

Radiative heating and cooling with spectrally selective surfaces

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Matter continuously exchanges energy with its surroundings. This exchange can be dominated by radiation, conduction, or convection. In this brief review we discuss how proper design of radiative surface properties can be used for heating and cooling purposes. The desired properties can be understood once it is realized that solar and terrestrial radiation take place in different wavelength ranges and that only part of the solar spectrum is useful for vision and for photosynthesis in plants. These facts allow the possibility of tailoring the spectral absorptance, emittance, reflectance, and transmittance of a surface to meet different demands in different wavelength intervals, i.e., to take advantage of spectral selectivity. One example is the selective surface for efficient photothermal conversion of solar energy, which has high absorptance over the solar spectrum but low emittance for the longer wavelengths relevant to thermal reradiation. Below we discuss the pertinent spectral radiative properties of our ambience. These data are then used as background to the subsequent sections treating four examples of spectrally selective surfaces. The first example is the previously mentioned selective surface for converting solar radiation to useful heat. The second example considers surfaces capable of reaching low temperatures by benefiting from the spectral emittance of the clear night sky. The third example concerns two related types of transparent heat mirror. The fourth example, finally, treats radiative cooling of green leaves; this part is included since it gives a nice example of how nature solves a difficult problem in an elegant and efficient way. This example hence provides an interesting background to the other cruder types of artificial selective surfaces. Throughout our discussion we treat the ideal spectral properties, give an illustrative experimental example of how well this goal can be realized, and—where this is possible—show a corresponding theoretical curve indicating to what extent the measured results can be theoretically understood.

I. Ambient Radiative Properties

A fundamental property of matter is its ability to emit radiation. This property is conveniently discussed starting from the ideal blackbody whose radiation spectrum, known as the Planck spectrum, is uniquely defined if the absolute temperature is known. Planck's law is a consequence of the quantum nature of electromagnetic radiation. The thermal radiation from a real body can be expressed as the blackbody spectrum times a wavelength dependent emittance lying in the interval zero to unity. Unoxidized metal surfaces, for example, can show an emittance as low as a few percent, whereas a soot layer can have an emittance of $\sim 99\%$. Figure 1(a) shows blackbody radiation spectra for four temperatures. These are bell-shaped curves peaked at $10\text{-}\mu\text{m}$ wavelength. The radiated power is seen to increase with increasing temperature, and at the same time the peak position moves toward shorter wavelength. The

most important fact is that the Planck spectrum is confined to the $3 < \lambda < 50\text{-}\mu\text{m}$ wavelength range for the temperatures of interest in connection with natural heating and cooling.

Figure 1(b) reproduces a solar spectrum^{1,2} for radiation outside the earth's atmosphere. The curve displays a bell shape which agrees well with a blackbody spectrum defined by the sun's surface temperature ($\sim 6000^\circ\text{C}$). The integrated area under the curve yields the solar constant ($1353 \pm 21 \text{ W/m}^2$). It is important to note that the solar radiation is limited to the $0.25 < \lambda < 3\text{-}\mu\text{m}$ wavelengths, so there is practically no overlap with the blackbody spectra shown in Fig. 1(a). Hence a surface may have entirely different properties with regard to solar and thermal radiation.

Figure 1(c) shows a typical atmospheric absorption spectrum at the level of the earth's surface.^{3,4} A number of absorption bands, mainly caused by water vapor, carbon dioxide, and ozone, are seen as well as intervening high transparency regions. Clearly most of the solar radiation is transmitted through the atmosphere, and only the UV tail ($\lambda < 0.3 \mu\text{m}$) and parts of the near IR tail ($\lambda > 0.7 \mu\text{m}$) are strongly damped. The thermal radiation from a freely radiating surface, however, is affected in a more significant way. The low atmospheric absorptance particularly in the $8 < \lambda < 13\text{-}\mu\text{m}$

