

Available online at www.sciencedirect.com



Energy



Energy Procedia 55 (2014) 865 - 872

4th International Conference on Silicon Photovoltaics, SiliconPV 2014

Sputtered hydrogenated amorphous silicon for silicon heterojunction solar cell fabrication

Xinyu Zhang^{a,} *, Andres Cuevas^a, Bénédicte Demaurex^b, and Stefaan De Wolf^b

^aAustralian National University, Research School of Engineering,31North Road, Canberra 0200, Australia ^bEcole Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Photovoltaics and Thin-Film Electronics Laboratory, Breguet 2, CH-2000 Neuchâtel, Switzerland

Abstract

This work shows that RF sputter-deposited hydrogenated amorphous silicon (a-Si:H) films are very effective in passivating silicon surfaces. We have previously found that sputter-deposited 45 nm thick intrinsic a-Si:H provides outstanding surface passivation on n-type silicon, similar to that achieved by 'classic' plasma enhanced chemical vapour deposition [1]. In this paper, we show that p-type silicon surfaces can be well passivated as well, achieving effective carrier lifetimes of 1.1 ms for a 1 Ω ·cm p-type wafer, compared to 4.5 ms for a 1.5 Ω ·cm n-type sample. Next, on n-type textured surfaces reasonable passivation is also achieved. Post-deposition annealing of our samples shows that sputtered a-Si:H films can perform similarly to PECVD deposited films in terms of thermal stability. Importantly, with stacks of intrinsic and doped (n or p) amorphous silicon effective carrier lifetimes of 1.9 ms and 1.6 ms on 1.5 Ω ·cm n-type wafers were obtained for i/n⁺ and i/p⁺ stacks respectively. These results underline the promise of sputter-deposited a-Si:H as an attractive alternative for heterojunction solar cell fabrication. However, dark conductivity measurements show that sputter-deposited doped a-Si:H films feature a relatively low conductivity, so far. We speculate that this may be caused by differences in microstructure compared to PECVD a-Si:H films, as suggested from the extracted optical band gap values for the respective films.

© 2014 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Peer-review under responsibility of the scientific committee of the SiliconPV 2014 conference

Keywords: Sputtering; heterojunction solar cells; intrinsic amorphous silicon; doped amorphous silicon; surface passivation

* Corresponding author: Xinyu Zhang Tel.: +61-2-61251763. *E-mail address:* xinyu.zhang@anu.edu.au.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) thin films are attracting increasing attention for their applications to silicon heterojunction (SHJ) solar cells [2]. The state-of-art deposition method is plasma enhanced chemical vapor deposition (PECVD) [2-4], by which both intrinsic and doped (n or p) a-Si:H are achievable, leading to a SHJ solar cell efficiency as high as 24.7% in a front/rear contacted structure [3], and 25.6% in an interdigitated rear contacted architecture [5]. Even though the precise processing complexity of these record devices is yet to be disclosed, SHJ devices with efficiencies well over 21% can be fabricated with fully industrially compatible methods, including rear-contacted SHJ solar cells [6]. Important cost-reductions are also possible by replacing the state-of-the-art screen-printed silver metallization by copper based solutions [7]. Alternative thin-film deposition methods may as well lead to further cost reductions. In that sense, the sputtering technique has become an attractive alternative deposition method for amorphous silicon films.

Sputtering is a mature industrial technology with advantages including fast and homogeneous deposition, no dangerous gasses, precise control of film thickness, and overall low running cost. It is of particular interest to SHJ solar cells because both the transparent conductive oxide and the metal contacts can be deposited by sputtering as well. Recently, it was found that sputter-deposited amorphous silicon, using a mixture of hydrogen and argon as carrier gas during the deposition process, can achieve outstanding silicon surface passivation, quite similar to that obtained by the conventional PECVD method [1]. In this work, we report next steps in the development of an all-sputtered SHJ solar cell. We test the passivation capabilities of sputtered a-Si:H films on both n-type and p-type silicon surfaces, on random textured surfaces and on phosphorus diffused surfaces. The latter surfaces are of particular interest for passivating contacts as reported in [8]. Furthermore, we also present first results for silicon surfaces passivated by device-relevant stacks of intrinsic and doped (boron or phosphorus) a-Si:H, needed for electron and hole collecting passivated contacts formation in our all-sputtered devices.

