency measurements the peripheral effect by illumination
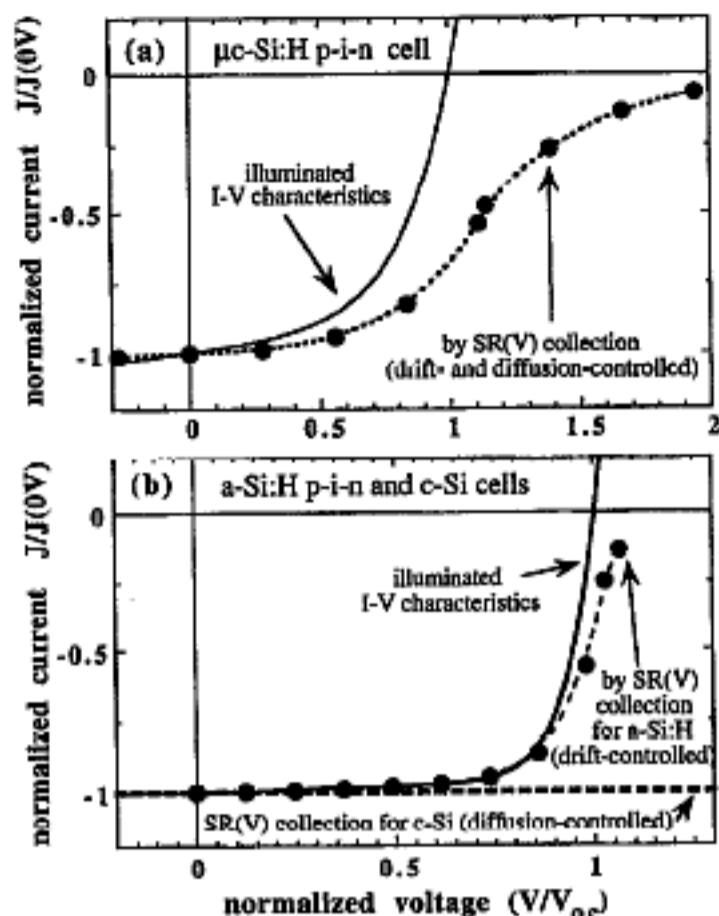
FIG. 4. Comparison of voltage-dependence collection and illuminated *I-V* characteristics of μc-Si:H, a-Si:H, and c-Si solar cells. The full points stand for the calculated current densities obtained by the SR collection at a given voltage V and the solar spectrum AM1.5.

through an orifice which corresponds to the active area and further we proved the existence of a strong peripheral contribution by light beam induced current (LBIC) measurements. Thus, special care is recommended when small active cell areas have to be characterized. If a large area light source is applied, too high efficiencies are measured[12]—as the authors have not mentioned this problem—we assume they did not take this effect into account.

The presented results have shown that μc-Si:H has the potential to become a new photovoltaic thin film material which merits broader investigations. The entirely μc-Si:H

cell is the first thin film device, exclusively based on silicon alone, that shows an enhanced sensitivity in the infrared above 800 nm. The limits of the V_{oc}, J_{sc}, and FF are still far from optimization and rest open. The highest potential in further increasing the efficiency is related to obtaining higher V_{oc} values. The μc-Si:H p-i-n cell could also contribute as germanium-free more stable bottom cell in tandem structures. The transport properties and mechanism clearly need further investigations.

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