Extremely broadband ultralight thermally-emissive optical coatings

ALI NAQAVI,1 SAMUEL P. LOKE,1 MICHAEL D. KELZENBERG,1 DENNIS M. CALLAHAN,1 TOM TIWALD,2 EMILY C. WARMANN,1 PILAR ESPINET-GONZÁLEZ,1 NINA VAIDYA,1 TATIANA A. ROY,1 JING-SHUN HUANG,1 TATIANA G. VINOGRADOVA,3 AND HARRY A. ATWATER1,*

1California Institute of Technology, Pasadena, CA 91125, USA
2J. A. Woollam Co., Inc., 645 M Street, Suite 102, Lincoln, NE 68508, USA
3Northrop Grumman Aerospace Systems, 1111 W 3rd St, Azusa, CA 91702, USA
*haa@caltech.edu

Abstract: We report the design, fabrication, and characterization of ultralight highly emissive structures with a record-low mass per area that emit thermal radiation efficiently over a broad spectral (2 to 30 microns) and angular (0–60°) range. The structures comprise one to three pairs of alternating metallic and dielectric thin films and have measured effective 300 K hemispherical emissivity of 0.7 to 0.9 (inferred from angular measurements which cover a bandwidth corresponding to 88% of 300K blackbody power). To our knowledge, these micron-scale-thickness structures, are the lightest reported optical coatings with comparable infrared emissivity. The superior optical properties, together with their mechanical flexibility, low outgassing, and low areal mass, suggest that these coatings are candidates for thermal management in applications demanding of ultralight flexible structures, including aerospace applications, ultralight photovoltaics, lightweight flexible electronics, and textiles for thermal insulation.

© 2018 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

OCIS codes: (310.0310) Thin films; (220.0220) Optical design and fabrication.

References and links
1. Z. Yu, N. P. Sergeant, T. Skauli, G. Zhang, H. Wang, and S. Fan, “Enhancing far-field thermal emission with thermal extraction,” Nat. Commun. 4(1), 1730 (2013).
2. S. V. Boriskina, L. A. Weinstein, J. K. Tong, W.-C. Hsu, and G. Chen, “Hybrid optical–thermal antennas for enhanced light focusing and local temperature control,” ACS Photonics 3(9), 1714–1722 (2016).
3. For a brief introduction on the primary works on this subject, the reader may read M. G. Hutchins, “Spectrally selective materials for efficient visible, color, solar and thermal radiation control,” in Solar thermal technologies for buildings: The state of the art, M. Santamouris. ed (Rotledge, 2014), pp. 37–38.
4. X. Liu, T. Tyler, T. Starr, A. F. Starr, N. M. Jokerst, and W. J. Padilla, “Taming the blackbody with infrared metamaterials as selective thermal emitters,” Phys. Rev. Lett. 107(4), 045901 (2011).
5. J. A. Mason, S. Smith, and D. Wasserman, “Strong absorption and selective thermal emission from a midinfrared metamaterial,” Appl. Phys. Lett. 98(24), 241105 (2011).
6. P. Bermel, M. Ghebrebrhan, M. Harradon, Y. X. Yeng, I. Celanovic, J. D. Joannopoulos, and M. Soljacic, “Tailoring photonic metamaterial resonances for thermal radiation,” Nanoscale Res. Lett. 6(1), 549 (2011).
7. J. Meseguer, I. Pérez-Grande, and A. Sanz-Andrés, “Spacecraft Thermal Control,” (Elsevier, 2012).
8. C. R. McInnes, Solar Sailing: Technology, Dynamics and Mission Applications, (Springer Science & Business Media, 2013).
9. S. A. Mann, S. Z. Oener, A. Cavalli, J. E. M. Haverkort, E. P. A. M. Bakkers, and E. C. Garnett, “Quantifying losses and thermodynamic limits in nanophotonic solar cells,” Nat. Nanotechnol. 11(12), 1071–1075 (2016).
10. L. Zhu, A. Raman, and S. Fan, “Color-preserving daytime radiative cooling,” Appl. Phys. Lett. 103(22), 223902 (2013).
11. K. A. Arpin, M. D. Losego, A. N. Cloud, H. Ning, J. Mallek, N. P. Sergeant, L. Zhu, Z. Yu, B. Kalanyan, G. N. Parsons, G. S. Girolami, J. R. Abeleson, S. Fan, and P. V. Braun, “Three-dimensional self-assembled photonic crystals with high temperature stability for thermal emission modification,” Nat. Commun. 4(1), 2630 (2013).
12. A. Manjavacas, S. Thongrattanasiri, J.-J. Greffet, and F. J. G. de Abajo, “Graphene optical-to-thermal converter,” Appl. Phys. Lett. 105(21), 211102 (2014).
13. M. H. Kryder, E. C. Gage, T. W. McDaniel, W. A. Challener, R. E. Rottmayer, G. Ju, Y.-T. Hsia, and M. F. Erden, “Heat Assisted Magnetic Recording,” Proc. IEEE 96(11), 1810–1835 (2008).
14. D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop, and L. Shi, “Nanoscale thermal transport. II. 2003–2012,” Appl. Phys. Rev. 1(1), 011305 (2014).

15. P. Li, X. Yang, T. W. W. Maß, J. Hanss, M. Lewin, A.-K. U. Michel, M. Wuttig, and T. Taubner, “Reversible optical switching of highly confined phonon-polaritons with an ultrathin phase-change material,” Nat. Mater. 15(8), 870–875 (2016).

16. H. T. Miyazaki, T. Kasaya, M. Iwanaga, B. Choi, Y. Sugimoto, and K. Sakoda, “Dual-band infrared metasurface thermal emitter for CO2 sensing,” Appl. Phys. Lett. 105(12), 121107 (2014).

17. S. J. Orfanidis, Electromagnetic Waves and Antennas, [Online]. Available: http://www.ece.rutgers.edu/~orfanidi/ewa/ [Accessed: 6-March-2018].

18. K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura, and K. Hata, “A black body absorber from vertically aligned single-walled carbon nanotubes,” Proc. Natl. Acad. Sci. U.S.A. 106(15), 6044–6047 (2009).