2. Experimental

In this work, intrinsic a-Si:H films were deposited by a AJA O8 RF magnetron sputtering system using a pure silicon target, where the hydrogenation of films was achieved by supplying 2% H₂ and 98% Ar mixed gas as carrier gas for the sputtering plasma. Boron and phosphorus doped silicon targets were used to achieve doped amorphous silicon films. N-type FZ 1.5 Ω ·cm and p-type CZ 1 Ω ·cm silicon wafers were used for passivation tests. Some n-type samples were random-pyramid textured using TMAH and IPA. Phosphorus diffusion was performed on 100 Ω ·cm p-type FZ substrates. All samples were RCA cleaned before loading into the sputter system for double-side depositions. Effective carrier lifetime and recombination current J₀ were measured with a Sinton Instruments WCT-120 system before and after a series of forming gas anneals at 300 °C. Thickness of deposited amorphous silicon films was measured using a J.A.Woollam N-2000 spectroscopic ellipsometry system, the measured data was also used to extract the optical band gap. A spectrophotometer was also used to measure the transmission of films, which can further allow to extract the optical band gap as well. The doping of boron and phosphorus doped amorphous silicon was tested through dark conductivity measurements. Films prepared for these purposes were deposited on glass slides.

3. Intrinsic amorphous silicon

3.1. Surface Passivation of N-type/p-type crystalline silicon on planar and textured surface

Fig. 1 shows the effective carrier lifetime of samples passivated by sputtered amorphous silicon using the optimised parameters we reported earlier [1]. Both n-type and p-type samples are well passivated. Effective lifetimes of 4.5 ms are achieved on n-type 1.5 Ω ·cm sample, corresponding to a surface recombination velocity upper limit S_{eff,UL} of 1.5 cm/s (using the Richter bulk lifetime [9]). In this work, 1.1 ms has been achieved for p-type 1 Ω ·cm samples, equivalent to S_{eff} of 11.7 cm/s. It is interesting to note that such sputtered intrinsic films show injection-dependent passivation trends that are quite similar to those discussed for PECVD layers: On n-type c-Si surfaces, towards low-injection levels, the measured carrier lifetimes remain high. Contrastingly, on p-type c-Si

surfaces, a drop in passivation quality is observed towards low injection levels. This difference was explained as arising from the asymmetry between electron and hole capture cross sections of silicon dangling bonds present at the wafer surface [4]. Comparing now the absolute passivation values we obtain here between sputtered and conventional PECVD deposited a-Si:H, we see that our PECVD samples have similar or slightly higher effective lifetime than sputtering samples, both of which are still significantly lower than the ideal surface passivation (~9 ms [9]), however. Importantly, for the same wafers we estimate the bulk lifetime to be 5.5 ms, using the HF passivation method, where the wafers are immersed in a HF bath during lifetime measurements (data not shown). Based on this, it is not unlikely that all our results are limited by the wafer bulk quality [1]. Considering this, surprisingly good surface passivation can be obtained with sputtering, indicating that this technique allows for gentle deposition (i.e. not leading to any c-Si surface plasma damage) while guaranteeing efficient incorporation of hydrogen into the films.

Using the same deposition parameters, the textured samples are not as well passivated as for the planar surfaces, possibly due to a non-uniform film thickness. The PL imaging of textured wafer shows a varying lifetime from substrate centre to edge. In our sputtering system the wafers are placed at an oblique angle with respect to the target, therefore, considering the directionality of the sputtering technique, some textured valley regions may be partially shaded by pyramid peaks. Adjusting the substrate-to-target distance and wafer loading position can possibly improve the quality and uniformity of the passivating layers. This will be subject to further research. Passivation of textured wafers can be significantly improved by post-deposition anneal, as shown in Fig. 1. After 1 hour forming gas anneal at 300° C an effective lifetime of 1.1 ms was achieved, while as-deposited films only resulted in $300 \,\mu$ s.



Fig 1. Injection dependent effective lifetime of samples coated by sputtering deposited a-Si:H.

