Special issue of the 2nd International Conference on Computational and Experimental Science and Engineering (ICCESEN 2015)

Fabrication of Pyramid/Nanowire Binary Structure on *n*-Type Silicon Using Chemical Etching

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A pyramid and nanowire binary structure of *n*-type monocrystalline silicon surface was fabricated by two-step chemical etching process. The nanowire surface is formed by electroless etching in HF-$AgNO_3$ aqueous solution after being textured in KOH/IPA solution. Optical absorption was compared between this structure and that of random pyramid arrays. The effective reflectance calculated between 400 and 1100 nm decreased from ≈40% to ≈15% after pyramidal texturing and ≈4% after formation of vertically aligned nanowires with a length less than 1 μm. This simple and low-cost surface structuring technique holds high potential for the manufacture of terrestrial silicon solar cells with reduced optical losses.

DOI: 10.12693/APhysPolA.130.385

PACS/topics: 88.40.jj

1. Introduction

The photovoltaic technology converts a portion of the sunlight energy directly into electricity by means of a photovoltaic module made up of inter-connected solar cells. Currently, 90% of commercially available solar cells are composed of silicon. To make the photovoltaic conversion competitive with other electricity sources, it is necessary to reduce the cost of manufacturing solar cells and increase their conversion efficiency. To achieve these goals, innovative technological approaches are essential. In particular, the reduction of reflection losses is very important since a planar silicon surface reflects more than 30% of the incident light. The reflected radiation cannot contribute to the conversion process in the solar cell and thus leads to a reduced performance. To overcome the reflective property of silicon, most manufacturers apply a low-cost chemical treatment to texturize the surface with random pyramids [1] or an antireflection coating, most often hydrogenated silicon nitride (SiN_x:H) deposited on the front surface by plasma enhanced chemical vapour deposition (PECVD) [2]. The reflection is then decreased to ≈10–12%. When both techniques are combined, the reflection losses still remain high (3–5%) [3, 4].

Currently, silicon nanowires (SiNWs) are a promising alternative because of their many advantages for the photovoltaic application, as shown by the extensive research work published in the literature [5, 6]. In particular, *n*-type SiNWs attract lots of attention to hybrid solar cells based polymer/ semiconductor [7]. The usage of SiNWs arrays can be categorized into two types. The first one is SiNWs-array core sheath *p*–*n* junction solar cells and the second one is for antireflection purpose.

Among the various techniques of implementation, the easiest method is based on electroless chemical dissolution of the surface in the presence of a metal catalyst [8]. The resulting SiNWs are vertically aligned, have usually a diameter of tens of nm and a length of up to several μm. These nanostructures promote strong absorption of the incident photons by light trapping. In this work SiNWs were synthesized by simple chemical etching of (100) *n*-type pyramid textured silicon wafers using a mixture of hydrofluoric acid (HF) and silver nitrate ($AgNO_3$). Prior to etching, a surface oxidation was applied using a piranha solution. A reflectivity of 4% over the wavelength range 400–1100 nm was obtained.

2. Experimental methods

The Si nanowires were prepared by chemical etching in HF-$AgNO_3$ solution. The starting material was mirror-polished front-side 4 inch diameter, *n*-type silicon wafer, (100) in orientation, with resistivity in the range 1–5 Ω cm. The wafers were cut into 1.5×1.5 cm^2 samples, degreased in trichlorethane and acetone at 50 °C (10 min each). The samples were first textured in KOH-IPA solution for different treatment times and concentrations to produce random (111) micro-pyramids. This was followed by cleaning in HCl for 5 min and a final dip in dilute HF for 30 s. They were then cleaned in a boiling piranha solution (H_2SO_4:H_2O_2) for 10 min, and dipped in 10% HF solution for 1 min to remove the surface oxide. As reported in [9], we found that performing an additional oxidation pre-treatment, just before the etching process, resulted in a better uniformity of the silicon nanowires over the sample surface and a lower

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reflection. The oxidized silicon wafers were etched various times in 5.6 M HF–0.023 M $AgNO_3$. After etching, the total hemispherical reflectance was measured in the wavelength range 300–1200 nm using a Varian Cary 500 UV-VIS-NIR spectrophotometer equipped with an integrating sphere. Surface morphology observation was carried out using a JEOL JSM 6360LV scanning electron microscope (SEM).

