Impact of secondary gas-phase reactions on microcrystalline silicon solar cells deposited at high rate

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The role of secondary gas-phase reactions during plasma-enhanced chemical vapor deposition of microcrystalline silicon is a controversial subject. In this paper, we show that the enhancement of such reactions is associated with the improvement of material properties of absorber layers deposited at high constant rate. We detect powder, a product of secondary gas-phase reactions, via infrared laser absorption spectroscopy, laser light scattering, and optical emission spectroscopy. As the powder formation is increased, we measure a systematic improvement of device performance. This demonstrates that secondary gas-phase reactions are not detrimental to the material quality of microcrystalline silicon deposited at high rate. © 2010 American Institute of Physics. [doi:10.1063/1.3449571]

Thin-film silicon solar cells are today a competitive alternative to traditional wafer-based photovoltaic technologies. Initial conversion efficiencies of over 13% have been demonstrated[1] for module-size tandem devices combining amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) (Ref. 2) solar cells. Nevertheless, the high cost of the equipment still accounts for around 30% of the total module cost. Increasing the throughput while keeping high conversion efficiency is the key to reduce cost. Currently, thick μc-Si:H absorber layers, of about 2 μm, are usually deposited in production lines at rates of 2.5 to 5 Å/s. High-rate deposition of device-grade μc-Si:H is, thus, one of the most important technological challenges in view of low manufacturing costs of thin-film silicon solar cells. This goal can be achieved by plasma-enhanced chemical vapor deposition (PECVD) of μc-Si:H films using a very-high excitation frequency (VHF) (Refs. 3–5) and a narrow interelectrode gap.[6,7] For this purpose, a high radical density in the gas-phase of the plasma must be realized. Nevertheless, as soon as this condition is met, secondary gas-phase reactions, which do not contribute to the film growth, gain in importance. Among such gas-phase reactions, we mention $SiH_2 + SiH_4 \rightarrow Si_2H_6$ that triggers the formation of powder.[8] Therefore, powder can be considered as an indicator of secondary gas-phase reactions.

Many studies have reported a drop in the quality and in the performance of μc-Si:H material and solar cells when the deposition rate of the absorber layer, R_d, is increased.[5,9–11] While the detrimental effect of strong ion bombardment[5,10,12] and of insufficient relaxation of growth precursors[11] have been well assessed, the role of powder is still controversial. Powder is identified as a possible additive source for the deterioration of device performance[5,9] and precautions are often taken to reduce its formation. On the other hand, it has been shown that the formation of powder under certain conditions is beneficial to the deposition of a-Si:H and μc-Si:H.[13,14] However, a systematic study of the effect of powder on the material quality of μc-Si:H films, per-formed at a constant ion bombardment and a constant R_d, is still lacking.

In this paper, we show that the formation of powder in its early stage is not detrimental to the deposition of device-quality μc-Si:H at high rate. We deposited μc-Si:H intrinsic layers (i-layers) using both dusty and nearly powder-free processes (*i*) at a fixed pressure, (*ii*) at a fixed excitation frequency, and (*iii*) at a constant $R_d = 10$ Å/s. Conditions (*i*) and (*ii*) result in comparable ion bombardment of the growing film. Condition (*iii*) ensures a comparable impingement rate and diffusion length of film precursors on the surface of the growing film. Therefore, these conditions enable us to isolate the effect of powder on the material quality of the deposited films. We present the results of *in situ* monitoring of plasma and powder dynamics during the film deposition. We then discuss the device performance of μc-Si:H solar cells. We deposited μc-Si:H p-i-n junctions in a medium-size (50×60 cm^2) and narrow gap (13 mm) version of the industrial large-area VHF-PECVD KAI™ (Ref. 15) reactor, operated at 40.68 MHz. We prepared solar cells and measured their electrical and optical performance as in Ref. 16. Thick μc-Si:H i-layers (1.8 μm) were deposited using a constant pressure $p = 4.5$ mbar and a constant input silane flow, $[SiH_4]$, while the input hydrogen flow, $[H_2]$, was reduced from process A to E. In Table I, we report only the variation in the input silane concentration c, where $c = [SiH_4]/([SiH_4]+[H_2])$. In our study, c increases as the total

TABLE I. Input silane concentration (c), ILSS measurements (η, c_p, and R_d^e), profilometric measurement (R_d) and LLS measurement for processes A to E.