3.2. Diffused-surface passivation

Intrinsic amorphous silicon films find important application as buffer layers in heterojunction solar cells. However, they may also be useful in homojunction solar cells. In such a case, the surfaces are usually much higher doped due to the homojunctions present (either as emitter or back surface field). In this section, we explore the properties of sputtered a-Si:H as passivating films for highly doped surfaces. Table 1 presents the passivation of phosphorus diffused samples with a variety of sheet resistances. It can be seen that sputtered amorphous silicon is able to provide effective passivation on diffused samples, especially after a forming gas anneal. Compared to PECVD deposited silicon nitride passivation results, which is the current industrial standard for phosphorous doped surfaces, sputtered a-Si:H films still give slightly higher J_{0n} . The sputter-deposited a-Si:H film is not ideal for

heavily doped surface passivation, however the reasonably low J_{0n} suggest that it may well be a promising alternative for passivating diffused surfaces. Another interesting finding is that also here the sputtered a-Si:H films are improving significantly with forming gas anneal at 300 °C, as shown in Table 1 the J_{0n} values are nearly halved after 2 hours anneal. Furthermore, the results are still slowly improving or keeping unchanged after overnight anneal, it shows that sputtering deposited a-Si:H films are thermally stable, which may enable easy process-integration.

Table 1. J₀ of phosphorus diffused regions passivated by sputtering deposited a-Si:H in fA/cm².

Passivation layer	50 Ω /□	75 Ω/□	100 Ω /□	120 Ω /□
Sputtered a-Si as-deposited	180	150	110	95
Sputtered a-Si 2 hour FGA	120	75	60	45
SiN _x from literature [10]	60	N/A	40	30

3.3. Post-deposition anneal

Earlier, we found that the (as-deposited) passivation quality of sputtering deposited a-Si:H is sensitive to the deposition (substrate) temperature T_{depo} [1]. The behaviour of samples deposited at different T_{depo} is also different. Fig 2 presents the post-deposition anneal experiments. All forming gas anneals were performed at 300 °C for a cumulated time. It is found that low T_{depo} samples can be significantly improved by anneal, while high T_{depo} samples are not sensitive to it and the prolonged anneal may even cause degradation. The results shown here are similar to the performance of PECVD deposited a-Si:H films [2, 11]. In practice, the a-Si:H films deposited by sputtering at high T_{depo} (> 250°C) is sufficient to provide good surface passivation without the need of any post-deposition anneal [1].



Fig 2. Seff as a function of anneal time. N-type silicon passivated by sputtering deposited a-Si at varied T_{depo}.

4. Intrinsic and doped amorphous silicon stacks

Amorphous silicon is widely used in heterojunction solar cell concepts, where thin intrinsic and doped a-Si:H film stacks are applied on top and rear of the silicon wafer [2-4]. In a typical HIT solar cell design, the intrinsic amorphous silicon layer between crystalline silicon bulk and the doped silicon layer works primarily as a passivating

layer. On top of the passivation layers, the boron and phosphorus doped amorphous silicon working as carrier selective layer. The challenge for sputter-deposited a-Si:H is to produce simultaneously sufficient doping and good passivation.

4.1. Passivation effect

Good passivation is the basic requirement of the stacked layers. It is previously found that sputtering deposited a-Si:H films with higher thickness (around 45nm) passivates silicon surfaces better. However, in order to reduce the absorption loses and barrier effect for charge carriers, the thickness of the (i)a-Si:H layer should be limited to a few nanometers [12, 13]. As a compromise, 10 nm (i)a-Si:H is used in this work. For doped amorphous silicon films, a thickness of 10 nm is used as well.

Fig. 3 shows initial results of passivation by sputtering deposited intrinsic and doped a-Si layers. Compared to a single 10 nm thick (i)a-Si:H layer, the subsequent deposition of an extra 10 nm of doped a-Si:H improves the passivation level. The effective lifetimes of 1.9 ms for the i/n+ stack and 1.6 ms for i/p+ stack are equivalent to S_{eff} of 4.5 cm/s and 5.5 cm/s. The lifetimes of these stack layers with 20 nm total thickness are higher than those obtained by intrinsic 10 nm a-Si:H and very close to that achieved by intrinsic 20 nm a-Si:H film. Intrinsic and doped silicon are deposited in a continuous process, during which the deposition conditions are kept unchanged.