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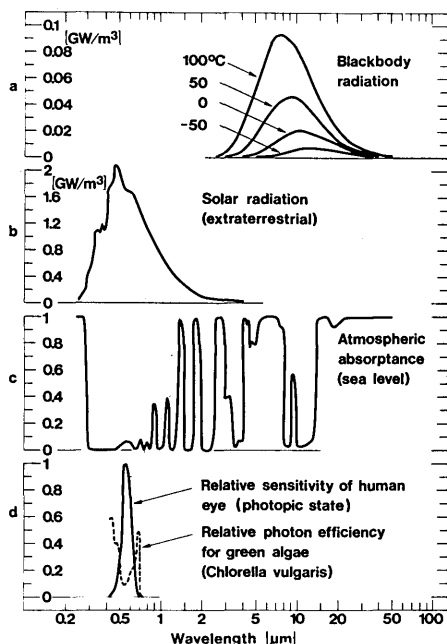


Fig. 1. Spectra for (a) blackbody exitance at four temperatures, (b) extraterrestrial solar irradiance, (c) typical absorptance across the atmospheric envelope, (d) relative sensitivity of the human eye and relative photon efficiency of photosynthesis in green plants.

interval allows radiative coupling at these wavelengths with the cold upper parts of the troposphere, so that the equivalent sky temperature lies below the ambient temperature.⁵ This effect thus offers a possibility for passive cooling.

Figure 1(d) presents two biophysical constraints which are important for considerations of heating and cooling. The solid curve shows the relative spectral sensitivity of the human eye in its light-adapted (photopic) state in which the retinal receptors are functioning for $0.4 < \lambda < 0.7\text{-}\mu\text{m}$ wavelengths. An eye in its dark-adapted (scotopic) state has its sensitivity curve displaced $\sim 0.05\text{ }\mu\text{m}$ toward shorter wavelengths. The dashed graph applies to the relative photon efficiency for photosynthesis in green plants; the particular curve pertains to a species of green algae (*Chlorella vulgaris*).⁶ We note that the photon efficiency drops to zero at $0.7\text{ }\mu\text{m}$, i.e., at the same wavelength as that where the eye's sensitivity vanishes. The two curves prove that a material which transmits light required for vision or for photosynthesis in green plants needs to be transparent only over a limited part of the solar spectrum, whereas it may be absorbing or reflecting outside this interval.

Applications related to the spectral curves in Fig. 1 will be discussed below. We then also need two fundamental relations:

$$a(\lambda) + r(\lambda) + t(\lambda) = 1, \quad (1)$$

$$a(\lambda) = e(\lambda), \quad (2)$$

where a is the absorptance, r is the reflectance, t is the transmittance, and e is the emittance. Equation (1)

follows from energy conservation. Equation (2), known as Kirchhoff's law, states that at a given wavelength the absorptance is equal to the emittance for matter in thermodynamical equilibrium.

II. Example 1: Surfaces with High Solar Absorptance and Low Thermal Emittance

A surface which efficiently converts solar radiation into useful heat should exhibit two properties: its absorptance should be near unity within the solar spectrum, whereas its emittance should be near zero for thermal reradiation. Thus the gained solar energy is retained and can be delivered to a suitable heat transfer fluid. It follows from Fig. 1 that a should be high for $0.3 < \lambda < 3\text{ }\mu\text{m}$ and e should be low for $3 < \lambda < 50\text{ }\mu\text{m}$. Equations (1) and (2) now yield that the ideal spectral reflectance for a nontransparent surface should be zero for $0.3 < \lambda < 3\text{ }\mu\text{m}$ and unity for $3 < \lambda < 50\text{ }\mu\text{m}$. This ideal curve is indicated by dotted lines in Fig. 2.

The role of spectral selectivity for obtaining specific radiative properties has been realized at least since 1909,⁷ and its importance for efficient photothermal conversion of solar energy was pointed out several decades ago.⁸⁻¹¹ Recently the much increased interest in solar energy applications has led to a very active development of selective surfaces having a spectral reflectance resembling the dotted curve in Fig. 2. This work has been the subject of detailed reviews¹²⁻¹⁵ as well as of more cursory surveys.¹⁶⁻²⁹ Surfaces that have been studied include