19. “AZ Technology | Materials, Paint and Coatings: AZ-93 White Thermal Control, Electrically Conductive Paint / Coating (AZ’s Z-93P),” [Online]. Available: http://www.azetechology.com/materials-coatings-az-93.html [Accessed: 19-Dec-2016].

20. Z. M. Zhang, G. Lefever-Button, and F. R. Powell, “Infrared refractive index and extinction coefficient of polyimide films,” Int. J. Thermophys. 19(3), 905–916 (1998).

21. S. W. W, “Absorbent body for electromagnetic waves,” US2599944 A, (10-Jun-1952).

22. R. L. Fante and M. T. McCormack, “Reflection properties of the Salisbury screen,” IEEE Trans. Antenn. Propag. 21(4), 484–490 (1973).

23. E. Knott and K. Langseth, “Performance degradation of Jaumann absorbers due to curvature,” IEEE Trans. Antenn. Propag. 28(1), 137–139 (1980).

24. B. M. Wells, C. M. Roberts, and V. A. Podolsky, “Metamaterials-based Salisbury screens with reduced angular sensitivity,” Appl. Phys. Lett. 105(16), 161105 (2014).

25. M. S. Jang, V. W. Brar, M. C. Sherrert, J. J. Lopez, L. Kim, S. Kim, M. Choi, and H. A. Atwater, “Tunable large resonant absorption in a midinfrared graphene Salisbury screen,” Phys. Rev. B 90(16), 165409 (2014).

26. W. Emerson, “Electromagnetic wave absorbers and anechoic chambers through the years,” IEEE Trans. Antenn. Propag. 21(4), 484–490 (1973).

27. L. J. du Toit and J. H. Cloete, “Advances in the design of Jaumann absorbers,” IEEE AP-S/URSI International Symposium Digest, Dallas, TX, 1212–1215 (1990).

28. Z. Li, E. Palacios, S. Butun, H. Kocer, and K. Aydin, “Omnidirectional, broadband light absorption using large-area, ultrathin lossy metallic film coatings,” Sci. Rep. 5(1), 15137 (2015).

29. F. J. Kelly, “On Kirchhoff's law and its generalized application to absorption and emission by cavities,” J. Res. Natl. Bur. Stand. Sec. 69(B), 165–171 (1965).

30. Validity of Kirchoff’s law is generally accepted in the literature. However, its experimental evidence is under question (See for example ref. [31]).

31. E. D. Palik, Handbook of Optical Constants of Solids. Academic (1998).

32. A. D. Rakic, “Algorithm for the determination of intrinsic optical constants of metal films: application to aluminum,” Appl. Opt. 34(22), 4755–4767 (1995).

33. We used Matlab optimization toolbox to optimize the multilayer thicknesses, and observed that there is more than one optimum set of layer thicknesses. However, as far as we calculated, the obtained emissivity values for the different optima were close to the values reported here.

34. The Brewster effect is commonly known as lack of the reflection for TM polarization of light at the interface between two dielectrics.

35. A planewave impinging on a planar multilayer may have two independent solutions: TE and TM. Since any solution for planewave reflection should be decomposable into these two solutions, and we assume in general both TE and TM may have the same probability of occurrence, so, unpolarized reflection can be obtained by averaging them.

36. J. A. Scholl, A. L. Koh, and J. A. Dionne, “Quantum plasmon resonances of individual metallic nanoparticles,” Nature 483(7390), 421–427 (2012).

37. H. Köppel, “Vibronic coupling effects in spectroscopy and non-adiabatic transitions in molecular photodynamics,” in Molecular Quantum Dynamics, F. Gatti, ed (Springer, 2014), pp. 147–180.

38. M. M. Finckenor and D. Dooling, “Multilayer insulation material guidelines,” NASA/TP-1999-209263 (1999).

39. M. M. Finckenor and D. Dooling, “Multilayer insulation material guidelines,” NASA/TP-1999-209263 (1999).

40. For spin coating, we used CP1 polyimide resin diluted in dyglyme (35% solution). After spin coating, we put the sample on the hot plate at approximately 100°C for one minute to vaporize the volatile gases. To our knowledge, this causes no relevant chemical reaction.

41. 2012,” Appl. Opt, “On the validity of Kirchoff’s law of thermal emission,” IEEE Trans. Plasma Sci. 31(6), 1263–1267 (2003).

42. R. H. Morf, “Exponentially convergent and numerically efficient solution of Maxwell’s equations for lamellar gratings,” J. Opt. Soc. Am. A 12(5), 1043–1056 (1995).

43. http://ee.sharif.edu/~khavasi/index_files/Page1077.htm [Accessed: 14-March-2018]
1. Introduction

Understanding the limits to far field radiative energy transfer and surpassing them is of longstanding scientific interest [1,2]. Beyond the traditional attraction of studying and engineering far field thermal radiation [3], this subject has enjoyed expanded interest and effort in recent years within the context of tailored electromagnetic materials [4–6]. Interest in the far field thermal radiation is multifold. First, it is to our knowledge the primary way of cooling objects in space [7], where convection is assumed lacking. Secondly, it provides a means to manipulate optical forces in space via radiation pressure management [8]. Finally, appropriate control of far field thermal radiation should be able to increase the efficiency of solar cells [9], and thus can have a global impact.

