Solar Energy Materials & Solar Cells ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Surface recombination analysis in silicon-heterojunction solar cells

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ARTICLE INFO

Article history:
Received 5 June 2009
Received in revised form
18 September 2009
Accepted 29 September 2009

Keywords:
Silicon
Amorphous
Heterojunction
PECVD

ABSTRACT

The origin of this work is the understanding of the correlation observed between efficiency and emitter-deposition temperature in single silicon-heterojunction solar cells prepared by depositing an n-doped hydrogenated-amorphous-silicon thin film onto a p-type crystalline-silicon wafer. In order to interpret these results, surface-recombination velocities have been determined by two methods, i.e. by fitting the current–voltage characteristics to a theoretical model and by means of the Quasi-Steady-State Photoconductance Technique (QSSPC). In addition, effective diffusion lengths have been estimated from internal quantum efficiencies. The analysis of these data has led to conclude that the performance of the cells studied is limited by back-surface recombination rather than by front-heterojunction quality. A 12%-efficient cell has been prepared by combining optimum emitter-deposition conditions with back-surface-field (BSF) formation by vacuum annealing of the back aluminium contact. This result has been achieved without using any transparent conductive oxide.

1. Introduction

Silicon-heterojunction (SHJ) solar cells have been gaining interest in the last years owing to the advantages derived from the combination of the good charge-transport properties of crystalline silicon and the versatility of thin-film technology [1]. This paper describes research originated in an attempt to find the optimum temperature for n-type amorphous-silicon emitter deposition in the preparation of this kind of devices. A correlation has been found between deposition temperature and cell performance, showing no evidence to be determined by thin-film emitter properties. Since silicon-heterojunction solar cells are critically affected by surface (or interface) properties [2,3], different experimental techniques have been applied in order to obtain information about the quality of the interfaces of the devices, and in particular about surface-recombination velocities (S). In addition, effective diffusion lengths (L_{eff}) have been estimated in order to have a more complete understanding of bulk- and back-interface recombination [4,5]. The present paper describes the research performed to understand the mechanisms responsible for the dependence of cell performance on emitter-deposition temperature. These mechanisms appear to be directly related to interface quality (particularly back-interface recombination) rather than to the properties of the emitter.

2. Experimental details

2.1. Preparation

Silicon-heterojunction cells are made by depositing thin (n) aSi:H emitters by 13.56 MHz plasma-enhanced chemical-vapour deposition (PECVD) onto 1 Ω cm-resistive, ⟨100⟩-oriented p-type boron-doped, float-zone double-polished monocrystalline-silicon wafers [(p) c-Si] with a previously evaporated aluminium back contact. The native oxide on the wafers is chemically etched by application of 1% FH:DIW (hydrogen fluoride 1% diluted in 18.2 MΩ cm-resistive de-ionised water at ambient temperature) for 2 min, following a previous work [6]. In order to ensure a proper sample thermalisation, substrates do remain in the sample holder within the reactor chamber at a temperature progressively approaching T_S for at least 4 h before (n) a-Si:H deposition. For the preparation of the samples of the present study, T_S has been varied from 195 to 330 °C. After PECVD deposition of the emitter, the sample is cooled down in vacuum and taken out from the reactor. Then, the front-grid (nickel+aluminium or titanium+silver) contact is evaporated immediately. In a small number of cells, the back aluminium electrode has been sintered immediately after its evaporation in order to induce the formation of a p^+ interface between the crystalline silicon and the aluminium electrode itself, i.e. the creation of a so-called Back-Surface-Field (BSF) rear contact. None of the cells prepared has a transparent conductive oxide (TCO).

All the a-Si:H layers have also been deposited by 13.56 MHz PECVD onto 10 × 10 cm² soda-lime glass substrates used for optical and electrical characterisation of the emitters. The same

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0927-0248/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.solmat.2009.09.017

deposition processes onto $10^4\,\Omega$ cm-resistive monocrystalline-silicon wafers has resulted in the samples for infrared-absorption spectrophotometry.