Noteworthy, it has been reported that PECVD deposited (n)/(p) a-Si:H layers are less efficient in terms of silicon surface passivation than intrinsic a-Si:H films [14, 15]. As for doped and intrinsic a-Si:H stacks, De Wolf *et al* [14] reported that n^+/i stack have slightly better passivation than intrinsic film, while p^+/i stack has much lower effective lifetime than intrinsic films. This effect was explained as arising from defect generation, mediated by a Fermi-level shift in the films, and is thus likely directly linked to the doping efficiency of the involved films. Based on dark conductivity measurements (discussed below), we find that our sputtered layers developed so far show a significantly lower conductivity, compared to typical PECVD layers. Hence, such layers will not be able to yield large shifts of their Fermi-level, causing defect generation and thus deteriorated passivation.

There are other side effects that can explain the less detrimental impact on passivation from sputtered films: during the sputtering of a-Si:H(p^+), the films are not directly exposed to a boron source like B₂H₆ (PECVD), as a result, the chance of forming defective aSiB_x:H layer at the p-i interface is reduced [14, 16, 17]; moreover, as the hydrogen plasma is not interrupted between the deposition of the intrinsic and doped layers, the interfacial layer between doped and intrinsic amorphous silicon could be better defined compared to other deposition techniques.



Fig 3. Effective lifetime of n-type 1.5 Ω cm samples passivated by intrinsic and doped a-Si stacks.

4.2. Doping Effect

Doped amorphous silicon layers on top of the passivating intrinsic a-Si:H layers are required to selectively transport carriers. The performance of this layer depends on the doping concentration of the film, which can be tested by measuring the conductivity and activation energy of the a-Si:H films in the dark. Table 2 lists first characterisation results. In addition, the optical band gap values extracted from spectroscopic ellipsometry (SE) measurement data are also presented. We also show the optical band gap results extracted from transmission data obtained from spectrophotometer measurements.

Table 2. Properties of doped amorphous silicon.

	a-Si:H (p ⁺)	a-Si:H (n^+)	Intrinsic a-Si:H
			(PECVD)
Dark conductivity (S/cm)	$(2.4\pm0.5)\times10^{-7}$	$(2.9\pm1.3)\times10^{-7}$	1.2×10^{-11}
Activation Energy (eV)	0.47	0.44	0.8
Ellipsometry extracted E_g^{opt} (eV)	1.59	1.52	1.80
Transmission extracted \tilde{E}_{g}^{opt} (eV)	1.60	1.43	1.73

The doping efficiency is reflected by the measured conductivity in the dark σ_{dark} . For PECVD deposited a-Si:H films, a typical σ_{dark} value for boron doped a-Si:H is in the range of 1×10^{-6} to 1×10^{-5} S/cm and for phosphorus doped films is 1×10^{-3} to 1×10^{-2} S/cm [18-20]. It can be seen that sputtering deposited a-Si:H is much less conductive. These initial results are obtained by process recipes used for passivation layers, which have relatively "gentle" conditions in order to avoid damage from sputtering. Furthermore, the doping concentration of our sputter target is quite low, boron doped silicon target has 1% boron and phosphorus doped silicon target has only 0.01% phosphorus. It is expected that higher doping efficiency can be achieved by further optimization of the process condition and of the target.

The optical band gap is another indicator of the doping conditions, since the E_g^{opt} value varies as the doping concentration is changed [19, 20]. It is commonly extracted from ellipsometry measurements. In this paper, we also present the transmission method which can provide fast, easy and reasonable estimation of the optical band gap for amorphous silicon films. Equation 1 describes the imaginary coefficient of the permittivity ε_i as a function of the absorption coefficient $\alpha(\hbar\omega)$ and photon energy $\hbar\omega$ [21]:

$$\epsilon_{i} = n \cdot k = n \cdot \frac{\alpha \lambda}{4\pi} = C_{1} \cdot \frac{\alpha(\hbar\omega)}{\hbar\omega}$$
 (1)

