

More stable low gap a-Si:H layers deposited by PE-CVD at moderately high temperature with hydrogen dilution

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Abstract

In the present work, several series with variation of deposition parameters such as hydrogen dilution ratio, VHF-power and plasma excitation frequency f_{exc} have been extensively analyzed. Compared with “conventional” more-stable layers obtained at 200–250°C and high H₂ dilution ratios of about 10, it was observed that electrical transport properties after light-induced degradation of layers deposited at “moderately high” temperatures (300–350°C) are equivalent but required lower H₂ dilution ratios (between 2 and 4). As a consequence, the deposition rate of more stable layers obtained at moderately high temperatures is increased by a factor of 2. Moreover, optical gaps of a-Si:H deposited at 300–350°C are significantly lower (by approx. 10 meV); furthermore, they decrease with f_{exc} .

Keywords: a-Si:H; Stability; VHF PE-CVD; Hydrogen dilution; High deposition temperatures

1. Introduction

Among the many tentatives to reduce light-induced degradation (Staebler–Wronski effect) in hydrogenated amorphous silicon a-Si:H films, the only method that has so far been successful in improving both material and solar cell stability against light soaking is the hydrogen dilution technique, introduced in 1981 by Guha et al. [1]. Because of its full compatibility with conventional a-Si:H-based solar cell deposition processes (PE-CVD), the hydrogen dilution technique is at present the fabrication method that is most widely used by amorphous silicon solar cell manufacturers (e.g. Refs. [2,3]).

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The use of the hydrogen dilution technique to produce more stable a-Si:H materials results in an increase of their optical gap E_{gap} ; thus, the open-circuit voltage V_{oc} of solar cells with such more stable hydrogen-diluted intrinsic layers is also increased (in comparison to the V_{oc} of similar solar cells with intrinsic layers deposited without hydrogen dilution). A second consequence of the higher optical gap E_{gap} is, however, that the optical absorption of layers deposited with hydrogen dilution is lower than that of a-Si:H layers deposited without hydrogen dilution; as a consequence, thicker intrinsic layers are needed to obtain sufficient current. However, as is well known (see e.g. Ref. [4]), the efficiency of solar cells with thicker intrinsic layers degrades more than that of cells with thinner intrinsic layers. Thus, the improvement of the cell stability obtained by incorporation of hydrogen-diluted intrinsic layers is partially compensated by the fact that the thickness of these intrinsic layers has to be increased.

The motivation of the present work is to reduce the optical gap of a-Si:H without any reduction in the transport quality of corresponding degraded layers. This will be achieved by systematically analyzing and optimizing layers deposited at moderately high temperatures (300–350°C) with different H_2 dilution ratios.

2. Experimental procedure

2.1. Deposition

Hydrogenated amorphous silicon layers with typical thicknesses of 1 μm are deposited by the VHF PE-CVD technique described in detail elsewhere [5]; deposition is done on glass for optical and electrical characterisation and on silicon wafer for infrared measurements. Two different deposition systems have been used to supply the series for the present work: a conventional one (with a total volume of 25 l) designed for depositions at plasma frequencies between 40 and 70 MHz. The second system, more compact (total volume of 2 l), was specially designed to deposit in the frequency range of 70–200 MHz with very low electrical losses.

2.2. Characterization

2.2.1. Optical

The absorption coefficient α is determined from reflection and transmission spectra measured with a commercial spectrophotometer; to improve the precision of α (to about 5% relative error), the dispersion of refraction index of the a-Si:H was taken into account [6]. The optical gap E_{gap} given here is evaluated by Tauc's method [7]. Microstructure factor R , given by the ratio of H bonds in the Si-H₂ configuration to the total bonded H is determined from infrared (IR) spectroscopy measurements.