- black chrome made by electroplating³⁰⁻⁵⁸,
- black nickel made by electroplating^{31,32,47,59-63} and chemical conversion⁶⁴,
- anodized aluminum black colored by electrolytic⁶⁵ and integral⁶⁶ techniques;
- metal-insulator composites made by coevaporation,⁶⁷⁻⁷¹ cosputtering,⁷²⁻⁷⁶ and ion implantation⁷⁷;
- cosputtering of semiconductors and insulators^{78,79};
- sputtering of metal carbides⁸⁰⁻⁸⁶ and silicides⁸⁵⁻⁸⁷;
- oxidation of copper,^{11,88-90} chrome,⁹¹ cobalt,⁹²⁻⁹⁴ zinc,⁹⁵ titanium,⁹⁶ and stainless steel^{64,97,98};
- multilayer interference stacks⁹⁹⁻¹⁰⁷;
- multilayer discontinuous films¹⁰⁸;
- carbon films with graphitic¹⁰⁹ and diamondlike structure¹¹⁰;
- gas evaporated particulate films of lead sulfide,¹¹¹ gold,¹¹²⁻¹¹⁶ chrome,^{117,118} cobalt,¹¹⁹ nickel,¹²⁰ and tellurium¹²¹;
- textured surfaces on metals¹²²⁻¹²⁴ and semiconductors^{125,126};
- dendritic surfaces¹²⁷⁻¹³⁰;
- amorphous silicon made by chemical vapor deposition¹³¹;
- films made by pyrolysis of molybdenum-containing compounds¹³²⁻¹³⁴;
- polymer films¹³⁵;
- enamel coatings¹³⁶⁻¹³⁷;
- paints.^{31,138,139}

Practical solar energy collectors use surfaces consisting of black chrome, black nickel, electrolytically colored anodic alumina, and copper oxide.

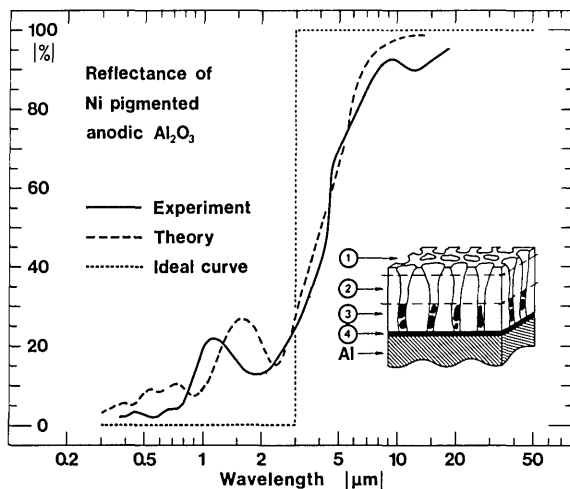


Fig. 2. Spectral reflectance of solar collector surfaces. Dotted curve shows the ideal properties, solid curve reproduces measurements on Ni pigmented anodized Al, and dashed curve represents computations based on the structural model indicated in the inset.

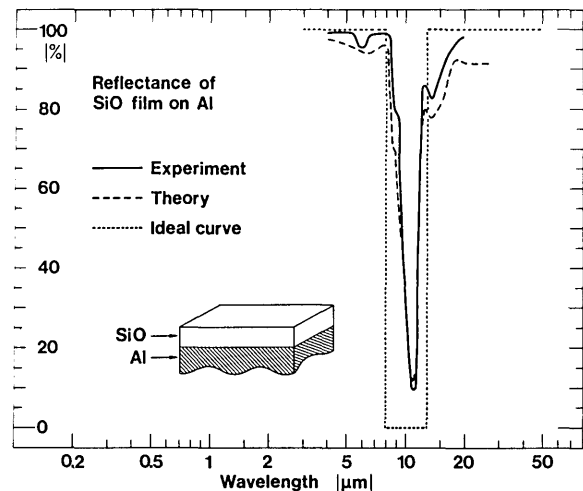


Fig. 3. Spectral reflectance of surfaces for radiative cooling to low temperatures. Dotted curve shows the ideal properties, solid curve reproduces measurements on SiO coated Al, and dashed curve represents computations for this configuration.

