backing layer, such a retroreflector would rely even more upon the specular reflection provided by the reflective layer since the critical angle for TIR is smaller, which, as pointed out earlier, reduces the intensity of the retroreflected light by about 39%.

[00010] To increase the critical angle for TIR, materials having an index of refraction lower than cryolite have been used in such retroreflectors. For example, a thin optical film formed from particulate metal oxide such as silicon dioxide or alumina mixed with a binder has been applied as a backing layer to retroreflected sheeting. The resulting layer is characterized by nanoporosity and can have an index of refraction *n* as low as 1.10.

SUMMARY

[0010a] In one aspect, there is provided a retroreflective article, comprising: a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction n1 that is at least about 1.40, a second transparent layer overlying the back surface of the first transparent layer having an index of refraction n2 that is no larger than about 1.20 and which includes a regular pattern of uniformly sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light, wherein the nanostructures include mutually parallel nanorods that are substantially parallel to one another and have one end connected to the back surface of the first transparent layer and an opposite end projecting away from the back surface of the first transparent layer, the nanorods having substantially the same length.

[0010b] In another aspect, there is provided retroreflective article, comprising: a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction n1 that is at least about 1.40, a second transparent layer overlying the back surface of the first transparent layer having an index of refraction n2 that is no larger than about 1.20 and which includes a regular pattern of uniformly sized nanostructures of transparent material that define pores having a width that is less than one

half of the wavelength of visible light, wherein the nanostructures include a grid-like array of tapered nano-ridges of uniform size that define tapered pores.

[0010c] In yet another aspect, there is provided a method for forming a retroreflective article, comprising: providing a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction n1 that is at least about 1.40, and providing a second transparent layer over the back surface of the first transparent layer having an index of refraction n2 that is no larger than about 1.20 and which includes a regular array of uniformly-sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light, wherein the nanostructures of the second transparent layer are nanorods deposited over the surfaces of the retroreflective prisms by e-beam evaporation and wherein one end of each of the nanorods is connected to the back surface of the first transparent layer and an opposite end of each of the nanorods projects away from the back surface of the first transparent layer, and the nanorods are substantially the same length.

[0010d] In a further aspect, there is provided a method for forming a retroreflective article, comprising: providing a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction n1 that is at least about 1.40, and providing a second transparent layer over the back surface of the first transparent layer having an index of refraction n2 that is no larger than about 1.20 and which includes a regular array of uniformly-sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light, wherein the nanostructures of the second transparent layer include a grid-like array of tapered nano-ridges of uniform size that define tapered pores.

[00011] While the use nanoporous films formed from a mixture of a particulate metal oxide and a binder is capable of producing a retroreflective sheeting or plates having a solid backing layer with a larger critical angle for TIR, the applicant has observed that such retroreflective articles

are difficult and expensive to manufacture due to the fact that such films must have a uniform porosity at scales on the order of a micron. It is thus an object of the invention to provide a retroreflector with a solid backing layer that exceeds all of the optical and structural advantages associated nanoporous films, but which is easier and less expensive to manufacture.

[00012] To this end, the retroreflective article of the invention may comprises a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1*, and a second transparent layer overlying the back surface of the first transparent layer having an index of refraction *n2* that is significantly less than the index of refraction *n1* and which includes an array of uniform nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light. The nanostructures may comprise an array of parallel, same-sized nanorods that are obliquely oriented at a same angle with respect to the first transparent layer and which have a porosity of 60% or greater so that the resulting index of

refraction *n1* is no larger than about 1.20. Alternatively, the nanostructures may comprise a uniform array of tapered ridges of uniform size and spacing incorporated into the first transparent layer that define pores having a width that is less than one half of the wavelength of visible light. The ridges may be arranged in parallel or in a grid-like pattern.

[00013] To increase the angle of incidence wherein TIR may be achieved, a reflective layer may be provided over the second transparent layer. The reflective layer may be formed from a specular reflective metallic layer such as aluminum or silver, or a diffuse reflective layer formed from a white material such as titanium dioxide. In all cases, the material forming the reflective layer is applied so that it bridges the projecting ends of the nanostructures of the second layer so that the pores defined between the nanorods are substantially devoid of material forming the reflective layer.

[00014] The retroreflective article of the invention may also include one or more structural features to increase the daytime brightness of the sheeting. For example, the retroreflective prisms may be cube corners having truncated tips that have been textured to increase their daytime reflectivity. The surfaces of the retroreflective prisms may include a light diffusive pattern or the front surface of the first transparent layer may be printed on selected areas to increase the daytime brightness of the sheeting. Finally, at least some of the retroreflective prisms may have one or both of canted optical axes and laterally displaced apices that result in some of the light being transmitted through walls of the prisms rather than being retroreflected in order to increase the daytime brightness of the sheeting.

