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Biomimetic broadband antireflection gratings on solar-grade multicrystalline silicon wafers

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(Received 30 August 2011; accepted 24 October 2011; published online 9 November 2011)

We report a simple and scalable bottom-up technique for fabricating broadband antireflection gratings on solar-grade multicrystalline silicon (mc-Si) wafers. A Langmuir-Blodgett process is developed to assemble close-packed silica microspheres on rough mc-Si substrates. Subwavelength moth-eye pillars can then be patterned on mc-Si by using the silica microspheres as structural template. Experimental results and theoretical prediction using a rigorous coupled-wave analysis model show that close-packed moth-eye arrays exhibit better antireflection performance than non-close-packed arrays due to a smoother refractive index gradient. © 2011 American Institute of Physics. [doi:10.1063/1.3660263]

Solar cells (or photovoltaics) produce electric power via conversion of the planet’s most abundant and renewable energy input: sunlight.1 The production of photovoltaic panels is dominated by crystalline silicon solar cells. More specifically, 36% of the 2004 production is based on single crystal silicon (sc-Si), 58% on multicrystalline silicon (mc-Si), and 4% on thin film amorphous silicon (a-Si).2 Unfortunately, traditional SiNx AR coatings suffer from high production cost, narrowband antireflection performance (i.e., they can only suppress reflection for a narrow range of wavelengths and incident angles), and poor thermal stability caused by the mismatch of thermal expansion coefficient between SiNx and Si.

Inspired by the excellent antireflection properties of microstructured corneas of some nocturnal moths,4,5 broadband moth-eye AR gratings consisting of periodic arrays of subwavelength pillars have been extensively exploited by both top-down and bottom-up approaches.6–15 We have recently developed a scalable spin-coating technology that enables the fabrication of moth-eye AR gratings by most of the available techniques such as spray deposition could create colloidal template on rough substrates,16–20 reproducible fabrication of monolayer colloidal crystals with good crystalline quality is still challenging.

Here, we report a simple and scalable colloidal templating technology that enables the fabrication of broadband moth-eye AR gratings on rough mc-Si wafers. Monodispersed silica microspheres with 250 nm diameter are synthesized by the standard Stöber method.21 The as-synthesized silica spheres are purified by repeated centrifugation/redispersion cycles in ethanol and are finally redispersed in ethylene glycol with particle volume fraction of 0.20. Solar-grade mc-Si wafers (p-type, 125 × 125 mm, University Wafers) with root mean square roughness of ~0.89 μm (provided by the vendor) are RCA-cleaned (immersed in a 1:1:7 mixture of hydrogen peroxide: ammonia hydroxide: de-ionized water at 70 °C for an hour) prior to use.

Using a clamp attached to a syringe pump (KD Scientific 780-230), the mc-Si wafer is vertically immersed in a Kimax crystallizing dish (170 × 90 mm) containing de-ionized water. The silica/ethylene glycol suspension is then added dropwise to the surface of the water. The suspension is spread to form a thin layer floating on the surface of the water. With the gradual dissolving of ethylene glycol in water, silica microspheres are accumulated at the water-air interface due to the high surface tension of water (72.75 mN/m at 20 °C). The capillary action between neighboring silica microspheres can then organize the floating particles into close-packed (CP) monolayer colloidal crystals which exhibit striking iridescence caused by light diffraction.22 Once the entire surface is covered with silica microspheres, it is left for 10 min for the silica spheres to form a homogeneous colloidal crystal. The mc-Si wafer is then slowly withdrawn at a rate of ~0.5 mm/min controlled by the syringe pump. As the wafer is withdrawn, the floating monolayer colloidal crystal is transferred onto the substrate. This simple colloidal self-assembly technology does not require sophisticated equipment (e.g., a Langmuir-Blodgett trough)15 to organize silica microspheres with diameter ranging from ~70 nm to ~30 μm over wafer-sized areas. In addition, our preliminary results show that this technique is...

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compatible with roll-to-roll processing, promising for scaling up to large volume production.