2.2.2. Electrical

Two coplanar aluminium contacts with a length of 1.5 mm and separated by 0.5 mm were thermally evaporated to perform electrical measurements. Steady-state

photoconductivity σ_{ph} (SSPC) and ambipolar diffusion length L_{amb} (via steady-state photocarrier grating (SSPG) method) are measured under Kr-laser (647 nm) illumination at an intensity of 2 mW cm^{-2} in the initial state (to minimize the light degradation during the measurement itself) and at 10 mW cm^{-2} in the degraded state (to improve the precision by increasing the signal). Combining L_{amb} and σ_{ph} we deduce the material quality parameter $\mu^0\tau^0$ [8].

$$\frac{b}{(b+1)^2} = \frac{L_{\text{amb}}^2 q^2 G}{kT\sigma_{\text{ph}}C}.$$

2.2.3. Accelerated light-induced degradation

The total degradation cycle is (as described in detail elsewhere [9]) composed of two phases: the first one is the accelerated degradation phase, based on the use of a pulsed laser ($\lambda = 700 \text{ nm}$, repetition rate of 20 Hz and pulse energy of 0.1 mJ) during 3 h . This accelerated and slightly “over-degraded” phase is followed by a relaxation phase based on continuous light illumination ($\lambda = 633 \text{ nm}$, $T_{\text{sample}} = 50^\circ\text{C}$ and intensity of 50 mW cm^{-2}) until saturation of the σ_{ph} is reached (typically after 2–3 days).

3. Results and discussion

3.1. Hydrogen dilution

Fig. 1 shows the effect of the H_2 dilution ratio on the material quality parameter $\mu^0\tau^0$ after light soaking (Fig. 1a); an optimum clearly appears for a H_2 dilution ratio of 2 in the special case of the series deposited at 350°C .

Furthermore, a rough anti-correlation between the stabilized value of $\mu^0\tau^0$ and the microstructure factor R can be observed (Fig. 1b), excepted in the case of the undiluted layer, where R -factor is low, although $\mu^0\tau^0$ is also low.

As already reported by other groups, the optical gap of a-Si:H deposited at “usual” temperatures ($200\text{--}250^\circ\text{C}$) increases with the H_2 dilution ratio during deposition. As shown in Fig. 1c, this behavior is also observed for materials deposited at 350°C in the H_2 dilution ratio range of 0–2. At higher H_2 dilution ratios, E_{gap} decreases again. This is due to the well-established fact that a high H_2 dilution ratio tends to produce microcrystalline material (in our special case, a non-negligible crystalline fraction has been detected by TEM in the sample deposited at 350°C with a H_2 dilution ratio of 9). Due to the fact that high T_{dep} also favors the crystallization, the H_2 dilution ratio point from where E_{gap} decreases again is lower at higher values of T_{dep} (this point is at H_2 dilution ratio = 15, 4 and 2 for $T_{\text{dep}} = 250^\circ\text{C}$, 300°C , and 350°C , resp.).

It is also important to recall that increasing H_2 dilution ratio considerably reduces the deposition rate (Fig. 1d). Accordingly, the use of moderately high temperatures should become attractive for industrial applications because high-quality materials deposited at $300\text{--}350^\circ\text{C}$ requiring low hydrogen dilution ratios can be deposited at higher rates (about 3 \AA/s).