Non-contacted silicon-heterojunction symmetrical structures (equal emitters deposited on both sides of c-Si) have been prepared with the same deposition parameters as for the a-Si:H emitters of the cells. The resulting samples have been used for Quasi-Steady-State Photoconductance (QSSPC) measurements.

2.2. Characterisation

The films deposited onto glass substrates have been characterised optically and electrically according to procedures formerly described [7]. The energy gaps (E_G) and the thicknesses (d) of the films have been evaluated from spectral transmittance and reflectance measurements. Optical gaps have been calculated using the method by Tauc et al. [8] for indirect optical transitions. Infrared-absorption spectra have been used as inputs to standard procedures [9,10] for the evaluation of the hydrogen content of the emitters.

The current–voltage characteristics (J–V) of the solar cells have been measured in dark and under calibrated 100 mW/cm^2 AM1.5G irradiance. The main photovoltaic parameters, i.e. short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and efficiency (η), have been obtained in the usual way. In addition, the experimental J–V characteristics have been fit to a theoretical model [11] specifically developed to describe the behaviour of cells such as those, whose interface defects usually dominate recombination. The following equation describes this model:

$$J = J_s(e^{(V-AJR_s)/(nV_T)} - 1) + \frac{V - AJR_s}{R_{sh}} - J_L \cdot H(V)$$

$$H(V) = \frac{1}{1 + S^*/\mu\xi(V)}$$

This equation is a variation of the expression for the standard model, to which the collection function, $H(V)$, has been added after multiplication by the photocurrent density term in order to take into account the effect of surface-recombination velocity (S^*). Here S^* is a fit parameter with velocity units (cm/s), μ represents the carrier mobility and $\xi(V)$ the electric field at the interface, given by

$$\xi(V) = \left[\frac{2q\,\varepsilon_{s2}\,N_{A1}N_{D2}}{\varepsilon_{s1}(\varepsilon_{s1}\,N_{A1} + \varepsilon_{s2}\,N_{D2})}\right]^{1/2} [V_{bi} - (V - AJR_s)]^{1/2}$$

Sub-indexes 1 and 2 represent the absorber and the emitter, respectively, with the rest of the variables retaining their usual meaning.

The QSSPC technique has been applied to measure the lifetime of free carriers in contactless SHJ structures in order to estimate the front-surface recombination velocity (S_{QSSPC}) and the so-called implicit open-circuit voltage (implicit V_{OC}) [12].

Internal quantum efficiencies (IQE) have been obtained from the spectral responses and the cell spectral reflectances. Minority-carrier effective diffusion lengths (L_{eff}) have been obtained from a plot of IQE^{-1} versus photon penetration depth in c-Si (α^{-1}) in the near-infrared wavelength regime ($900 < \lambda < 1000$ nm) [13,14]. The plot is linear, and it can be expressed approximately by

$$1/IQE = 1 + 1/(\alpha L_{\mathrm{eff}})$$

L_{eff} is a valuable parameter to extract information about the bulk- and back-surface recombination of the devices.

3. Results and discussion

The most relevant parameters obtained from the electrical and optical characterisation of the (n) a-Si:H films deposited onto glass as a function of the preparation parameter having been scanned, i.e. the substrate temperature during deposition T_s, are shown in Table 1.

As can be expected, the values of E_G decrease with deposition temperature (T_S). This behaviour is attributed to a decrease in the hydrogen content of the films (see Fig. 1) [15,16]. In fact, the optical gap linearly increases with the hydrogen content ([H]) according to $E_G = 1.57 + 0.021[H]$ ($R^2 = 0.958$). The coefficient of correlation is not very high, probably owing to the error associated with the calculation of [H] (see again Fig. 1). This linear relation is similar to the equation obtained by Papadopoulos et al. [16] with the same independent term. No significant variations in conductivity with deposition temperature can be appreciated.

