Research Article

Wafer Surface Charge Reversal as a Method of Simplifying Nanosphere Lithography for Reactive Ion Etch Texturing of Solar Cells

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A simplified nanosphere lithography process has been developed which allows fast and low-waste maskings of Si surfaces for subsequent reactive ion etching (RIE) texturing. Initially, a positive surface charge is applied to a wafer surface by dipping in a solution of aluminum nitrate. Dipping the positive-coated wafer into a solution of negatively charged silica beads (nanospheres) results in the spheres becoming electrostatically attracted to the wafer surface. These nanospheres form an etch mask for RIE. After RIE texturing, the reflection of the surface is reduced as effectively as any other nanosphere lithography method, while this batch process used for masking is much faster, making it more industrially relevant.

1. INTRODUCTION

Multicrystalline Si wafers make up the majority of the photovoltaic market. Due to the variety of grain orientations, they cannot be textured cheaply by the anisotropic wet chemical etches used for monocrystalline silicon. One possibility for texturing is reactive ion etching (RIE). RIE can randomly texture a Si surface, with the minimum reflectance of below 5% achieved vcommentWe changed "masking" to "maskings" for the sake of clarity. Please check. [1, 2]. This maskless RIE requires the etching of several microns of Si and has the resulting long process times. The use of a mask during RIE allows greater control over the surface topography than maskless RIE and results in shallower textures with reduced etch times. The best reflection achieved to date using an RIE mask applied a photolithography process to form pyramids [3], with minimum reflectances around 5% achieved.

As an alternate to a photolithography mask, RIE masks can be formed by nanospheres. Nanospheres are highly uniform spheres (typically of silica or polystyrene) and are commercially available and very cheap. In previous work with nanosphere masks, the mask has been formed by spin-coating, resulting in a uniform monolayer of spheres across the surface. These particles are then the etch mask for subsequent RIE [4]. Without an antireflection coating, the minimum reflectance is reduced around 13% by etching less than 500 nm of Si—making the process fast and high-throughput compared to other RIE textures, with or without masks.

Spinning-on of the nanosphere mask requires very careful control of the nanoparticle solution used, with many critical factors including spin speed, substrate surface treatments, and particulate concentration [5]. The typically rough wafer surface complicates spinning as some large regions are left unmasked [4]. Additionally, the throughput would be low and the masking solution wastes high for a factory application. A solution with a high nanosphere solids content is required for this spinning process and accentuates the waste problem.

Dipping a wafer into a masking solution would be attractive in a manufacturing environment, as the batch process could have very high throughput. Dipping could also coat large area wafers, 1 m^2 glass sheets, or other objects which are not suitable for spinning due to size, asymmetry, or weight. For some applications, it would also be an advantage to mask both sides of a wafer at once, to achieve a double-sided texture. Silicon dioxide, which comprises the surface of the standard wafer and the silica beads commonly used for the masking, has a negative surface charge when immersed in a solution with a pH above its isoelectric point of ~2.5 [6]. To electrostatically attract the negative spheres to the negative wafer
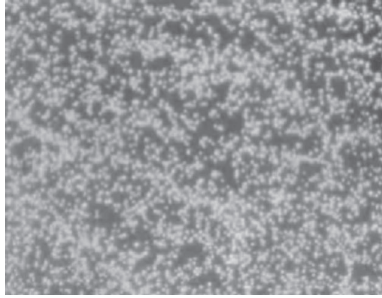
FIGURE 1: Dark field optical microscope image of the nanosphere mask applied to a wafer by reversing its surface charge. The image is $180 \times 160\,\mu$m.

surface, the surface charge of the wafer must be reversed by the application of a positive coating.

This work shows that a simple dipping process can reverse the surface charge of a wafer, and another dip can mask the surface. Masking based on this idea can lead to high-nanosphere surface coverage, and etching through the nanosphere masks is well controlled by RIE. A variety of textures can be formed and very good reflectance reduction achieved. The geometry of the texture features can be altered by changing RIE processing parameters (primarily pressure and gas mixtures), which also controls the etch rate of the nanospheres that act as the mask.

2. EXPERIMENTS AND DISCUSSION

Below is outlined the process used to optimize the two solutions used for dip coating wafers, first for wafer surface charge reversal, followed by electrostatic attraction of a nanosphere lithography mask. Afterwards, some RIE textured surfaces are examined by SEM and the reflectance of the best texture assessed.

2.1. Reversing the surface charge of silicon wafers

Layer-by-layer coating can be used to build up a variety of types of films, by alternate deposition of positive followed by negative ions, molecules, or colloids [7]. The use of colloidal particles such as nanospheres in the layer-by-layer method was pioneered by Iler [8]. In this work, Iler's technique was used to deposit a single bilayer of hydrolyzed Al^+ ions followed by negatively charged SiO_2 nanospheres. The composition of the Al^+ solution and the pH of the nanosphere solution were adjusted to optimize the mask coatings.