Fig. 1(a) shows a photograph of a 5-in. solar-grade mc-Si wafer with the right half (yellowish region) covered by a uniform monolayer of 250 nm silica microspheres. The typical top-view scanning electron microscope (SEM) images in Figs. 1(b) and 1(c) illustrate the left and right parts of the wafer. The high surface roughness of the wafer as evidenced by the randomly distributed, micrometer-sized pits and the uniform coverage of the rough surface by silica microspheres over large areas are clearly shown by these images. The magnified SEM image in Fig. 1(d) demonstrates that the hexagonal close-packing of the floating colloidal monolayers is retained during the colloidal transferring and drying processes. This is reasonable as the transferred colloidal monolayers are observed to float on a thin water wetting layer at the early stage of the particle transfer process. The high flexibility of this water layer renders the observed conformal coating of silica spheres on the rough mc-Si surface.

The close-packed silica microspheres can then be used as etching masks during a chlorine reactive ion etching (RIE) process (5 mTorr pressure, 20 SCCM chlorine flow rate, and 80 W) to create moth-eye AR gratings. As the etching rate of silica is much lower than that of silicon under the above RIE conditions, silica microspheres protect silicon immediately underneath them from being etched, resulting in the formation of pillar arrays directly on mc-Si wafers. Importantly, the different crystalline orientations (or domains) of mc-Si wafers do not affect the dry etching rate of silicon during chlorine RIE. The templating silica microspheres can finally be removed by dissolving in a 2 vol. % hydrofluoric acid aqueous solution.

Fig. 2(a) shows a photograph of the wafer in Fig. 1(a) after 30 min RIE etching. The wafer here is cut to be circular to fit inside of our Unaxis Shuttlelock RIE/ICP (inductively coupled plasma) reactive-ion etcher chamber which requires samples to have a maximum diameter of 4-in. The dark part of the wafer is the area that is exposed to the reactive ions. The top-view SEM images in Figs. 2(b) and 2(c) show that hexagonally ordered pillars uniformly cover the dark region. The cross-sectional SEM image in Fig. 2(d) illustrates the close-packing of the templated pillars and the height of the pillars is determined to be \( \sim 1 \mu m \).

Spectral hemispherical reflectance measurements of the templated moth-eye AR gratings are carried out using a HR4000 UV-Vis spectrometer and an ISP-REF reflectance integrating sphere (both from Ocean Optics). Figure 3 compares the hemispherical reflectance obtained from a polished sc-Si wafer, a solar-grade mc-Si wafer, and the templated mc-Si grating in Fig. 2. The flat sc-Si wafer exhibits 30%-50% hemispherical reflectance for wavelengths from 400 to 900 nm, matching with early measurements in the literature. The rough surface of the commercial mc-Si facilitates to reduce the hemispherical reflectance to 20%-30%. By contrast, the templated mc-Si grating shows excellent broadband antireflection property and the hemispherical reflectance is near zero for a wide range of wavelengths from \( \sim 500 \text{ nm} \) to \( \sim 850 \text{ nm} \). The antireflection performance of the moth-eye AR gratings templated from CP colloidal crystals assembled at air-

![Fig. 1](image1.png)

![Fig. 2](image2.png)

![Fig. 3](image3.png)
normal-incidence specular reflection of CP and NCP arrays with 1000 nm pillar height templated from 250 nm spheres. The reflection of the NCP array is apparently much higher than that of CP array. This is caused by the significant difference in the calculated refractive index profiles of the CP and NCP arrays as shown in Fig. 4(b). For the NCP array, the effective refractive index first changes gradually from 1.0 (air) to ~2.1 (at the bottom of the nipples) and then increases sharply to 3.774 (the index of silicon at 600 nm wavelength);26 while for the CP array, the refractive index changes much more smoothly from 1.0 to ~3.44 and then to 3.774. This smooth refractive index gradient leads to the very low reflection over a wide range of wavelengths.5

In summary, we have developed a simple yet scalable bottom-up technology for fabricating broadband AR gratings directly on rough mc-Si wafers. Optical measurements and RCWA simulations reveal that subwavelength gratings with CP structure exhibit improved antireflection performance than NCP arrays. Further structural optimization and integration of moth-eye AR gratings in mc-Si photovoltaic cells are underway and the optoelectronic properties of the final cells will be reported in our future publications.

This work was supported in part by DTRA and NSF under Grant Nos. CBET-0744879 and CMMI-1000686.

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