Highly efficient microcrystalline silicon solar cells deposited from a pure SiH$_4$ flow

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A time-resolved optical emission spectroscopic study identified transient behavior of the excited SiH emission in a parallel plate SiH$_4$/H$_2$ plasma. The transient behavior could be prevented by filling the background gas with H$_2$ prior to plasma ignition. Applying this condition, state-of-the-art microcrystalline silicon (μc-Si:H) could be deposited irrespective of the applied H$_2$ flow, ultimately demonstrated by a 9.5% efficient solar cell deposited from pure SiH$_4$. The results are discussed in terms of SiH$_4$ back diffusion: an initial diffusion flux of SiH$_4$ from the reactor's dead volume back into the plasma. © 2005 American Institute of Physics. [DOI: 10.1063/1.2152115]

Plasma deposition of the intrinsic microcrystalline silicon (μc-Si:H) film is a key process in the fabrication of highly efficient thin-film silicon solar cells. High-quality μc-Si:H is deposited in a narrow regime close to the phase transition to amorphous growth,[1] generally tuned by the feed gas dilution ratio R=[H$_2$]/[SiH$_4$].[1–5] Commonly applied dilution ratios (R) range between approximately 10 and 300. These high values reflect the important role of H in the growth process.[6] Nonetheless, recent studies[7,8] revealed that it is possible to deposit μc-Si:H at much lower R by using the H that is created upon dissociation of SiH$_4$. However, solar cells prepared under these conditions showed poor performance.[7] Roschek *et al.* tried to solve this by grading the process flows during deposition,[8] but still could not achieve state-of-the-art devices. These studies indicated that high R is an essential prerequisite for obtaining high-quality material.

In this letter, we will demonstrate that state-of-the-art μc-Si:H solar cells can be deposited from a pure SiH$_4$ flow. We will make plausible that the previously reported drop of performance at low R was in fact caused by an initial diffusion flux of SiH$_4$ from the reactor's dead volume back into the plasma. Our findings are important from a fundamental point of view, demonstrating that the common belief that a high feed gas dilution ratio R is essential for obtaining high-quality μc-Si:H needs reinterpretation. Moreover, the newly developed process makes ultimate effective use of the SiH$_4$ and strongly reduces the need for H$_2$ as additional process gas, with obvious cost reduction promises for industry.

We conducted our study in the 13.56-MHz high pressure depletion regime, which has been developed recently for parallel plate plasma reactors to allow deposition of high-quality material at high rates.[9–11] The reactor used for intrinsic μc-Si:H deposition, described in more detail elsewhere,[12] encompassed a showerhead electrode for gas injection, and consisted of a volume of 11 liter, an interelectrode distance of 1.0 cm, and an electrode area of 150 cm^2. We applied a power of 0.5 W/cm^2, a pressure of 10 Torr(1.3×10^3 Pa), a

SiH$_4$ flow of up to 3.3 sccm (1.0 standard cm^3 min^{-1}, or sccm, equals 7.4×10^{-7} mol s^{-1}), and an H$_2$ flow of up to 1000 sccm. The substrate was kept at 196±12 °C.[12] These parameters, in particular the SiH$_4$ flow, were optimized beforehand in a deposition series[1,5,8] in order to make sure that the conditions were close to the phase transition to amorphous growth. A spectrometer equipped with a charge-coupled device (CCD) camera was used to measure the time resolved emission intensities of certain spectral lines.

Figure 1(a) shows the recorded emission intensity at 414.3 nm, originating from SiH* created by electron impact dissociation of SiH$_4$,[13] during the first minute after plasma ignition for various values of R. We also measured the emis-
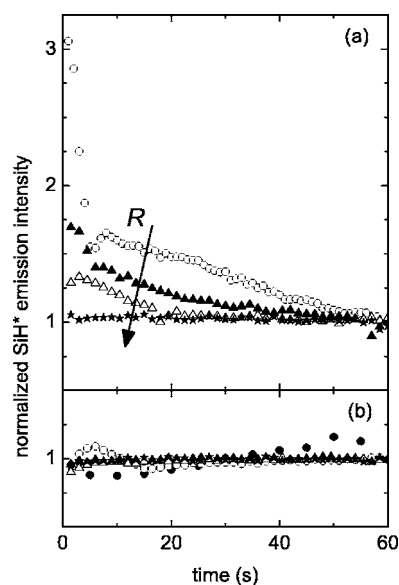

FIG. 1. Recorded SiH* emission as function of time for various values of the H$_2$ dilution ratio R, in (a) the standard process and (b) the H$_2$ background gas condition that prevents SiH$_4$ back diffusion. Data is shown for R=0 with total flow $\sim$2 sccm (closed circles), R=50 with total flow $\sim$50 sccm (open circles), R=90 with total flow $\sim$130 sccm (closed triangles), R=150 with total flow $\sim$360 sccm (open triangles), and R=300 with total flow $\sim$1000 sccm (closed stars). In (a), the R=0 case could not be recorded because the plasma did not ignite.

