Investigation of room temperature deposited silicon dioxide thin films for surface texturisation of monocrystalline {100} silicon

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In the fabrication of crystalline silicon-based solar cells, silicon surface is usually texturised by wet anisotropic etchant without using any masking pattern. This method provides randomly oriented upright pyramids (or hillocks) of varying sizes. However, a surface textured with inverted pyramids yields high efficiency compared with the one textured with normal pyramids. Silicon dioxide thin films synthesised using anodic oxidation technique at room temperature are explored as etch mask in KOH solutions to texturise the Si{100} surface with inverted pyramids without patterning of the oxide layer using lithography. Oxide films of ~50 nm thickness are synthesised in different compositions of the electrolyte under potentiodynamic regime. Thickness uniformity and refractive index of the as-grown oxide films are measured using spectroscopic ellipsometry. Scanning electron microscope is primarily used to inspect the etched surface morphology. The composition of the electrolyte, KOH concentration and etching time are optimised for the maximum surface coverage of inverted pyramids. The surface texturing process demonstrated is very simple and economic as it utilises anodic silicon dioxide as an etch mask, which is deposited by a simple experimental setup and the process does not involve any lithography step.

1. Introduction: The efficiency of solar cells can be improved by several methods [1–4]. The surface texturing is one of the common practices in silicon-based solar cells for reducing light reflectance to improve their efficiency. It is achieved by different techniques such as plasma etching, chemical etching and so on [4, 5], but wet chemical anisotropic etching using alkaline solutions (e.g. KOH, TMAH etc.) is a popular method because of its low cost and simple experimental setup [6–9]. These etchants are commonly used in silicon micromachining for microelectromechanical system (MEMS) fabrication [10, 11]. The texturing of silicon surface is realised by forming either random upright pyramids or inverted pyramids. The surface textured with inverted pyramids yields high efficiency compared with the surface textured with normal pyramids [4, 12–14]. The inverted pyramids are fabricated using selective wet anisotropic etching by patterning of mask layer using the lithographic technique [12, 13]. The involvement of the lithography step adds extra cost in the surface texturing process. If wet anisotropic etching of silicon is employed using the porous mask layer (e.g. low-density oxide layer), it will yield a textured surface with randomly oriented inverted pyramids. However low-density oxide can be deposited using conventional techniques such as plasma-enhanced chemical vapour deposition, anodic oxidation method is an attractive alternative as it has distinctive advantages over conventional deposition methods such as simple experimental set-up, inexpensive, easy control over oxide growth, no requirement of toxic. Moreover, oxide properties can easily be tailored by varying the electrolyte composition and/or the deposition parameters (e.g. current, gap between electrodes etc.).

In our previous paper, we explored as-grown anodic SiO_2 thin films for different applications [10, 15]. In this Letter, as-grown SiO_2 thin films are thoroughly investigated for the texturing of Si {100} surface with inverted pyramids without using any lithographic process. The effect of electrolyte composition, KOH concentration and etching time on the surface texturing of Si{100} is studied in detail. Oxide films are synthesised in different electrolyte compositions at room temperature. Wet anisotropic etching is performed in KOH solution for the formation of inverted pyramids using as-grown oxide film as an etch mask.

