

Progress in a-Si:H / c-Si heterojunction emitters obtained by Hot-Wire CVD at 200 °C

D. Muñoz¹, C. Voz¹, I. Martín¹, A. Orpella¹, J. Puigdollers¹, R. Alcubilla¹

F. Villar², J. Bertomeu², J. Andreu²

J. Damon-Lacoste³, P. Roca i Cabarrocas³

¹Universitat Politècnica de Catalunya, Grup de Recerca en Micro i Nanotecnologies,
Jordi Girona 1-3, Barcelona 08034, Spain

²CeRMAE -Universitat de Barcelona, Departament de Física Aplicada i Òptica,
Diagonal 647, Barcelona 08028, Spain

³Laboratoire de Physique des Interfaces et des Couches Minces, CNRS, Ecole
Polytechnique, 91128 Palaiseau, France

Abstract

In this work, we investigate heterojunction emitters deposited by Hot-Wire CVD on p-type crystalline silicon. The emitter structure consists of an n-doped film (20 nm) combined with a very thin intrinsic hydrogenated amorphous silicon buffer layer (5 nm). The microstructure of these films has been studied by Spectroscopic Ellipsometry in the UV-visible range. These measurements reveal that the microstructure of the n-doped film is strongly influenced by the amorphous silicon buffer. The Quasi-Steady-State Photoconductance (QSS-PC) technique allows estimating implicit open-circuit voltages near 700 mV for heterojunction emitters on p-type (0.8 $\Omega\cdot\text{cm}$) FZ silicon wafers. Finally, 1 cm^2 heterojunction solar cells with 15.1 % conversion efficiency

(total area) have been fabricated on flat p-type ($14\ \Omega\cdot\text{cm}$) CZ silicon wafers with aluminum back-surface-field contact.

Keywords

Hot-wire deposition, Solar cell, Heterostructure

1. Introduction

Heterojunction solar cells with thin hydrogenated amorphous silicon (a-Si:H) films deposited at low temperature on crystalline silicon (c-Si) wafers have attracted the interest of the photovoltaic community due to their potential high-efficiency and cost-effective fabrication process. Sanyo Electric Co. has reported conversion efficiencies (η) over 19% for mass produced solar cells with the so-called Heterojunction with Intrinsic Thin-layer (HIT) structure [1]. In this device a very thin (5 nm) intrinsic a-Si:H buffer reduces interface recombination, which leads to impressing open-circuit voltages (V_{oc}) over 700 mV. Most groups, included Sanyo, use the Plasma-Enhanced CVD technique to grow the a-Si:H films.

Recently, the Hot-Wire CVD (HWCVD) technique has also demonstrated its potential to fabricate high efficiency heterojunction silicon solar cells [2]. In the HWCVD technique, besides some technological advantages, the absence of ion bombardment reduces the damage to the c-Si surface. During the last years, our group has also obtained promising results in heterojunction solar cells by HWCVD [3,4]. In this work, we concentrate our effort in optimizing the heterojunction emitter on p-type c-Si. Besides, the importance of the thin intrinsic a-Si:H buffer and the influence of hydrogen pre-treatment are discussed in detail.

2. Experimental

In this work, the wire configuration has been modified with respect to our previous works to enlarge the homogeneous deposition area to $4 \times 4 \text{ cm}^2$. Two parallel tantalum wires separated 3 cm have been installed, with the gas inlet centered 1 cm below the wires. The substrate is placed 4 cm above the plane of the wires. The diameter of the wires is 0.5 mm. The deposition conditions have been extensively investigated for this new configuration. The optimized intrinsic a-Si:H layer is grown at a substrate temperature of 100 °C, with a silane flow of 2 sccm under a process pressure of 10^{-2} mbar. On the other hand, the n-doped layer is grown at 200°C under a higher process pressure of $8 \cdot 10^{-2}$ mbar. In this case, the gas flow consists of 4 sccm of silane mixed with 28 sccm of hydrogen and 0.04 sccm of phosphine. The wire temperature is 1600 °C in all cases. In addition, the convenience of hydrogen pre-treatment has been investigated. In such case, the c-Si surface is exposed to 20 sccm of hydrogen dissociated by the wire at 1700 °C under a process pressure of $3 \cdot 10^{-2}$ mbar. The chemical procedure to clean the c-Si wafers before being introduced into the HWCVD chamber is described elsewhere [4]. In this work, we have considered three different structures as n-type heterojunction emitters. First, an n-doped layer 20 nm thick deposited directly onto the cleaned c-Si surface (sample A). Second, a stack consisting of a very thin a-Si:H buffer layer (5 nm) followed by a 20 nm thick n-doped layer (sample B). Finally, the same stack in sample B but preceded by a hydrogen pre-treatment during 1 minute (sample C).