44. https://www.lp2n.institutoptique.fr/Membres-Services/Responsables-d-equipe/LALANNE-Philippe [Accessed: 14-March-2018]
45. P. Willis and C. H Hsieh, “Space applications of polymeric materials,” Society of Polymer Science Meeting-Kobunshi (1999).
46. W.-L. Qu, T.-M. Ko, R. H. Vora, and T.-S. Chung, “Anisotropic dielectric properties of polyimides consisting of various molar ratios of meta to para diamine with trifluoromethyl group,” Polym. Eng. Sci. 41(10), 1783–1793 (2001).
47. G. Yu, H. Ishikawa, T. Egawa, T. Soga, J. Watanabe, T. Jimbo, and M. Umeno, “Polarized reflectance spectroscopy and spectroscopic ellipsometry determination of the optical anisotropy of gallium nitride on sapphire,” J. Appl. Phys. Part 2 36(4A), L1029–L1031 (1997).
48. D. E. Aspnes, “Approximate solution of ellipsometric equations for optically biaxial crystals,” J. Opt. Soc. Am. 70(10), 1275–1277 (1980).
49. G. E. Jellison, Jr. and J. S. Baba, “Pseudodielectric functions of uniaxial materials in certain symmetry directions,” J. Opt. Soc. Am. A 23(2), 468–475 (2006).
50. S. A. Francis and A. H. Ellison, “Infrared spectra of monolayers on metal mirrors,” J. Opt. Soc. Am. 49(2), 131–138 (1959).
51. R. G. Greenler, “Infrared study of adsorbed molecules on metal surfaces by reflection techniques,” J. Chem. Phys. 44(1), 310–315 (1966).
52. G. E. Jellison, Jr., “Data analysis for spectroscopic ellipsometry,” Thin Solid Films 234(1–2), 416–422 (1993).
53. G. E. Jellison, “Data analysis for spectroscopic ellipsometry,” in Handbook of Ellipsometry, J.G. Tompkins and E.A. Irene, eds. (William Andrew, 2005) pp 237 – 296.
54. C. M. Herzinger, P. G. Snyder, B. Johns, and J. A. Woollam, “InP optical constants between 0.75 and 5.0 eV determined by variable-angle spectroscopic ellipsometry,” J. Appl. Phys. 77(4), 1715–1724 (1995).
55. C. M. Herzinger, B. Johns, W. A. McGahan, J. A. Woollam, and W. Paulson, “Ellipsometric determination of optical constants for silicon and thermally grown silicon dioxide via a multi-sample, multi-wavelength, multi-angle investigation,” J. Appl. Phys. 83(6), 3323–3336 (1998).
56. C. M. Herzinger, H. Yao, P. G. Snyder, F. G. Celii, Y.-C. Kao, B. Johns, and J. A. Woollam, “Determination of AlAs optical constants by variable angle spectroscopic ellipsometry and a multisample analysis,” J. Appl. Phys. 77(9), 4677–4687 (1995).
57. D. De Sousa Meneses, M. Malki, and P. Echegut, “Structure and lattice dynamics of binary lead silicate glasses investigated by infrared spectroscopy,” J. Non-Cryst. Solids 352(8), 769–776 (2006).
58. A. Naqavi, S. P. Loke, M. D. Kelzenberg, D. M. Callahan, T. Tiwald, E. C. Warmann, P. Espinet-González, N. Vaidya, T. A. Roy, J.-S. Huang, T. G. Vinogroda, and H. A. Atwater, “n, k data and model parameters,” figshare (2018) [retrieved 5 July 2018], https://doi.org/10.6084/m9.figshare.6387395.
59. We used different data sets for gold from https://refractiveindex.info. [Accessed: 20-May-2018], which in turn obtained data from Refs. [61–65].
60. P. B. Johnson and R. W. Christy, “Optical constants of the noble metals,” Phys. Rev. B 6(12), 4370–4379 (1972).
61. K. M. McPeak, S. V. Jayanti, S. J. P. Kress, S. Meyer, S. Iotti, A. Rossinelli, and D. J. Norris, “Plasmonic films can easily be better: Rules and recipes,” ACS Photonics 2(3), 326–333 (2015).
62. A. Ciesielski, L. Skowronski, M. Trzciński, E. Görecka, P. Trautman, and T. Szoplik, “Evidence of germanium segregation in gold thin films,” Surf. Sci. 674, 73–78 (2018).
63. H.-J. Hagemann, W. Gudat, and C. Kunz, “Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al2O3,” J. Opt. Soc. Am. 65(6), 742–744 (1975).
64. H.-J. Hagemann, W. Gudat, and C. Kunz, “Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al2O3,” DESY report SR-74/7 (1974).
65. We used different data sets for gold from https://refractiveindex.info/download/data/1974/Hagemann%201974%20-%20DESY%20report%20SR-74-7.pdf [Accessed: 27-May-2018].
66. A. L. Wasserman, Thermal Physics (Cambridge University, 2012). Ch. 14, Eq. (14.39) (p. 218).
67. These measurements were done at the Northrop Grumman Corporation and we have no information on the approach they were obtained. Nevertheless, we speculate that these are reflection measurements.
From a practical viewpoint, tailoring the emission of thermal radiation has the potential to benefit a wide range of applications including radiative cooling for terrestrial use [10], thermophotovoltaic energy harvesting [11], optoelectronics and plasmonics of two-dimensional materials [12], heat-assisted magnetic recording [13], cooling of nanoscale electronic devices [14], developing reconfigurable optical platforms and devices [15], sensing [16], and thermal management of aircraft and spacecraft [7]. Specifically, realizing structures that efficiently emit infrared radiation in the 8 to 14-micron range can enable passive thermal management of devices operating near room temperature, as this spectral range corresponds to the peak of the blackbody spectrum at a temperature of 300°K-400°K. Appropriate radiative cooling at this temperature range benefits applications including the efficient performance of photovoltaic cells, metabolism of living organisms and thermal signature control.

A key factor motivating our work is the design and realization of thermally emissive structures that are as lightweight as possible, a feature that is important for space-based technologies where design of active structures with lowest possible mass per unit area is a critical metric. For a homogeneous dielectric medium, reducing the thickness also inevitably reduces the optical absorptivity and emissivity, particularly as the thickness is reduced to less than several wavelengths. Thus the challenge for ultralight structures is to achieve high emissivity at subwavelength structural thicknesses. Multilayer coatings have promise to minimize the emitter mass, as they enable one to manipulate electromagnetic wave spectrum in reflection and transmission [17].

