Stability of a-Si:H prepared by hot-wire and glow discharge using H₂ dilution evaluated by pulsed laser degradation

Ch. Hof *, Y. Ziegler, R. Platz, N. Wyrsch, A. Shah
Institute de Microtechnique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

Abstract

The quality of intrinsic amorphous silicon films prepared by different deposition techniques was investigated. For very high frequency glow discharge, both the substrate temperature as well as the hydrogen dilution were varied. These layers were compared to hot wire material produced at comparable temperatures. To study the stability of these films, an optimised degradation method was developed in which a pulsed dye laser was used in combination with a monochromatic steady beam to achieve a relatively fast stabilisation of the light induced degradation. The film quality was monitored by the photoconductivity and by the ambipolar diffusion length from which the material parameter, \( \mu_0 t_0 \), was extracted. Taking into account the transport properties after light soaking as well as the optical absorption we concluded that the hot wire material could lead to more stable solar cells in comparison with plasma enhanced chemical vapor deposition material.

Keywords: Amorphous silicon; Hot-wire; Glow discharge; Pulsed laser degradation

1. Introduction

The optimisation of the deposition technique of hydrogenated amorphous silicon (a-Si:H) for solar cell applications is motivated by the goal of finding materials which have optoelectronic properties suitable for devices after stabilisation of the light induced degradation process (Staebler–Wronski effect). In this context, there are two main aspects that are rendering the development of such high quality a-Si:H material difficult.

The first one concerns the evaluation of material quality. Various parameters can be measured for this purpose. However, many of them do not account for all relevant microscopic parameters limiting the carrier collection in solar cells or they depend on the prevailing experimental conditions. To address this problem, a reliable material quality parameter, \( \mu_0 t_0 \), has been recently introduced. This parameter combines steady state photocarrier grating (SSPG) and photoconductivity data to give a Fermi-level independent mobility-lifetime product [1]. It has been shown to correlate well with solar cell efficiencies incorporating corresponding materials.

The second problem is related to the degradation process itself which, under conditions as experienced typically by photovoltaic modules (1 sun, 50°C), lasts up to several months [2]. Moreover, the kinetics depends on the type of sample under test. It has been shown that the degradation time can be reduced, at the same temperature and even lower average generation rates, if a pulsed source is used [3]. It is, however, necessary to study the conditions applied.

* Corresponding author. Fax: +41-32 718 3201; e-mail: hof@imt.unine.ch.
In fact, when using this technique, time-consuming relaxation phenomena may take place before reaching a stable state [4]. We have optimised a degradation procedure using a dye laser which allows us to obtain a saturation of the defect creation in a reasonable amount of time (typically about 30 h).

Using these two tools for the evaluation of the stability of a-Si:H layers, we are now able to compare different materials produced by distinct deposition techniques. As far as glow discharge material is concerned, layers deposited using H2-dilution at comparatively low temperatures have shown promising results in the past [5]. P−i−n structures which incorporated these layers turned out to be more stable when compared to solar cells made of ‘standard’ material. In this paper, we are presented measurements on films which were obtained by applying different dilutions and deposition temperatures.

On the other hand, we will consider as well the hot-wire deposition technique. Using the approach cited above, it is possible to evaluate directly the potential of this material as a photovoltaically active layer as well as the current state of optimisation of this technology.

2. Experimental procedures

In this study, the a-Si:H layers were deposited by employing the very high frequency glow discharge (VHF-GD) technique at 70 MHz. The substrate temperature during deposition was varied between 190°C and 290°C. For each temperature, three films with different H2 dilution ratios (defined as [H2]/[SiH4]) were made to study the effect of the H2 dilution. The H2 dilution was set to 0 (undiluted), 2 and 9. These series of VHF-GD samples were compared to hot-wire (HW) samples which were deposited at 320°C and 270°C. While for the 320°C sample, no H2 was added, a dilution of 1 was used during the growth of the low temperature sample.

The measurement of the film quality was done by measuring the photoconductivity, \( \sigma_{\text{photo}} \), and the ambipolar diffusion length, \( L_{\text{amb}} \) [6]. Both were measured using a HeNe Laser emitting at 633 nm. The light intensity was kept at the smallest possible intensity to avoid degradation during the measurement but large enough to get a reasonable signal to noise ratio for the SSPG measurement: 2 mW cm\(^{-2}\) in the initial state, 10 mW cm\(^{-2}\) in the degraded state. The thickness of the films was determined by means of an alpha step profiler and varied between 0.9 µm and 1.5 µm. The optical absorption was measured using a reflection and transmission measurements to allow for corrections of the generation rate. The ohmic behaviour of the electrical coplanar contacts (Al or ITO) was measured and less than 10% variation of the photocurrent between 0 and 100 V was tolerated. From the \( \sigma_{\text{photo}} \) and \( L_{\text{amb}} \) measurements the quality parameter, \( \mu \tau_{\text{eff}} \) [1], was extracted. This product corresponds to the mobility lifetime product which would be measured in an a-Si:H layer (by both, \( \sigma_{\text{photo}} \) and \( L_{\text{amb}} \)) if all its defects were neutral. It has been recently introduced by our group to account for the effect of the Fermi level on the recombination function via the occupation of the dangling bonds.