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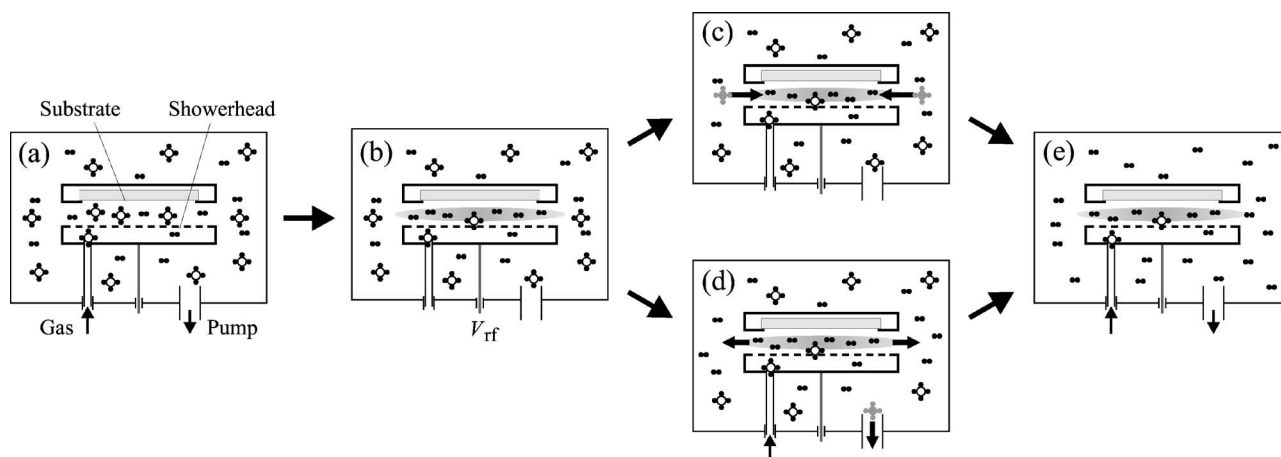[b)]Electronic mail: M.C.M.v.d.Sanden@tue.nl

FIG. 2. Schematic representation of the sequence of processes that occur after plasma ignition: (a) stable situation before plasma ignition, (b) plasma ignition and initial SiH_4 depletion in the plasma zone, (c) SiH_4 back diffusion, (d) purging, (e) stable situation after plasma ignition.

sion at 390.5 nm, originating from Si^*, which showed the same behavior in all cases. One clearly observes a transient behavior; the initial SiH^* emission intensity is higher than the stable one. This effect is particularly large for low R, and it occurs on a typical times cale of ~ 60 s. Figure 1(b) shows the time-resolved optical emission intensity for a special case that will be discussed later.

We explain the transient behavior in terms of a transformation of the gas composition, as sketched in Fig. 2. Before plasma ignition [Fig. 2(a)] the entire reactor is filled with the SiH_4/H_2 gas mixture, whereas in the stable situation after plasma ignition [Fig. 2(e)] the SiH_4 is heavily depleted[8–11] and the reactor is predominantly filled with H_2. During the transformation, the SiH_4 depletion in the plasma zone [Fig. 2(b)] drives a diffusion flux of SiH_4 from the reactor's dead volume back into the plasma[14] [Fig. 2(c)]. A high R limits the time scale on which this SiH_4 back diffusion may take place by purging [Fig. 2(d)]: For the $R=0$ condition at ~ 2 sccm total flow we roughly estimate the gas residence time (via gas density at room temperature $\times$ reactor volume/gas flow) to be as long as 4×10^3 s. For the $R=300$ condition at ~ 1000 sccm total flow, we estimate it to be only 8 s. The SiH_4 diffusion flux should be proportional to the initial SiH_4 density, so this effect should be largest for low R. Thus, it is our tentative view that the SiH_4 back diffusion is responsible for the initial enhancement and subsequent relaxation of the SiH^* emission.