Conventional thermally-emissive structures include a broad range of particulate and bulk materials and composites. Black or white paints and different types of materials such as anodized metals, carbon fiber and carbon nanotubes [18] are widely used in current thermal radiation applications. Despite their ease of use, application of paints as emissive materials is limited in a practical sense as their thickness cannot be typically made thinner than about several tens of microns [19], i.e., a thickness of several infrared wavelengths. Fundamentally, the absorbance and emittance decreases correspondingly as the layer is made thinner than a few wavelengths. Metals (e.g., Al, Cr, Ag and Au) are characterized by a large imaginary permittivity component at infrared wavelengths and have potential for high infrared emissivity. However, the drawback of homogeneous metallic structures is that they have relatively high areal mass densities and are also very reflective. Polymeric organic materials such as polyimides are among other alternatives that are very lightweight and show strong vibronic resonances at wavelengths less than 10 microns, however, they are weakly absorptive and emissive at long wavelengths [20], and typically require thicknesses of tens of microns to achieve high effective emissivity in the 300-400°K range. To manipulate thermal radiation in structures made of thin polymers, multilayer design can be used to alter effective optical properties over the thermal infrared wavelength range.

Here, we report the design, fabrication and characterization of polymeric thermally emissive multilayers based on Salisbury screen [21,22] and Jaumann absorber [23] concepts. The Salisbury screen is a widely-employed electromagnetic wave absorber that consists of a quarter-wavelength dielectric layer placed between a metallic back reflector and a very thin conductive layer. The high absorption by the Salisbury screen may be explained by destructive interference of the incident and the reflected waves [24,25] and therefore, depends on the incident wavelength and angle. The absorption bandwidth of Salisbury screens can be increased by adding additional dielectric-metallic bilayers, yielding multilayered structures that have been termed Jaumann absorbers [26,27]. Thus the Salisbury screen is the simplest form of a Jaumann absorber, and one can view it as a Jaumann absorber with a single layer pair on the back reflector.

Recently, Z. Li et al. [28] have shown omnidirectional and broadband light absorption of light by a Salisbury screen, which similar to our structure, has Cr as back reflector and the top thin metal layer. However, their work is different from ours from several points: Their study
considers visible and near infrared frequencies mainly (400-800 nm), but we mainly investigate thermal infrared (>2µm). The dielectric spacer between the metal layers in their work is an SiO$_2$ layer but we use CP1 polyimide for the spacer. SiO$_2$ is transparent at visible and near infrared but absorbs light at 300K thermal wavelengths relatively strongly: it has pronounced and wide absorption peaks at approximately 10 and 20 µm. However, CP1 has much less absorption over thermal wavelengths. Besides, we consider adding more layer to the Salisbury screen to realize Jaumann absorbers (emitters).

We realize our structures using polyimides as the dielectric, and thin metallic layers that are much thinner than the optical skin depth for thermal infrared radiation.

During ellipsometric material characterization, we considered CP1 polyimide as an anisotropic material obtained its optical data (See Appendix A). However, in our simulations and optimizations, we assumed it isotropic data and used its in-plane optical data. This makes the simulations easier, and we expect it to provide the similar results, practically.

Finally, in our design and measurement procedures, we use the reciprocity relations between the emission and absorption inherent to Kirchhoff’s thermal radiation law, which dictates that the absorptance and emittance of a surface are equal at a given wavelength (and we assume it holds for each polarization separately), angle and polarization [29,30]. Thus, emissivity data presented herein is based on measurements or calculations of absorption, or equivalently reflection.

2. Design of the emissive multilayers

In our designs, we utilized a back reflector, dielectric spacer and top metallic layer comprised of Cr, CP1 polyimide and Cr respectively (see experimental for details). Optimization of the top metallic layer and dielectric layer thicknesses by rigorous calculations leads to emissivity values depicted in Fig. 1(a). Two high-emissivity regions exist which correspond to small and large dielectric thicknesses. High emissivity at large dielectric thickness is expected because the dielectric can absorb and emit thermal radiation more efficiently over large thicknesses according to the Beer-Lambert law. In contrast, the high emissivity region at small dielectric thicknesses is due to interference effects that are the basis of a Salisbury screen. This phenomenon is more clearly demonstrated in Fig. 1(b), which shows the spectral emissivity as the Cr layer thickness changes and for a polyimide layer thickness fixed at its optimal thickness. Spectral emissivity is defined as the ratio of the power emitted from the surface at a particular wavelength to the power emitted from the blackbody at the same wavelength. The high-emissivity region at a wavelength near10 microns and Cr thickness of 2 nm is the signature of the mentioned interference. The sharp peaks in emissivity in the range from 5 to 10 microns may be related to vibronic resonances related to molecular vibrational modes of the polyimide material, to our knowledge. To achieve a design that minimizes areal mass density, we find optimal thicknesses of 2.1 microns and 2 nm for the polyimide and the Cr layer respectively, which corresponds to an emissivity of 0.65 and an areal mass of 3.3 g/m$^2$ (assuming CP1 density of 1.54 g/cm$^3$).

An interesting question is whether we can replace Cr by other metals. Changing the back reflector material to Al, Ag, or Au has negligible effect on the results. However, the optimization of the front metal layer thickness depends strongly on the optical properties of the metal used. Figure 1(c) shows the emissivity optimization assuming the top metallic layer is made of Al. Notably, high emissivity values can still be obtained, but only if the Al layer is significantly thinner (~10x) than the optimal thickness range for Cr. Furthermore, the emissivity values are very sensitive to the Al layer thickness and drop dramatically with slight changes in Al thickness, as Al quickly becomes opaque and reflective with increasing thickness. The reason can be found by comparing the optical permittivity of the two metals. Figure 1(d) illustrates the real and imaginary parts of the relative permittivity of Cr [31] and Al [32]. These values are about an order of magnitude smaller for Cr than for Al.
Interestingly, for both Cr and Al structures, the optimal emissivity obtained is about 0.65. However, we note that the optimal thickness predicted for Al is on the order of the atomic spacing, and thus our calculations based on bulk optical properties may be inadequate. Furthermore, fabrication of such thin layers would likely require advanced methods, especially considering the tendency of Al to oxidize. We therefore conclude that Cr is suited for experimental realization of these structures, due to its low relative permittivity among metals, and because it can be readily deposited at optimal thickness using physical vapor deposition (e.g., electron-beam evaporation as employed in this work). To limit the effects of oxidation or other chemical reactions with the Cr, in our experimental work, we follow each Cr deposition by depositing a $\geq 10$ nm layer of SiO$_2$, without breaking vacuum. This layer only slightly affects the optical behavior of the multilayer in the infrared range, but is included in the remainder of our calculations and measurements below.