The microstructure of the films is obtained by fitting the pseudodielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) measured by Spectroscopic Ellipsometry (SE) with the Bruggeman model [5]. On the other hand, the quality of the emitter was assessed by the contactless QSS-PC technique for the same samples. In this technique, the minority carrier effective

lifetime (τ_{eff}) is measured as a function of an averaged excess minority carrier density (Δn_{avg}). P-type (0.8 $\Omega\cdot\text{cm}$) FZ silicon wafers were used for these experiments to avoid the influence of bulk recombination in the QSS-PC data.

Finally, flat p-type (14 $\Omega\cdot\text{cm}$) CZ silicon wafers with aluminum back-surface-field (Al-BSF) contact were used to fabricate complete heterojunction solar cells. The front contact consisted in an indium-tin-oxide (ITO) anti-reflecting coating (80 nm) deposited by RF magnetron sputtering, followed by an evaporated silver grid with 8% shadowing. The active area of the solar cell is 1 cm².

3. Results and Discussion

In figure 1 the imaginary part of the pseudodielectric function (ϵ_2) measured by SE is compared for the three samples previously described (symbols). The a-Si:H and c-Si models used to fit the experimental data are also shown in the same plot (lines). The two-peak characteristic of sample A, resembling the c-Si model, is typical of epitaxial growth [6]. Actually, the fit with the Bruggemann model leads to a high crystalline fraction (F_c) of 90% for this sample. By contrast, the broad bands observed in sample B indicate an essentially amorphous growth, even though the deposition conditions of the n-doped layer are the same. In this case, the fit only indicates a F_c value close to 20% in a very thin superficial layer (2-3 nm). The lower ϵ_2 values measured in sample B compared to A indicate a higher porosity, with a void fraction (F_v) close to 40%. A similar F_v value can be estimated for sample C. However, in this case the fit indicates a higher microcrystalline phase with F_c about 30% in the whole structure. This indicates a strong influence of the hydrogen pre-treatment on the emitter microstructure.

Figure 2 shows the QSS-PC data of the same samples studied by SE. As it can be observed, the intrinsic a-Si:H buffer improves the effective lifetime at one-sun

irradiance (τ_{eff}) from 17 μs in sample A to 750 μs in B. The hydrogenation pretreatment used in sample C results in a drastically reduced τ_{eff} value of 4 μs , even with the presence of the intrinsic layer. In addition, the QSS-PC data implicitly contain information about the maximum V_{oc} value that could be expected from the heterojunction emitter [7]. As it is shown in fig. 3, the long τ_{eff} value measured in sample B leads to an excellent implicit- V_{oc} of 695 mV at one-sun irradiance, whereas it is limited to 590 mV in sample A. Even lower is the value of 570 mV measured in sample C, in agreement with the shorter τ_{eff} value.

The group at NREL has clearly demonstrated that an abrupt heterojunction is preferred to reduce interface recombination [8]. In this sense, high-quality a-Si:H films are far more effective passivating layers than mixed-phase or highly defective epitaxial ones. Then, the highest performance of sample B agrees with its negligible crystalline fraction. However, the absence of a-Si:H buffer (sample A) results in a defective low-temperature epitaxy with moderate passivating properties. Finally, the hydrogen pretreatment (sample C) evidences a clear detrimental effect, leading to the growth of low quality microcrystalline films.

Complete heterojunction solar cells have been fabricated on flat CZ silicon wafers with Al-BSF contact. The structure B was selected as heterojunction emitter due to its excellent QSS-PC data. Actually, two different thicknesses have been considered for the n-doped layer, which are labeled as sample B1 (10 nm) and B2 (20 nm) in figure 4. The thin a-Si:H buffer layer was around 5 nm thick for both samples. The fabricated devices were isolated by a dry-etching process with CF_4 diluted into O_2 (20%). This treatment reduces lateral leakage currents in about three orders of magnitude (inset of Fig. 4).

