

Gradient-Porosity Porous Silicon (GPSi) as Anti-reflection Coating in Solar Cells Applications

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Received on: 3/9/2014 & Accepted on: 8/1/2015

ABSTRACT

Laser Assisted Etching (LAE) technique with short laser wavelength was used to provide a gradient-porosity porous silicon (GPSi) layer. Morphological aspects, reflectivity and photoelectric properties of (GPSi) layer were studied based on a bare solar cell substrate (p-n). The results show that the (GPSi) layer has a lower reflectivity of about (1.3%) comparing with bulk silicon (reference sample 50%) and single layer PSi of about (10.5%) at wavelength regime (400 nm). The surface morphology and x-section images present the formation of (GPSi) with layer thickness of about (400 nm) less than the junction depth. The photoelectrical properties of (GPSi) layer shows that an increase of short circuit current density of (2.8 mA/cm²) compared with the ordinary solar cell of (2.15 mA/cm²) while for single layer PSi is about (2.05 mA/cm²).

Keywords: porous silicon, gradient-porosity porous silicon, reflectivity, solar cell.

السليكون المسامي المتدرج- المساميه لتطبيقات الطبقات المضادة للانعكاس في الخلايا الشمسية

الخلاصة

في هذا البحث تم استخدام طريقة التنميش المساند بالليزر باستخدام اطوال موجية ليزرية قصيرة لإنتاج سيليكون مسامي متدرج الطبقات من شرائح سليكونية مجردة (p-n). وقد تم دراسة خصائصه التركيبية والبصرية. وقد اظهرت نتائج الانعكاسية ان السيليكون متدرج المسامية يمتاز بانعكاسية واطئة جدا ولحد 1.3% مقارنة مع السيليكون الاعتيادي والتي تصل الى 50% وللسيليكون المسامي احادي الطبقة 10.5% عند منطقة الطول الموجي (400) نانو متر. وقد بينت نتائج صور المقطع العرضي للمجهر الالكتروني الماسح ان سمك طبقة (GPSi) هو اقل من 400 نانو متر (اقل من عمق المفرق). ان الخصائص الكهربائية لطبقة (GPSi) بينت حصول زيادة ملموسة في تيار

دائرة القصر حيث كانت 2.8 ملي امبير/سم² لطبقة السيلكون متدرج المسامية 2.05 ملي امبير/سم² للسيلكون احادي الطبقة و 2.15 ملي امبير/سم² للخلية الشمسية الاعتيادية.

INTRODUCTION

Porous silicon (PSi) has recently been shown to have potential in highly efficient solar cells as a reflector due to large light-trapping. The role of the PSi layer is to increase the photon absorption in the active layer for low energy photons and therefore to increase the photo generation of photo carriers and resulting short circuit current of the solar cell. Various morphologies and porosities of PSi were employed to enhance the light trapping in solar cell. These included by convert the conventional single-layer PSi to gradient-porosity (GPSi) [1, 2, 3].

The gradient- porosity resulting from localized formation of PSi gives rise to a variation of the refractive index which can be used to fabricate waveguides [4] to obtain photonic crystals. One important issue in silicon photovoltaic is the reduction of optical losses in polycrystalline silicon solar cells by texturing of their surface [5].

The high reflectivity of a silicon solar cell in the (350–1000) nm spectral range is due to the large refractive index discontinuity that exists at the air-silicon interface [Fig. 1(a)]. By placing a single layer ARC of intermediate refractive index on the silicon surface, this large index discontinuity is broken into two smaller steps [Fig. 1(b)] resulting in a lower broadband reflectivity. Very low narrow band reflectivity can also be achieved by exploiting the interference of light reflected from the two interfaces [6]. Further reduction in broadband reflectivity can be achieved by adding additional intermediate index layers, thus breaking the air- silicon index discontinuity into smaller and smaller steps [7]. Therefore, a gradient index ARC is the limit of this progression, where a single index discontinuity is replaced by a continuous transition from a low to a high index material [Fig. 1(c)]. If this continuous index transition occurs over several wavelengths of optical path length, broadband reflectivity approaching zero can be achieved [1].