Before any surface treatments, a polished and oxide-free Cz Si wafer surface was oxidized by a 5-minute piranha clean ($H_2SO_4 : H_2O_2$ solution, 2 : 1 mixture) and then rinsed for 10 minutes. A polished surface was chosen as its predictably high reflection is best for quantifying the benefits of the resulting texture. In order to attach a positive Al coating to the wafer, a set of $AlNO_3$ solutions (concentration varying from 400–800 μM) was prepared, and small amounts of 50 mM NaOH were added to adjust the pH and concentration of the solutions. The cleaned wafer was dipped into the solution
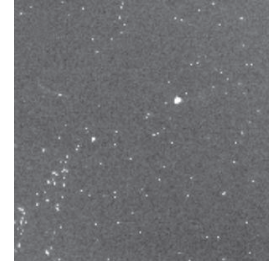
(a)
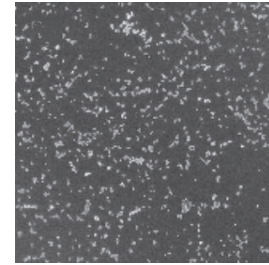
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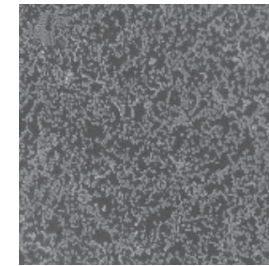
(c)

FIGURE 2: SEM images of the nanosphere masks attached to a silicon wafer surface using 3 different pH masking solutions: (a) pH = 4, (b) pH = 3.5, (c) pH = 3.2. The images are $80\,\mu$m $\times$ $80\,\mu$m.

for 30 seconds to allow adsorption of a positive layer. Immediately afterwards, a 10 seconds dip-in-deionized water was followed by a nitrogen gas blow dry to remove excess liquid.

To test the effectiveness of the positive coating solutions, the positive coated wafers were dipped in a masking solution of negative nanospheres. The nanospheres used in this study are 400 nm diameter silica beads from Bangs Labs, product code SS02N, which comes in a colloid solution with 10% by weight nanospheres. A 3.5 pH solution of acetic acid was used, containing 2% by weight nanospheres. A 3.5 pH was chosen as it is greater than the isoelectric point of SiO_2 and much less than the isoelectric point of Al and Al_2O_3 (the composition of the positive coating layer), giving opposite charged surfaces.

Optical microscope imaging in dark field mode revealed that a combination of 650 μM $AlNO_3$ with 125 μM NaOH resulted in the most dense coating of nanospheres onto the wafer. This mixture of chemicals gives the mask solution a pH of 4.1. A picture of the surface is shown in Figure 1. It should be reiterated at this stage that an oxide was formed on the wafer by a piranha clean. Vastly, different nanosphere masks result when using a wafer which has a different surface,
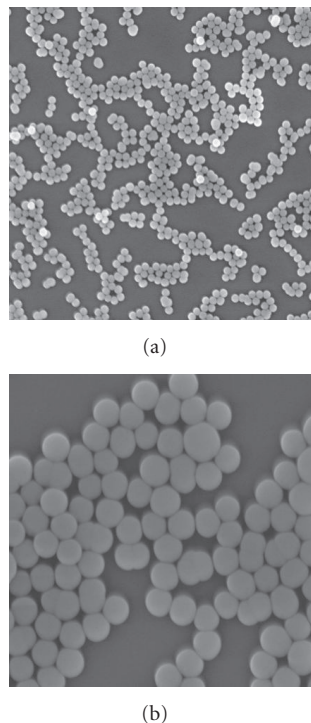
(a)

(b)

FIGURE 3: SEM images of the nanosphere coatings from the 3.2 pH masking solution. Scale can be taken from the 400 nm diameter sphere diameters.

such as a thick thermal oxide, native oxide, or no oxide at all. In addition, masking of multicrystalline wafers may require a slightly different composition due to their surface roughness. The solutions used here must be optimized for each type of surface, and each application.

2.2. Electrostatically attaching nanosphere masks

Varying the pH of the masking solution strongly alters the surface charge of the solids in solution and hence influences the electrostatic attraction between the positive coated wafer and the negative nanospheres. Mixtures of 50 mM acetic acid and 50 mM NaOH were used to tailor the pH of the nanosphere solutions. After pH was determined, a small volume of nanospheres was added to make the solution 2% by weight nanospheres. As expected for such a buffer solution, this amount of dilution with nanosphere solution was found to have negligible effect on the pH. The solution pH was varied upwards of 3.2 by this process, and the nanosphere masks examined by SEM. Figure 2 shows the nanosphere masks achieved.