![Fig. 1](image)

**Fig. 1.** (a): The emissivity (300°K) of the Salisbury screen versus the Cr and the polyimide layer thickness. (b): Spectral emissivity of the Salisbury screen as the Cr layer thickness changes, for dielectric thickness of 2.1µm. Note that the scale is different from (a). (c): Same as (a) except that the top Cr sheet is replaced by an Al sheet. (d): Magnitude of the real and imaginary part of the relative permittivity of Cr [31] (blue) and Al [32] (red). The real and imaginary part of the permittivity are indicated by the solid and dashed lines respectively. In (a) to (c) the top pink layer is the metallic sheet made of either Al or Cr, the yellow spacer is the CP1 layer and the bottom black layer is the back reflector.

We next consider multilayer structures comprised of alternating thin metallic layers and dielectric spacers (Jaumann absorbers) in pursuit of even higher emissivity. Using the above
approach, we calculated optimal layer thicknesses for structures having one, two, and three Salisbury screen layer pairs [33]. It is instructive to analyze the fraction of thermal emission arising from the different layers in these structures. Figure 2 shows the layer-by-layer contribution to the spectral emissivity at normal incidence for the three optimized emissive surfaces. For clearer illustration, the emission spectra are plotted in a cumulative fashion. The top-most curve shows the total spectral emissivity at normal incidence and the shaded areas between successive curves show the proportional contribution of each corresponding layer. The additional SiO₂ layers are present to avoid interfacial reactions in the layered structure. In all cases, the very thin Cr layers dominate the absorption (hence emission), particularly at long wavelengths. In all cases, the back reflector emission is negligible based on the calculations.

Until now, we considered only emission in the direction normal to the interfaces. To have an accurate estimate of the total power that is emitted by the multilayer at each temperature, the angular dependence of thermal radiation should also be taken into account. Figure 3(a) shows the directional emissivity—which is defined here as the weighted average of spectral
emissivity by the blackbody spectral radiance weighting—versus the emission angle for all three designed structures, in both TE and TM polarizations. The TM-polarized emissivity is in all cases larger than the TE-polarized emissivity similar to the Brewster effect [34], which occurs close to 70 degrees. The unpolarized directional emissivity [35] is almost constant over a large angular range, from normal to 70 degrees, as the drop in the TE-polarized emissivity is compensated by the TM-polarized emissivity. The total power radiated from any of the planar structures can be obtained by applying the Lambert cosine law. Therefore, the hemispherical emissivity, which is the total power radiated from the structure at all angles, to the total power radiated from a blackbody can be obtained by

\[
\frac{\varepsilon_\theta}{\varepsilon_{rad, BB}} = \frac{\int d\Omega \cos \theta \int d\lambda I_{BB} (\lambda, T) \cos \theta (\lambda, \Omega)}{\int d\Omega \cos \theta \int d\lambda I_{BB} (\lambda, T)}
\]

(1)

where \(\lambda\) is wavelength, \(T\) is temperature, \(\Omega\) is solid angle and \(I_{BB}\) is the blackbody spectral radiance. Figure 3(b) shows the emissivity of the structures versus their areal mass for both normal and hemispherical emission. Increasing the number of layers yields a higher emissivity and a correspondingly larger areal mass. The emissivity of the three-layer structure reaches 90% (normal) and 84% (hemispherical). Even for the simplest structure—a Salisbury screen—a high emissivity value of 65% is calculated for emission in the normal direction. The areal mass of each of these emissive surfaces is less than 10 g/m\(^2\). Specifically, the Salisbury screen weighs only 3.3 g/m\(^2\), which is to our knowledge, the lightest structure with this level of emissivity. Here, the mass of the back reflector is excluded from the calculation of areal mass, because we consider the metal as an existing surface whose emissivity we seek to increase by addition of the additional layers. Should we instead desire to fabricate a free-standing membrane, or to modify the emissivity of a transparent surface, we could add a 40-nm Al layer beneath the dielectric, increasing the areal mass by 0.1 g/m\(^2\).

A reasonable question is why such wideband spectral emissivity is predicted for even the single-layer structure, despite the general narrowband nature of the Salisbury screens. As expected, in Fig. 2(a), the emissivity for the Salisbury screen is large at a wavelength near 10 microns in agreement with this wavelength being close to the blackbody spectrum peak at
approximately 300 K. However, the associated resonance falls off rapidly as the wavelength increases. The broad peak at 20 microns may exist because the permittivity of Cr becomes very large at longer wavelengths [see Fig. 1(d)]. For the details of the angular dependence of the spectral emissivity in different polarizations, see Fig. 8.

Figure 4(a) shows a SEM image of the cross section of a Salisbury screen that was fabricated. Due to the multiscale dimensions of the structure, the Cr layer and the SiO₂ layer are observed as one very thin layer on top. Figure 4(b) compares the infrared spectral emissivity of the Salisbury screen that is obtained from two different measurements with the spectroscopic ellipsometer and Fourier transform infrared (FTIR) microscope, which are in excellent agreement [See Fig. 9 for similar plots of two- and three-layer structures, and angle-resolved spectra for all three samples]. The angle-resolved data presented here represent the average of TE and TM polarization measurements.) Weighting by the 300 K blackbody spectrum and integrating over wavelength gives the directional emissivity of each sample versus angle, which is depicted in Fig. 4(c). The thermal emissivity of all three structures is more than 0.7 for angles up to almost 60 degrees. Expectedly, as the number of layers increases, the emissivity is enhanced, especially at long wavelengths and at shallower angles. Our measurement facility could measure only within the range from 2 to 30 µm, which corresponds to 88% of the 300K blackbody power (See Appendix E).