2. Experimental details: Czochralski (Cz) grown 3 in diameter *P*-type boron-doped (resistivity 1–10 Ω cm) {100} oriented single-sided polished silicon wafers are used for the deposition of SiO_2 thin films using anodic oxidation technique at room temperature. To obtain the ohmic contact on one side of the wafer, aluminium is deposited on the rough surface side using the DC sputtering system. A two-electrode electrochemical set-up is used for oxide deposition. A customarily designed wafer holder is used to provide a metal contact on its backside (i.e. the side with the aluminium layer). In the wafer holder, 2.4 in diameter area of the wafer surface is exposed to the electrolyte in the oxidation process. In the experimental set-up, silicon wafer is fixed as the anode and the platinum gauge mesh (90% Pt, 10% Ir) as the cathode. The electrodes are separated by a fixed distance of 1.5 cm. Anodic oxidation is carried out in a solution of 0.04 M KNO_3 in ethylene glycol with a small addition of water (2.7 or 3.7 vol%). The pH of the solution is maintained at 4. The oxide films are deposited under the potentiodynamic regime. In this process, initial oxide is grown in galvanostatic mode at a constant current density of 8 mA/cm^2 until the forming voltage attains the predetermined voltage of 110 V. Thereafter, the process is continued in constant voltage (i.e. potentiostatic) mode at 110 V for 15 min. Prior to the anodic oxidation process, silicon wafers are cleaned sequentially in acetone and deionised (DI) water for 5 min using ultrasonic cleaning method. Afterwards, wafers are dipped in 2% hydrofluoric acid (HF) followed by a thorough rinse in DI water. This step is attempted to remove native oxide. After the deposition of oxide layer by anodic oxidation, wafers are properly cleaned in DI water to get rid of the adsorbed glycol solvents. Ellipsometry (J.A. Woolam, model: M-2000D) is used to determine the thickness and the refractive index of as-grown oxide films.

To investigate the effect of KOH concentration on the surface texture of Si{100} surface using the as-grown oxide as an etch mask, etching is performed in KOH solution of different concentrations (2.5, 5, 10, 15 and 35 wt%) at 60°C. To determine the optimal etching time for maximum surface coverage of inverted pyramids, a number of samples are etched under the same condition and collected one by one at 1 min interval till the oxide layer is etched

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out completely. All etching experiments are performed in a container made of Teflon and equipped with a reflux condenser to prevent evaporation of the etchant solution (or to avoid concentration change) during the etching process. The vessel filled with the etchant is inserted into a constant temperature bath. Each time, 1 l fresh KOH solution of desired concentration is used. The samples are held in a chip holder made of Perfluoroalkoxy (PFA), which can accommodate a number of samples at a time. No mechanical stirring of the etching solution is provided during etching. The scanning electron microscope (SEM) is used to examine the surface morphology of the etched samples.

3. Results and discussion

3.1. Growth characteristics: The concentration of H_2O in the electrolyte is a key parameter that influences the oxide growth, density (or porosity) and morphology of the oxide films [16, 17]. In this Letter, oxide films are synthesised in 2.7 and 3.7 vol% H_2O-added electrolytes. To study the effect of H_2O concentration on oxide growth behaviour, the cell voltage during oxide growth is recorded at 1 min intervals until the forming voltage reaches the predetermined voltage of 110 V. This voltage value is chosen to produce oxide films of ∼50 nm thickness [18, 19].

Fig. 1 presents a graph showing the relationship between the oxidation time and forming voltage for the films grown in the electrolyte containing 2.7 and 3.7 vol% H_2O. It can be observed from the figure that the voltage increases continuously with time until the forming voltage reaches the predetermined value (i.e. 110 V) in order to maintain a constant current density as the film grows with time [20]. Moreover, it can be noted that the oxide growth rate is not significantly affected by a small percentage increase in the H_2O concentration since the time required to attain the predetermined voltage (i.e. 110 V) is almost same in different concentrations of water-added electrolytes.

3.2. Thickness and refractive index: Variable angle spectroscopic ellipsometry is used to measure the thickness and refractive index of the as-grown oxide films.

The measurements are performed at 65°, 70° and 75° incidence angles. In electrolytes of different compositions (i.e. 2.7 and 3.7 vol% H_2O-added electrolytes), oxide thicknesses are measured to be 53 ± 0.5 nm. To determine the thickness uniformity on 3 in wafer, oxide thicknesses are measured at different locations as shown in Fig. 2. The variation in oxide thickness is <6 Å which manifests a high degree of thickness uniformity.

