Dopant Diffusion through Selective Surface Regions to Improve Efficiency in Micro/Nano Textured Thin Solar Cells

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Abstract — **We introduce a simple method to improve efficiency in micro/nano textured solar cells by diffusing a dopant through selective surface regions. This method is effective when the texture size is comparable to or smaller than the characteristic diffusion length. In this size regime, strong inhomogeneity in the dopant concentration often develops in the cells. In our case, the texture is an array of nanopyramidal dips on thin crystalline silicon solar cells. Our simulations for the texture show strong inhomogeneity in the dopant concentration along the textured surface. The strong inhomogeneity creates electrically inactive regions in the texture. With our doping method, our simulations show that the inhomogeneity can be significantly reduced to enhance charge collection efficiency. We confirm this prediction by directly measuring photovoltaic efficiencies of solar cells fabricated with and without using our doping method of selective diffusion. Our experiments demonstrate that our selective dopant diffusion enhances the efficiency from 12.5% to 13.3% for free-standing 15-μm-thick silicon solar cells textured with periodic nanopyramidal dips. Our method would be generally applicable for other micro/nano structures, semiconductor materials, and optoelectronic devices.**

Index Terms — **Power engineering and energy, energy, photovoltaic cells, generation, solar power generation, photovoltaic systems**

I. INTRODUCTION

Semiconductor surfaces in solar cells are conventionally textured to enhance light trapping. For thin solar cells, light trapping structures are desired to be on a micro/nano scale [1]. To fabricate a pn-junction in homojunction cells, diffusion processes are commonly used where dopants are diffused into the textured substrates. With the diffusion process, strong inhomogeneity in the dopant concentration typically develops along the textured surface when the structural dimension of the texture is comparable to or smaller than the characteristic diffusion length. In this case, the inhomogeneity can result in overdoped and/or underdoped regions that decrease photovoltaic efficiency of the cells. Moreover, because overall charge concentration is high in thin cells with efficient light-trapping structures, the volume fraction of such inactive regions is high in thin films, potentially resulting in significant degradation in photovoltaic efficiency.

We recently reported that well-designed periodic nanostructures can enhance optical absorption of thin crystalline silicon (c-Si) solar cells to enable reduction of the cell thickness by two orders of magnitude [1,2]. To fully harness the advantage of such structures, the electronic transport properties in the structures should also be carefully engineered. For example, the doping concentration should be sufficiently uniform along the textured surfaces. In this work, we introduce a simple method for rendering the doping concentration uniform by diffusing a dopant through selective surface regions. We demonstrate that this method enhances the efficiency of 15-μm-thick c-Si solar cells by 0.8%.

II. INHOMOGENEOUS DOPING

Alkaline etching on c-Si surfaces with a periodically perforated mask results in an array of pyramidal dips called inverted pyramids. We demonstrated that the thickness of c-Si solar cells can be reduced by more than an order of magnitude at the same solar absorbing power when an array of inverted nanopyramids is used for light trapping [3]. Maximum solar absorption for these structures is obtained when the periodicity is 700 nm. Because typical dopant diffusion length, which is on the order of 500 nm, is comparable to the periodicity, conventional doping often results in significant inhomogeneity along the structure surface.
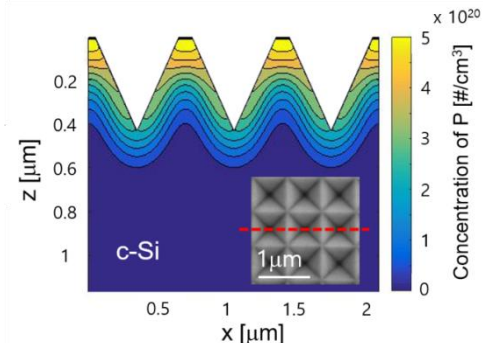

Fig. 1. Calculated dopant concentration profile in a c-Si substrate with periodic triangular grooves. The concentration profile roughly represents that in a cross section of an inverted nanopyramid array (top view in the inset) marked by a red-dashed line.

Figure 1 shows calculated dopant concentration profile in a cross section of a c-Si substrate with a grooved surface when the doping is performed by diffusion. The dopant in the calculation is phosphorus (P) and the grooves are triangular in a cross-sectional plane. The concentration profile in the 2D structure can be regarded as a rough approximation to that of a cross section of a periodic inverted nanopyramid structure indicated as a red dashed line in Fig. 1 inset. After the dopant is placed on the structured surface, the dopant is diffused into the substrate in two steps, which are termed pre-deposition and drive-in. This process will be employed in our experiment in

Section IV. In pre-deposition, the dopant is infiltrated into the vicinity of the surface. The dopant remaining on the surface is subsequently removed. Then, with drive-in, the dopant is diffused deep into the substrate with a depth of ~ 500 nm. In our calculations and experiments, pre-deposition and drive-in are performed at 960 °C for 2 hours and 950 °C for 3 hours, respectively. These conditions lead to a fill factor of 75% in our experiment, as will be shown in Section IV.

