Periodic upright nanopyramid fabricated by ultraviolet curable nanoimprint lithography for thin film solar cells

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Abstract: In this work, a periodic upright nanopyramid structure was developed for light harvesting applications suitable for thin film solar cells. The periodic inverted nanopyramid structure was fabricated on Si substrate by laser interference lithography (LIL) and subsequent pattern transfer by combined reactive ion etching and KOH wet etching. The silicon substrate was used as a master mould in the replication process utilising ultraviolet curable nanoimprint lithography (UV-NIL) process. The inverted nanopyramid patterns were transferred onto OrmoStamp resist layer to form upright pyramids on glass substrates by UV-NIL. The replicated periodic upright nanopyramid structures can be used as light trapping structures in thin film solar cells and as soft mould in the 3D imprint process.

Keywords: nanopyramid; thin film solar cells; nanoimprint lithography; NIL; light trapping; interference lithography.


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1 Introduction

Light trapping technique has been utilised in the development of high performance and low cost thin film solar cells by enhancing light absorption without requiring thicker active layers. The most widely used light trapping techniques in industry are the upright or inverted pyramid structure[1,2]or random texturing for texturing crystalline silicon solar cells, which has a characteristic feature size of typically 3–10 µm [3,4]. Such large-scale geometries are not suitable for thin film solar cells where the active region itself is only a few microns or even few hundred nanometres in thickness. In addition, micron scale features require deep etching and is known to introduce defects in the material [5]. Therefore, nanoscale structures are needed in order to reduce reflections and achieve light trapping in thin film solar cells. The use of nanoscale surface structures for improving the light absorption of thin film solar cells is a promising method compared with the traditional micro sized surface texturing for crystalline silicon solar cells [6,7]. This is because the reduced etching depths required to form the nanoscale features subsequently results in a decreased level of damage to the substrates. Furthermore reflections are reduced over wide range of wavelengths in sub-wavelength nanophotonic structures. It has also been theoretically illustrated that nanophotonic structures can achieve the optical path length enhancement factors beyond the Yablonovitch conventional limit [8]. A variety of three-dimensional nanoscale structures, such as nanowires [9,10], nanocones [11], nanopillars [12], nanorods [13], nanowells [14], nanopyramids [15,16] and nanospheres [17], have been extensively investigated in thin film solar cells to enhance light harvesting.

Nanostructures can be fabricated by various techniques including electron beam lithography [18], focused ion beam lithography (FIB) [19], laser interference lithography (LIL) [20,21], nanoimprint lithography (NIL) [22,23], nanosphere lithography (NSL) [24] and block copolymer lithography (BCPL) [25]. However, for large scale, low cost implementation, mask-less interference lithography is more suitable especially when combined with nanoimprint technology. The ultraviolet curable nanoimprint lithography (UV-NIL) is an emerging technique for fabricating nanoscale structures on a surface with very simple, high throughput, low cost, and high resolution manufacturing technology [26]. Generally, UV-NIL achieves high pattern transfer accuracy combined with simple fabrication steps, requires low pressure and can be carried out at room temperature. The UV curable resists with high transmittance [27] in the visible and near infrared region of the solar spectrum make it possible to achieve different types of nanostructure on glass, even on ones when the master stamp surface is non-transparent. In the last few years, several authors [27–29] demonstrated that UV-NIL could be
Periodic upright nanopyramid fabricated by ultraviolet

successfully utilised in thin film solar cells. Although the above mentioned three-dimensional nanoscale structures have been shown to be very efficient in thin film solar cells, periodic upright nanopyramid structures have never been demonstrated by means of UV-NIL.

The objective of this work was to develop the fabrication process for manufacturing periodic upright nanopyramid structures on glass substrate with low cost and scalable approach. The upright nanopyramid can be easily produced through a single step imprint from the inverted nanopyramid that we developed on silicon substrates. The resultant upright nanopyramid can be transferred onto glass or other types of substrates through the use of UV curable polymers. Furthermore, Liang et al. [30] have performed numerical analysis on meta-nano pyramid arrays and showed near 100% absorbing property over the wavelength range from 200 nm to 2500 nm.

In this study, UV-NIL was applied to texture glass as the base substrates for the fabrication of thin film solar cells. The periodic upright nanopyramid structures were obtained from a periodic inverted pyramid structures on Si master stamp that was fabricated by LIL and subsequent pattern transfer by combined reactive ion etching and KOH wet etching. The fabrication of the master stamp on Si substrate and pattern transfer on glass substrates have been demonstrated in this work.