Where n is the refractive index and k is the imaginary part of the refractive index, λ is the wavelength and C₁ is a constant. In addition, by defining and calculating the joint density of states D_j for conduction and valence bands, we can get ε_i for amorphous silicon thin films from equation 2 [21]:

$$\varepsilon_{i} = C_{2} \cdot \frac{1}{\omega^{2}} \cdot |P_{cv}| \cdot D_{j} = C_{3} \cdot \frac{1}{\omega^{2}} \cdot (\hbar\omega - E_{g})^{2}$$
(2)

Where P_{cv} is the transition matrix element, C_2 and C_3 are both constants. As a result, we can derive the fowling relation shown in Equation 3:

$$\alpha(\hbar\omega) \cdot \hbar\omega = C \cdot (\hbar\omega - E_g)^2 \tag{3}$$

Through the spectrophotometry measurement, we can get the absorption coefficient data from the normalized transmission signal as a function of photon energy. Fig. 4 presents an example of optical band gap extraction for sputtering deposited boron doped amorphous silicon. According to the above derived equation, we can fit the linear part of the curve and estimate the E_g^{opt} to be 1.60 eV, which is in agreement with the ellipsometry extracted value.



Fig 4. Example of optical bandgap (boron doped a-Si:H) extraction from spectrophotometer measured transmission data.

Using this method, we can get a reasonable estimation of the optical band gap values for amorphous silicon thin films. However, there are some limitations to this method: it is assumed that interface reflection between thin film and the underneath glass substrate is negligible; the surface scattering of measured films is not considered; the model for permittivity calculation from joint density states D_j is not particularly based on amorphous material which leads to some errors. However, due to the measurement simplicity, it can be a useful characterization tool for a-Si:H films.

5. Summary

In this work, we present progress in the area of sputtering deposited a-Si:H thin films. The best surface passivation result has been achieved with S_{eff} of 1.5 cm/s on n-type 1.5 Ω -cm silicon, while p-type 1 Ω -cm sample results in S_{eff} of 11.7 cm/s. The doped a-Si:H films deposited by sputtering have also been studied, which is a crucial path towards heterojuction solar cells fully prepared by sputter-deposition . Promising results on the passivation effect of the doped (boron or phosphorus) a-Si:H and intrinsic a-Si:H stacks have been found, where no detrimental impact was found after doped amorphous silicon deposition. However, initial characterizations show that the doping efficiencies of sputtering deposited a-Si:H films with either boron or phosphorus is not sufficient yet for making heterojunction devices. Further investigation aims to improve the doping content of sputtered films.

Acknowledgements

This program has been supported by the Australian Government through the Australian Renewable Energy Agency (ARENA). Responsibility for the views, information or advice expressed herein is not accepted by the Australian Government. The authors from EPFL thank the Axpo Naturstrom Fonds, the European Commission (FP7 project Hercules), the EuroTech Universities Alliance and the Swiss Commission for Technology and Innovation for their financial support. Special appreciations are given to Niels Holm and James Bullock for their assistance with

characterizations. The authors would also like to thank Di Yan for help with wafer texturing. Thanks also to Stuart Hargreaves for maintaining the sputtering system.