The lowest pH gives a denser mask, covering more of the surface. SEM images of 2 different areas of the best mask can be seen in Figure 3. Around 60% of the surface is masked with large 2D nanosphere arrays, with unmasked regions usually closer than 3 sphere diameters from a nanosphere. Stronger concentrations of acetic acid were used to achieve a lower pH, but the masks were very sparse and gave poorer surface coverage than that shown in Figure 3. This may have
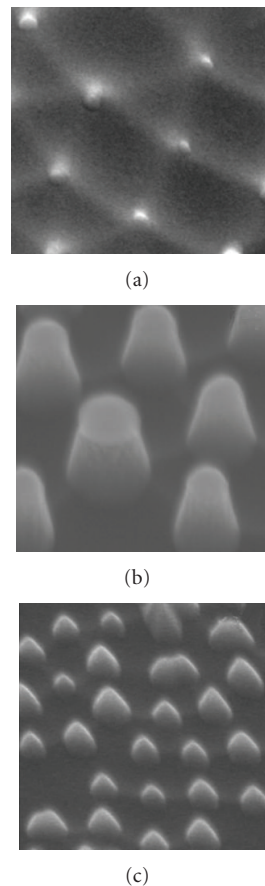

(a)

(b)

(c)

FIGURE 4: SEM images (taken on a 45° tilt) of different RIE textures made using SF_6 plasmas during RIE. (a) Shallow honeycomb feature. (b) Flat-topped cones, with best antireflection properties. (c) Small pointed structures.

been because the nanosphere surface charge/wafer surface charge was not well balanced, or the positive coating partially dissolved in the stronger acid. Other acids are likely to give different results, as they will have a different pH at this 50 mM concentration, and they will interact differently with the positive wafer coating. A denser or more homogeneous coating than that shown in Figure 3 may be possible using the surface charge reversal masking process. All previous work on nanosphere lithography has assumed a requirement for a continuous monolayer mask, although the merits of this have not been demonstrated. Using these simple-to-apply lithography masks and then forming an RIE texture, the reflection is shown to be as good as anything achieved using a spun on, more homogeneous monolayer mask.

2.3. RIE texturing results

RIE is commonly used in the microelectronic industries and the equipment appears in many labs and photovoltaics manufacturing plants where it is used for edge isolation. A handful of different textures were created by RIE using SF_6 gas and the best mask as shown in Figure 3. Figure 4 shows some different shaped features that were created. The surfaces were
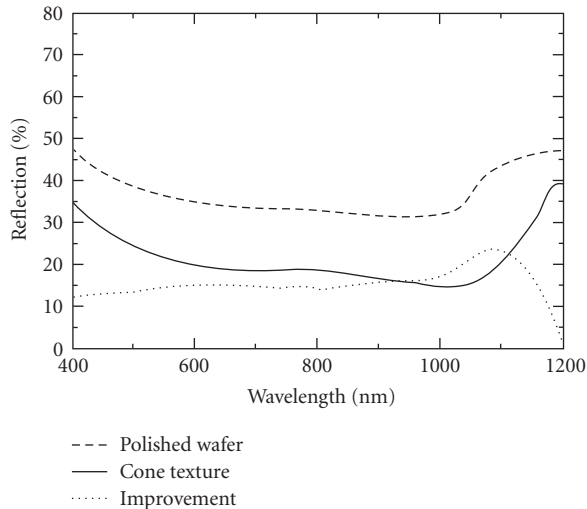
FIGURE 5: Reflectance of a polished silicon wafer, and an RIE textured wafer using the simplified nanosphere lithography mask. The difference between the two is also shown.

etched with different SF_6 pressures and flow rates. The shallow honeycomb features in Figure 4(a) were made with a process pressure of 6.9 Pa in 10 minutes. The flat-topped cone-shaped texture from Figure 4(b) has the best antireflection effect, and was made using the highest process pressure of 7.5 Pa in 4 minutes. The small pointed structures in Figure 4(c) are made with 3.5 Pa and took 8 min. On the regions where there were no nanospheres, the surface is gently curved and almost flat.

After texturing, the wafers were dipped into a solution of 5% HF which removed the remains of the nanospheres and removed the oxide from the silicon surface. The hemispherical reflectance of the silicon surfaces were then measured using an integrating sphere accessory with a Varian CARY 500 spectrophotometer. As the small RIE system used in this study only etches uniformly across a 3 cm diameter area, only the central region of the wafer was measured. Figure 5 shows that the cone texture performs well across the full wavelength range, with a minimum reflectance of 14.5%.

3. CONCLUSION

Nanospheres are a suitable etch mask for RIE texturing. The masks are usually spun on, but this is a slow serial process and wastes a great deal of nanosphere solution. By reversing the surface charge of a polished silicon wafer, the mask has been applied by simply dipping into a dilute acidic solution of nanospheres. This process is suitable for a manufacturing environment, as the masking and drying process takes only 2 minutes, and the RIE texturing (which uses standard equipment) takes only 4 minutes.

The nanosphere masks used do not fully coat the surface in a homogeneous monolayer as seen in spun-on masks. The mask is more like a random arrangement of tendrils, stretching over the wafer surface in 2D arrays. This has proven to be no disadvantage, as the minimum front sur-

face reflectance produced with this process is as low as has been achieved by any other nanosphere lithography masking process [4]. The added advantage of the masking process developed here is the increased processing speed that should translate to factory throughput and cost savings. The application for these colloidal masks stretches beyond polished silicon wafers, as the simple dipping process could also create nanosphere coatings onto very large multicrystalline wafers or to heavy glass sheets, which would not be suitable for spinning.

ACKNOWLEDGMENTS

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