The electrical parameters corresponding to the current density-voltage characteristics measured under AM1.5 irradiance are summarized in table 1. Especially remarkable are

the relatively high V_{oc} values. In fact, since the implicit- V_{oc} measured by QSS-PC was close to 700 mV for sample B, the actual values around 620 mV could be limited by the quality of the Al-BSF contact. The n-doped layer could be thinned to only 10 nm without any loss in V_{oc} .

Finally, figure 5 shows the Internal Quantum Efficiency (IQE) curves of the fabricated solar cells. As it could be expected, the thinner emitter device (B1) presents higher IQE values in the short wavelength range ($\lambda < 600$ nm). The same IQE curves are measured for longer wavelengths, since identical Al-BSF contacts were used in both cases.

4. Conclusions

Heterojunction emitters obtained by HWCVD at 200 °C on p-type c-Si showed implicit- V_{oc} values close to 700 mV. Such excellent result was obtained when a thin intrinsic buffer was directly deposited onto the c-Si before the n-doped layer. This buffer promotes the formation of an abrupt heterojunction, making the n-doped layer to grow essentially amorphous. Hydrogen pre-treatments, at least under the studied process conditions, evidenced detrimental effects on the quality of these heterojunctions. Complete solar cells with conversion efficiency 15.4% have been fabricated. In the future, low-temperature back surface passivation strategies will be used to get the maximum performance of this emitter structure.

Acknowledgments

This work was developed in the framework of CeRMAE. It has also been supported by the Spanish Government under programme ENE2004-07376-C03-01 and TEC2005-02716/MIC. One of the authors (D.Muñoz) acknowledges the support for the grant

program (FI/BE) of the Catalan Government. The work at LPICM has been supported by the French Agency for Environment and Energy Management.

References

1. M. Tanaka, S. Okamoto, S. Tsuge and S. Kiyama, Proc. 3rd World Conference on Photovoltaic Energy Conversion, Osaka (2003), 955-958.
2. T.H. Wang, E. Iwaniczko, M.R. Page, D.H. Levi, Y. Yan, H.M. Branz and Q. Wang, Thin Solid Films, 501 (2006) 284.
3. C. Voz, I. Martin, A. Orpella, J. Puigdollers, M. Vetter, R. Alcubilla, D. Soler, M. Fonrodona, J. Bertomeu and J. Andreu, Thin Solid Films, 430 (2003) 270.
4. D. Muñoz, C. Voz, M. Fonrodona, M. Garin, A. Orpella, M. Vetter, J. Puigdollers, R. Alcubilla, F. Villar, J. Bertomeu and J. Andreu, Journal of Non Crystalline Solids, 352 (2006) 1953.
5. A. Fontcuberta-i-Morral, P. Roca-i-Cabarrocas, C. Clerc, Physical Review B, 69 (2004) 125307.
6. D. Levi, E. Iwaniczko, M. Page, Q. Wang, H. Branz and T. Wang, Proc. 4th World Conference on Photovoltaic Energy Conversion, Waikoloa, Hawaii (2006).
7. R.A. Sinton, A. Cuevas, Appl. Phys. Lett. **69**, 2510 (1996).
8. T.H. Wang, Q. Wang, E. Iwaniczko, M.R. Page, D.H. Levi, Y. Yan, C.W. Teplin, Y. Xu, X.Z. Wu and H.M. Branz, Proc. 19th European Photovoltaic Solar Energy Conference, Paris (2004), 1296-1299.

List of table and figure captions

Table 1 Comparison of the different parameters measured for the solar cells B1 and B2.

Fig. 1 Imaginary part of the pseudodielectric function (ϵ_2) measured by SE for samples A, B and C. The models of c-Si and a-Si:H used are also shown.

Fig. 2 Effective surface recombination velocity (τ_{eff}) as a function of the excess minority carrier density for samples A, B and C. The arrows point the values at one sun.

Fig. 3 Implicit V_{OC} versus irradiance for samples A, B and C deduced from the QSSPC measurements.

Fig. 4 J-V characteristics measured under AM1.5 illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$) for the solar cells B1 and B2. In the inset, initial and dry-etched JV characteristics measured in dark.

Fig. 5 IQE curves of solar cells B1 and B2. The influence of the emitter thickness clearly affects the absorption between 300nm and 600nm.

SAMPLE	Open circuit Voltage, V_{oc} (mV)	Short circuit current, J_{sc} (mA/cm ²)	Fill Factor, FF (%)	Efficiency, η (%)
B1	622	32.7	75.7	15.4
B2	616	31.4	75.5	14.6