Interestingly, the reflectance measurements for all three samples indicates slightly higher emissivity than predicted by the calculations and optimizations above. Different processes may be responsible for the large emissivity of these multilayers. The thin Cr layer is not a uniform layer and may consists of small nanoparticles with various sizes. For metal nanoparticles with nanometer-sized diameters, the energy levels in the conduction band become discretized due to quantum size effects [36]. Besides, the polyimide layer has a large molecular composition and may support a considerable number of resonances [37]. As electrons in the thin Cr layer get hot, they give some part of their energy through thermalization to the Cr lattice and subsequently to the surrounding media. The energy of the hot electrons at the metal-polyimide interface can get coupled to the vibronic and phononic resonances of the polyimide layer. Also, the Cr hot electron energy can be coupled to the phonon resonances in SiO₂. Furthermore, the adjacent SiO₂ and Cr layers may exchange energy. Even if we neglect other possibilities such as the role of atom nuclei, calculations of the exact role of each effect on the reflection is well beyond the scope of this manuscript, and can be an extremely challenging task.

We also fabricated a free-standing Salisbury screen membrane, shown in Fig. 4(d). The 300 K emissivity of this sample was 0.60 as inferred from spectroscopic reflectance measurements at 30° incidence angle [see Fig. 11]. This value is slightly less than that obtained for the Salisbury screen that was fabricated on a rigid substrate (above). The primary reason for this difference is that the free-standing membrane has a dielectric thickness of 1.8 µm, which is slightly less than optimal dielectric thickness of 2.1 µm [see Fig. 1]. The rigid structure fabricated above used this optimal dielectric thickness of 2.1 µm.

The high emissivity of the free-standing membrane is nonetheless remarkable considering that its total thickness is less than 2 µm, corresponding to a calculated areal mass of 3 g/m². For comparison, the aluminized polyimide (Kapton) layer typically used in spacecraft multilayer insulation must be 25 microns thick (36 g/m²) in order to achieve a similar value of emissivity (0.62) [38]. Although working with such thin membranes may be challenging in terms of fabrication, handling, and impact damage, the ability to achieve moderate to high emissivity with 3–10 g/m² areal mass may be beneficial to numerous aerospace applications. And, although achieving high emissivity with these structures requires precise control of dielectric layer thickness as well as extremely thin layers of Cr metallization, this should be within the capabilities of established roll-to-roll fabrication processes, to our knowledge.
Thus, ultralight high-emissivity films can be prepared and subsequently integrated or laminated onto other surfaces, enabling the thermal emittance of a structure to be designed and manufactured separately from its other functions.

3. Experimental

Fabrication. We fabricate the Salisbury screen by evaporating a 100 nm thick Cr back reflector layer on a Si substrate, followed by spin coating the Nexolve CP1 polyimide layer [39,40], then electron beam evaporating the thin Cr layer. Without breaking vacuum, a 10-nm SiO$_2$ layer is then deposited to protect the Cr from oxidization. Since the SiO$_2$ layer is very thin, it should have only a marginal effect on the optical properties of the Salisbury screen [see Fig. 2]. For the two-and three-layer surfaces, we repeat the single-layer steps in succession, but increase the interfacial SiO$_2$ layer thickness to 50 nm, to prevent the solvent from penetrating into underlying polyimide layers during spin coating.

The free-standing Salisbury screen was fabricated from a 1.8 micron CP1 film, onto which we evaporated 100 nm Cr as the back reflector. For ease of handling, the CP1 film was

---

Fig. 4. (a): The SEM micrograph of the fabricated Salisbury screen. (b): Infrared spectral absorption (inferred from reflection) of the Salisbury screen as obtained by FTIR (yellow) and ellipsometer (30° incidence, blue). The measurements were done with a Nicolet iS50 FTIR coupled to a Continuum microscope with a 100 µm spot size (c): The angle-dependent emissivity for the three fabricated multilayers. (d) The fabricated free-standing Salisbury screen installed on a frame for better demonstration. The flat central part is the Salisbury screen with a total thickness of around 2.1 µm. The surrounding parts meet the underneath frame, hence appear differently.
supplied on a polypropylene backing film. Following the first evaporation step, the membrane was glued to an acrylic frame, and then the backing film was removed. On the opposite side, we evaporated 2 nm Cr and 10 nm SiO₂.

We inform the reader that not all our trials to fabricate the Salisbury screens provided the results we reported here. Indeed, some of our trials led to considerably lower emissivity values. Since electron beam evaporation is the least certain part of the fabrication process, we conclude that the reflection values and thus emissivity depends highly on this step, particularly for the fabrication of the very thin metal layer.

**Optical measurements.** We obtained the emissivity of our samples by measuring their specular reflectance over wavelengths from 2 to 30 microns with the J. A. Woollam IR-VASE infrared spectroscopic ellipsometry system. Because the metallic back reflector is opaque at all wavelengths, we may calculate absorption (and thus emissivity) directly from the reflectance measurements [41]. We also measured the reflectance with a Nicolet iS50 FTIR coupled to a continuum microscope with a 100 μm spot size, over wavelengths from 2.5 to 15 microns. The FTIR microscope illuminates and collects from the surface of the sample with a Cassegrain lens within an angular range from about 15 to 35 degrees, therefore the obtained emissivity is averaged over that angular range. Nevertheless, we observed that the results of the measurements with the FTIR correspond very well in all cases to the results of the reflection measurements with the ellipsometer at 30 degrees, in agreement with the intuition that the emission from these structures should not be sensitive to angle.

**4. Simulations**

Full-wave electromagnetic simulations were performed using in-home codes based on the transfer matrix method from Prof. Khashayar Mehrany, the free codes based on the Legendre Polynomial Expansion Method [42], available online (LPEM package) [43] and the free Reticolo package available online [44].

In the simulations we considered all materials isotropic. Although we extracted anisotropic optical data for CP1 polyimide from ellipsometric measurements, we used its in-plane optical data for the simulations.

**5. Conclusions**

Ultralight multilayers have been designed and fabricated, exhibiting 300 K emissivity up to 0.9 in the surface normal direction (0.85 hemispherical). The total thickness of these structures is only 20–50% of the design free-space wavelength, and their areal mass is less than 10 g/m². The high spectral emissivity of these structures may be due to different phenomena including phononic resonances in its dielectric layers and transfer of energy of quantum-confined hot electrons in the metallic particulates to the vibrons in the adjacent polyimide.