References

- Zhang X, Hargreaves S, Wan Y, Cuevas A. Surface passivation of crystalline silicon by sputter deposited hydrogenated amorphous silicon. Phys. Status Solidi RRL. Physica Status Solidi rrl 2014; 8:3-231.
- [2] De Wolf S, Descoeudres A, Holman ZC, Ballif C. High-efficiency Silicon Heterojunction Solar Cells: A Review. Green 2012; 2:7-7.
- [3] Taguchi M, Yano A, Tohoda S, Matsuyama K, Nakamura Y, Nishiwaki T, Fujita K, Maruyama E. 24.7% Record Efficiency HIT Solar Cell onThin Silicon Wafer. IEEE Journal of Photovoltaics 2014; 4:1-96.
- [4] Descoeudres A, Holman Z, Barraud L, Morel S, De Wolf S, Ballif C. >21% efficient silicon heterojunction solar cells on n-and p-type wafers compared. IEEE Journal of Photovoltaics 2013; 3:1-83.
- [5] Panasonic. Panasonic HIT(R) Solar Cell Achieves World's Highest Energy Conversion Efficiency of 25.6% at Research Level. Available: http://panasonic.co.jp/corp/news/official.data/data.dir/2014/04/en140410-4/en140410-4.html. 2014.
- [6] Tomasi A, Paviet-Salomon B, Lachenal D, De Nicolas S, Descoeudres A, Geissbuhler J, De Wolf S, Ballif C. Back-contacted silicon heterojunction solar cells with efficiency >21%. IEEE Journal of Photovoltaics 2014; DOI: 10.1109/JPHOTOV.2014.2320586.
- [7] Geissbuhler J, De Wolf S, Faes A, Badel N, Jeangros Q, Tomasi A, Barraud L, Descoeudres A, Despeisse M, Ballif C. Silicon heterojunction solar cells with copper-plated grid electrodes: status and comparison with silver thick-film techniques. IEEE Journal of Photovoltaics 2014; DOI: 10.1109/JPHOTOV.2014.2321663.
- [8] Bullock J, Yan D, Wan Y, Cuevas A, Demaurex B, Hessler-Wyser A, De Wolf S. Amorphous silicon passivated contacts for diffused junction silicon solar cells. Journal of Applied Physics 2014; 115:16-163703.
- [9] Richter A, Glunz SW, Werner F, Schmidt J, Cuevas A. Improved quantitative description of Auger recombination in crystalline silicon. Physical Review B 2012; 86:16-165202.
- [10] Kerr MJ, Schmidt J, Cuevas A, Bultman JH. Surface recombination velocity of phosphorus-diffused silicon solar cell emitters passivated with plasma enhanced chemical vapor deposited silicon nitride and thermal silicon oxide. Journal of Applied Physics 2001; 89:7-3821.
- [11] De Wolf S, Olibet S, Ballif C. Stretched-exponential a-Si:H/c-Si interface recombination decay. Applied Physics Letters 2008; 93:3-032101.
- [12] Fujiwara H, Kondo M. Effects of a Si : H layer thicknesses on the performance of a-Si:H c-Si heterojunction solar cells. Journal of Applied Physics 2007; 101:5-054516.
- [13] Holman Z, Descoeudres A, Barraud L, Fernandez F, Seif J, De Wolf S, Ballif C. Current losses at the front silicon heterojunction solar cells. IEEE Journal of Photovoltaics 2012; 2:1-7.
- [14] De Wolf S, Kondo M. Nature of doped a-Si:H/c-Si interface recombination. Journal of Applied Physics 2007; 105:10-103707.
- [15] De Wolf S. Intrinsic and doped a-Si:H/c-Si interface passivation. In: van Sark W, Korte L, Roca F, editors. Physics and technology of amorphous-crystalline heterostructure silicon solar cells. Berlin Heidelberg: Springer-Verlag; 2012.
- [16] Collins R. Insitu study of ptype amorphous silicon growth from B2H6:SiH4 mixtures: Surface reactivity and interface effects. Applied Physics Letters 1988; 53:12-1086.
- [17] Catalano A, Wood G. A method for improved short wavelength response in hydrogenated amorphous silicon based solar cells. Journal of Applied Physics 1988; 63:4-1220.
- [18] Tucci M, Serenelli L, De Iuliis S, Izzi M, De Cesare G, Caputo D. Contact formation on a-Si:H/c-Si heterostructure solar cells. In: van Sark W, Korte L, Roca F, editors. Physics and technology of amorphous-crystalline heterostructure silicon solar cells. Berlin Heidelberg: Springer-Verlag; 2012.
- [19] Cabarrocas P. Deposition of intrinsic, phosphorus doped, and boron doped hydrogenated amorphous silicon films at 50°C. Applied Physics Letters 1994; 65:13-1674.
- [20] Nicolas S, Munoz D, Ozanne A, Nguyen N, Ribeyron P. Optimisation of doped amorphous silicon layers applied to heterojunction solar cells. Energy Procedia 2011; 8:-226.
- [21] Yu P, Cardona M. Fundamentals of semiconductors: Physics and materials properties. 3rd ed. Berlin Heidelberg: Springer-Verlag; 2005.