Refractive index of the as-grown oxide films measured using ellipsometry at 632.8 nm is presented in Table 1. It can be noted that the refractive index of the as-grown oxides is decreasing with an increase in H_2O concentration in the electrolyte. The decrease in refractive index is due to the increase in O_2 concentration incorporated into the oxide or increase in film porosity as the H_2O

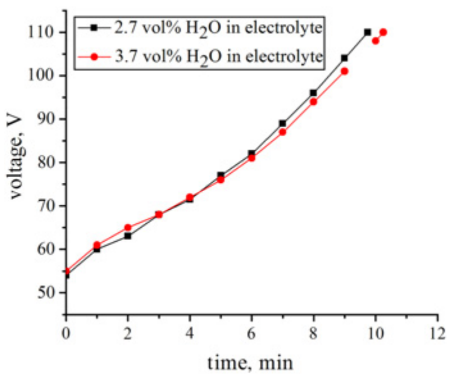

Fig. 1 *Cell voltage versus oxidation time for different electrolyte compositions*

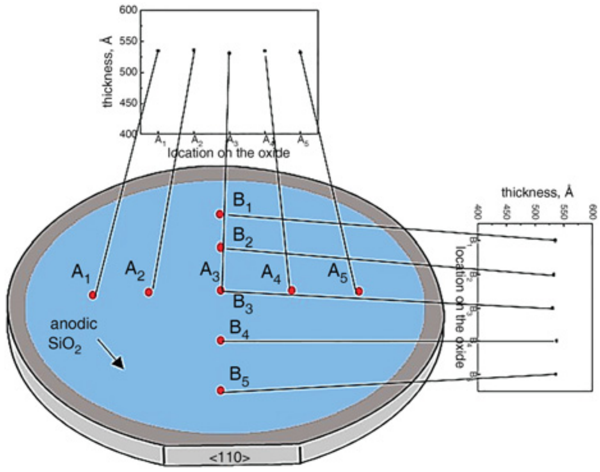

Fig. 2 *Oxide thickness at different locations on 3 in wafer for the film deposited in 3.7 vol% H_2O-added electrolyte*

concentration increases in the electrolyte [21, 22]. However, the refractive index of the as-grown oxides is greater than the thermally grown SiO_2 films (1.46) [23]. This could be due to the higher concentration of silicon (or oxygen deficiency) in the as-grown oxide films [24].

3.3. Surface texturing of Si{100}: The main objective of this Letter is the surface texturisation of Si{100} with inverted pyramids using as-grown anodic SiO_2 film as an etch mask. To optimise the deposition and etching conditions for achieving better surface coverage of inverted pyramids, the effect of electrolyte composition, KOH concentration and etching time is investigated. These are discussed in the following subsections.

3.4. Effect of oxide composition: To optimise the electrolyte composition for improved coverage of inverted pyramids, silicon samples with the as-grown oxide film deposited under different electrolyte compositions are etched in 5 wt% KOH solution at 60°C. Etched surface morphologies are examined using the SEM.

Table 1 Refractive index of oxide films developed in two different electrolyte compositions

Regime: potentiodynamic, pH = 4	
H_2O concentration	Refractive index (n)
2.7	1.482
3.7	1.480

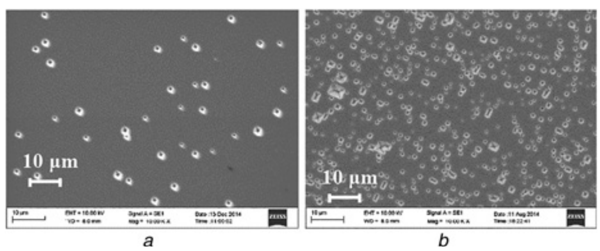

Fig. 3 *Surface morphology of the samples etched in 5 wt% KOH at 60°C for 28 min using SiO_2 films deposited in H_2O-added electrolytes as an etch mask*
a 2.7 vol%
b 3.7 vol%
The SEM images have been taken after removal of the oxide layer

The etched surface morphologies of the {100} silicon samples on which oxide films are grown in 2.7 and 3.7 vol% H_2O-added electrolytes used as an etch mask are presented in Figs. 3*a* and *b*, respectively.