We also fabricated a free-standing Salisbury screen with an emissivity of 0.6 and weighing only 3 g/m². These multilayers have substantial mechanical flexibility, are made of low outgassing materials [45], and the extremely low areal mass density of only a few g/m², making them of considerable interest for space-based and other ultralight flexible technology applications.

**Appendix A. Optical data of CP1 visible, near-infrared and infrared wavelengths**

In order to extract the refractive index (n) and extinction coefficient (k) for CP1, two samples were prepared and measured. For the first sample, CP1 was spin-coated onto a Si wafer; for the second sample, CP1 was spin-coated onto an e-beam evaporated gold mirror on silicon. The gold film was sufficiently thick that it was opaque (See Appendix B for more details); and therefore, had the optical behavior of a semi-infinite gold substrate. For spinning, we mixed with CP1 resin in diglyme to make it thinner. After spinning, a heater was used to
evaporate the diglyme solvent. To our knowledge, this should not practically change the optical properties of CP1 resin, although further analysis of this issue may be beneficial. We assume the resulting CP1 film is uniaxially anisotropic, with the optic axis oriented normal to the surface, which has been previously observed in polyimide films [46]. This assumption turns out consistent to our findings of the refractive index of the film.

In order to determine the refractive index for CP1 at visible and near-infrared wavelengths, variable angle spectroscopic ellipsometry data were acquired from the CP1-on-silicon sample using a V-VASE ellipsometer (J. A. Woollam Co., Lincoln NE). Data were acquired over the 0.4 to 2.1 μm wavelength range, and at incident angles of 55°, 65° and 75°.

The infrared CP1 optical functions were determined by measuring both the CP1-on-silicon and CP1-on-gold samples using an IR-VASE ellipsometer (J. A. Woollam Co., Lincoln NE). The measurement wavelengths were 2 to 39 μm. The incident angles were 45° and 60° for the CP1-on-silicon sample measurements, and at 75° for the CP1-on-gold sample measurements. The backside of the CP1-on-silicon sample was abraded in order to suppress back surface reflections, in order to simplify the data analysis of this sample. Also, prior to spin-coating, the gold mirror was measured in order to determine the optical function of the gold surface without a film.

Because this uniaxially anisotropic film is transparent over the 0.4 to 5 μm spectral range, it is relatively easy to determine not only the thickness but also the refractive indices in-the film-plane (ordinary, $n_o$) and normal-to-film-plane (extraordinary, $n_e$) [47]. These three quantities can be unambiguously determined by fitting a uniaxial film model to the amplitude, separation and shape of the oscillations present in the $\Psi$ and $\Delta$ curves [47].

For the CP1 on Si sample, refraction at the ambient-film interface tends to direct the beam towards surface normal, so both the p- (TM) and s- (TE) components of the electric field is oriented mostly parallel to the film surface, which causes the optical response in the film’s absorbing regions to be dominated by projection of the dielectric tensor on the sample surface [48,49].

To overcome this limitation, infrared ellipsometric data were also acquired on the CP1-on-gold sample, at an angle of incident of 75°. When the light beam illuminates a highly conductive surface like gold at near-grazing angles, the electric fields normal to the surface (and normal to film plane) are maximized in the near surface region, and the electric fields parallel to the surface are minimized [50,51]. This ensures maximum electric field interaction with (and sensitivity to) the IR-active modes in the film that are normal to the film plane. Simultaneous analysis of the IR-data from both samples allows us to determine both the in-film-plane (ordinary) and out-of-film plane (extraordinary) optical functions at IR wavelengths.

The data were analyzed with WVASE software (J. A. Woollam Co., Lincoln NE), using the standard numerical analysis methods similar to those described by Jellison [52,53], and Herzinger, et al. [54] and others. Model parameters were optimized to minimize the difference between measured and model-generated data, using the Mean Squared Error (MSE) figure of merit that is defined by Eq. (4) in Ref. [54].

In order to generate self-consistent CP1 ordinary and extraordinary optical functions across all wavelengths, the data from both samples and all wavelengths – visible, near infrared, and infrared – were simultaneously analyzed in a multi-sample, multi-data set analysis [55,56]. This multi-sample analysis required the assumption that the CP1 optical properties remain the same for all samples (only the thickness changes).

In the model, the silicon substrate was represented by the optical function described in Ref [53], which covers 0.19 to 7 μm, but can extrapolated very accurately to 40 μm range (silicon has no strong infrared-active phonons). An ellipsometric measurement of the silicon substrate prior to coating of the CP1 showed no evidence of free carrier effects in the silicon. This indicates that the doping was below the measurement sensitivity limit, at least for these wavelengths. Therefore, no Drude oscillator function was required for this analysis.
The gold substrate optical properties from 2 to 30 $\mu$m were determined by measurement and analysis of the gold surface prior to application of the CP1 film. The CP1 films were modeled using the same uniaxial model for the ordinary (in-plane) and extraordinary (out-of-plane) relative permittivity. They consist of a pole function to represent the dispersion in the visible and near infrared spectral regions, combined with a number of Kramers-Kronig consistent Gaussian oscillators.

\[
\epsilon(E) = \epsilon_1(E) - i\epsilon_2(E) = 1 + \frac{A_1}{E_1^2 - E^2} + \sum_{n=1}^{k} \left( e^{G}_{1n} - i e^{G}_{2n} \right)
\]  

(2)

where $\epsilon$ is relative permittivity, $\epsilon_1$ and $\epsilon_2$ are its real and imaginary parts, $E$ is energy and $E_1$ is the pole energy, and $e^{G}_{1n}$ and $e^{G}_{2n}$ are the real and imaginary part of the Gaussian oscillators.

The complex Gaussian oscillator functions \((e^{G}_{1n} - i e^{G}_{2n})\) closely describe the combined infrared absorption modes for many disordered films [57].

\[
e^{G}_{2n} = A_n \left( e^{\frac{E-E_1}{\sigma}} - e^{\frac{E+E_1}{\sigma}} \right)
\]

(3)

In the last equation, $\sigma = \frac{Br}{2\sqrt{\ln(2)}}$, where $Br$ is the full width at half maximum (FWHM) of the oscillator. The real part of the function, $e^{G}_{1n}$, is the Kramers Kronig integral transform of $e^{G}_{2n}$, and is related to the Error function [57].