[00015] ~~The invention further encompasses~~Herein disclosed is a method for forming a retroreflective article, comprising the steps of providing a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1*, and providing a second transparent layer over the back surface of the first transparent layer having an index of refraction *n2* that is significantly less

than the index of refraction *n1* and which includes an array of nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light

[00016] In one embodiment of the method, the nanostructures are an array of parallel, obliquely-oriented nanorods deposited over the surfaces of the retroreflective prisms by oblique angle e-beam evaporation. This embodiment of the method exploits the fact that certain evaporated materials, such as silicon dioxide, will inherently self-organize into parallel nanorods defining pores having a width that is less than one half of the wavelength of visible light when they condense on a cold surface. This embodiment further exploits the fact that because the faces of retroreflective prisms are already oriented at about a 45° angle to the substrate, the substrate only needs to be tilted between about 40° and 44° to a vertically oriented stream of evaporated silicon dioxide to form obliquely-oriented nanorods having a porosity of 80% or higher.

[00017] In an alternative embodiment of the method, the second transparent layer may be embossed over the surface of the first transparent layer by the tooling used to form the prisms. The surface of the tooling may include nanostructures that are half or less than the wavelength of visible light (such as tapered nano-grooves in a parallel or grid-like pattern) etched into the surface of the tooling by 3-D grey-scale e-beam or x-ray lithography. Such tooling is capable of embossing an array of tapered nano-ridges in a parallel, grid-like or even "moth-eye" pattern over the back surface of the first transparent layer having an index of refraction *n2* on the order of 1.20 or less that is significantly less than the index of refraction *n1* of the first transparent layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[00018] Figure 1 is a plan view of a cube corner retroreflective sheeting;

[00019] Figure 2 is a cross-sectional view of the sheeting of Figure 1 along the line 2-2, illustrating the first and second transparent layers of the sheeting;

What is claimed is:

1. A retroreflective article, comprising:

a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1* that is at least about 1.40,

a second transparent layer overlying the back surface of the first transparent layer having an index of refraction *n2* that is no larger than about 1.20 ~~significantly less than the index of refraction *n1*~~ and which includes a regular pattern of uniformly sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light.

~~2. The retroreflective article defined in claim 1,~~

wherein the nanostructures include mutually parallel nanorods that are substantially parallel to one another and have one end connected to the back surface of the first transparent layer and an opposite end projecting away from the back surface of the first transparent layer, the nanorods having substantially the same length.

~~3~~2. A retroreflective article, comprising:

a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1* that is at least about 1.40,

a second transparent layer overlying the back surface of the first transparent layer having an index of refraction *n2* that is no larger than about 1.20 and which includes a regular pattern of uniformly sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light~~The retroreflective article defined in claim 1 or claim 2~~, wherein the nanostructures include a grid-like array of tapered nano-ridges of uniform size that define tapered pores.

43. The retroreflective article defined in any one of claims 1-3 or 2, wherein the porosity of the second transparent layer is at least about 60%. or

~~5. The retroreflective article defined in any one of claims 1-4, wherein the porosity of the second transparent layer is~~ at least about 80%.

~~6. The retroreflective article defined in any one of claims 1-5, wherein *n2* is no larger than about 1.20 and *n1* is at least about 1.40.~~

74. The retroreflective article defined in ~~any one of~~ claims 1-~~6~~, wherein the axes of rotation of the nanorods are non-orthogonal to the surfaces of the retroreflective prisms which they overlie.

85. The retroreflective article defined in any one of claims 1-~~7~~ or 4, wherein the nanorods are formed from silicon dioxide and are deposited over the surfaces of the retroreflective prisms by e-beam evaporation.

96. The retroreflective article defined in any one of claims 1-~~8~~5, wherein the nanostructures are integrally formed from the same material as the first transparent layer.

~~10~~7. The retroreflective article defined in any one of claims 1-~~9~~ or 4 or 5, further comprising a reflective layer overlying the second transparent layer and bridging the projecting ends of the nanorods of the second layer such that the pores defined between the nanorods are substantially devoid of material forming the reflective layer.

~~11~~8. The retroreflective article defined in ~~any one of~~ claims 7~~1~~-10, wherein the reflective layer is a specular reflective metallic layer.

~~12~~9. The retroreflective article defined in any one of claims ~~1-11~~7 or 8, wherein the reflective layer is a diffuse reflective layer formed from a white material.

