Light Trapping Enhancement in Thin Film Solar Cells by Breaking Symmetry in Nanostructures

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***Abstract* — We experimentally demonstrate highly efficient light-trapping structures that is achieved by breaking the symmetry in inverted nanopyramids on c-Si. The fabrication of these structures is cost-effective and scalable. Our optical measurement for the structures on 10-μm-thick c-Si cells shows the Shockley-Queisser efficiency of 27.9%. We further fabricate plasmonic metal structures on the symmetry-breaking inverted nanopyramids. When a light-absorbing polymer layer is deposited on top of the plasmonic structures, we observe that the plasmonic light trapping exceeds the Lambertian limit. The remarkable light trapping increases the short circuit current by 2.5 times. We expect the symmetry-breaking structures to be broadly applicable to thin-film solar cells.**

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

I. Introduction

Light trapping is a well-established technique to enhance the photovoltaic efficiency of solar cells. For example, optimized light trapping has achieved the record efficiency of 25.6% for thick crystalline silicon (c-Si) single junction solar cells [1]. However, for thin-film solar cells with a thickness less than 10 microns, macroscopic light-trapping structures cannot be applied. With nanoscale structures, the physical principles of light trapping are radically different. For example, the ray-tracing technique that is based on geometric optics is no longer valid for nanophotonic structures. Various nanophotonic structures have been investigated for efficient light trapping. While many promising nanoscale structures have been suggested, it has been difficult to fabricate these structures in a cost-effective and manufacturable manner. Without the solution to the problem of expensive manufacturing, the scientific research would have little economic values. Therefore, toward the goal of the development of inexpensive light trapping for thin films, care has to be taken to find the nanophotonic structures that can be manufactured with inexpensive techniques.

A promising nanophotonic principle to light trapping, recently developed by Han *et al.* is that proper symmetry breaking in periodic nanostructures enhances absorption over the broad solar spectrum [2]. The absorption enhancement can reduce the c-Si solar cell thickness by two orders of magnitude, while achieving the same efficiency as thick flat c-Si films with an antireflection coating. In this work, we introduce a new approach to systematically break the symmetry in inverted nanopyramid arrays [3]. The fabrication relies on simple, low-cost, wet etching process steps, and does not rely on the use of off-cut Si wafers [4]. This method also provides a convenient platform to rapidly fabricate a large range of geometries and study the effect of symmetry breaking on light trapping. More importantly, our method does not add any fabrication steps to the existing processes that are used for symmetric structures. Therefore, without any added effort, the light-trapping efficiency can be improved by our method to break the symmetry. Our method represents a very useful advancement in the thin-film c-Si solar cell technology because symmetric inverted nanopyramid arrays have already achieved a remarkable efficiency of 15.7% with only a 10-μm-thick c-Si films [5].

II. Symmetry-breaking approach

Our symmetry-breaking method for inverted nanopyramid arrays is illustrated in Fig. 1. The left column of Fig. 1 shows a variety of etch templates represented by yellow mask with perforation. The open windows in the template are defined by lithography and dry etching. The exposed underlying c-Si is then etched in an alkaline solution to create the inverted nanopyramids shown in the right column of Fig. 1. The underetching of c-Si for the circular perforation in the mask leads to square-based inverted nanopyramids.

In conventional method, the square lattice perforation with one of its lattice vector parallel to the [110] direction leads to the inverted pyramid arrays with C_{4v} symmetry. This structure exhibits 4 mirror symmetry planes and 4-fold rotation symmetry. The first level of symmetry breaking can be achieved by rotating the etch template and therefore the side of the square lattice around the [001] axis from the [110] direction. This lattice rotation effectively results in each inverted nanopyramid rotated around its own apex. Consequently, the mirror symmetry is completely broken while the 4-fold rotational symmetry is preserved in the C_4 symmetry structure. In addition to the rotation, the symmetry can be further broken by arranging the etch windows in non-square lattices. For example, we use a rectangular lattice as shown in Fig. 1. With the previously described sequence of

symmetry-breaking, we can reduce the symmetry of inverted nanopyramid arrays down to C_2.