The main photovoltaic parameters of the SHJ cells prepared with different emitter-deposition temperatures have been obtained from their experimental J–V characteristics, as measured under 100 mW/cm^2 AM1.5G simulated sunlight. As can be seen in Fig. 2, the efficiencies (η) of the cells improve with deposition temperature (T_S) except for the highest T_S. In addition, the effect of the two different front contacts is also shown. A slight increase in cell efficiency is generally found in cells with Ti–Ag front contact over those with an Ni–Al one, probably because the barrier height between (n) a-Si:H and the front contact is lower for Ti–Ag than for Ni–Al [17,18]. The maximum efficiencies obtained are 9.7% and 12.2% for cells without and with a BSF, respectively, both

Table 1.
Properties of the thin-film (n) a-Si:H emitters used, as deduced from their optical and electrical characterisation.

T_s (°C)	d (nm)	E_G (eV)	σ (S/cm)
195	187	1.80	2×10^{-2}
240	221	1.84	1×10^{-2}
265	216	1.83	2×10^{-2}
285	244	1.75	3×10^{-2}
310	248	1.69	6×10^{-2}
330	257	1.67	7×10^{-2}

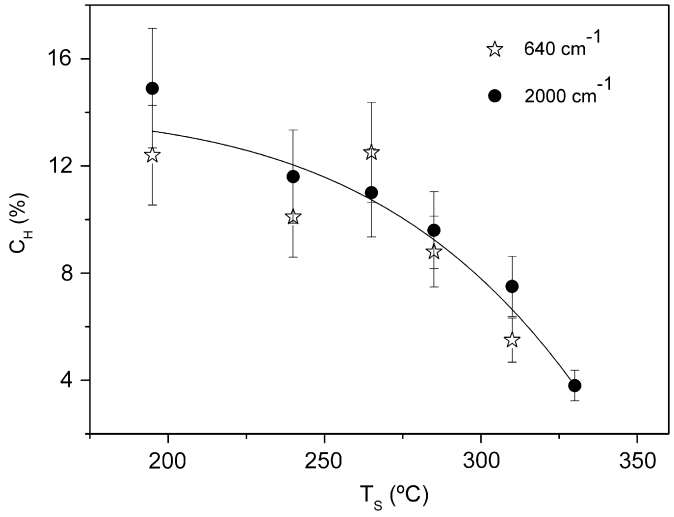

Fig. 1. Hydrogen content of the n-type a-Si:H films deposited onto high-resistivity crystalline-silicon wafers vs. substrate temperature (T_S), as deduced from infrared spectra at 640 and 2000 cm^{-1} absorption peaks.

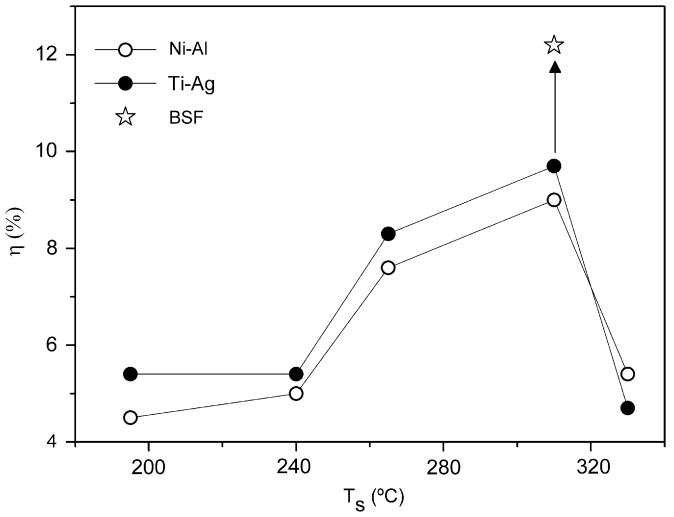

Fig. 2. Efficiency of the cells (η) vs. substrate temperature (T_S) as obtained from the experimental J–V characteristics under 100 mW/cm^2 AM1.5G.