In the present work, we focused on using (LAE) process to prepare thin ARC layer and study the characteristics of (GPSi) layer with thickness less than the junction depth of industrial solar cell, where in this process we can controlled on the depth and the morphology of (GPSi) by varying the laser wavelength and current density. The involved characteristics are about the morphological, reflectivity and photoelectrical characteristics reading to prepare excellent (ARC) layer.

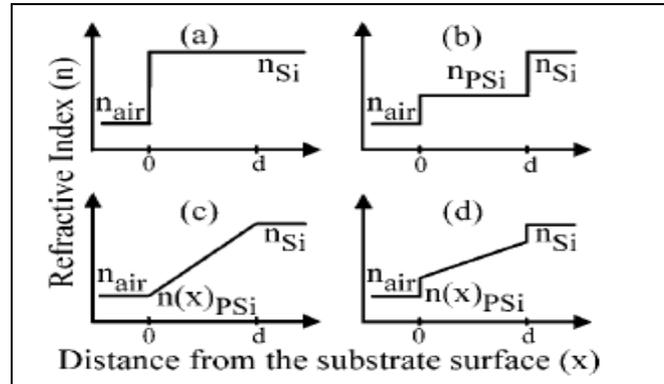


Figure (1): Four basic spatial refractive index profiles of thickness d . (a) No AR film, (b) Standard single layer AR film (or constant-current PSi etching), (c) Theoretical 100% graded film [$n(x)$ is arbitrary], and (d) PSi film with a partial gradient [1].

Experimental details

In our etching procedure a gradient-porosity porous silicon (GPSi) layer was formed on (p-n) type silicon bare solar cell with (100 Ω .cm) resistivity using Laser Assisted Etching (LAE) with a step-gradient current density as a function of etching time. All wafers were etched in (3:2) HF/ethanol electrolyte in Teflon electrochemical etching cell with (405 nm) blue laser diode wavelength and (50 mW/cm^2) laser illumination intensity, as shown in figure (2).

A step-gradient current density from higher value of (18 mA/cm^2) to minimum value of (6.25 mA/cm^2) was applied with etching time is (5 min) which divided to four steps, to form a gradient-porosity layer (GPSi) layer. For comparison, some Si wafers were etched with a constant-current density to form a conventional single-layer PSi. We have studied the morphological aspects across the porous layer thickness to investigate how the morphological aspects could be governed by effective parameters. Surface morphology and x-sectional properties of (GPSi) layer thickness of the films were determined from scanning electron microscopy (SEM) and cross-sectional images respectively.

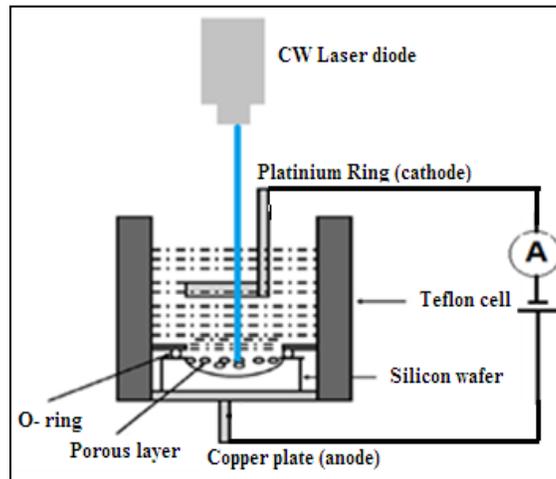


Figure (2): schematic diagram of Laser Assisted Etching (LAE) setup.

Results and discussion

The surface morphology of single-layer PSi and gradient-porosity (GPSi) is shown in figure (3), (a) and (b) respectively, this figure shows SEM image (top – view) of single-layer PSi and (GPSi) layer produced at constant-current density (18 mA/cm^2) with etching time (5 min) for single-layer PSi while etching time periodic with (1 min) interval with step-gradient current density of maximum value of (18 mA/cm^2) for gradient-porosity (GPSi). The illumination has been achieved by using blue diode laser (405 nm) of (50 mW/cm^2) power density on (p-n) type silicon immersed in 32% HF concentration. From figure (3), (a) and (b) we observed the porosity of single-layer PSi is larger than the porosity of gradient-porosity (GPSi), this is due to that the charge carrier during the

etching process get big opportunity for initiating and growth of pores while the contrary is right for gradient-porosity (GPSi) samples.

