Inverted nanopyramid texturing for silicon solar cells using interference lithography

Senthuran Sivasubramaniam *, Maan M. Alkaisi

Department of Electrical and Computer Engineering, University of Canterbury, Christchurch, New Zealand

Abstract

We report on a maskless and scalable technique for fabricating nano-scale inverted pyramid structures suitable for light management in crystalline silicon solar cells. This technique utilizes interference lithography and subsequent combined dry and KOH wet pattern transfer etching techniques. The inverted nanopyramid structures suppress the total reflection at normal incidence to below 10% over the entire visible range. The overall efficiency of the solar cell has been increased by 67% with the inverted nanopyramid texturing. The standard dual MgF₂/ZnS anti-reflection coating further enhanced the overall efficiency by 5.79%.

1. Introduction

Surface texturing is a key process in silicon solar cell fabrication. It reduces the optical reflection losses to well below 10%, compared to a polished silicon surface which reflects about 30% of the incident light in the visible region. The dominant techniques in commercial and high efficiency laboratory crystalline silicon solar cells are micron sized random pyramids and periodic inverted pyramids respectively. These are formed by alkali etching combined with silicon nitride anti-reflection coating by plasma enhanced chemical vapor deposition (PECVD) [1]. The effect of this is to reduce the light reflections from the surface and create multiple internal reflections to obtain total internal reflection. By trapping the light inside the cell, optical path length increases to a value close to Yablonovitch limit of 4n², where n is refractive index of silicon[2]. The size of these pyramids range from 5 to 10 μm and thus is not suitable for thin wafers or films because of the thickness limitation of the absorbing layer in next generation photovoltaic devices. Therefore light trapping schemes with submicron periodicity are needed. Furthermore, It has been theoretically shown that the optical path length enhancement beyond the Yablonovitch limit is possible with nanophotonic structures [3].

There are many variety of photonic nanostructures such as nanowires [4], nanocones [5] and nanoholes [6] which are being extensively studied. Despite their excellent light trapping capability, the performance of these nanostructured solar cells is largely suppressed by poor charge carrier collection due to high surface recombination loss resulting from increased surface area. Pyramids have relatively low surface area enhancement of about 70% and their gradient refractive index tapered profile makes them more suitable candidates for efficient light trapping. It has been recently shown that 700 nm period inverted nanopyramid arrays with 100 nm separation fabricated on 10 μm thick crystalline silicon thin film can absorb as much light as planar silicon wafers of thickness about 300 μm [7]. Sub-wavelength structures cannot be fabricated by conventional optical lithography techniques due to diffraction limits and as such, ordered nanostructures have been fabricated by electron beam lithography (EBL) [8], focused ion beam lithography (FIB) [9], interference lithography (IL) [10], nanoimprint lithography (NL) [11], nanosphere lithography (NSL) [12] and Block copolymer lithography (BCPL) [13]. EBL and FIB produce high spatial resolution features but they suffer from low throughput, high cost and charging effects whereas NL and BCPL are capable of producing feature sizes down to a few tens of nanometers and are also suitable for non-planar substrates. However, NL needs a high quality master mold and NSL and BCPL have long range order issues.
In this paper, we present a fabrication process for inverted nanopyramid texturing by interference lithography and subsequent pattern transfer by dry etching and wet KOH etching. Finally, the performance of nanopyramid textured solar cell is compared with planar solar cell using current–voltage measurements and external quantum efficiency (EQE) measurements.

2. Experimental

2.1. Interference lithography

Fig. 1 shows the schematic diagram of the Lloyd’s mirror interference lithography experimental setup used for this work. It is a very simple interference lithography setup and the period of interference fringes can be easily changed without readjusting the optics by simply rotating the mirror-sample assembly. A 325 nm HeCd laser was used as a light source. The spatial filter consists of a lens and a pinhole which expands the laser beam and gives a gaussian beam profile. The rotatable, UV-enhanced, aluminum coated mirror-sample holder assembly was mounted in such a way to allow half the portion of the expanded beam to be reflected by a mirror and another half to fall directly on the substrate. Both portions of the beams undergo interference and fringes are recorded on the imaging photoresist layer. The period of the fringes is given by:

\[ p = \frac{\lambda}{2 \sin \theta} \]  

where \( \lambda \) is the wavelength of the laser source, and \( \theta \) is the half angle of intersection of the two beams. Single exposure gives line gratings. The holes and post with different lattice configurations such as squares, hexagonal arrays can be generated by double exposure. Fig. 2(a)–(c) shows a MATLAB simulation of interference intensity distribution on the photoresist for single and double exposures. Depending on the tone (negative/positive) of the photoresist that is used, the resultant pattern on the photoresist can be either an array of holes or pillars. Fig. 2(d)–(f) shows SEM images of line gratings and pillar arrays in square and hexagonal lattice arrangements fabricated by using AZMI701 positive tone resist. The experimental results agree well with the simulated intensity distribution.