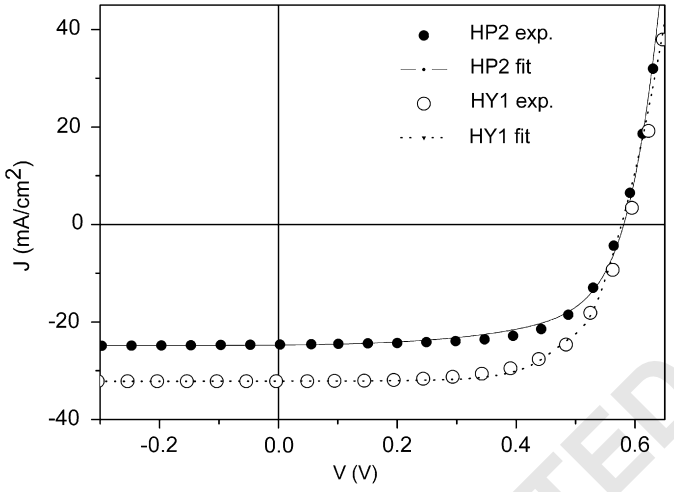

Fig. 3. Fits (solid and dash lines) of the experimental J–V characteristics under 100 mW/cm^2 AM1.5G (symbols) of the cells HP2 and HY1 (without and with BSF rear contact, respectively) using the surface recombination model described previously in the text. Emitters in both cells were deposited at 310 °C.

corresponding to an emitter-deposition temperature T_S=310 °C. These efficiencies are considered highly satisfactory, taking into account that the devices do not have any transparent conductive oxide. Series-resistance and particularly optical-reflectance reductions related to the deposition of a TCO are responsible for efficiency improvements typically of the order of relative 40% in cells of this kind. The fits of the J–V experimental curves to the surface-recombination model are illustrated in Fig. 3.

Surface-recombination velocities have been obtained from fits of the experimental J–V curves to the surface-recombination model (S^*) described previously. As can be seen in Table 2, increasing T_S up to 310 ºC results in a decrease of parameter S^*. Furthermore, a non-surprising correlation between S^* and J_{SC} has been observed (see Fig. 4). The improvement of the interface recombination found for increasing temperatures is also translated to cell efficiency and short-circuit current density. The maximum efficiencies obtained at 310 ºC coincide with a minimum S^* and a maximum J_{SC}.

However, the values of S^* obtained from the best fits are orders of magnitude higher than those expected for SHJ cells with a good front interface (see again Table 2). In fact, the values of S_{QSSPC}

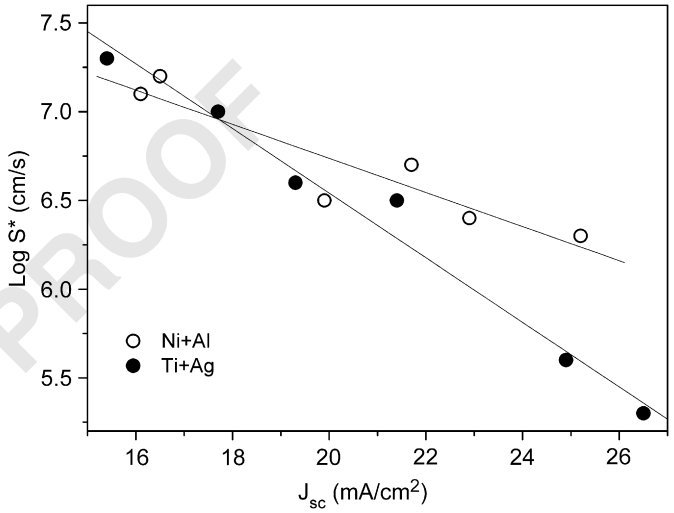

Fig. 4. Correlation between surface recombination velocity (S^*) as obtained from the surface-recombination model, and short-circuit current density (J_{SC}) as derived from the experimental J–V characteristics.