In thin etched films, the transition region at each interface significantly affects the porosity profile. Small interface undulations in these regions will extend the effective porosity values at each interface, allowing a greater porosity range to be achieved [8]. This effect can be observed in the SEM image of Figure (3), where high porosity fine structure near the film surface and relatively large undulations at the substrate interface extend the porosity range.

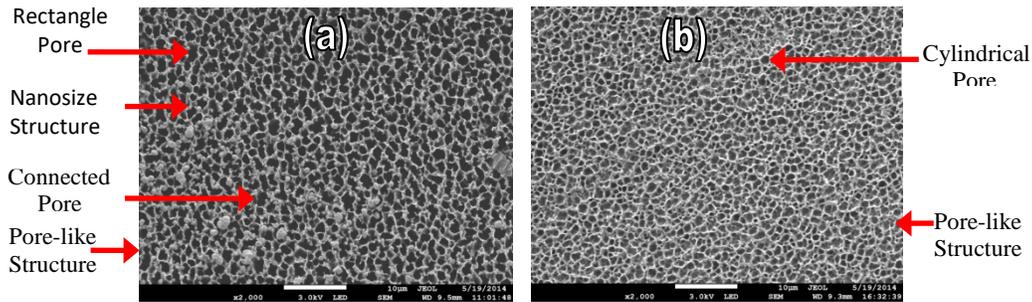


Figure (3): SEM images (top-view) of (a): single-layer PSi (b): gradient-porosity (GPSi) prepared at Blue (405nm) etching wavelength with 50mw/cm² laser illumination intensity.

The cross-sectional images of the gradient-porosity (GPSi) has attracted a great attention since it describes the variation of pore width and diameter along the pore depth [8], figure (4), shows the cross-sectional images of gradient-porosity (GPSi). The morphology of pores along the layer thickness depends on the formation parameters and is governed by generation rate and recombination of holes (h^+) to the surface [5].

From this figure we can reach to several results as follows:

1. The pores depth has different sizes due to the variation of current density of step-gradient form.
2. The spatial (electron-hole) pairs generated inside the substrate lead to determine the pore- shape inside the pore- like structure as stated below:
The generated (electron-hole) pairs in the deep porous regions will increase the pore sizes as shown in figure (4), whereas the generated (electron-hole) pairs near the porous surface (interface region between the silicon and porous region) lead to increase the etching at the porous surface rather than inside the porous substrate.
3. The cross-sectional shape of the resulting pores have (v-shape) as that obtained by J. D. Hwang et al., [5].
4. Wide scatter in diameter of etched pores as shown in figure (4). The width depends on local efficiency in capturing minority carriers which have been determined by initial position of pore in the random pore pattern.

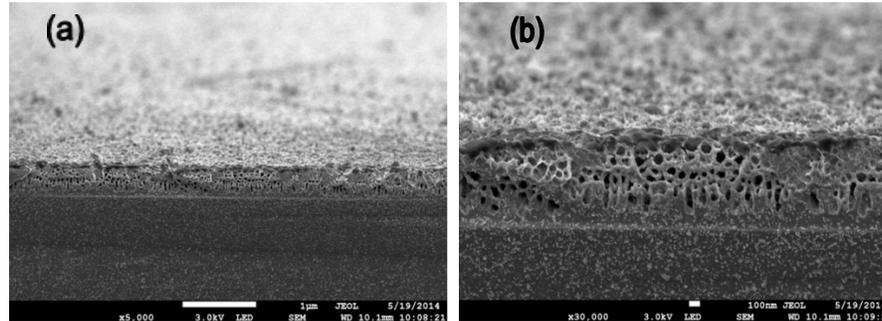


Figure (4): shows cross-sectional SEM image of gradient-porosity (GPSi) with different magnification. (a) 5,000, (b) 30,000.

The reflectance spectra of polished silicon surface and (p-n) type single layer porous silicon and (GPSi) layer which prepared in laser-assisted etching process at laser illumination intensity of (50 mw/cm^2) at fixed etching time (5 min) and etching current density (18 mA/cm^2) were studied. Blue laser diode (405 nm) illumination wavelength is employed in this process to achieve porous layer of minimum porous layer thickness where theoretically the porous layer thickness is inverse of absorption depth. This thickness is about (400 nm).