Sorokin *et al.*[14] already discussed the effect of the SiH_4 back diffusion on the dust formation process in the plasma. Since our conditions are very close to the phase transition to amorphous growth, the SiH_4 back diffusion mainly affects film crystallinity: Either the first minute of deposition occurs on the amorphous side of the transition, or the deposition after the first minute occurs too far inwards on the microcrystalline side of the transition. Both cases lead to poor film quality: the former because of thick amorphous incubation layers[4,7] and the latter because of the too-high crystallinity.[1]

A background gas consisting predominantly of H_2 would prevent the SiH_4 back diffusion from happening. We realized this experimentally by first filling the entire reactor with H_2. Then, after flushing the reactor for a short time period with the process flows of dilution R, the plasma was ignited. The flushing time was crucial to this method. If it was too short, a pure H_2 plasma would be ignited. In this case, the SiH^*

emission would gradually increase to its stable value. If it was too long, the SiH_4 back diffusion process would be observed again to some degree. The time-resolved optical emission spectroscopy was used in this matter as a process control tool to determine the correct flushing times: Using values varying from 2 s at $R=300$ to 30 s at $R=0$, we obtained the stable SiH^* emission signals of Fig. 1(b). It shows only the first 60 s after plasma ignition, in which initial SiH^* emission enhancements of more than a factor of 2 were prevented. On longer time scales, the SiH^* emission intensity decreased further by about 20%. We compensated for this by proportionally increasing the SiH_4 flow during deposition.

Note that in the $R=0$ case the reactor consisted almost completely of H_2 upon plasma ignition, since the flushing time was negligible compared to the gas residence time. The SiH^* emission, hence SiH_4 density, remained stable at this low value after ignition notwithstanding the applied pure SiH_4 flow. This confirms our previous statement about the heavy SiH_4 depletion.

Solar cells are very sensitive to changes in structure or optoelectronic properties of the μc-Si:H film and its interfaces. Therefore, to test the H_2 background condition deposited material, intrinsic μc-Si:H layers were incorporated in *p-i-n* solar cell structures with an *i*-layer thickness of 1.0 ± 0.1 μm. Texture-etched ZnO:Al-coated glass substrates[15] served as transparent front contacts, while several 1×1 cm^2 Ag back contacts defined the solar cell area. We applied the same deposition conditions as were used in the recording of Fig. 1(a) (the standard process) and Fig. 1(b) (the H_2 background gas condition).

Figure 3 shows the solar cell properties obtained at various H_2 dilution ratios R. For the standard process, solar cells deposited at $R<100$ showed poor performance, mainly due to lower fill factor and open circuit voltage, consistent with previous observations.[8] In contrast, high-quality solar cells could be deposited at all H_2 dilutions, down to $R=0$, when the H_2 background gas condition was applied. We provided one sample, deposited at 0.4 nm/s, $R=0$, and a total gas flow of only 2.0 sccm, with a ZnO/Ag back contact for better light trapping. The cell showed excellent electronic performance with an open circuit voltage of 564 mV and a fill factor of 74.8%. Together with the short circuit current of 22.5 mA/cm^2, the solar energy conversion efficiency was 9.5%. Depth-profiled Raman spectroscopy measurements[5]
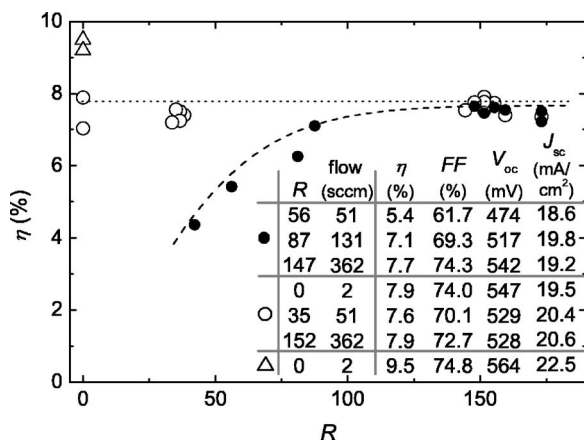
FIG. 3. Optimized solar cells deposited at various SiH_4 and H_2 flows represented by their efficiency η against H_2 dilution ratio R, for the standard process (closed circles), for the H_2 background gas condition (open circles) and for the H_2 background gas condition after which the solar cell was provided with a ZnO/Ag back reflector (open triangles). The dashed and dotted lines are guides to the eye. The inset shows a table containing the dilution ratio (R) and total flow for some characteristic depositions, plus the resulting solar cell parameters efficiency (η), fill factor (FF), open circuit voltage (V_{oc}), and short circuit current (J_{sc}).

	R	flow (sccm)	η (%)	FF (%)	V_{oc} (mV)	J_{sc} (mA/cm²)
●	56	51	5.4	61.7	474	18.6
	87	131	7.1	69.3	517	19.8
	147	362	7.7	74.3	542	19.2
○	0	2	7.9	74.0	547	19.5
	35	51	7.6	70.1	529	20.4
	152	362	7.9	72.7	528	20.6
△	0	2	9.5	74.8	564	22.5

revealed a homogeneously structured film crystallinity around 70%.

In summary, the aforementioned results lead to a reinterpretation of the role of H_2 dilution: The high H_2 flow generally applied during deposition of μc-Si:H is needed to suppress SiH_4 back diffusion. When it is suppressed in other ways, e.g., by applying a H_2 background prior to plasma ignition, high-quality μc-Si:H can be deposited irrespective of the applied H_2 flow.

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