The final ordinary dielectric function had 26 Gaussian oscillators, and the extraordinary dielectric function had 56 Gaussian oscillators. Figure 5 shows the resulting refractive indices and extinction coefficients. Figure 6 shows the ordinary and extraordinary refractive indices \(n_o(\lambda)\) and \(n_e(\lambda)\), for 0.4 to 2.5 $\mu$m. Note that both ordinary and extraordinary extinction coefficients \(k_o(\lambda)\) and \(k_e(\lambda)\) are almost zero in this spectral range, therefore we did not plot them.
Our results of modeling of the permittivity of the CP1 polyimide film in terms of parameters of the pole and Gaussian functions, and the obtained n and k are included in Dataset 1 (Ref. [58]).

Appendix B. Obtaining the skin depth of gold

Penetration depth (of electric field) can be approximated by $\delta = \frac{\lambda}{2\pi k}$ where $\lambda$ is wavelength and $k$ is the imaginary part of the refractive index. We compared several material optical data for gold from the literature [59–64], and observed that the values for the refractive index (n) and the extinction coefficient (k) correspond well to each other in the reported wavelength ranges. We then obtained the penetration depths from the data reported in [62] and [63,64], which is shown in Fig. 7. Despite the peak at 0.5 µm, over all shown
wavelengths, the penetration depth is smaller than 50 nm. Since the Au film we fabricated was much thicker than this value, the film can be practically considered infinite.

Fig. 7. (a): penetration depth of Au from 0.3 to 40 µm. (b): Same as (a), zoomed in at wavelengths from 0.3 to 3µm.

Appendix C. Polarized spectral emissivity of the Salisbury screen

Figure 8 shows the angle dependence of the spectral emissivity in both polarizations for the Salisbury screen. The width of the pronounced Fabry-Perot resonance is a few microns due to the subwavelength thickness of the dielectric spacer layer. As the incidence angle increases, the resonance experiences a blue shift in both polarizations, but these changes are not very significant due to the large width of the resonance. In TM polarization, we observe a Brewster-like effect [34], which appears in Fig. 8(b) as higher emissivity over a broad angular range for long wavelengths up to almost 25 microns. Also the phononic resonance of polyimide near 8 microns gets amplified at large angles. These two phenomena lead to a considerable amount of absorption in the polyimide layer and maximize the TM-polarized absorption at around 70 degrees. Therefore, the TE and TM polarized results combined give rise to nearly constant absorption and emissivity over a very wide angular range.

Fig. 8. Spectral emissivity of the Salisbury screen versus the emission angle and the wavelength for (a): TE-polarized emission, and (b): TM-polarized emission.
Appendix D. Measured emissivities

Fig. 9. Infrared spectral emissivity of the fabricated structures [66]. (a) at 30 degrees, (b): 1-layer structure, (c): 2-layer structure, (d): 3-layer structure.

Appendix E. Amount of blackbody power captured in the experiments

We measure IR reflection by the J. A. Woollam IR-VASE infrared spectroscopic ellipsometry system, which can measure reflection reliably from 2 to 30 μm. We thus need to verify how much of the reflected wave we actually capture.

We use the 300K blackbody spectrum as reference for thermal radiation from the Salisbury screen. Since the measurement facility do not capture all of emitted wavelengths, their measurements can be valid only within a certain range, as depicted in Fig. 10(a).
Fig. 10. (a): measurement bandwidth (yellow region) can cover spectral range of the (300 K) blackbody partially. (b): the amount of total power contained within the measurement bandwidth.

For thermal radiation spectral intensity, the following formula is used [65]:

\[
I(\lambda) = \frac{1}{\lambda^2} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1},
\]

where \( \lambda \) is wavelength, \( h \) is Planck’s constant, \( T \) is temperature and \( k \) is Boltzmann’s constant.

Note that plotting the spectral density versus frequency (energy per unit volume per unit frequency) is a different function from the spectral density versus wavelength (energy per unit volume per unit frequency). We consider the latter one here.

Now, we can verify how much of the energy of the blackbody is contained within the measured bandwidth, i.e. the colored box in Fig. 10(a). We assume that at short wavelength (\( \lambda_1 \)) we cover effectively the blackbody spectrum, we change the upper wavelength limit (\( \lambda_2 \)) only. We numerically calculate the amount of total power that is contained within the range from \( \lambda_1 \) to \( \lambda_2 \). We normalized the wavelength axis by the wavelength of the blackbody spectrum peak, and obtain a universal curve, depicted in Fig. 10(b). The peak wavelength for the 300 K blackbody occurs at 9.67 μm.

For the 300K blackbody, by having \( \lambda_2 = 30 \mu \text{m} \), we obtain approximately 88% of the blackbody power.
Appendix F. Free-standing CP1 foil

Fig. 11. The spectral emissivity (inferred from specular reflectance measurements at 30 degrees) of CP1 film with (a): Al back reflector and nothing on top, (b): Al back reflector and 2 nm Cr and 10 nm SiO2 on top, and (c) Cr back reflector and 2 nm Cr and 10 nm SiO2 on top. The emissivity of the free-standing foils is notably less than that of those fabricated on Si wafers because the thickness of the CP1 layer is not ideal for the free-standing foils.

Funding

Northrop Grumman Corporation and the Caltech Space Solar Power Project; Emily Warmann and Harry Atwater were partially supported by the DOE “Light-Material Interactions in Energy Conversion’ Energy Frontier Research Center under grant DE-SC0001293. Ali Naqavi acknowledges support from the Swiss Science National Foundation.

Acknowledgment

We acknowledge all those who supported this research, in particular Lynn Rodman of Nexolve for providing materials and guidance in fabricating the thin polyimide layers. We also thank Mark Kruer, George Rossman, Laura Kim, Victoria Chernow, Michelle Sherrot and Will Whitney for assisting with emissivity measurements; Dagny Fleischman, Rebecca Glaudell, Cristofer Flowers and Rebecca Saive for their support during the fabrication and measurements; and Colton Bukowsky and Krishnan Thyagarajan for technical discussions. We thank a reviewer for his comment on the manuscripts which helped us improve it.