Figure (5), presents the reflectivity of reference sample (mirror-like) silicon surface as a function to wavelengths, the reflectivity has a maximum value of about 50% at wavelength of 400 nm and its value decrease with increasing wavelength and a minimum value reflectivity of about 33% is reached at wavelength of 850 nm. This relatively high reflectivity of silicon solar cell in the (400 nm – 850 nm) spectral range is due to the large reflective index discontinuity that exists at the air-silicon interface.

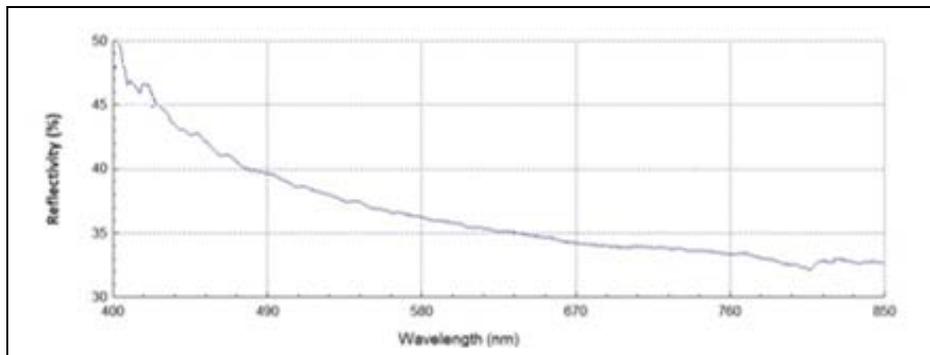


Figure (5): presents the reflectivity of reference silicon (mirror-like) sample as a function to wavelength.

Figure (6) shows the reflectivity for porous sample which prepared at illumination intensity of (50 mw/cm^2) with (405 nm) blue laser diode wavelength. As shown in this figure, it can be seen that the reflectivity of porous silicon surface is much lower than that

of silicon surface (reference sample). This variation in reflectivity may be due to the effect of the porosity on the refractive index and these fluctuations attributed to the excessive etching process and removing the formed porous layer (pillar) form.

The changing in porous reflectivity is generally due to the nature of porous layer, where this layer have light scattering regions and also due to the large value of the surface area to volume ratio of about $1000 \text{ m}^2/\text{cm}^3$, which improve the optical absorption inside the porous structure and hence, a low reflectivity is reached [6]. The effect of the porosity values on the reflectivity may be due to the fact that the effective dielectric constant of porous material system can be expressed as [9]:

$$P \left(\frac{\epsilon_1 - \epsilon_{eff}}{\epsilon_1 + 2\epsilon_{eff}} \right) + (1 - P) \frac{\epsilon_2 - \epsilon_{eff}}{\epsilon_2 + 2\epsilon_{eff}} = 0 \quad \dots (1)$$

Where

(P) is the porosity, ϵ_1 and ϵ_2 are the complex dielectric of host material and filling material and ϵ_{eff} is the effective dielectric function of mixed material (porous). The value of refractive index of porous silicon is expected to have a very small value than that of crystalline silicon and decrease with increasing porosity of the porous layer, because porous silicon is basically a mixture of silicon and air. Based on the above the single-layer porous silicon can act as broadband antireflection coating.

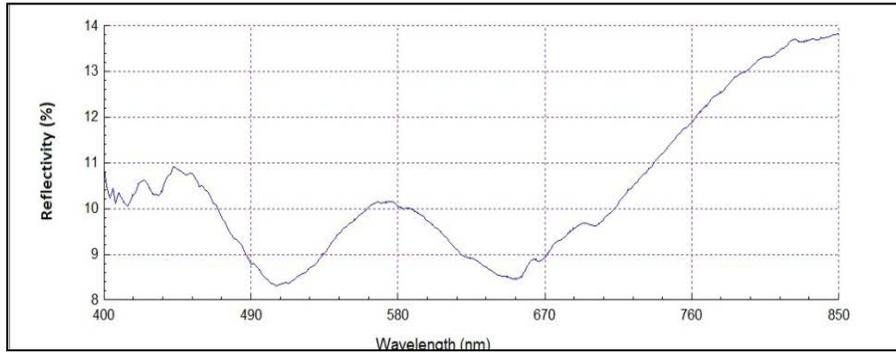


Figure (6): shows the reflectivity of single layer PSi prepared by (LAE) with blue (405 nm) wavelength and illumination intensity ($50 \text{ mw}/\text{cm}^2$) of etching current density ($18 \text{ mA}/\text{cm}^2$) and etching time (5 min).

