Ordered Nanostructures for Organic Photovoltaic Cells

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Abstract:

Though potentially a source of clean, renewable energy at a cost even lower than conventional power, organic solar cells are at present far too inefficient. The leading strategy for making efficient organic cells is to create nanoscale ordered bulk heterojunctions.

In this work, we used Nanosphere Lithography and Block Copolymer Lithography as methods to pattern Cr nano-dots on Si for use as masks during reactive ion etching (RIE). With these techniques we were able to produce arrays of Si pillars on the order of 120 nm tall and 20 nm wide, which are very close to the ideal length scale. Devices employing these nanostructured substrates have not yet been tested, but exciton splitting, charge collection and overall cell efficiency are expected to be improved.

Background:

Due to their high cost of production, the use of inorganic solar cells has been relatively limited. Organic semiconductor devices are inherently much less expensive to manufacture, but less efficient due to low charge mobility in the polymer. The most common strategy for making more efficient organic photovoltaics is to use a bulk heterojunction in which excitons (coupled electron-hole pairs) are split at an interface between two semiconductors with offset energy levels [1, 2]. Since excitons only diffuse 4-20 nm in most organic semiconductors, the interface must be patterned at this scale.

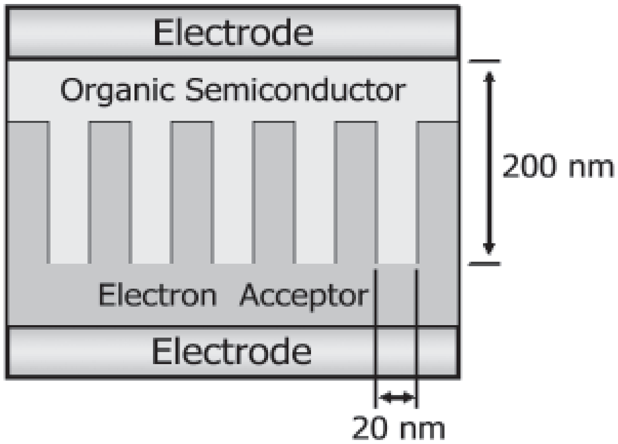

Figure 1: Schematic cross section of the ideal nanostructured heterojunction showing nanoscale interpenetration of the two semiconductor materials.

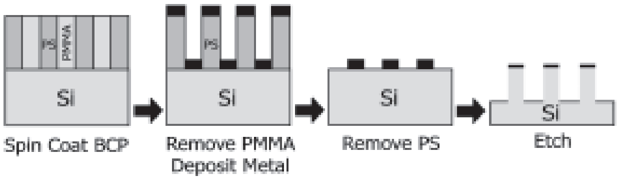

Figure 2: Schematic cross-sectional view of the Block Copolymer Lithography process.

An ideal bulk heterojunction consists of a 100-300 nm thick film of one semiconductor with arrays of 10-20 nm wide pores filled with the other semiconductor, shown schematically in Figure 1 [3]. The electron acceptor material could be any semi-conductor with the right energy levels, and is typically inorganic. Ideally this would be something inexpensive such as titania, but for the purposes of proving the concept of the nanostructured interface, we chose to try to obtain the ideal structure in silicon, which has better understood properties and processing techniques.

We used nanosphere lithography and block copolymer lithography along with reactive ion etching to produce pillars of Si that could be infiltrated with organic semiconductor to create photovoltaic cells.

Nanosphere Lithography:

With this technique, a monolayer of polystyrene nanospheres ~ 34 nm in diameter were spin cast from aqueous suspension onto Si substrates. Next, an electron beam evaporator was used to deposit ~ 5 nm of Cr onto the samples. Because the particles are spherical, even when perfectly packed, there are spaces between them which allows metal to be deposited directly onto the Si surface, but only in small islands.

We then removed the spheres by dissolving them away in toluene, which left only the small islands of metal on the surface. By choosing a plasma highly selective to Si (NF_3), the metal islands acted as a mask during RIE leaving behind pillars of Si.