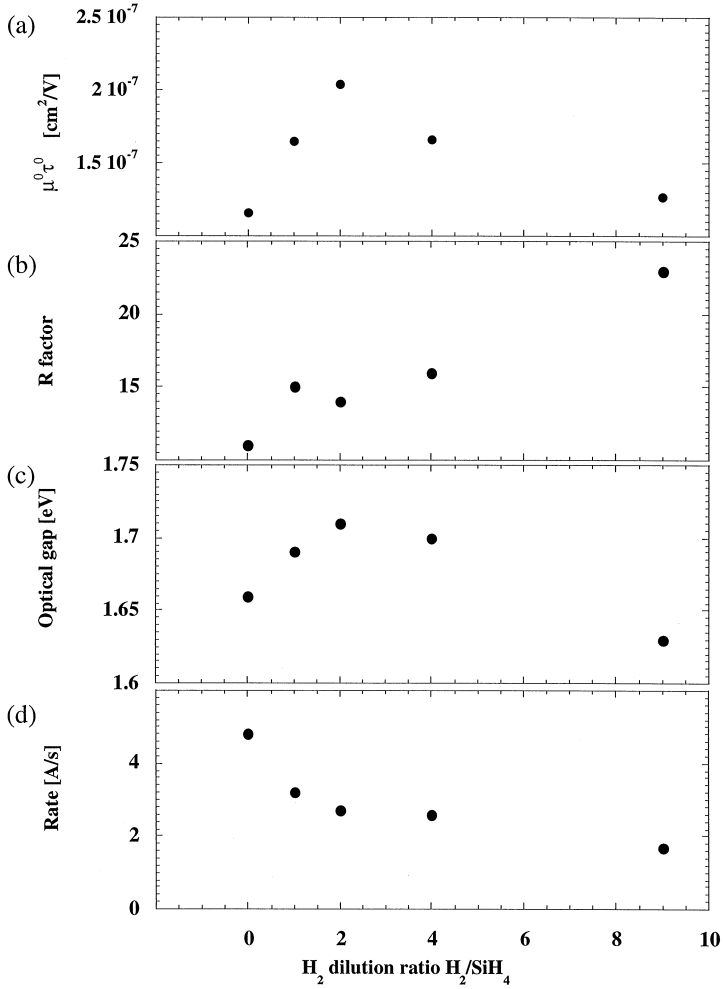


Fig. 1. Effect of H₂ dilution ratio on (a) the “stabilized” quality parameter $\mu^0\tau^0$ (after degradation), on (b) the microstructure factor R , on (c) the optical gap E_{gap} and on (d) the deposition rate; this series has been deposited in the “conventional” deposition system with $T_{\text{dep}} = 350^\circ\text{C}$, VHF-power = 5 W and $f_{\text{exc}} = 70$ MHz.

3.2. Plasma excitation frequency

First, it is interesting to mention that the deposition at higher plasma excitation frequencies tends to produce layers with reduced optical gaps (Fig. 2b). The reduction of the optical gap can be associated with a reduction in hydrogen content C_{H} (from $C_{\text{H}} = 12\%$ at 40 to $C_{\text{H}} = 9\%$ at 70 MHz). It would see from this latter that the use of increased plasma excitation frequency has a similar effect in layer properties as the use of higher substrate temperatures.

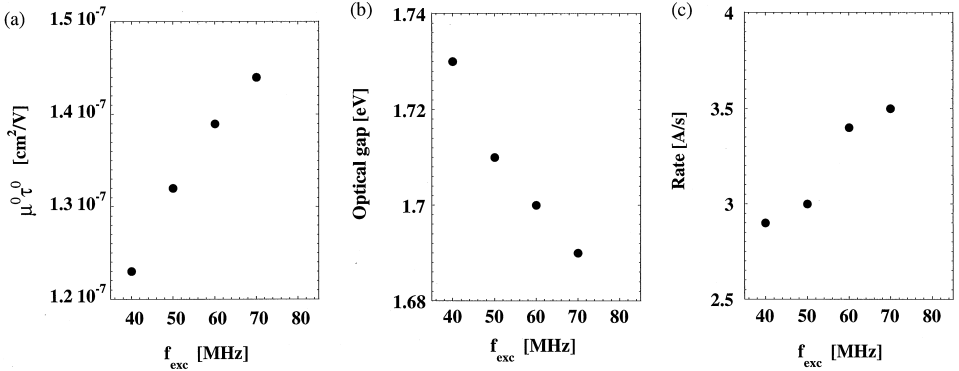


Fig. 2. Effect of the plasma excitation frequency on (a) the “stabilized” quality parameter $\mu^0 \tau^0$ (degraded state), on (b) the optical gap E_{gap} and on (c) the deposition rate. This series has been deposited in the “conventional” deposition system at $T_{\text{dep}} = 300^\circ\text{C}$, H_2 dilution ratio = 1 and VHF-power = 2 W.

Secondly, the stability of a-Si:H layers (i.e. the “stabilized” value of $\mu^0 \tau^0$ after degradation) increases slightly with the excitation frequency (Fig. 2a). As already mentioned in the past, one of the reasons for this may be the fact that at higher frequencies, the average energy of ions involved in ion bombardment of the growing layer is reduced [10].

Finally, as already shown in the past (see e.g. Ref. [5]), the deposition rate increases with plasma excitation frequency (Fig. 2c); this effect is also observed when depositing at moderately high temperatures with hydrogen dilution (in the case where $T_{\text{dep}} = 300^\circ\text{C}$, H_2 dilution ratio = 1 and VHF-power = 2 W an increase of 30% of the rate is observed by increasing f_{exc} from 40 to 70 MHz).

