Antireflection Coatings with Sub-wavelength Structures

Junwen He

Literature Seminar

Fresnel refractions occur at interfaces with a sudden change in refractive index (RI). Antireflection (AR) coatings can reduce reflection and increase quality of optical systems. They have wide applications ranging from camera manufacturing, flat screen displays, high performance lenses, and photovoltaic devices. Traditional single-, double- and multiple-layered quarter-wavelength dielectric AR coatings take advantage of the destructive interference of reflective waves, and can suppress reflection to nearly zero at a specific wavelength. These types of coatings, however, are effective only at narrow wavelength bands and incident angles.

In order to overcome the shortcomings of homogenously layered AR coatings, Lord Rayleigh proposed a coating that comprises a gradient transition of RI from one medium to another². As the incident ray "meets no optical discontinuity", Fresnel reflection can be eliminated. Experimental progress, however, lags far behind theory. One challenge is the lack of transparent materials with a low enough RI to air. The lowest RI dielectric material is MgF₂, which has a RI of 1.35— much higher than 1.0 of air. An additional challenge is the difficulty in engineering dense materials to obtain a large enough index modulation to meet the demanding requirement of an AR coating. For example, doping and other methods are effective at changing the RI no more than 0.1^3 .

The observation of moth eye structures⁵, however, has opened up a new approach for an effective AR coating. For camouflage during the night, moths possess a cornea with extremely low reflection. Electron microscopy reveals that there are pillar-like arrays on the corneal surface of the moth's eye. These arrays have sub-wavelength (SW) height protuberances and are 100 nm in diameter and 200 nm apart from each other⁷. Photoresist moth eye structures on glass, fabricated by recording the interference fringes of two collimated laser beams, were able to reduce the air/glass reflection over the entire visible spectrum from 4% to less than 0.5%⁷.

How exactly do these SW structures reduce reflections across the broad band? The first theory to describe this system is known as effective medium theory (EMT), which was introduced to describe the effective dielectric constant of homogenously mixed materials⁹. The theory⁷ states that as the fraction of air around these structures decreases gradually from the top of the tip to its base, the effective RI changes gradually. Therefore, the incident light goes through the surface as if it is going through a gradient index environment, thus rendering low reflectance. The theory works generally well for both regular fine surface relief and random porous structures.

Another available theory is to view moth eye structures as SW gratings. Diffraction theory⁴ states that when the period of the grating is sufficiently smaller than the wavelength of incident light, non-zeroth order reflective diffraction is evanescent over a broad range of wavelengths and incident angles. Unfortunately, this theory provides minimal visual intuition and it is hard to predict the reflectance of these gratings other than solving Maxwell's equations rigorously. Rigorous coupled-wave analysis (RCWA)¹⁰ and finite-difference time-domain (FDTD)¹¹ methods can be employed to model such systems. Numerical simulation¹² reveals that

high aspect ratio gratings that resemble nanotips have a reflectance smaller than that of nanopillar-like structures. The reason for this discrepancy is the difference in size from the tip of the structure to its base. Having a different distribution of air across the structure is the key to minimizing reflections. This result, to an extent, agrees with what EMT predicts.

Direct etching of a surface is perhaps the most straightforward way to obtain high aspect ratio surface structures. For example, high-density electron cyclotron resonance plasma etching was employed to create nanotips on a 6-inch silicon wafer that are microns in height¹. The densely-packed sharp nanotips (Fig. 1a) showed reflectance values of less than 1% between 0.5-



Figure 1. Different sub-wavelength surface morphologies. a, silicon nanotips¹. **b**, silica pyramidal structures⁴. **c**, silica nano-columns⁶. **d**, PS porous structures⁸.

2.5 µm light over broad incident angles. Direct etching, however, generally has poor control over the morphology of SW structures. Although electron-beam lithography can be exploited, a different controllable lithography method that is low-cost is highly desirable. In one study⁴, a pyramidal Si texture profile was obtained by employing RIE on a Si substrate dip-coated with closepacked polystyrene spheres (Fig. 1b). With a periodicity of 350 nm, the pyramidal texture showed a reflectance of less than 2.5% over the visible regime.

Instead of the top-down etching methods, bottom-up fabrication techniques are also possible. By changing the deposition angle during e-beam evaporation, the RI of the as-prepared porous dielectric thin film can be tuned over a wide range¹³, from 1.05 to 1.46 for SiO₂ (Fig. 1c), and from 1.3 to 2.7 for TiO_2^{6} . A five-layered TiO_2 -SiO₂ coating, with different RI for each layer, was deposited on AlN (n=2.05) substrate, mimicking a quantic-index profile¹⁴. The reflection was found to be less than 0.5% omnidirectionally in both visible and NIR.

Polymeric AR coating can also be fabricated by introducing SW pores through fast phase separation of immiscible polymers. For example, polystyrene-block-polymethylmethacrylate (PS-b-PMMA)/PMMA blend was spin-coated onto an octadecyltrichlorosilane (OTS)-modified glass⁸. The alkyl chains of OTS help hydrophobic PS blocks wet the bottom surface, while the PMMA blocks and free PMMA chains will prefer to relax or migrate to the upper air interface. After selective removal of PMMA, the PS thin film can be fabricated (Fig. 1d), which has

gradient-like porosity. This structure resulted in a 97% transmittance on glass in visible and NIR compared to 90% transmittance of bare glass without the polymeric coating.

In conclusion, SW structures prove to be effective in suppressing Fresnel reflection. Different etching and deposition schemes were proposed to construct dielectric AR coatings with SW structures. Phase separation can be used for polymer AR coatings with SW pores. A more facile theory, however, rather than numerically solving Maxwell's equations, may be needed to relate SW structures to their antireflection efficacy.

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