Block Copolymer Lithography:

With this technique, thin films of PS-PMMA (polystyrene-poly methyl methacrylate) block copolymer were spin cast from toluene solution onto Si substrates during which the polymer phase-separated into a periodic array of 25 nm PMMA cylinders in a matrix of PS. Ultraviolet light was used to selectively degrade and remove the PMMA cylinders leaving an array of pores, allowing Cr to deposit directly onto the Si surface at the bottom of the pores during subsequent e-beam evaporation. The PS was then removed leaving a periodic array of 25 nm Cr nano-dots on the Si surface. This process is shown schematically in Figure 2.

Results and Discussion:

The Si pillars created using both lithography techniques were characterized using ultra high resolution scanning electron microscopy (UHR SEM). In Figure 3, which shows the best results obtained with the nanosphere lithography technique, we see that the spatially irregular pillars are ~ 130 nm tall, ~ 25 nm wide, and ~ 25 nm apart.

In Figure 4, which shows the best results obtained with the block copolymer lithography technique, we see that the pillars are ~ 120 nm tall, ~ 20 nm wide, and ~ 15 nm apart, and much more geometrically homogeneous than the results of the nanosphere technique. These structures are very close to the ideal nanostructure that we are trying to create. Ideally we would like the pillars to be somewhat taller, but in terms of width and separation these structures are nearly perfect. Additionally, these pillars have relatively straight sides, which would allow for greater ordering and better transport characteristics in the infiltrated organic semiconductor.

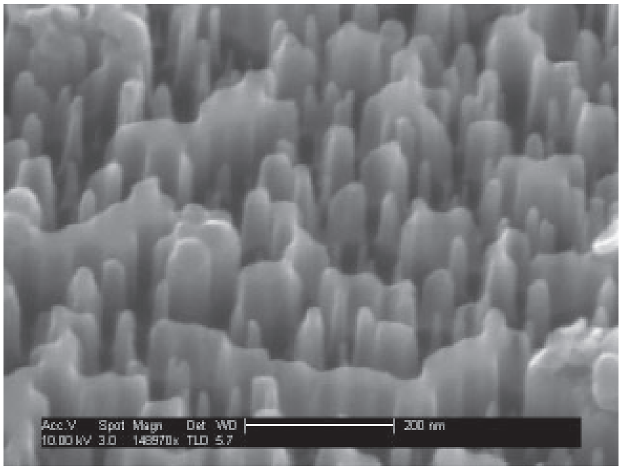

Figure 3: UHR SEM image of structure made using Nanosphere Lithography showing ~ 130 nm tall Si pillars

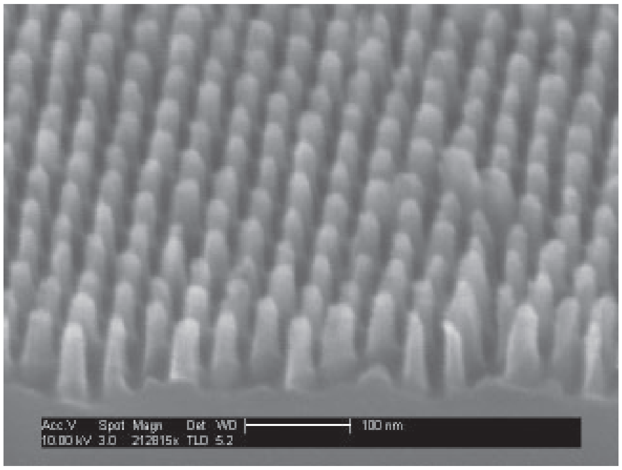

Figure 4: UHR SEM image of structure made using Block Copolymer Lithography showing ~ 120 nm tall Si pillars.

The nanosphere technique is an easier process and has so far produced slightly taller pillars, but the block copolymer technique produces a much more ordered structure. Furthermore, this technique has the advantage that it lends itself to greater geometric control since it is relatively trivial to change the molecular weight of the block polymers, which directly affects the size and spacing of the resulting pillars.

Summary and Future Work:

We have created highly ordered nanostructures in Si, which are very close to the desired size and shape. In the near future, devices utilizing these structures in the heterojunction will be made and tested. Additionally, the entire process of making the pillars and devices should be optimized to maximize efficiency. Ultimately, this knowledge and technology may need to be transferred to some material other than Si, such as titania.

Acknowledgements:

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References:

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