![Fig. 1. Sketch of Lloyd’s mirror interference lithography system used to fabricate the initial nanohole array on photoresist.](image)

![Fig. 3. Process flow of inverted nanopyramid fabrication (a) Deposition of tri-layer stack on thermal oxide coated silicon (b) Patterning the resist with interference lithography (c) Formation of inverted pyramids by KOH etching on hole array patterned oxide mask layer (d) Removal of mask by buffered oxide etching.](image)

![Fig. 2. (a–c) Simulated intensity distribution on photoresist for single exposure, double exposure by 90° rotation and double exposure by 30° rotation respectively. (d–f) SEM images of corresponding photoresist patterns.](image)
2.2. Fabrication of inverted nanopyramids

Boron doped p-type (100) c-Si CZ wafers with resistivity of 0.5–1 Ω cm and thickness of 350 μm were used. Fig. 3(a)-(d) shows the important process steps in an inverted nanopyramids fabrication. After standard RCA cleaning and 1:10 dilute HF dipping, 100 nm thick oxide layer was grown on silicon at 1000 °C in a furnace. The tri-layer stack was comprised of 200 nm thick AZ Barli II anti-reflection coating, 20 nm thick thermally evaporated silicon dioxide and 150 nm thick diluted AZMiR701 coated on the thermal oxide. The samples were double exposed with interference fringes. The exposure dose was chosen to underexpose the resist in order to create a hole array instead of the usual post pattern on positive resist. The pattern on the photoresist was transferred onto the thermal oxide through a series of dry etching steps. All the dry etchings were performed in an Oxford Instruments PlasmaLab80 reactive ion etching system. Before starting the actual pattern transfer etching steps, a very short O2 etching was performed to remove any residual photoresist left in the bottom of the nanoholes. The nanoholes pattern on photoresist was transferred onto the thin SiO2 interlayer using CHF3/Ar plasma etching. Then, the O2 plasma etching was performed to transfer the pattern onto the AZ Barli II. The SiO2 interlayer provides good selectivity for O2 plasma etching. Again, the CHF3/Ar plasma etching was performed to transfer the pattern onto the thermal oxide layer. Finally, the inverted pyramids were fabricated by wet etching in 30% KOH solution at 80 °C for 160 s.

2.3. Fabrication of nanopyramid solar cell

Nanopyramid textured samples were cleaned with HCl:H2O2:H2O 1:1:5 at 80 °C for 10 min to remove the potassium impurities which can cause degradation of solar cell performance. The backside of the substrates were doped with boron dopant to produce a back-surface field effect. The emitter junction was formed by solid source diffusion using PH-950 planar phosphorus source from Saint-Gobain Ceramic Materials Corp. The source consists of active component silicon pyrophosphate (SiP2O7) carried on an inert porous silicon carbide substrate. The diffusion was performed in a tube furnace at 875 °C for 30 min in nitrogen ambient. After phosphosilicate glass removal etching in 10:1 diluted HF, the 350 nm thick aluminum front contact grid and back contact were formed by DC sputtering and metal lift off. Finally, four isolated cells were defined by photolithography followed by plasma etching using SF6/O2 gases to remove the exposed emitter and isolate the cells.

3. Results and discussion

Fig. 4 illustrates the effect of pyramid size on the reflectance over the broad wavelength range. The optical simulation was carried out using finite difference time domain (FDTD) method. Fig. 4(b) clearly shows that the low reflectance region broadens and shifted to the long wavelengths as the pyramid size increases. The low reflectance region span from wavelength 780 nm to 950 nm for 700 nm size pyramids. Silicon usually has low absorption coefficient in this wavelength range.

Fig. 5(a) shows the 700 nm base size inverted nanopyramids with 100 nm separation. The base size of the pyramids was slightly larger than the diameter of thermal oxide nanoholes. This is due to slight undercutting during KOH etching. The conformal deposition of dual ARC was clearly seen from the cross-sectional SEM image in Fig. 5(b).

Fig. 6 shows that the 700 nm pyramids exhibits superior anti-reflection performance than 500 nm pyramids due to less flat surface area and greater depth of pyramids. The reflectivity of the 700 nm pyramid is below 10% over the entire visible region with the minimum of 3.77% near the band edge of silicon where the absorption of bare silicon is usually low. It is interesting to note

![Figure 4](image1.png)

**Fig. 4.** (a) Contour plot of simulated reflectance spectra as a function of pyramid size (100 nm to 700 nm) over broad wavelength range. (b) magnified contour plot shows reflectance below 12%.

