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# Patterning of SiO<sub>2</sub> interfaces for radiative cooling applications

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**Abstract.** Silicon dioxide (SiO<sub>2</sub>) is a prominent material for radiative cooling applications due to its negligible absorption at solar wavelengths (0.25-2.5  $\mu\text{m}$ ) and exceptional stability. However, at thermal infrared wavelengths, its bulk phonon-polariton band introduces a strong reflection peak inside the atmospheric transparency window (8-13  $\mu\text{m}$ ) which is detrimental to its selective emissivity. Herein, we demonstrate scalable strategies for the patterning of ordered and disordered SiO<sub>2</sub> metasurfaces enhancing their thermal emissivity and enabling sub-ambient passive cooling under direct sunlight.

## 1 Introduction

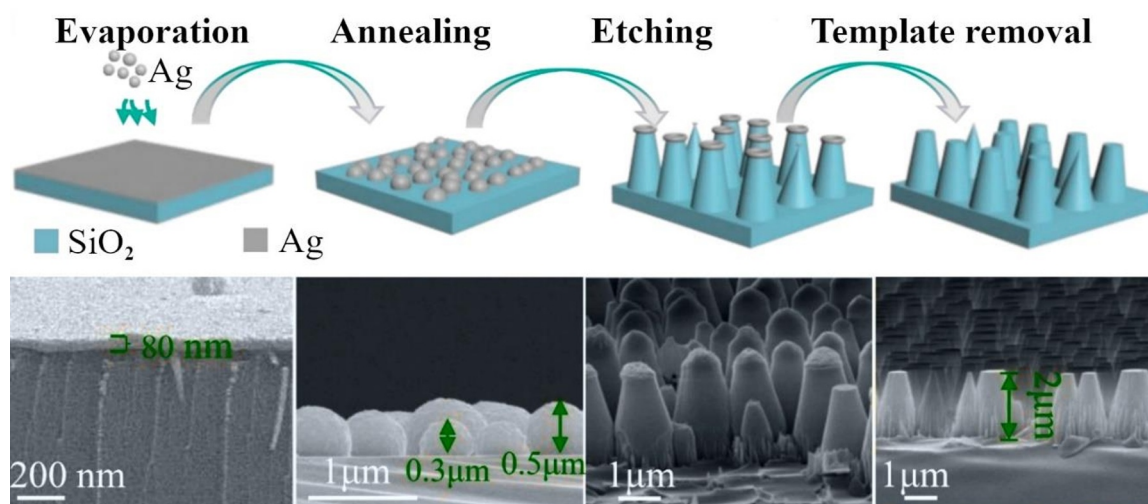
Radiative cooling materials are a special class of materials characterized by a strong emissivity in the wavelength range of the atmospheric transparency window (8-13  $\mu\text{m}$ ) which allows them to dissipate their thermal energy directly into space and cool down to sub-ambient temperatures when exposed to the sky. As such, they hold promise for addressing the growing cooling needs exacerbated by global warming, without requiring any electricity input thanks to their passive operation mode [1].

Due to their inherent outdoor application, however, passive radiative cooling materials should also exhibit exceptional resistance to weathering agents, non-toxicity and be environmentally friendly. Silicon dioxide (SiO<sub>2</sub>) is an excellent candidate due to its low cost, large availability and superior stability. For these reasons, it is

often used as a component in some of the radiative coolers proposed up to date, by adding either bulk layers or glass microparticles to composite materials. These strategies, however, fail to address the inherent emissivity limitations of bulk SiO<sub>2</sub> which are due to its characteristic phonon-polariton resonances causing a large impedance mismatch around 9  $\mu\text{m}$ .