Process	c (%)	η (%)	c_p (%)	R_d^e (Å/s)	R_d (Å/s)	LLS (mV)
A	4.58	75.1	1.1	13.6	9.7	43.6
B	5.66	77.6	1.3	14.0	10	73.0
C	6.98	80.2	1.4	14.5	10	114.3
D	9.09	81.8	1.7	14.8	10	136.4
E	13.04	86.6	1.8	15.7	10	267.6

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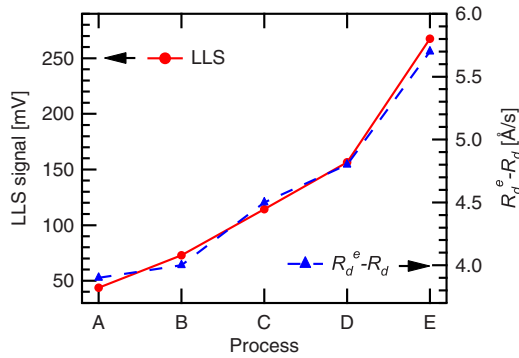
FIG. 1. (Color online) Quantification of powder by ILSS and LLS. Processes A to E correspond to the deposition of μc-Si:H absorber layers at 10 Å/s. Lines are guides for the eye.

FIG. 2. (Color online) Time evolution of I_{Ful} measured via OES during processes A to E.

input gas flow decreases. We further adjusted the feed-in power density, P_d, by a few percent to obtain films with comparable Raman crystalline fraction. The influence of the small variation in P_d on the ion bombardment is negligible. During the deposition of the i-layers, we characterized the plasma dynamic via infrared laser absorption spectroscopy. A high spectral resolution (0.001 cm^{-1}) infrared laser-based silane sensor (ILSS) developed in house[17] allowed us to monitor the silane dissociation efficiency, η. From the measurement of η, we determined the silane concentration in the plasma, c_p,[18] and estimated the film deposition rate, R_d^e, in the hypothesis that all the dissociated silane contributed to the deposition of a uniform film.[17] The actual R_d was determined by measuring the thickness of the film via profilometry. $R_d^e - R_d$ is an indirect quantification of the powder produced during the PECVD process. Simultaneously to the ILSS measurement, we monitored the production of powder at the gas exhaust via visible laser light scattering (LLS) (Ref. 19) and in the reactor via optical emission spectroscopy (OES). The ILSS, LLS, and OES allow us to monitor the production of powder and to quantify them. The evolution of nanoparticle sizes, as can be characterized via Rayleigh–Mie ellipsometry (Refs. 13 and 14) or cavity ringdown spectroscopy,[20] is beyond the scope of this paper.

In Table I we give the results of the ILSS and profilometric measurements, as well as the intensity of the LLS signal measured during processes A to E. The silane dissociation efficiency measured via ILSS monotonically increases from process A to E due to the increase in the gas residence time, τ_r, as $\tau_r \propto p/([H_2]+[SiH_4])$ (since [SiH$_4$] is constant in our study, we have $\tau_r \propto pc$). The gas residence time is of the order of the second and increases by roughly a factor three from process A to E. While the estimated R_d^e increases from 13.6 to 15.7 Å/s from process A to E, the R_d measured via profilometry is constantly equal to 10 Å/s. This apparent contradiction is explained by the fact that the SiH$_4$ molecules that are dissociated in excess are lost in secondary gas-phase reactions and are expelled from the reactor in the form of polysilane and powder, as confirmed by the LLS measurement (Table I). In Fig. 1, we compare $R_d^e - R_d$ with the intensity of the LLS signal, and show that the two independent detections of powder production are in good qualitative agreement. We calculate $c_p = c(1-D)$, where D is the silane depletion, assuming $D = \eta$ when $c \ll 100\%$.[18] c_p is the crucial parameter to determine if the PECVD process will result in amorphous or microcrystalline film growth.[18] Using
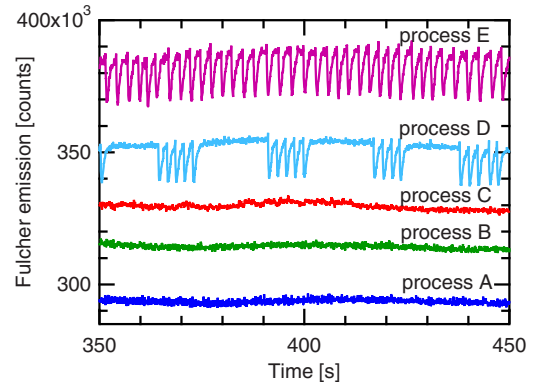
the procedure defined in Ref. 18, we determined via ILSS that, in our reactor, μc-Si:H material is deposited at the amorphous-to-microcrystalline transition when $1\% < c_p < 2.8\%$. All the values of c_p in Table I are included within this interval, meaning that we were working in suitable conditions for the deposition of device-grade μc-Si:H. The variations in c_p are very small because the increase in η systematically compensates the increase in c, and this explains why the Raman crystalline fraction of the deposited films is almost constant despite the large variation in c.