Table 2
Cell-performance parameters as a function of substrate-deposition temperature (T_S). Surface-recombination velocities have been obtained from fits of the experimental J–V characteristics to the surface recombination model (S^*) and from QSSPC (S_{QSSPC}). Open-circuit voltages have been drawn from experimental J–V curves (V_{OC}) and from *QSSPC* (implicit V_{OC}) measurements. Effective diffusion lengths (L_{eff}) have been derived from internal quantum efficiency.

T_s (°C)	Front contact	Back contact	*FF* (%)	S^* (cm/s)	S_{QSSPC} (cm/s)	V_{oc} (mV)	*Impl.* V_{oc} (mV)	L_{eff} (μm)
195	Ni–Al	Al	51	1×10^7	1×10^2	556	639	102
	Ti–Ag		53	1×10^7		570		118
240	Ni–Al	Al	46	4×10^6	2×10^2	555	626	192
	Ti–Ag		50	4×10^6		560		167
265	Ni–Al	Al	57	3×10^6	1×10^2	580	643	250
	Ti–Ag		58	4×10^5		580		250
285	Ni–Al	Al	59	5×10^6	3×10^2	584	617	167
	Ti–Ag		55	3×10^6		580		233
310	Ni–Al	Al	61	2×10^6	4×10^2	580	608	286
	Ti–Ag		63	2×10^5		580		270
330	Ni–Al	Al	55	2×10^7	1×10^3	590	580	172
	Ti–Ag		54	2×10^7		580		164
310	Ni–Al	*Al-BSF*	64	3×10^4	5×10^2	590	604	417

Please cite this article as: R. Barrio, et al., Sol. Energy Mater. Sol. Cells (2009), doi:10.1016/j.solmat.2009.09.017

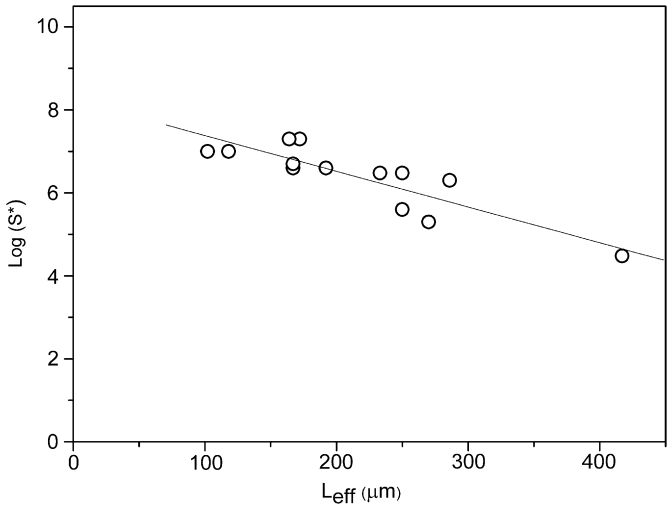

Fig. 5. Correlation between surface recombination velocity (S^*) as obtained from the theoretical surface-recombination model, and effective diffusion length (L_{eff}) as derived from internal quantum efficiencies.

measured are much lower than S^* and more in accordance with the efficiencies obtained. In order to understand these results, a number of experimental considerations have to be taken into account. QSSPC samples are fully symmetrical structures having the same interface on both sides of the sample. This means that S_{QSSPC} is sensitive to recombination mechanisms at the (n) a-Si:H/(p) c-Si heterojunction, i.e. on the front side of the absorber. S^*, on the other hand, is derived from the fit of the cell J–V curve to a theoretical model taking into account interface recombination. There is no way for S^* to discriminate recombination taking place on the front interface from that having its origin on the back one. Furthermore, the surface-recombination velocities reported in the literature for (p) c-Si/Al ohmic contacts are very high ($S > 10^5$ cm/s), whereas those for (p) c-Si/(p^+) c-Si/Al BSF contacts are significantly lower [19,4]. All this leads to the conclusion that S^*, being an effective surface-recombination velocity with contributions from both sides of the cell absorber, is dominated in our cells by a very important recombination on the back c-Si/Al interface. Keeping this in mind, the values in Table 2 can be interpreted as S_{QSSPC} being the surface-recombination velocity at the front side, whereas S^* represents that of at back interface. The correlated improvement in S^*, J_{sc} and η when the BSF concept is applied is fully consistent with this vision and can be easily understood as a consequence of a significant reduction of back-interface recombination. Finally, this interpretation allows to explain the improvement of cell performance and S^* with deposition temperatures increasing up to 310 °C. Since, as described above, the samples are thermalised for at least 4 h in the PECVD-chamber sample holder, cells made using higher emitter-deposition temperatures do have a lower back recombination as a consequence of a partial annealing of the c-Si/Al interface.