It can easily be observed from the figures that the density of the inverted pyramids is more for the oxide film synthesised in 3.7 vol % H_2O-added electrolyte compared with the film developed in 2.7 vol% H_2O-added electrolyte. The density of pyramids can directly be correlated with the number of pin holes generated in the oxide during oxide deposition and/or during the etching processes in KOH solution. Since the oxide grown in 3.7 vol% H_2O-added electrolyte provides a higher density of inverted pyramids (better coverage), further study is focused on the oxide films deposited in this electrolyte composition.

3.5. Effect of KOH concentration: To elucidate the effect of KOH concentration on the size and density of inverted pyramids, etching is carried out in a wide range of KOH solutions (2.5, 5, 10, 15 and 35 wt%) at 60°C using the oxide grown in 3.7 vol% H_2O-added electrolyte as an etch mask. In all cases, etching is continued till the surface is covered with the maximum number of inverted pyramids. To optimise the etching time in each KOH concentration for maximum coverage of inverted pyramids, large number of samples are etched under the same etching condition for different periods of time, ranging from 1 to 45 min. Samples are collected one by one at 1 min intervals until the oxide layer is completely etched out. The maximum coverage of inverted pyramids is observed before all etch pits coalesces (or before the oxide layer is completely etched out). Thus, the optimal etch time for various KOH concentrations is the time corresponding to the maximum coverage of inverted pyramids. A detailed description of the effect of etching time is elaborated in the next section.

Table 2 Size of the inverted pyramids for the samples etched in different concentrations of KOH at 60°C

Concentration of KOH, wt%	Size of the inverted pyramids	
	Width, μm	Depth, μm
2.5	~2.5–1.25	~1.76–0.88
5	~1.42–0.83	~1.0–0.59
10	~1.33–0.76	~0.94–0.54
15	~0.98–0.58	~0.69–0.41
35	~0.53–0.34	~0.37–0.24

Figs. 4*a*–*e* present the surface morphologies of the samples etched in different concentrations of KOH solution at 60°C. From the figure, it can be observed that the variation in the density of pyramids with KOH concentration is not significant; however, the pit size decreases with an increase of KOH concentration. Similarly the optimised etching time for maximum coverage of inverted pyramids decreases with KOH concentration. It is well known that the oxide etch rate increases with KOH concentration [25]. In wet anisotropic etching, inverted pyramids form due to the existence of pinholes in the oxide layer and/or their generation during the etching process. The size of the inverted pyramids depends on the time for which the silicon surface through pinholes is exposed to the etchant. As the oxide etch rate increases with KOH concentration, the silicon surface through the pinholes is exposed for less time and therefore results in smaller sized pyramids.

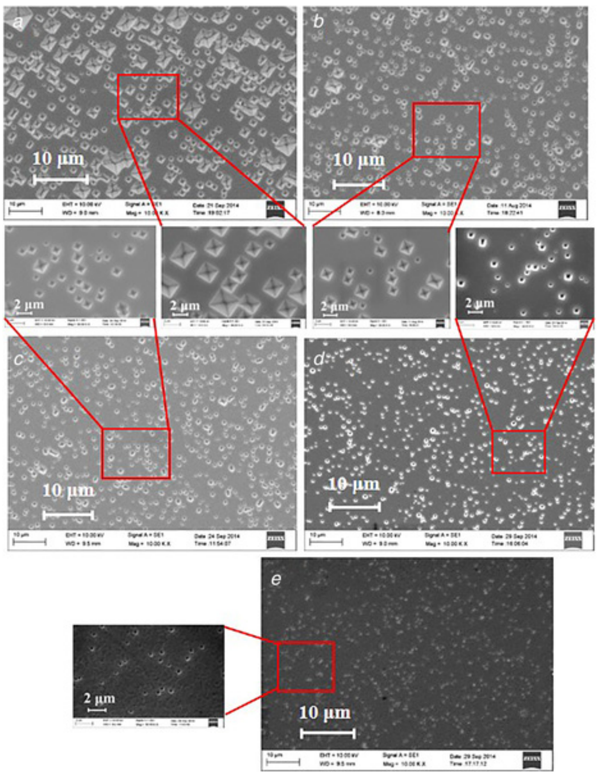

Fig. 4 *Surface morphology of Si{100} etched in various concentrations of KOH solutions at 60°C for different time periods using the oxide layer deposited in 3.7 vol% H_2O-added electrolyte as an etch mask*
a 2.5 wt% KOH, 39 min
b 5 wt% KOH, 28 min
c 10 wt% KOH, 20 min
d 15 wt% KOH, 17 min
e 35 wt% KOH, 6 min
The SEM images are taken after removing the oxide layer