3. Results and discussion

In this work, we have started studying the optical properties of the different samples labelled T1, T2, T3, and T4 obtained varying the texturization process. We have optimized the conditions to obtain the lower reflectivity and the optimized result was utilized to fabricate the binary structure. As a figure of merit, we used the solar weighted spectral reflectance, R_w, given by the following relation:

$$R_w = \int_{400}^{1100} R(\lambda)\, \Phi(\lambda)\, \mathrm{d}\lambda \Big/ \int_{400}^{1100} \Phi(\lambda)\, \mathrm{d}\lambda,$$

where R is the reflectivity and Φ — the solar flux at each wavelength under AM1.5 standard conditions. The different reflectivity obtained on n-type Si(100) samples calculated in the spectral range 400–1100 nm are summarized in Table I with their corresponding etching conditions. A mirror-polished sample (MPS) has been used as a reference. As shown in Fig. 1, the lowest value was obtained for the sample T3 after etching in 1.5 wt% KOH/3.8 vol.% IPA in H_2O for 40 min. Figure 2 shows the SEM picture of the simple T3 before and after fabrication of binary structure after etching for 10 min in HF-$AgNO_3$ solution.

TABLE I

Conditions of texturization used in this work for the different reflections.

Sample	KOH [wt%]	IPA [vol.%]	T [°C]	t [min]	R_w [%]
T1	1	1	70	40	23
T2	1	1	70	60	19.48
T3	1.5	3.8	70	40	15.45
T4	1.5	3.8	70	60	18.80
MPS	–	–	–	–	≈40

Without oxidation pre-treatment (b), the etching is not uniform as can be observed by naked eye where it can be noted that the etching occurs only on some regions. However, the pretreatment with oxidation (c) gives a surface completely dark black, indicating the uniformity of the nanowire formation.

The reflection of a nanowire covered silicon surface depends mainly on the nanowire length, diameter, and density. In the literature, a nanowire length of several μm was found necessary to reduce the reflectivity to less than 2% in a much smaller portion of the wavelength range considered in the present study [10, 11]. In this study, the reflectivity could be reduced over the entire range 400–1100 nm to 4% by the binary structure silicon pyramid/nanowires. This value can be reduced further with increasing etching time. It can even reach values lower than 2% provided it does not destroy the pyramids.

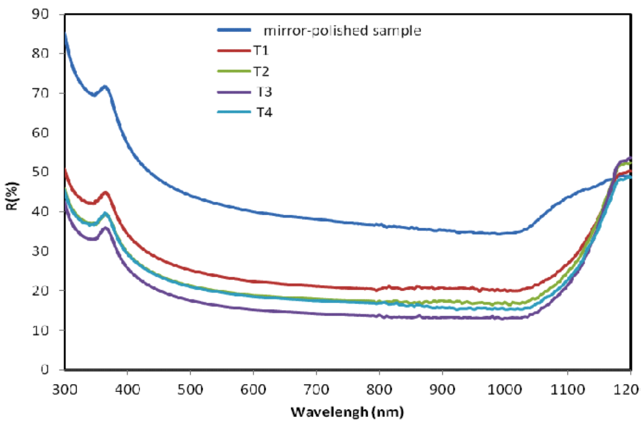

Fig. 1. Measured reflectance spectra of mirror polished silicon, pyramidal textured silicon under different etching conditions.

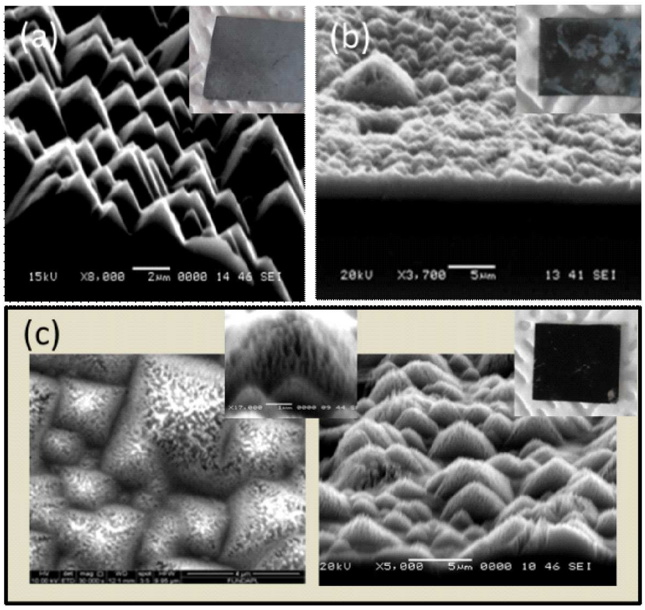

Fig. 2. SEM micrographs of T3 surface (a) before formation of nanowire ((b) and (c)); after formation of a silicon nanowire for 10 min in HF-$AgNO_3$ solution without oxidation, and with oxidation pretreatment respectively. In the left of (c) — top view, in the right — cross-section.

