Symmetry-Breaking Nanostructures for Enhanced Light-Trapping in Thin Film Solar Cells

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***Abstract* — We introduce a manufacturable method to break the symmetry in inverted nanopyramids on c-Si. This method broadly enhances light trapping and would increase the efficiency from 25 to 26.4% for thick c-Si cells. We further use the nanopyramids as a template to deposit plasmonic metal structures and demonstrate enhanced light absorption in organic solar cells. The enhancement exceeds 100% in some cases by concentrating the plasmonic bands tuned to the polymer absorption. The result agrees well with our measured surface plasmon polariton band structures. We expect our approach 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

Thin-film photovoltaic technology is gaining significant interest because of its low cost and high efficiency. Gallium Arsenide based thin-film single junction cells have achieved an efficiency of 28.8% which exceeds that of thick crystalline silicon (c-Si) solar cells which is currently 25.6% [1]. Typically, the film thickness is on the order of 1-10 microns or less. Further reduction of the film thickness would decrease the module cost by using less material which, in some cases, contains scarce and toxic elements. In addition, bulk recombination of charge carriers is less in thinner films, which is advantageous with regard to cell performance. However, as the photovoltaic cells become thinner, they absorb less light which reduces photovoltaic efficiency. Thus, light trapping in thin layers is essential to reduce the cost and enhance the performance of thin-film solar cells.

Han *et al.* recently reported that proper symmetry-breaking in periodic nanostructures enhances light-trapping [2]. This improvement 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. However, fabricating such structures in a scalable, cost-effective, manufacturable manner remains elusive. 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. We note that our light-trapping structures inherently minimize parasitic losses. Our approach eliminates the need for metal nanostructures for light scattering and therefore reduces metal loss. In addition, the total increase in surface area is either comparable to the microscale inverted pyramids or much less than that of nanorod arrays. These advantages make the symmetry-breaking nanostructure exceptionally suitable for high-efficiency solar cells.

II. Symmetry-breaking approach

Figure 1 illustrates our approach to break the symmetry in inverted nanopyramid arrays with each symmetry group denoted by the Schönflies notation. The top row of Fig. 1 shows a variety of etch templates represented by white 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 bottom row of Fig. 1.

In Figure 1, we use a square lattice with C_{4v} symmetry with its side parallel to the [110] direction as the basis of comparison. 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 addition to the rotation, the symmetry can be further broken by arranging the etch windows in non-square-lattice patterns. The possible two-dimensional non-square lattices are rectangular, triangular, centered-rectangular, and oblique lattices. With the previously described sequence of symmetry-breaking, we can reduce the symmetry of inverted nanopyramid arrays down to C_2.

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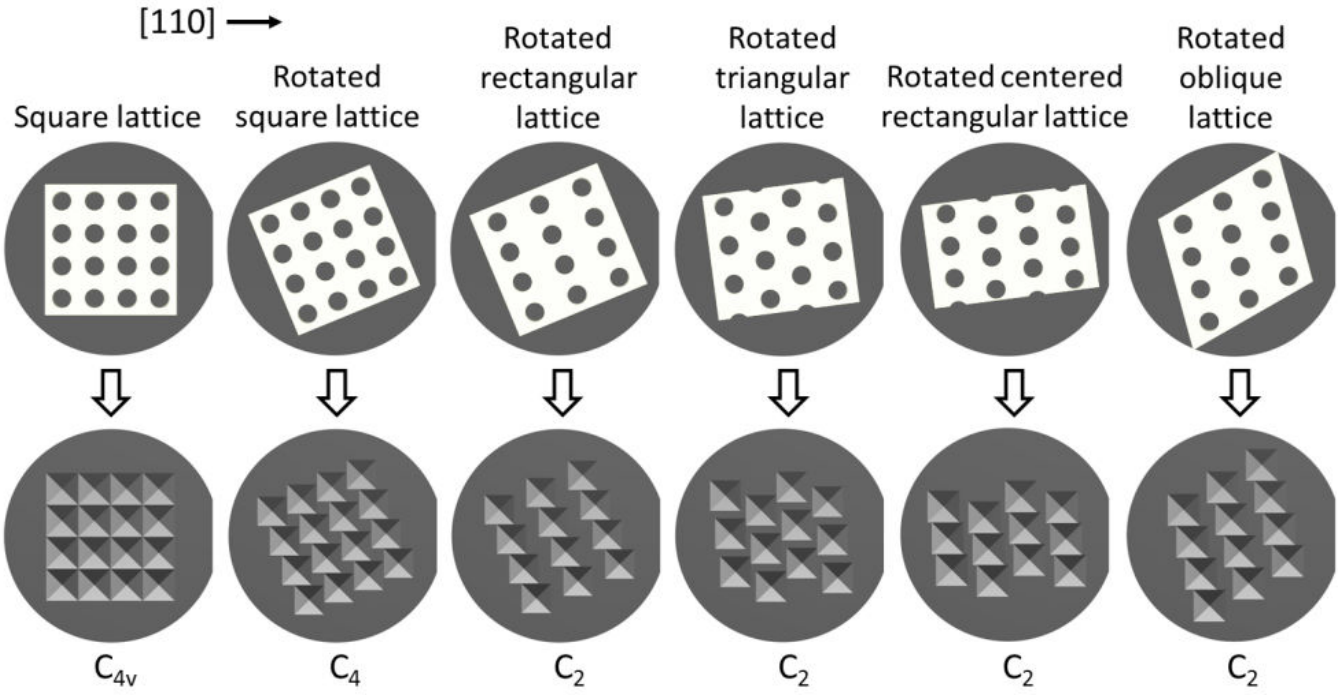