~~13. The retroreflective article defined in any one of claims 1-12, wherein the reflective layer is a combination of a specular reflective metallic layer and a diffuse reflective layer formed from a white material.~~

~~14~~10. The retroreflective article defined in any one of claims 1-~~13~~9, wherein the retroreflective prisms are cube corners having truncated tips that have been textured that increases the daytime brightness of the sheeting.

~~15~~11. The retroreflective article defined in any one of claims ~~1-14~~1-10, wherein portions of the article include a light diffusive pattern that increases the daytime brightness of the sheeting.

~~16~~12. The retroreflective article defined in any one of claims ~~1-15~~1-11, wherein the front surface of the first transparent layer is printed on selected areas that increase the daytime brightness of the printed areas of the front surface.

~~17~~13. The retroreflective article defined in any one of claims ~~1-16~~1-12, further comprising a printed layer overlying the front surface of the first transparent layer ~~transparent layer~~on selected areas that increases the daytime brightness of the printed areas of the printed layer.

~~18~~14. The retroreflective article defined in any one of claims ~~2-17~~1 or 4 or 5, further comprising an adhesive layer overlying the second transparent layer and bridging the projecting ends of the nanorods of the second layer such that the pores defined between the nanorods are substantially devoid of material forming the adhesive layer.

~~19~~15. The retroreflective article defined in ~~any one of claims 2-18~~claim 14, wherein the adhesive ~~material~~ layer is white.

~~20~~16. The retroreflective article defined in any one of claims 1-~~19~~14, wherein at least some of the retroreflective prisms are cube corners having one or both of canted optical axes and laterally displaced apices that retroreflect near normal incident light to an angle of about 45° with respect to the planar front surface in order to increase the daytime brightness of the sheeting.

~~21~~17. The retroreflective article defined in any one of claims 1-~~20~~14 and 16, wherein at least some of the retroreflective prisms are cube corners having one or both of canted optical axes and laterally displaced apices that result in some of the light being transmitted through walls of the prisms rather than being retroreflected in order to increase the daytime brightness of the sheeting.

~~22~~18. The retroreflective article defined in any one of claims 1-~~21~~14 and 16-17, wherein the retroreflective prisms are rectangular prisms including corners having one or both of canted optical axes and laterally displaced apices such that, for some of the corners, some of the light is not retroreflected but rather is transmitted through walls of the rectangular corners in order to increase the daytime brightness of the sheeting.

~~23~~19. A method for forming a retroreflective article, comprising:

providing a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1* that is at least about 1.40, ~~———~~and

providing a second transparent layer over the back surface of the first transparent layer having an index of refraction *n2* that is no larger than about 1.20 ~~significantly less than the index of refraction *n1*~~and which includes a regular array of uniformly-sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light~~.~~

~~24. The method of claim 23~~, wherein the nanostructures of the second transparent layer are nanorods deposited over the surfaces of the retroreflective prisms by e-beam evaporation and wherein one end of each of the nanorods is connected to the back surface of the first transparent layer and an opposite end of each of the nanorods projects away from the back surface of the first transparent layer, and the nanorods are substantially the same length.

~~25~~20. A method for forming a retroreflective article, comprising:

providing a first transparent layer having a back surface that includes a plurality of retroreflective prisms, and a planar front surface that receives incident light, and an index of refraction *n1* that is at least about 1.40,and

providing a second transparent layer over the back surface of the first transparent layer having an index of refraction *n2* that is no larger than about 1.20 and which includes a regular array of uniformly-sized nanostructures of transparent material that define pores having a width that is less than one half of the wavelength of visible light~~The method of claim 23 or claim 24~~, wherein the nanostructures of the second transparent layer include a grid-like array of tapered nano-ridges of uniform size that define tapered pores.

~~26. The method of any one of claims 23-25, wherein one end of each of the nanorods is connected to the back surface of the first transparent layer and an opposite end of each of the nanorods projects away from the back surface of the first transparent layer, and the nanorods are substantially the same length.~~

~~27~~21. The method of any one of claims ~~23-26~~19 or 20, wherein the pore width is between about 2 and 8 nanometers.

~~28~~22. The method of ~~any one of~~ claims~~23-27~~19, wherein the thickness of the e-beam deposited second transparent layer is between about 150-2000 nanometers.

~~29~~23. The method of ~~any one of~~ claims ~~23-28~~19, wherein the second transparent layer is formed from silicon dioxide.

~~30~~24. The method of ~~any one of~~ claims~~23-29~~ 20, wherein the second transparent layer is embossed over the surface of the first transparent layer.

~~31~~25. The method of any one of claims ~~23-30~~19-24, further comprising applying a reflective layer over the second transparent layer that bridges the projecting ends of the nanorods of the second layer such that the pores defined between the nanorods are substantially devoid of material forming the reflective layer.