3.3. VHF-power

One of the major handicaps of the hydrogen dilution method for producing more stable material is the decrease of the deposition rate in comparison to deposition processes with pure silane. Apart from the plasma excitation frequency (described above) the most important of these parameters is the power coupled into the plasma. Note that the latter has not been measured in the present work, only the value of the VHF-power measured before the match-box is given here.

VHF-power series have been deposited both in the compact and in the conventional deposition systems. In both cases, one observes a substantial increase of the deposition rate in the VHF-power range between 2 and 5 W (Fig. 3b). However, for a given VHF-power, the deposition rate in the compact system is much higher than one obtained in the conventional system. This is due to the fact that electrical losses in the compact system are less than the losses in the conventional one, and as a consequence, more power is coupled into the plasma (in other words, one needs more electrical input power in the conventional system than the compact system for the same effective plasma power).

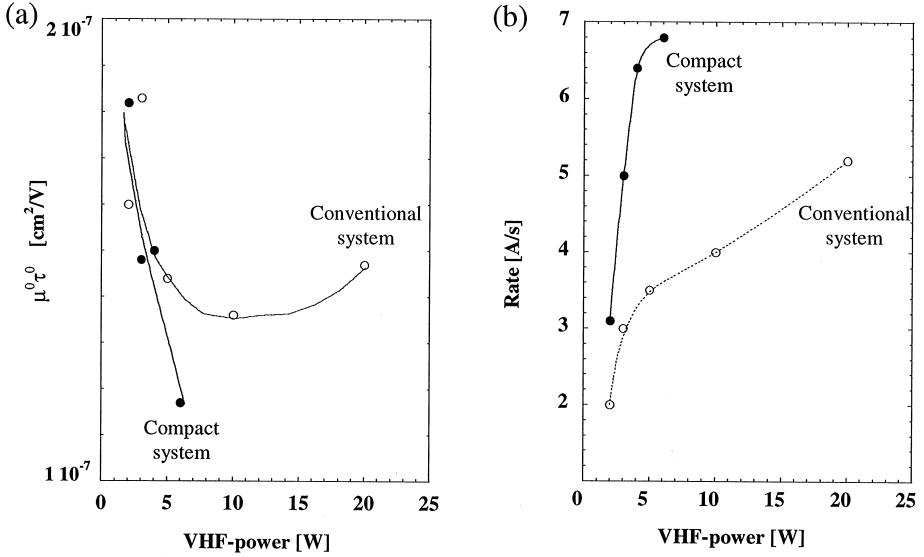


Fig. 3. Effect of VHF-power on (a) the "stabilized" quality parameter $\mu^0\tau^0$ (in degraded state) and on (b) the deposition rate; layers of this series have been deposited in both deposition systems with $T_{\text{dep}} = 300^\circ\text{C}$ and $f_{\text{exc}} = 70$ MHz.

One also observes that at low VHF-power (< 5 W), the quality of layers deposited in both systems present similar values of "stabilized" $\mu^0\tau^0$ after light soaking (Fig. 3a). Nevertheless, at higher values of VHF-power, the quality of layers obtained in the compact system is reduced compared with the quality of layers deposited in the conventional system. This effect is probably due to powder formation that can take place in the compact system, even at low values of VHF-power.

4. Conclusions

It has been shown that for VHF plasma deposition a combination of both moderately high deposition temperatures and relatively low hydrogen dilution ratio allows one to produce high-quality material with a reduced optical gap; in the case of layers deposited at 350°C , their stability, evaluated with the quality parameter $\mu^0\tau^0$ after light soaking, is improved by a factor of 2, and the absorption coefficient at 700 nm is about a factor of 5 higher than the value of "standard" a-Si:H deposited at 250°C without hydrogen dilution.

On the other hand, the use of hydrogen dilution for producing more stable material reduces, in general, considerably the deposition rate (of about a factor 2 in comparison to deposition process with pure silane); this is problematic for the integration of such material into production lines for low cost solar cells. In the present work it has been

demonstrated that the increase of the plasma excitation frequency increases the deposition rate, and the absolute value of the deposition rate of more stable material obtained at 70 MHz remains higher than the rate of films with relatively poor stability deposited at 13.56 MHz with pure silane. This effect has yet to be confirmed by the fabrication and testing of complete n-i-p solar cells; if confirmed, it should be of considerable industrial interest.

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