Figure 2 shows the time evolution of the intensity of the Fulcher (600–630 nm) emission of molecular hydrogen, I_{Ful}, measured via OES. During processes A to C, which are nearly-powder free, I_{Ful} is constant, while its sharp oscillations during process E are likely related to the cycle of powder production and ejection from the reactor. In fact, I_{Ful} is proportional to the electron density, which fluctuates due to the interaction between electrons and silicon clusters formed in the plasma.[21,22] An interesting intermediate behavior is observed during process D, which is characterized by a cyclic alternation of dusty and powder-free plasma conditions. Our results of OES plasma monitoring are in good qualitative agreement with the ILSS and LLS powder measurements presented in Fig. 1.

We repeated the full study at two higher values of the process pressure, namely, $p = 5.5$ mbar and $p = 7.0$ mbar, and adapted the feed-in power density to keep comparable I_c and $R_d = 10$ Å/s. The input SiH$_4$ flow remained unchanged. The input silane concentration was varied by changing the input H$_2$ flow only. In Fig. 3 we plot the conversion efficiency of the solar cells versus c for $p = 4.5$, 5.5, and 7.0 mbar. For a given p, the formation of powder increases with increasing c, as discussed above. For a given c, the formation of powder increases as p increases. A monotonous increase in the efficiency is obtained both with increasing c at a fixed p, and with increasing p at a fixed c. In both cases, the variation in process parameters is such that secondary gas-phase reactions are favored. We conclude that powder formation and, in general, secondary gas-phase reactions are not detrimental to the deposition of μc-Si:H at high rate. We even argue that some gas-phase reactions are beneficial to the high-rate deposition of device-grade μc-Si:H material. We point out that, for a given c, the improvement of cell performance with increasing p could be partly due to additional effects, such as a reduced ion-bombardment on the growing surface.[12] The best conversion efficiency we
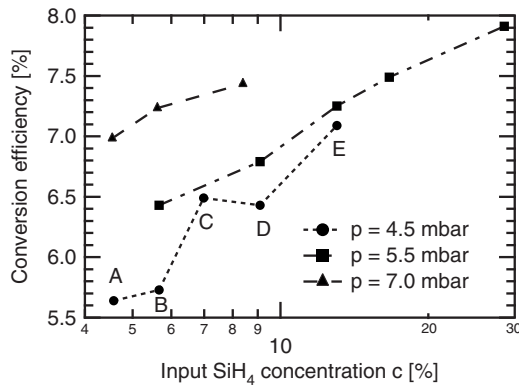
FIG. 3. Conversion efficiency of solar cells deposited at $R_d = 10$ Å/s using process pressures p = 4.5 (corresponding to processes A to E), 5.5 and 7.0 mbar, vs input silane concentration. Lines are guides for the eye.

achieved in this study is 7.9%. We used one of the best μc-Si:H cells in Fig. 3 as bottom cell for a a-Si:H/μc-Si:H tandem device, and achieved 11.9% initial efficiency. The i-layers of the top and bottom cells were 250 nm and 2.5 μm thick, respectively. No further optimization of the μc-Si:H or tandem solar cell design were undertaken.

The concept of powder formation covers a wide range of possible phenomena. In fact, the beginning of powder particle growth is a homogeneous process but not the following coagulation process leading to large size powder particles and resulting in an inhomogeneous plasma discharge, non-uniform deposition and plasma time-instability.[23,24] However, it cannot be excluded that the early stage of powder formation has a beneficial effect on the material quality and on the performance of μc-Si:H devices. Powder is only one product of gas-phase reactions taking place in the volume of a plasma discharge but it is not yet clear in which way these reactions influence the material quality of the deposited film. In this paper, we have shown that the formation of powder during the PECVD process is not detrimental to the performance of μc-Si:H devices.

In summary, we have studied the plasma dynamic during deposition of μc-Si:H i-layers at a high rate. While maintaining a constant deposition rate of 10 Å/s, we increased the input silane concentration and the process pressure, in order to favor the formation of powder. Powder is regarded here as a product of secondary gas-phase reactions that is expelled from the PECVD reactor. Using LLS, OES, and ILLS we show that powder-rich processes are favorable for the deposition of device-grade μc-Si:H. Our conclusion is supported by state of the art single-junction and multijunction devices

having initial conversion efficiencies of 7.9% and 11.9%, respectively.

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