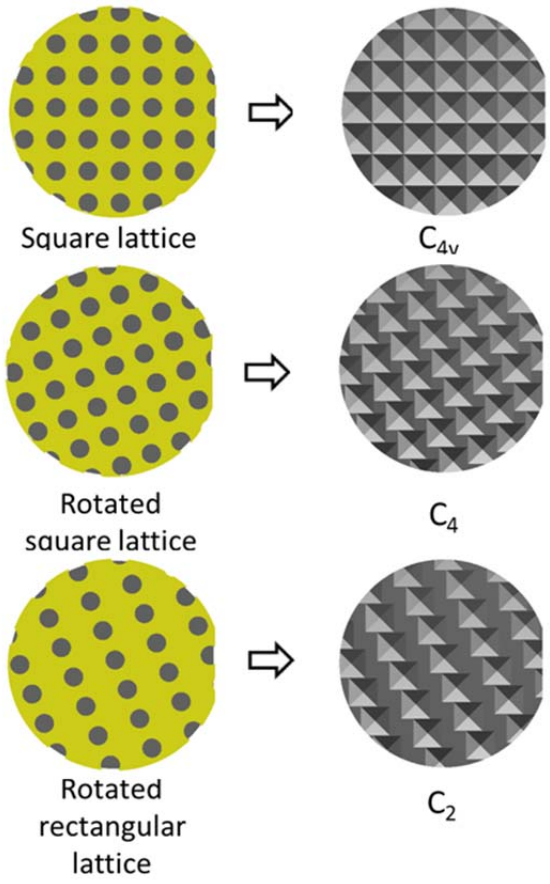

Fig. 1. Our approach to systematically break the symmetry by rotating the etch template and arranging the openings in various lattice types. Left figures show the etch template rotated about the [001] axis. The flat region on the right side of each c-Si wafer indicates the [110] direction. Subsequent etching in an alkaline solution defines inverted nanopyramids on c-Si (001) surfaces (right figures). The resulting symmetries are labeled in Schönflies notation. Adapted from Ref. [3].

III. Symmetry-Breaking Structures for c-Si Photovoltaics

Following this approach, in our experiment, we have broken the symmetry of inverted nanopyramid arrays from C_{4v} to C_4 and C_2 symmetry as shown in Fig. 2(a)-(c). Double exposure in a Lloyd's mirror type interference lithography and dry etching create the etch template pattern on a 25×25 mm^2 area of c-Si wafers. For the C_4 and C_2 structures, the rotation angle is approximately 22.5°. This angle is chosen to be one half of 45° to further reduce the symmetry from C_{4v} or C_{2v}, either of which results from 0 and 45° rotations. The unetched flat area, which lessens light trapping, is reduced by subsequently performing isotropic etching in HNO_3/HF. The isotropic etching can completely remove these unetched regions. Using Silicon-On-Insulator (SOI) wafers, we fabricate 10-μm-thick c-Si films with the light-trapping structures on top. We deposit Ag on the oxide layer on the backside of the film. The absorption in c-Si is determined by subtracting calculated absorption in Ag from experimentally measured total absorptance. The total absorptance values obtained by experiment and calculation agree well with each other. Figure 2(d) shows the obtained absorptance in c-Si. In general, the absorptance increases as the symmetry is reduced. The Shockley-Queisser efficiencies obtained for the C_{4v}, C_4, and C_2 symmetry in inverted nanopyramids on 10-μm-thick c-Si films are 27.0, 27.5, and 27.9%, respectively. Further optimization results in 28.1, 29.1, and 30.0%, corresponding to each symmetry structure, based on our calculations for 20-μm-thick films.