2 Experimental details

2.1 Sample preparation and pattern definition for master mould fabrication

Single-side polished, Czochralski (CZ) grown, 350 µm thick, boron doped p-type silicon wafer with <100> crystal orientation and resistivity of 0.5–1.0 Ωcm was used as the substrate. The wafer was cleaned with piranha solution (H₂SO₄:H₂O₂=3:1) for 10 min. After that 100 nm thermal oxide was grown onto the wafer using quartz tube furnace and oxidation was done at 1000°C for 12 min. Next, 200 nm anti-reflection coating (ARC) (AZ BARLi II) was deposited onto the substrate by spin coating at 2250 rpm for 60 s. Spin-coating is a very widely used method for resist spinning. The sample was then soft baked at 200°C for 60 s and then a 50 nm SiO₂ deposition was performed onto the ARC layer using vacuum thermal evaporation. After that hexamethyldisilazane (HMDS) was spun onto the SiO₂ and a 400 nm commercially available i-line photoresist (AZMiR 701 i-line positive resist diluted in 1 : 3 with PGMEA (1-methoxy-2-propyl-acetate)) was immediately spun coated using a spin speed of 3000 rpm for 60 s and soft baked at 90°C for 60 s. Adhesion promoter HDMS was used to improve the adhesion between SiO₂ and the photoresist.

2.2 Fabrication of inverted nanopyramid

Interference lithography (IL) set up as shown in Figure 1 was used to define the nanoholes pattern through double exposure of the imaging resist after rotating the substrate by 90 degrees for each exposure. To fabricate the inverted nanopyramid, the nanohole patterned photoresist was transferred onto the thermal oxide coated silicon substrate through a subsequent dry etching steps. An Oxford PlasmaLab80 reactive ion etching system was utilised for all the dry etching steps. The process flow used in the fabrication of inverted nanopyramid structures are shown in Figure 2. Initially, CHF₃/Ar
plasma etching was performed to transfer the nanoholes pattern onto thin evaporated SiO₂ interlayer. Then, an O₂ plasma etching was performed to transfer the pattern onto ARC layer with thin SiO₂ as mask. After that, the pattern was transferred onto the thermal oxide layer using CHF₃/Ar plasma etching. Then, the inverted pyramid structure on Si substrate was fabricated by wet etching in 30% KOH solution at 80°C for 170 s. Finally, the thermal oxide layer was removed by buffered Hydrofluoric acid etching. The inverted nanopyramid on Si substrate was used as master mould in the replication process for NIL.

**Figure 1** The schematic diagram of Lloyd’s mirror interferometer employed in this study setup for pattern definition on photoresist (see online version for colours)

**Figure 2** Process steps for the fabrication of inverted nanopyramid on Si substrate: (a) defined pattern formed by interference lithography; (b) pattern transferred onto the SiO₂ thin layer using CHF₃/Ar plasma etching; (c) O₂ etch to transfer pattern onto the ARC layer; (d) CHF₃/Ar plasma etch to transfer nanoholes pattern onto the thermal oxide layer; (e) inverted nanopyramids formed by KOH wet etching on nanoholes patterned thermal oxide mask layer and (f) thermal oxide mask layer removed by buffered oxide etching (see online version for colours)
2.3 Preparation of anti-sticking layer for master mould

Anti-sticking or anti-adhesion materials are essential components in all imprint processes. A (1H, 1H, 2H, 2H-perfluorooctyl) trichlorosilane also known as F\textsubscript{13}-OTCS solution from Sigma-Aldrich was used as an anti-sticking layer placed on moulds and imprint resists. A self-assembled monolayer (SAM) coating can be achieved on the sample surfaces by using a slow natural evaporation/convection deposition method at room temperature [31]. In this method, the sample was baked in the oven at 90°C for 30 min to fully dry the surface from water moisture and then cooled down to room temperature. A 20 µl droplet of the anti-sticking solution (F\textsubscript{13}-OTCS) was dispensed at the centre of a petri dish and the sample was placed in close proximity as shown in Figure 3. They were then covered with the petri dish lid and left for 2 h at room temperature.