Fig. 1. Our approach to systematically break the symmetry by rotating the etch template and arranging the openings in various lattice types. Top figures show the etch template rotated about the [001] axis. The flat region on the right side of each c-Si wafer indicates the [110] direction. Subsequent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

III. Symmetry-breaking structures for c-Si photovoltaics

Using this approach, we have fabricated inverted nanopyramid arrays with C_{4v}, C_4, and C_2 symmetry as shown in Figure 2(a)-(c), respectively. In this experiment, we use a Lloyd's mirror type interference lithography and dry etching to pattern the etch template on a 25×25 mm^2 area of c-Si wafers. The C_4 and the C_2 structures are obtained by rotating the square and rectangular template lattices according to our scheme in Fig. 1. 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 in Fig. 2(b), which lessens light-trapping, is reduced to that in Fig. 2(c) by subsequently performing isotropic etching in HNO_3/HF. Further isotropic etching completely removes these unetched regions. The calculated absorptance in Fig. 2(d) shows the comparative increase in absorptance with reduced symmetry. The optimum Shockley-Queisser efficiencies obtained for C_{4v}, C_4, and C_2 symmetry in inverted nanopyramids on 20-μm-thick c-Si films are 26.2, 26.9, and 27.6%, respectively. Achieving near 25% efficiency with a 20-μm-thick film, and increasing it further by symmetry breaking (1.4 % increase) are considered substantial in Si photovoltaics.

IV. Symmetry-breaking structures for organic photovoltaics

To investigate the symmetry breaking effect on light trapping in organic photovoltaics, we use the nanostructures created on Si(001) as a negative mold to create nanoscale positive relief patterns on thin Ag films. The SEM image in Fig 3(a) shows a magnified view of rectangular, positive, nanopyramid Ag relief pattern. These metal patterns are then used to deposit light-absorbing polymers on top. For a 100-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 deposited on the nanostructured Ag films, Fig. 3(b) shows that the overall light absorptance increases significantly with symmetric nanostructures, compared to flat Ag film, and even further with asymmetric nanostructures. The surface plasmon polariton band structure measured on (c) symmetric and (d) asymmetric Ag inverted nanopyramid arrays shows that symmetry breaking increases the number of resonances around wavelengths of ~0.46 and ~0.7 μm in the normal direction (zero wavevector), corresponding to the spectral regions of absorption enhancement in Fig. 3(b).