![Figure 5](image2.png)

**Fig. 5.** SEM images of (a) 700 nm inverted nanopyramids (b) cross sectional view of inverted nanopyramids with conformal dual ARC (c) optical image of fabricated nanopyramid (black) and planar solar cells.
that the reflectivity of the nanopyramid structures in the UV region outperforms their micron size counterpart. The low reflectivity in the UV region improves the absorption of the high-energy photons, the loss of which limit current solar cells efficiency. To allow a quantitative comparison between inverted pyramid cell and planar cell, their weighted absorption (\(A_w\)) have been calculated using the following formula.

\[
A_w = \frac{\int_{280 \text{ nm}}^{1110 \text{ nm}} A(\lambda) I(\lambda)_{\text{AM1.5}} d\lambda}{\int_{280 \text{ nm}}^{1110 \text{ nm}} I(\lambda)_{\text{AM1.5}} d\lambda}
\]

where \(R(\lambda)\) is the reflectance at wavelength \(\lambda\) and \(I(\lambda)_{\text{AM1.5}}\) is the standard air mass 1.5 solar spectral irradiance.

The ratio between calculated weighted absorption of inverted pyramid cell and planar cell was 1.5 and the ratio between measured short-circuit current densities was 1.7. In the absorption calculation, we assumed that there was no transmission. At long wavelength region, there will be some transmission which is more prominent in planar solar cell. The long wavelength transmission is less in inverted pyramid solar cell due to light trapping effect. So, the actual absorption ratio would be slightly higher than the calculated absorption ratio. The

\[
A(\lambda) = 1 - R(\lambda)
\]

Fig. 6. Reflectivity of nanopyramid silicon substrates.

Fig. 7. Current density-Voltage (J-V) characteristics of nanopyramid solar cell under illumination and I-V under dark conditions (inset).

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ZnS/MgF\(_2\) dual ARC brings the reflectivity of 700 nm pyramids below 2.5% over broad wavelength range of 400 nm to 1030 nm.

Fig. 7 shows the current density–voltage characterization of solar cells under illuminated and dark conditions. It is clearly seen that the inverted pyramid texturing enhanced the short circuit current density from 9.43 mA cm\(^{-2}\) to 16.06 mA cm\(^{-2}\). This increment is mainly due to the low reflectivity of nanopyramids over the broad wavelength region. The high dark reverse saturation current density is attributed to surface area enhancement in nanopyramid cells. This also leads to reduced fill factor of the pyramid textured cell to 76.2% compared to 79.2% for planar cell. Despite the slight decrease in fill factor, the overall power conversion efficiency is increased from 4.03% to 6.73%, corresponding to a significant 66.9% enhancement compared to the planar cell. Dual anti-reflection coating (ARC) consist of 35 nm ZnS and 110 nm MgF\(_2\) further increases the current density to 17.19 mA cm\(^{-2}\) and fill factor to 76.7%. The slight increase in fill factor indicates that ARC coating not only decrease the reflection but also act as an efficient surface passivation layer. Table 1 summarized the basic solar cell parameters of both planar and nanopyramid solar cell and the efficiency enhancement percentage with respect to the planar cell.

To understand the impact of nanopyramid texturing on spectral response of the solar cells, the external quantum efficiencies (EQEs) of the solar cells were measured as shown in the Fig. 8. The EQE of inverted nanopyramid solar cell is higher than the reference planar cell over the measured wavelength range. The large enhancement of EQE was observed from 500 nm to 1000 nm. This is due to the reduced reflection. The improvement of EQE in short-wavelength (350–500 nm) was small. This can be attributed to the lost of carriers due to front-surface recombination more than the extra absorbed photons owing to low reflectance. However, Dual anti-reflection coating increases the EQE largely in short-wavelength region. This could be due to both reduced reflection of ARC coating and partially from the efficient surface passivation.

Table 1

<table>
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<tr>
<th></th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
<th>Enhancement (%)</th>
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<td>Planar cell</td>
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<tr>
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<td>0.54</td>
<td>76.7</td>
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<td>76.6</td>
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4. Conclusion

We have demonstrated the fabrication of nanopyramid structures with feature sizes of 700 nm that have improved the overall efficiency of crystalline silicon solar cells by 67%. The dual MgF2/ZnS anti-reflection coating further enhanced the overall efficiency by 5.79%. The patterning was performed using inexpensive, maskless and scalable interference lithography and combined dry and wet etching techniques.

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References