Figure 3 illustrates the variation of the measured reflection spectra for the polished silicon wafer surface, the textured surface and the silicon nanowire covering the surface shown in Fig. 2c.

In the useful wavelength range for solar cells, 400–1100 nm, R_w was reduced by pyramidal texturization using different chemical solutions. The lower reflectivity (15%) was obtained for the solution 1.5 wt% KOH/3.8 vol.% IPA in H_2O for 40 min as shown in Fig. 1 (curve T3). The reflectivity became 11%, when the sil-

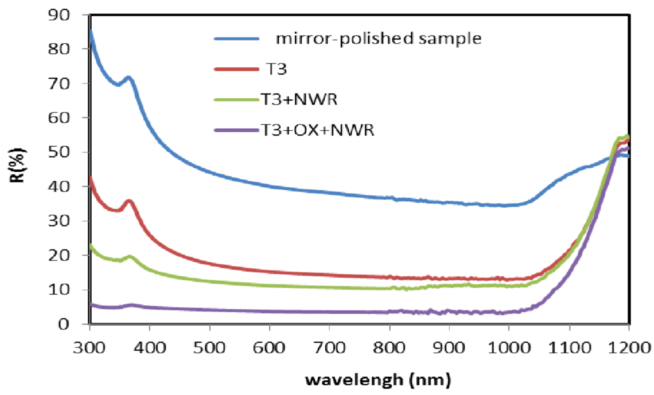

Fig. 3. Measured reflectance spectra of mirror polished silicon, textured silicon with and without silicon nanowires.

icon nanowires were formed on the pyramids without an oxidation pretreatment, curve T3+NWR of Fig. 3. The lowest reflectivity (4%) was obtained when the oxidized pyramids were nanotexturized with SiNWs, see curve T3+Ox+NWR of Fig. 3. This means that silicon nanowires fabricated using inexpensive chemical etching lead to a reduction of optical losses which is much better than that achieved with a pyramidally texturized surface covered by a SiN_x antireflection coating which requires a costly plasma reactor with flammable and toxic precursor gases such as silane and ammonia.

4. Conclusion

In this work, n-type silicon nanowires have been fabricated using a simple, low-cost technology based exclusively on chemical etching steps. Vertically aligned, silicon nanowires were obtained on random pyramidally-textured silicon samples. A remarkable reduction in surface reflectivity over the entire spectral range 300 to 1200 nm was obtained. The lowest weighted reflectance reached ≈4% between 400 and 1100 nm. The reflection losses are lower than obtained using a pyramidally textured surface covered with a SiN_x PECVD antireflection coating which is the standard procedure in the photovoltaic industry. Such low reflection of the silicon nanowires presented in this study hold a great potential to increase the photocurrent of silicon solar cells.

Acknowledgments

This work was supported by the Algerian Ministry for Higher Education and Scientific Research (DGRSDT).

References

[1] U. Gangopadhyay, K.H. Kimb, S.K. Dhungel,. U. Manna, P.K. Basu, M. Banerjee, H. Saha, J. Yi, *Sol. Energy Mater. Sol. Cells* **90**, 3557 (2006).

[2] J. Yoo, J. So, G. Yu, J. Yi, *Sol. Energy Mater. Sol. Cells* **95**, 7 (2011).

[3] P.K. Singh, R. Kumar, M. Lal, S.N. Singh, B.K. Das, *Sol. Energy Mater. Sol. Cells* **70**, 103 (2001).

[4] M.A. Green, *Solar Cells: Operating Principles, Technology and System Applications*, Prentice-Hall, Englewood Cliffs, NJ 1982, p. 164.

[5] L. Hu, G. Chen, *Nano Lett.* **7**, 3249 (2007).

[6] V. Sivakov, G. Andrä, A. Gawlik, A. Berger, J. Plentz, F. Falk, S.H. Christiansen, *Nano Lett.* **9**, 1549 (2009).

[7] Hong-Jhang Syu, Shu-Chia Shiu, Ching-Fuh Lin, *Sol. Energy Mater. Sol. Cells* **98**, 267 (2012).

[8] K. Peng, Y. Xu, Y. Wu, Y. Yan, S.T. Lee, J. Zu, *Small* **1**, 1062 (2005).

[9] S.C. Shiu, S.B. Lin, S.C. Hung, C.F. Lin, *Appl. Surf. Sci.* **257**, 8566 (2011).

[10] S.K. Srivastava, D. Kumar, P.K. Singh, M. Kar, V. Kumar, M. Husain, *Sol. Energy Mater. Sol. Cells* **94**, 1506 (2010).

[11] B. Ozdemir, M. Kulakci, R. Turan, H.E. Unalan, *Nanotechnology* **22**, 155606 (2011).