For the degradation experiments, we used a combination of a continuous wave (CW) light source and an pulsed laser beam in order to achieve a faster stabilisation. The continuous light beam (HeNe laser) had an intensity of 100 mW cm\(^{-2}\) and was divided into two equal parts illuminating the sample from each side to give a generation profile of acceptable uniformity across the layer. As a sample holder, we used a transparent heating plate, which allowed us to control the temperature at 50°C. During the degradation, the changes in the photoconductivity were monitored.

On a red bias light, the beam of a pulsed (20 Hz) dye laser was superimposed. Its mean intensity was slightly less than the steady beam (50 mW cm\(^{-2}\)).

The wavelength was chosen at \( \lambda_{\text{dye}} = 700 \text{ nm} \). Due to the absorption coefficient of the a-Si:H at such wavelengths, the flux of photons ‘seen’ by the film amounted to less than 5% of the bias light and the corresponding photoconductivity was only about 2% of the total photoconductivity. Nevertheless, since the energy is concentrated into flashes of a duration of only about 10 ns one gets peak generation rates which are 10\(^3\) times higher than the average generation rate. Therefore, the degradation kinetics is substantially accelerated [3].

Previous experiments [7] have shown that the stabilised photoconductivity under pulsed light depends on the intensity of the latter, which makes the result of such an accelerated degradation question-
able. In fact, the saturation level of the degradation under pulsed light is less than the corresponding value obtained after exposure under standard conditions. However, with our degradation procedure, as soon as the pulsed light source is interrupted relaxation occurs which brings the sample to the same stable state that would have been found under CW light only (see Fig. 1). It was experimentally verified that this stable state is independent of the intensity of the pulsed light over a large range. Although the relaxation is notable in the dark (at 50°C) it was found to be accelerated under the bias light (light induced annealing). In fact the annealing rate could be enhanced by a factor 4. Typically, it lasts about 20 to 50 h before the stabilisation is reached. This time can be reduced if the intensity of the pulsed source is adjusted to a relatively low value such as to reach a saturation of the defect creation not very much deeper than the CW light stable state.

3. Results

Following the experimental procedures described above, we compare in Fig. 2 the $\mu^0\tau^0$ of the layers deposited by VHF-GD and hot wire in the initial state (after annealing at 200°C during 2 h). Taking into account the precision of the measurement of about 20% no variation of the material quality with deposition temperature is observed for the glow discharge films. The diluted films, however, have a smaller $\mu^0\tau^0$ product in the initial state. These films showed also a relatively larger $b$ ($b$ is defined as $b = \mu^0_N N_t / \mu^0_P P_t$ where the $\mu$ refer to the mobilities of free carriers while $N_t$ and $P_t$ represent their density) indicating that they are slightly extrinsic [8] when compared to the others. This difference may be attributed to the reduction (by a factor 2) of the growth rate at a dilution of 9 which would result in a higher contamination (outgassing of O from reactor
walls, etc. [9]). On the other hand, one should note that with such dilutions one starts to approach a phase transition region (photothermal deflection spectroscopy shows that at a temperature of 290°C and with a dilution of 9 the films show microcrystalline infrared absorption) which may also affect the transport properties. For the hot wire material, a clear decrease of the material quality at lower deposition temperature was observed. At 270°C, a reasonable \( \mu^0 \tau^0 \) product could only be obtained by applying H\(_2\) dilution.

After the full accelerated degradation procedure, the \( \mu^0 \tau^0 \) products as represented in Fig. 3 were measured. One observes an increase of the stability with deposition temperature in the case of undiluted samples. The largest increase of stability was observed in samples with H\(_2\) dilution. The highest quality, however, was measured on the 320°C HW sample.

4. Discussion

In view of incorporation into a solar cell, it is important to consider also their optical properties. The bandgap of diluted layers has a tendency to increase. Therefore, the \( i\)-layer thickness would have to be adapted accordingly to avoid current losses due to photons which are not absorbed. This effect means, in a first order approximation, that a \( p-i-n \) structure incorporating a material with a reduced absorption coefficient in the relevant wavelength region should be made thicker by the same factor. The collection length should thereby, in a first order, also be bigger by this same factor to get a comparable stability of the cell. The importance of this consideration is illustrated by Fig. 4, where we show the absorption coefficients of the different layers measured at 633 nm (in the case of a matched micromorph tandem the spectral response of the top cell is about one half at this wavelength). One notes typically a reduction of the absorption coefficient of 15% when diluting the silane by 2 with H\(_2\) whereas the gain on the degraded \( \mu^0 \tau^0 \) product amounts to more than 50% (Fig. 3). Cells made using this dilution would therefore be expected to be more stable in spite of the thicker \( i\)-layer required. In the case of the HW samples, one observes also a higher absorption coefficient when compared to the most stable (diluted) VHF-GD material. Therefore, we would expect it to give very interesting results when successfully incorporated in a cell.

5. Conclusions

It was shown that the same stabilised state reached after relaxation could be obtained independently of the intensity of the pulsed source. The transport properties of the films were compared in the initial as well as in the degraded state. It was found that even relatively small H\(_2\) dilutions lead to an increase in stability of the films which could not be increased by applying larger dilutions. The HW layers mea-
sured were found to have even better $\mu^0\tau^0$ products in the degraded state when compared to the diluted VHF-GD material. For solar cell applications changes in the optical absorption should be considered which was shown to decrease with $H_2$ dilution as well as with the deposition temperature. Our HW layers being deposited at somewhat higher temperatures showed also the largest absorption and bear therefore an interesting potential for solar cell applications.

References