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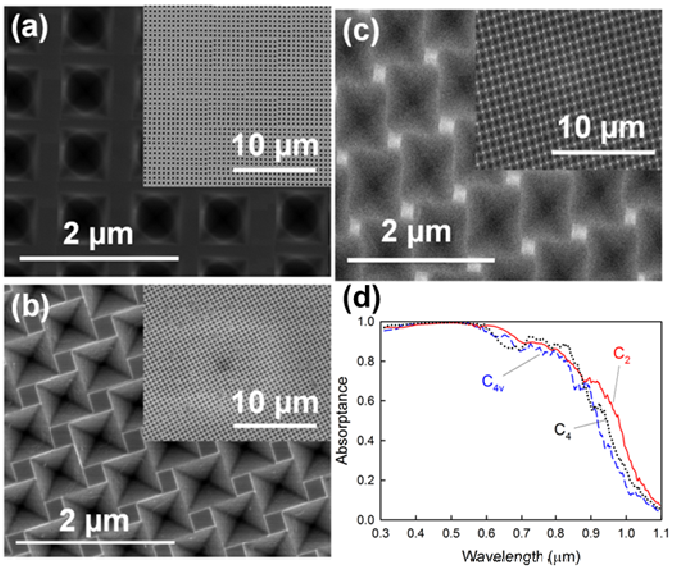

Fig. 2. Scanning electron micrographs of the inverted nanopyramid arrays with (a) C_{4v}, (b) C_4, and (c) C_2 symmetry. The insets are zoomed-out views of the structures. (d) Calculated absorptance spectrum in c-Si for the inverted nanopyramid arrays of C_{4v} (dashed), C_4 (dotted), and C_2 (solid line) symmetry. Adapted from Ref. [3].

V. Conclusion

In conclusion, we have introduced a simple method to systematically break the symmetry on c-Si(001) surface for enhanced optical absorption in solar photovoltaics. This method uses cost-effective, manufacturable, wet etching steps, and does not rely on expensive off-cut wafers. The symmetry of inverted nanopyramids can be reduced by rotating the etch template about the [001] axis and using five different lattice types. Following this approach, the symmetry is reduced from C_{4v} to C_4 to C_2. Our calculations demonstrate 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 also demonstrate that our symmetry-breaking scheme is useful for organic photovoltaics. Using the symmetric/asymmetric light-trapping structures on silicon surfaces as a negative mold, we create positive relief patterns on metal films. Symmetry-breaking in these plasmonic structures enhances light absorption in thin organic materials coated on the metal films. By controlling the lattice symmetry, we increase the number of available plasmonic bands and concentrate the bands at the desired optical frequencies. Therefore, our symmetry-breaking approach is broadly applicable to various material systems in photovoltaics. Further, our symmetry-breaking scheme provides a versatile experimental platform to study the effect of nanostructure symmetries on various optical phenomena.

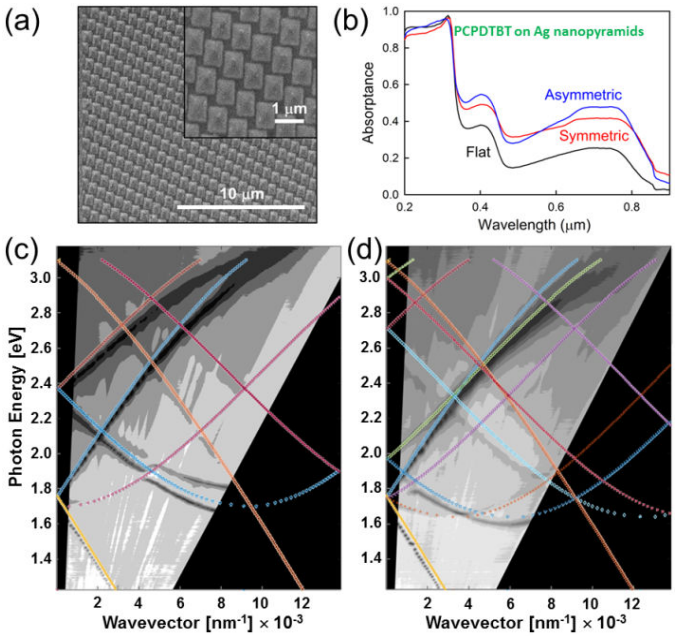

Fig. 3. (a) SEM image of a Ag nanopyramid array with C_2 symmetry, (b) experimentally measured normal absorptance for a 100-nm-thick PCPDTBT layer on Ag films with symmetric/asymmetric nanopyramids vs. without them and the surface plasmon polariton band structures measured on (c) symmetric and (d) asymmetric Ag inverted nanopyramid arrays. In (c) and (d), the brightness represents reflectance and theoretical predictions on flat surfaces are also shown.

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