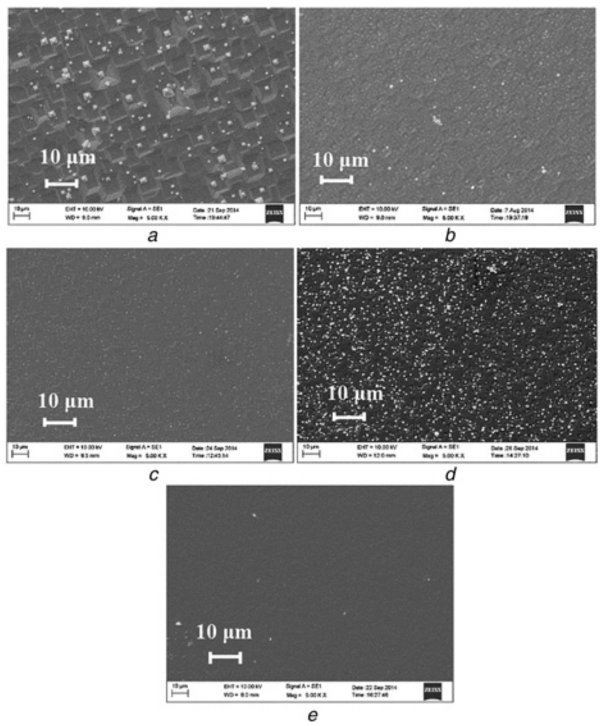

Fig. 5 *Surface morphology of etched Si{100} after the masking layer (SiO_2) is completely etched in different concentrations of KOH solutions at 60°C*
a 2.5 wt% KOH, 40 min
b 5 wt% KOH, 30 min
c 10 wt% KOH, 21 min
d 15 wt% KOH, 19 min
e 35 wt% KOH, 7 min
In all cases, oxide films are deposited in 3.7 vol% H_2O-added electrolyte

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It can be noted from the SEM micrographs that the shape and size of the inverted pyramids are not identical. Moreover they are randomly distributed. This is due to the fact that the pinholes generate randomly during the oxide growth and during anisotropic etching processes. The etch depth (d) of the inverted pyramids can be calculated using the trigonometric relation $d = 0.707 \times w$, where w is the width (or smaller side) of the inverted pyramid and can easily be estimated from the SEM images. The range of pyramids' size (width and depth) for the samples etched in different concentrations of KOH at 60°C is presented in Table 2. It is apparent from Table 2 and Fig. 4 that the large-sized inverted pyramids develop in low-concentration KOH solutions (or low oxide etch rate etchant) and the size decreases with an increase in KOH concentration (i.e. high oxide etch rate etchant).

Figs. 5*a–e* present the etched surface morphologies of silicon in different concentrations of KOH solutions after the SiO_2 film (i.e. masking layer) is completely etched out. It is evident from the SEM images that the inverted pyramids have disappeared (or the surface with inverted pyramids has transformed to the surface with rounded pits) when the oxide layer is completely etched out. It happens due to the fact that the silicon surface is directly exposed to the etchant after the removal of oxide film during the etching process. The etched silicon surface morphology depends on the concentration of KOH concentration and the time for which the silicon surface is exposed to the etchant after oxide etching. The equilibrium between the oxidation rate of silicon and desorption of byproducts during the etching of bare silicon in high-concentration KOH leads to a better etched surface morphology [25, 26].