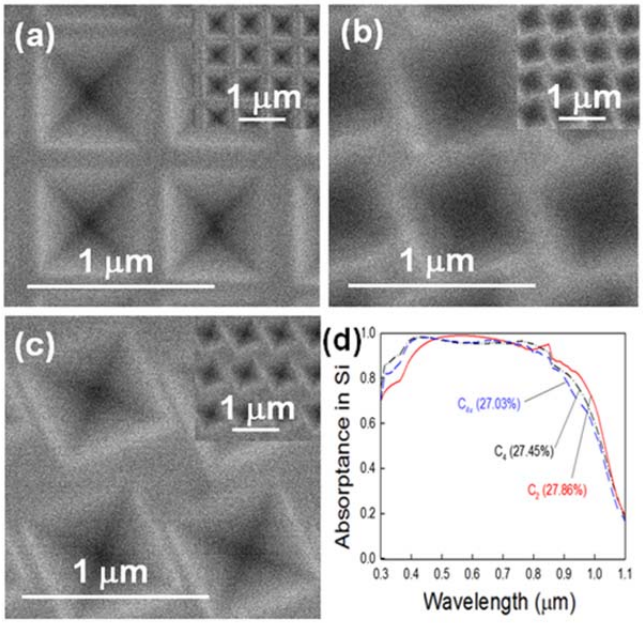

Fig. 2. Scanning electron micrographs of the inverted nanopyramid arrays with (a) C_{4v}, (b) C_4, and (c) C_2 symmetry. The insets are zoomed-out views of the structures. (d) Experimentally determined absorptance spectrum in c-Si for the inverted nanopyramid arrays of C_{4v} (blue dashed), C_4 (black dotted), and C_2 (red solid line) symmetry. The calculated small absorption in the back metal is subtracted from experimentally obtained total absorption. Adapted from Ref. [3].

IV. Symmetry-Breaking Structures for Thin-Film Photovoltaics

Our symmetry-breaking method can be extended to plasmonic light-trapping structures. For plasmonic structures, we deposit thin Ag films on both the symmetric (C_{4v}) and asymmetric (C_2) inverted nanopyramid structures created on

Si(001). The asymmetric structure exhibits a greater number of resonances, which is useful for light trapping. For solar photovoltaic structures, we deposit light-absorbing polymers on top of these patterned metal surfaces. For the polymers, we use a 30-nm-thick poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b]dithiophene-2,6-diyl]] (PCPDTBT) layer. Fig. 3(a) shows that the overall light absorptance increases significantly with patterned nanostructures, compared to flat Ag film. Absorption in PCPDTBT is determined by subtracting the Ag absorption from the total absorption. The measured absorption spectra agree with calculations in general, but the detailed features show some discrepancies. Thus, with the experimentally determined optical constants of PCPDTBT, we obtain absorption in the polymer from calculations. Figure 3(b) compares the results with the Lambertian light-trapping limit. For the asymmetric structure, the absorption enhancement in PCPDTBT exceeds the Lambertian light-trapping limit over most of the spectrum. This remarkable light trapping enhances the short circuit current by 2.5 times. While other structures can surpass the limit, our symmetry-breaking structures can be directly integrated into photovoltaic architectures. Moreover, our plasmonic structures can be manufactured with a cost-effective method.

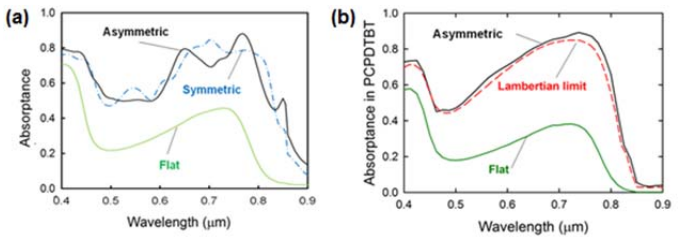

Fig. 3. (a) Experimentally measured normal absorptance for a 30-nm-thick PCPDTBT layer on Ag films with symmetric/asymmetric nanopyramids vs. without them. (b) Absorption in PCPDTBT for the asymmetric and flat structures compared to the Lambertian limit.

V. Conclusion

To conclude, we have demonstrated that symmetry-breaking inverted nanopyramid arrays are exceptionally suitable for light trapping in solar cells. A simple symmetry-breaking fabrication method is introduced. The method does not rely on expensive off-cut c-Si wafers and uses cost-effective, manufacturable, wet etching steps. The symmetry of inverted nanopyramids can be reduced by rotating the etch template about the [001] axis and using non-square lattices. This approach can fabricate inverted nanopyramids with C_{4v}, C_4, and C_2 symmetry. We have experimentally demonstrated that, as the symmetry of the inverted nanopyramids is broken in the $C_{4v} \rightarrow C_4 \rightarrow C_2$ sequence, the photovoltaic efficiency increases along the path. We have also demonstrated that our symmetry-breaking scheme is useful for plasmonic light trapping. Plasmonic structures are created by depositing thin metal films on the symmetric/asymmetric light-trapping structures on silicon surfaces. Symmetry breaking in these plasmonic structures enhances light absorption in thin organic materials coated on the metal films. By breaking the symmetry, we achieve exceptionally strong plasmonic light trapping that surpasses the Lambertian limit. For cost reduction, the silicon structures can be used as a negative mold to create positive relief patterns on metal films repeatedly. Therefore, our symmetry-breaking method is directly applicable to various solar cells. Moreover, the method involves inexpensive fabrication steps and has great potential for wide commercial use.

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