The reflectance spectra of gradient-porosity porous silicon sample are shown in figure (7). When compared with the single-layer PSi, the reflectivity of gradient-porosity (GPSi) is much lower than that of single-layer PSi at wavelengths ranging between (400 nm- 850 nm), this suggesting it has a property of broadband antireflection. Porous silicon layer contains light scattering voids and large surface-area to volume ratio, which enhance the optical absorption and, hence, a low reflectivity is obtained [10]. Moreover, the gradient-porosity (GPSi) has a rather low reflectivity, this attributed to the morphology of multiple reflection in gradient-porosity (GPSi) [11, 12].

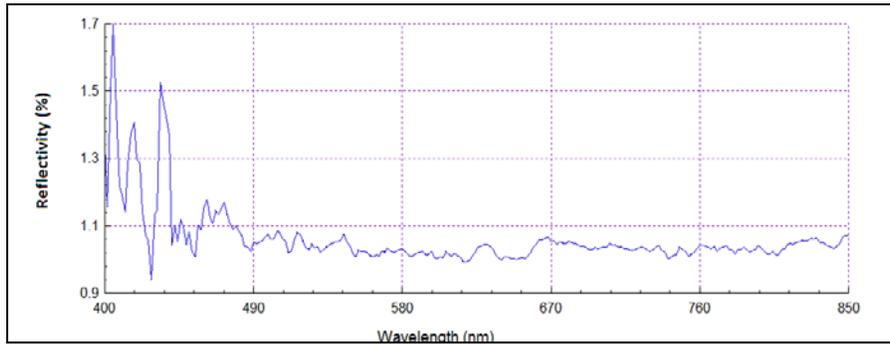


Figure (7): shows the reflectivity of gradient- porosity GPSi sample prepared by Blue (405nm) wavelength and illumination intensity (50 mw/cm²), under step-gradient current density of 20mA/cm² and etching time 5min.

The photoelectrical properties of (GPSi) layer and single (PSi) layer of bare solar cell sample are tabulated in table (1). This table shows the results from the two kind of solar cells samples (before and after porous layer formation).

Table (1): The results from the three samples of solar cell

Solar cell parameters	Ordinary solar cell	With PSi layer	With GPSi layer
Jsc (mA/cm ²)	2.15	2.05	2.8
Voc (mV)	427	410	435
Layer thickness (μm)	/	2.6	0.38

Where

Jsc is the short circuit density, **Voc** is the open circuit voltage.

From this table can be seen that the short circuit current density of solar cell sample with (GPSi) layer has a higher value of about 2.8% compare with that of ordinary solar cell which is about of 2.15%. This improvement in the short circuit current density is due to the reduction in the reflectivity of the upper porous layer (GPSi), which acts as a broadband antireflection coating.

Conclusions

The laser- assisted etching process with short laser wavelength of 405 nm can be used to prepare a (ARCs) layer through preparing a (GPSi) layer as a top-layer on a solar cell. The reflectivity measurements of (GPSi) layer show a minimum value of 1.3% comparing with the bulk silicon of 50%. The short circuit current density of (GPSi) layer was improved to (2.8 mA/cm²) for (GPSi) compared with the ordinary solar cell of (2.15 mA/cm²) while for single layer PSi of about (2.05 mA/cm²).

Acknowledgements

The SEM and cross- sectional measurements were carried out in the school of material engineering at the University Sains Malaysia in Penang.

The reflectivity measurements were carried out in the range (400 nm – 850 nm) by using (TF Probe, Spectroscopic Reflectometer Film Thickness Measurement System, Angstrom Sun Technologies Inc. made in U.S.A) in University Sains, penang – Malaysia.

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