3.6. Effect of etching time: To investigate the etched surface morphology of silicon with time, etching experiments are carried out in 5 wt% KOH. Various samples with the as-grown oxide layer synthesised in 3.7 vol% H_2O-added electrolyte are etched under the same etching condition, but each sample is removed from the etchant after a different etching time. Fig. 6 shows the surface morphologies before and after etching for different periods of etching time. Fig. 6*a* reveals that the oxide surface is smooth and uniform. Figs. 6*b–e* present the sequence of the formation of inverted pyramids and their annihilation at the point when the oxide layer is etched out completely. As etching proceeds, the size of the pyramids increases due to the exposure of silicon to the etchant through the pinholes in the oxide film. Initially the number of pinholes increases with time, but after a certain time of etching, the pinholes (or adjacent pyramids) start merging with each other which results in the annihilation of pyramids. As soon as the oxide layer is etched out, the silicon surface is directly exposed to the anisotropic etchant. Therefore, the surface with inverted pyramids changes to the surface with rounded pits as shown in Fig. 6*e*. It can be concluded here that the maximum coverage of inverted pyramids occurs before complete removal of oxide layer. Low-concentration KOH is preferable for a better surface coverage of the large-sized inverted pyramids.

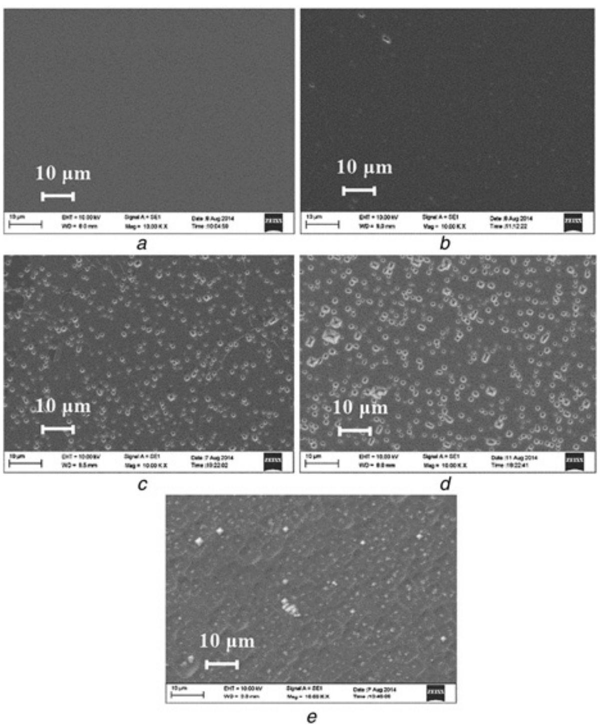

Fig. 6 *Surface morphology of the samples etched in 5 wt% KOH at 60°C using the oxide grown in 3.7 vol% H_2O-added electrolyte as the etch mask*
a 0 min
b 9 min
c 19 min
d 28 min
e 30 min

It may be emphasised here that the main objective of this Letter is to study the surface texturisation of Si{100} with inverted pyramids using anodic SiO_2 as an etch mask. The measurement of UV reflectance spectra is important to determine the surface morphology with high absorbance (or low reflectance); however, it is beyond the scope of this Letter and hence not attempted.

4. Conclusions: In summary, we have established a simple and cost-effective technique to texturise the Si{100} surface with inverted pyramids without using lithography. The as-grown oxide layer deposited at room temperature using an anodic oxidation method is successfully demonstrated as an etch mask in KOH solution for surface texturing without using lithography. The films deposited in 3.7 vol% H_2O-added electrolyte at 110 V provide a better coverage of inverted pyramids. In the case of the etchant, low-concentration KOH solution is an optimal choice to achieve improved surface coverage of large-sized inverted pyramids. However, there is a scope for future research to improve the surface coverage and the size of inverted pyramids by varying the electrolyte composition, oxide growth parameters, etching temperature, etchant and its concentration. The present technique of surface texturisation with inverted pyramids requires neither lithography nor great consumption of silicon. Moreover, the oxide films are deposited using the low-cost experimental set-up. Considering these major advantages, the method demonstrated in this Letter can be adopted for surface texturisation of c-Si in order to reduce the front surface light reflectance for improving the efficiency of silicon-based solar cells.

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