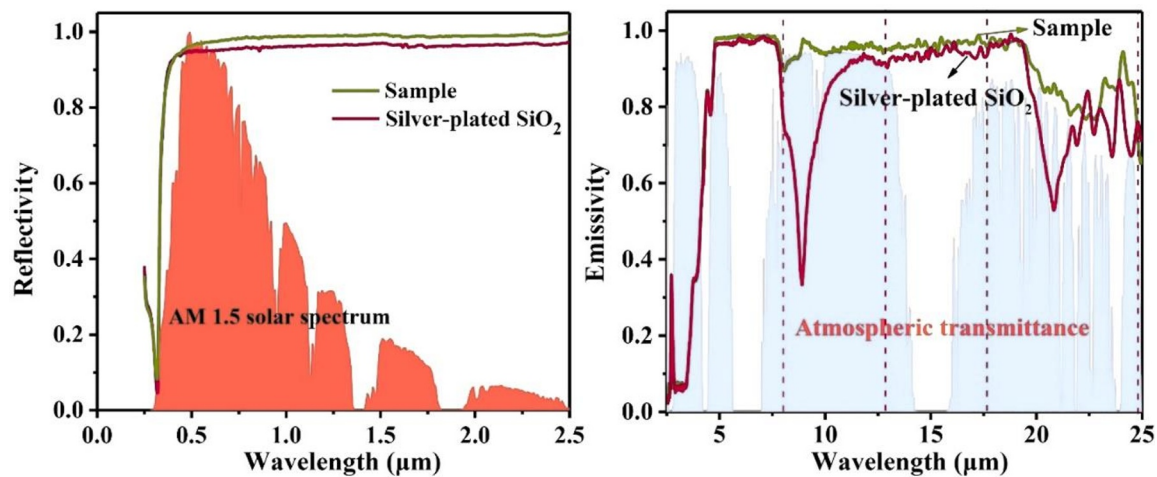
To this end, several groups have considered different strategies to prepare patterned or grated SiO<sub>2</sub> structures. Examples reported to date, however, are typically characterized by deeply etched (> 5  $\mu\text{m}$ ) structures with large periods, which result in high manufacturing costs, long etching times, and low compatibility with existing technologies.

Here, we present numerical and experimental evidence that sub- $\mu\text{m}$  patterning can be optimized to yield a comparable or even superior emissivity enhancement of



**Figure 1** Steps in the fabrication process of the truncated microcone array on the surface of SiO<sub>2</sub>. Adapted from [2].

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**Figure 1** Left panel: Measured reflectivity over the solar spectrum (0.25–2.5  $\mu\text{m}$ ) for the silver-coated flat and patterned samples. Right panel: Measured emissivity/absorptivity at thermal infrared wavelengths from 2.5 to 25  $\mu\text{m}$ , together with the atmospheric transmittance. Adapted from [2].

silica substrates, ensuring increased compatibility with different manufacturing processes.

The micro-pattern designs are first optimized numerically by means of FDTD and RCWA simulations, and then fabricated by different techniques based on self-assembled etching masks.

## 2 Results

Numerical simulations were performed targeting pillar-like patterns compatible with etching processes. A large parameter space was tested including feature sizes, periodicity and height, revealing that significant emissivity enhancement in the thermal infrared range can be obtained using pattern designs with sub-wavelength features below or comparable with a  $\mu\text{m}$  length scale, in contrast with previously reported structures, thus allowing considerable time and cost savings at etching stage. The resulting optimized structures have been then fabricated using two different techniques [2, 3]. In the first case (Figure 1), we start by depositing an 80 nm thick Ag layer on the  $\text{SiO}_2$  substrate, which is then annealed at 550  $^\circ\text{C}$  to spontaneously form Ag micro-islands with a diameter of about 0.2–1  $\mu\text{m}$ , and a height between 0.2–0.5  $\mu\text{m}$ . A correlated micro-cone pattern with a height of about 2  $\mu\text{m}$  is then obtained by etching the  $\text{SiO}_2$  layer using the Ag micro-islands as the etching masks.

Alternatively, a more ordered pillar array can be obtained starting from a self-assembled monolayer of polystyrene microspheres, followed by Argon plasma etching to tune the inter-pillar separation, and finally by a similar dry etching process using trifluoromethane and argon, leading to an emitter with enhanced emissivity due to the improved index matching at the air-glass interface (Figure 2). Based on the size of the pillar and micro-cone structures, the resulting emitters can also be endowed by structural iridescent coloration free of any absorption peak, as inspired by the structural color display of the rainbow peacock spider (*Maratus spp.*).

During outdoor tests inside an insulated measurement box covered by a thin polyethylene film, these patterned samples exhibited a net cooling power exceeding 100

$\text{W/m}^2$  and temperature drops up to 7 degrees Celsius, in contrast with the case of a flat silica layer of the same thickness, which was unable to deliver any net cooling. Additionally, the etching process induces the formation of F/C compounds on the patterned surface, endowing the resulting sample with a hydrophobic surface that is highly desirable for its self-cleaning and anti-soiling properties.

## 3 Conclusions

Bulk silicon dioxide cover layers are commonly used in several sky-facing applications where thermal management is crucial, such as Optical solar reflectors (OSR) and photovoltaic cells. We showed that the thermal emissivity of such flat interfaces can be significantly enhanced by etching sub-wavelength patterns to mitigate the characteristic impedance mismatch of silica in the atmospheric transparency window.

The exceptional stability of silica against ageing and weathering agents is also promising towards the fabrication of reference radiative coolers, which could be used to improve the comparability and reproducibility of radiative cooling tests available in the literature.

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