With the diffusion process, the dopant is concentrated in the top-most region of the structure as shown in Fig. 1. The concentration at the top is more than twice that at the bottom of the grooves. When doping is performed enough to avoid underdoped regions, the top region would be overdoped resulting in a reduction in minority carrier lifetime. Oppositely, when overall doping level is low to avoid overdoped regions, the bottom regions would be underdoped and the series resistance of solar cells would increase. Thus, in both cases, the solar cell efficiency decreases in general due to the doping inhomogeneity.

III. CALCULATIONS FOR SELECTIVE DIFFUSION

Periodic surface structures are typically fabricated by etching through a mask. The etch mask is fabricated by various methods including optical/interferometric lithography and nanoimprint lithography. For diode fabrication, after etching, the etch mask is removed and subsequently a pn-junction is created. In our selective dopant diffusion, the etch mask is used as a diffusion barrier for a dopant in the pre-deposition process. Figure 2 illustrates our process flow for selective dopant diffusion by an etch mask. When a perforated mask is placed on a c-Si substrate, etching is performed to define an inverted nanopyramid array. A spin-on-dopant (SOD) is spin coated on the structure which includes the etch mask. During pre-deposition, the dopant is infiltrated selectively through the c-Si surface regions that directly contact the SOD. The etch mask and SOD are subsequently removed and the dopant drive-in is performed to obtain a Gaussian concentration profile.
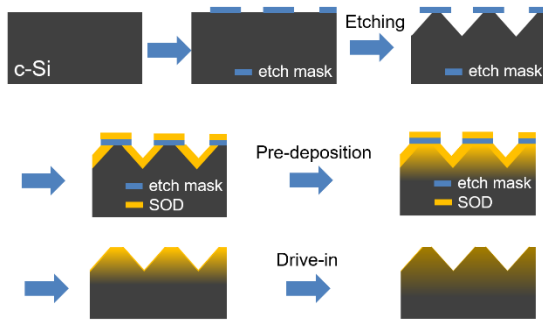

Fig. 2. Process flow for pn-junction fabrication by selective dopant diffusion into micro/nano textured c-Si substrate.

As a rough approximation, we calculate the phosphorus concentration profile in the 2D groove structure in Fig. 1 using the finite difference method. In this case, when selective diffusion is performed, the top of the groove structure in a c-Si substrate is covered by an etch mask. Figure 3 compares the concentration profile with (a) and without (b) using the etch mask, both after pre-deposition and after drive-in. After both steps, when the etch mask is used, the dopant concentration near the top is significantly reduced whereas that near the bottom of the grooves is negligibly altered.
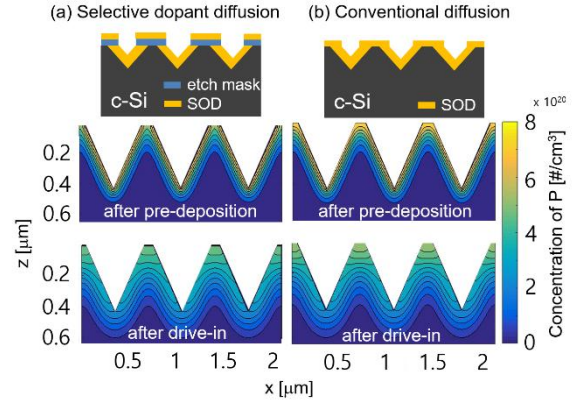

Fig. 3. Calculated dopant concentration profile in periodic triangular grooves for (a) selective dopant diffusion and (b) conventional diffusion after pre-deposition and drive-in.

When the dopant concentration is below 3.7×10^{20} cm^{-3} at the diffusion temperature of 950 °C and the thickness of the doped region is on the order of 500 nm, the solar cell would function well [4]. In our calculations, after drive-in, the doped region thickness at the bottom is ~270 nm and the concentration at the top region without selective diffusion is above 3.7×10^{20} cm^{-3}. These results indicate that the underdoped bottom region may lead to relatively high sheet resistance and the overdoped top region would result in strong charge recombination. In this work, we focus on the effect of selective diffusion on the doping concentration in the top region. Figure 4 displays excess dopant concentration above 3.7×10^{20} cm^{-3}, which represents the concentration of excess dopant that is electrically inactive. By the selective diffusion, the excess concentration is reduced by a factor of two under the same diffusion conditions. Thus, our selective diffusion method would increase open circuit voltage (V_{oc}), fill factor (FF), and photovoltaic efficiency of the cells by reducing the concentration of inactive dopant.
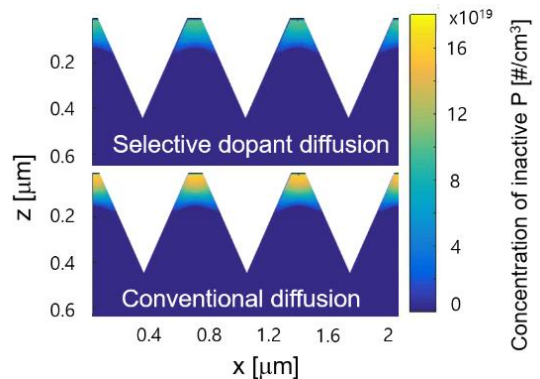

Fig. 4. Excess dopant concentration extracted from Fig. 3.