The implicit open-circuit voltage has also been estimated by QSSPC in the SHJ symmetrical structures. A value of 618 ± 15 meV has been found on average at 1 sun. The V_{oc} value on average of our finished solar cells with front and back contacts obtained from J–V curves is, however, only 576 ± 15 meV, in agreement with the much higher values of S^* as compared to those of S_{QSSPC}. These important losses of 44 ± 23 meV in the values of the open-circuit voltage evince an additional interface recombination being present in the cells but absent in QSSPC samples [12].

Finally, effective diffusion length values obtained from quantum efficiencies do confirm the hypothesis about the improvement of the cells with a good annealing of the back electrode. L_{eff} increases when the bulk and back recombination decrease, even up to values exceeding device thickness ($d \approx 300$ μm). The best values of L_{eff} are obtained when the emitter is deposited at 310 °C and cell performance is improved with a BSF rear contact, in agreement with a minimum of S^* (see again Table 2). In fact, a linear correlation between S^* and L_{eff} has been found (see Fig. 5). A new theoretical model is presently being developed in order to better fit the experimental J–V characteristics. This model is aimed at discriminating the effects of the recombination in either of the interfaces. The back-interface recombination is described through the dependence of L_{eff} on the voltage applied.

It is worth noticing the significant drop in η together with the increase of S_{QSSPC} and S^* observed at the highest deposition temperature (330 °C). The effect is accompanied with a decrease in the hydrogen content down to less than 5% (see Fig. 1). This low value is very probably the origin of the problem, since it corresponds to a solid lattice in which a very significant fraction of the dangling bonds do not have hydrogen atoms to be saturated. Consequently, the density of localised states in the band gap becomes significant, thus worsening cell performance [16,20].

4. Conclusions

A correlation has been found between emitter-deposition temperature and cell performance in a series of single silicon-heterojunction solar cells. This correlation cannot be explained in terms of emitter quality. Surface-recombination velocities obtained in different ways have allowed to interpret these results as being a consequence of the improvement of back-interface quality, derived in turn from annealing during the warm-up process. Additional measurements (effective diffusion lengths from internal quantum efficiencies) have confirmed this vision.

A 12%-efficient cell has been prepared by combining optimum emitter-deposition conditions and back-surface-field at the rear aluminium contact. This result has been based on the understanding of the limiting mechanisms of the devices after an analysis of interface-recombination velocities, effective diffusion lengths and implicit open-circuit voltages of the devices. The dominant limiting factor has been found to be back-interface recombination.

A drop in cell efficiency occurs for relatively high emitter-deposition temperatures. The effect is attributed to an increase of dangling-bond density, associated with a lowering of the hydrogen content.

None of the cells reported had a transparent conductive oxide. Theoretically, the efficiency of the best of them could be raised up to at least about 15% if an optimum anti-reflection coating or transparent conductive oxide is employed.

Acknowledgments

This work has been partially supported by the Spanish Ministry of Science and Innovation under projects CLÁSICO (ENE2007-67742-004-01/ALT) and MICROSIL (PSE-120000-2007-7).

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Please cite this article as: R. Barrio, et al., Sol. Energy Mater. Sol. Cells (2009), doi:10.1016/j.solmat.2009.09.017