![Figure 3](image)

2.4 Substrate preparation for imprint process

Prior to coating, the glass substrate was normally cleaned with acetone, methanol, and isopropyl alcohol (IPA) solvents in an ultrasonic bath and then rinsed with deionised water and finally dried with nitrogen gas. Next, the substrate surface was treated using oxygen plasma to enhance optimum adhesion at the interface between the glass and the OrmoPrime08. The OrmoPrime08 from micro resist technology was used as an adhesion promoter solution based on organo functional silanes. It has been designed to promote the adhesion of OrmoStamp to various substrates such as silicon, glass and quartz. After that the substrate was baked using an Oven at 200°C for 30 min and cooled down to room temperature immediately before coating. OrmoPrime08 was deposited onto the glass substrate by spin coating at a spin speed of 4000 rpm for 60 s. The spin-coated film was then baked on a hot plate at 150°C for 5 min and cooled down to room temperature. The OrmoPrime08 layer was cured by this treatment. Finally, the OrmoStamp was spun coated onto the OrmoPrime08 layer coated substrate at a spin speed of 6000 rpm for 60 s and pre baked on a hot plate at 80°C for 2 min.

2.5 Imprint process

To perform the imprint experiments, a vacuum operated manual imprint tool was attached onto the UV illumination source of the Karl Suss Mask Aligner (MA-6) system. This created a vacuum environment in order to reduce the air bubbles trapped in-between the mould and resist during the imprint process. The first imprint produces the inverted
shape of the master mould into a UV curable resist. Figure 4 illustrates the schematic diagram of the imprint process steps. The F13-OTCS coated inverted nanopyramids master mould was placed face up at the bottom of the imprint tool and an OrmoStamp resist coated on the quartz substrate with face down was manually aligned on top of the master mould. The top holder of this imprint tool which weighs about 350 g, was used as an applied force/load during the imprint process. A vacuum pressure of 4 mbar and the Mask Aligner (MA-6) system were then activated and the resist was cured under a UV exposure for 4 min using 4.4 mW/cm² illumination intensity with 365 nm UV source. The recommended dose for curing the OrmoStamp is 1000 mJ/cm² intensity. Finally, a manual de-moulding process was utilised by applying gradual force using a scalpel at one corner of the mould in order to delaminate between the two material surfaces. The replicated periodic upright nanopyramid samples were formed and imaged using atomic force microscope (AFM).

Figure 4  The schematic diagram of the imprint process steps (a) OrmoStamp and anti-sticking layer deposition; (b) curing of resist by exposure to UV light and (c) separation of mould from substrate after exposure (see online version for colours)

3 Results and discussion

Line gratings and holes patterns can be generated using IL in positive photoresist by two consecutive exposures with sample rotation by 90° between the two exposures respectively. Figure 5(a) shows line grating patterns with a period of 650 nm onto photoresist formed by single exposure. In this work, a 50 mWHeCd laser at a wavelength of 325 nm was used as a light source. A commercial spatial filter was employed.
It consists of a UV objective lens and a pinhole of 5 µm in diameter, which expands the laser beam and creates a Gaussian beam profile. The period, \( p \), of the pattern can be described by the following equation (1).

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

where \( \lambda \) is the wavelength of the laser, and \( \theta \) is the half angle between the incidence beams.

**Figure 5** SEM images of (a) line grating patterns embossed onto the photoresist with a period of 650 nm by single exposure and (b) nanoholes array with a 475 nm diameter formed onto the photoresist by double exposure and 90° rotation between the two exposures.

To achieve a period of 650 nm, the angle of incidence was adjusted to 14.5°. The holes formed onto the photoresist show a good uniformity as shown in the Figure 5(b), which was achieved using ARC layer between the Si and the photoresist. During the interference lithography exposure, the standing wave formed parallel as well as perpendicular waves with respect to the substrate, because the silicon substrate is reflective. An ARC layer played an important role to suppress vertical standing wave during the exposure. The sample as shown in the Figure 6(a) was used for the final fabrication of the pyramids.

**Figure 6** shows the SEM images of holes and dots patterns formed onto the photoresist by double exposure with increasing exposure dosage. The exposure dose was calculated by multiplying the intensity of the incident laser light by the time of exposure, yielding a value in energy per unit area [32]. With the exposure dose increasing, the size of the holes increased as shown in the Figures 6(a)–(c), then holes disappeared but some dots are still linked as shown in the Figure 6(d). Increasing the exposure dose further, result in creating discrete dot arrays as shown in the Figure 6(f). It can be clearly seen that the exposure time is an important factor to consider which can significantly influence the size and type of structure.