IV. Experiment

To confirm the effect of our selective diffusion on the solar cell efficiency, we have fabricated thin c-Si solar cells with an inverted nanopyramid array using our selective diffusion method. For the fabrication, we reduced the thickness of p-type c-Si wafers (1-10 ohm-cm) from 250 µm to 15 µm by etching in a 50% potassium hydroxide (KOH) solution at 90 °C. After thinning the wafers, a 30-nm-thick Si_3N_4 layer was deposited on the wafers by plasma-enhanced chemical vapor deposition (PECVD). The Si_3N_4 etch mask layer was perforated in a square lattice of a 700 nm periodicity using interference lithography and dry etching. The c-Si surface regions exposed by the perforations were etched in the form of inverted nanopyramids in a KOH solution. A top-view electron micrograph in Fig. 5(a) shows circular holes in the etch mask and the inverted nanopyramids underneath. For selective diffusion, the etch mask was used as a barrier for pre-deposition of a phosphorus SOD. After pre-deposition and SOD removal, for passivation, a 1.5-nm-thick SiO_2 layer was grown by thermal oxidation and a 50-nm-thick amorphous Si (a-Si) layer was deposited by PECVD on the SiO_2 layer. Then, the temperature was slowly increased at a rate of 83 °C/hour to 950 °C to crystallize the a-Si into poly-Si. At 950 °C, the dopant was diffused into the c-Si substrate by drive-in for 3 hours. After drive-in, Pd/Ag/Ti (20nm/1500nm/20nm) was evaporated on the passivated surface through a mask to define metal bus bars and fingers. On the backside of the cell, a 1500-nm-thick Ag layer was deposited using e-beam evaporation for both electrical contact and back reflection. Figure 5(b) shows a photograph of our free-standing thin solar cell.
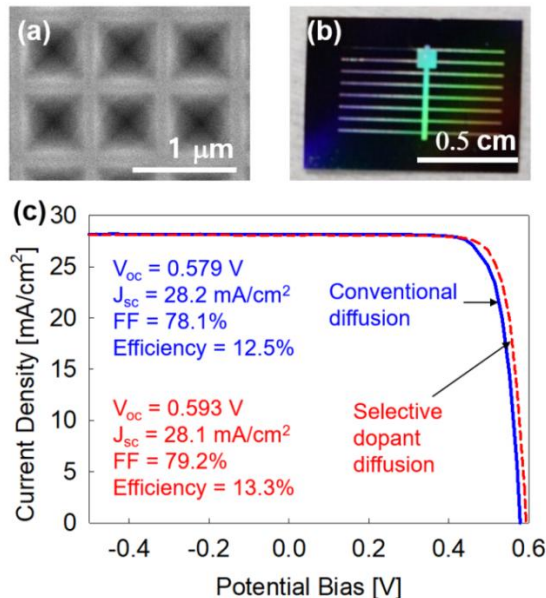
We obtained current-voltage (IV) curves for our thin c-Si solar cells fabricated with and without using selective diffusion. The cells were illuminated by a light beam of the AM1.5G spectrum from a solar simulator (ABET, LS-150). The IV curves in Fig. 5(c) demonstrate that our selective dopant diffusion increases both FF and V_{oc}. This effect amounts to an increase of photovoltaic efficiency from 12.5% to 13.3%.

V. Conclusion

In conclusion, we have introduced a simple method of selective dopant diffusion to reduce the inhomogeneity in the dopant concentration for micro/nano textured solar cells. Our calculations show that a dopant concentration along a textured surface can vary by a factor of two when conventional diffusion is performed. Such inhomogeneity often develops when the texture size is comparable to or smaller than the characteristic diffusion length and decreases solar cell efficiency significantly. In our method, the inhomogeneity is reduced by diffusing a dopant through selective surface regions exposed by an etch mask remaining on the surface after texturing. Our 15-µm-thick c-Si solar cells fabricated by the selective dopant diffusion process increased photovoltaic efficiency from 12.5% to 13.3% by increasing both open circuit voltage and fill factor. While we demonstrate the effectiveness of the selective dopant diffusion in thin c-Si solar cells, our method would be broadly applicable to other semiconductor materials, light-trapping structures, and optoelectronic devices.

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Fig. 5. (a) Top-view electron micrograph of inverted nanopyramids underneath an etch mask with circular holes. (b) Photograph of our 15-µm-thick c-Si solar cell integrated with the light trapping structure in (a). (c) Comparison of IV curves of thin c-Si solar cells between conventional diffusion and selective dopant diffusion.