**Figure 7(a)** shows an SEM image of the nanoholes array fabricated onto the thermal oxide layer by IL and subsequent reactive ion etching step. To obtain a high etching selectivity between the ARC and photoresist, a thin SiO2 film was deposited between the two layers. It solved the selectivity problem between the photoresist and the ARC during O2 plasma etch. It can be observed that the RIE etching process induced a slight enlargement of the nanoholes diameter while the uniformity was improved. **Figure 7(b)** shows an SEM images for the 500 nm inverted nanopyramid structures with 150 nm separation on the Si substrate formed by KOH wet etching, obtained on the same sample.
as shown in Figure 6(a). It is evident from the SEM image that all the inverted pyramid structures have been completely formed and centred without showing any overlapping between neighbouring structures. However, the size of the inverted pyramid increased slightly compared with the diameter of the nanoholes as demonstrated in Figure 7(a) due to undercutting during KOH wet etching. Figure 7(b) shows the final inverted nanopyramid structure formed by this technique on Si substrate. This structure was used in this work as master mould in the replication process for UV-NIL to form the upright nanopyramids.

The AFM image and cross sectional traces of the periodic inverted nanopyramid structures on the Si substrate master mould are shown in the Figure 8. This demonstrates the successful creation of the inverted pyramids with periodic structure and smooth surfaces onto the Si substrate employing LIL and subsequent pattern transfer by combined reactive ion etching and KOH wet etching. Figure 9(a) shows the AFM image of 3-D view of the periodic upright nanopyramid formed onto OrmoStamp resist on glass substrate as the result of imprint process. It can also be seen that the upright nanopyramids with periodic features in the order of 500 nm and smooth surfaces have been precisely reproduced onto the OrmoStamp resist.

**Figure 6** SEM images of array of holes and dots onto the photoresist by double exposure with different exposure time (a) 70 s; (b) 80 s; (c) 90 s; (d) 100 s; (e) 110 s and (f) 120 s

(a) ![SEM image](image1)  
(b) ![SEM image](image2)  
(c) ![SEM image](image3)  
(d) ![SEM image](image4)  
(e) ![SEM image](image5)  
(f) ![SEM image](image6)

The AFM images for each master and imprinted sample were compared and dimensions measured from randomly selected areas but with the same scanned area of 5 µm × 5 µm. Figures 8(b) and 9(b) reveal that no significant differences can be found between the master mould and inverted shape of master mould replica. These results further confirm that excellent fidelity periodic upright nanopyramid structures can be achieved by UV-NIL imprinting. This high fidelity replication offers high flexibility in designing new light trapping schemes for thin film solar cells. The UV curable resist can be incorporated into a range of solar cells configuration because of its low optical absorption [27,29,33]. Therefore, the replicated periodic upright nanopyramid structures onto the OrmoStamp resist on glass substrate can be utilised as light trapping
Periodic upright nanopyramid fabricated by ultraviolet structures in thin film solar cells. This process can be continued and a daughter mould can be created from the upright pyramids and used as a mould for direct 3D imprint process. It should be noted that there is no direct technique for forming periodic and ordered upright pyramids on crystalline silicon because of the limitation imposed by the crystal orientation.

**Figure 7** SEM images of (a) nanoholes pattern on the thermal oxide SiO$_2$ layer (b) top view of the inverted nanopyramid structure on Si

![SEM images](image)

**Figure 8** AFM image of inverted nanopyramid master mould (a) 3-D view and (b) cross sectional traces (see online version for colours)

![AFM images](image)
4 Conclusions

This work has demonstrated the fabrication of upright nanopyramids (500 nm period) with ordered periodic array onto OrmoStamp resist on glass substrates by a UV-NIL process. The inverted nanopyramid master mould structures were fabricated using LIL and subsequent pattern transfer by combined reactive ion etching and KOH wet etching. The UV-NIL can be used to invert original structures with an excellent fidelity down to nanometre scale accuracy. The periodic upright nanopyramid formed onto OrmoStamp resist on glass substrates can be utilised for thin film solar cells application including organic solar cells as well as soft mould in the 3D imprint process. The combined maskless lithography and nanoimprint technology provides a low cost platform for high throughput process.

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References