Our example of a spectrally selective surface for efficient photothermal conversion of solar energy is nickel pigmented anodic alumina.⁶⁵ These surfaces are commercially produced on a scale exceeding 10000 m²/year.¹⁴⁰ The coatings are made by first anodizing 99.5% pure aluminum sheet in dilute phosphoric acid so that a porous coating of Al₂O₃ is formed.¹⁴¹⁻¹⁴⁴ In a second step, an electrolysis in a bath containing NiSO₄ is used to precipitate metallic Ni inside the pores.¹⁴⁵⁻¹⁵¹ The resulting surface coating is sketched in the inset of Fig. 2. Directly on top of the Al base material is the barrier (layer 4) comprised of compact Al₂O₃ with a thickness of ~10 nm. The rest of the 0.7-μm thick coating is porous alumina, whose lowest 0.3 μm (layer 3) contains ~25 vol % metallic Ni as particles occluded in the oxide. The upper part of the coating (layers 1 and 2) can be separated into two, since the pores widen toward their openings. The spectral hemispherical reflectance of such a material is shown by the solid curve in Fig. 2. It is seen to be in fair agreement with the ideal curve. This degree of correspondence is typical for Ni pigmented anodic Al₂O₃ as well as for other types of practically useful solar collecting surfaces.

Our theoretical interpretation⁶⁵ of the measured reflectance spectrum is based on the published bulk dielectric permeabilities of Ni,¹⁵²⁻¹⁵⁶ Al,¹⁵⁷⁻¹⁵⁹ and anodic Al₂O₃.^{160,161} The most crucial part of the model is to account for the Ni pigmented layer. The metal particles are much smaller than the wavelengths of the electromagnetic radiation, implying that an effective medium description is appropriate.¹⁶² We employed the formulation by Bruggeman,¹⁶³ which assumes structural equivalence between metallic and insulating components of the inhomogeneous material.¹⁶⁴⁻¹⁶⁸ This theory was then used together with a matrix formulation¹⁶⁹ of Fresnel's equations to account for the four-layer nature of the Ni pigmented anodic Al₂O₃ coatings. The final computations, which also assumed

a slight elongation of the particles in the direction perpendicular to the film surface, are shown by the dashed curve in Fig. 2. It agrees well with the measurement, so that the spectrally selective properties of this kind of surface can be theoretically understood in considerable detail.

III. Example 2: Surfaces for Radiative Cooling to Low Temperatures

The earth gains energy from the sun and dissipates the same amount of energy as thermal radiation so that heat balance is maintained on a global scale. The back radiation is strongly dependent on wavelength, as may be realized by inspecting Fig. 1(c) which shows a strong split minimum for the $8 < \lambda < 13$ -μm wavelengths. In this atmospheric window the transparency is so high as to permit direct radiative coupling to the cold upper parts of the troposphere. This effect causes a cooling which is most noticeable during clear nights^{5,170,171}; it has been consciously used for centuries for climatization¹⁷² and water desalination by freezing.¹⁷³

The atmospheric downward radiation during clear nights is of prime importance for assessing the potential of radiative cooling of surfaces at earth level. This radiation has three important sources⁴: water vapor whose emittance is strong in a band around 6.3 μm and also at $\lambda \gtrsim 20$ μm; carbon dioxide which emits in a band centered at 15 μm; and ozone whose most prominent feature is a narrow emittance peak at 9.6 μm, i.e., in the range which is otherwise highly transparent for dry air. Judging from Fig. 1(c), the atmospheric emittance can be low in the main part of the $8 < \lambda < 13$ -μm interval but near unity elsewhere. This has been verified by spectral IR radiometry^{4,174-179} and by computations based on elaborate models of the atmosphere.^{4,178-182} An upward facing surface which benefits from this atmospheric window to reach low temperatures in the night should hence emit predominantly in the 8-13-μm

range. From Eqs. (1) and (2) it now follows that the ideal spectral reflectance is zero for $8 < \lambda < 13 \mu\text{m}$ but unity for $3 < \lambda < 8 \mu\text{m}$ and for $13 < \lambda < 50 \mu\text{m}$; this property is indicated by the dotted lines in Fig. 3. If the surface is to be used during daytime also, its reflectance must be high even for $0.3 < \lambda < 3 \mu\text{m}$. Considering radiation balance only, such an ideal surface would be able to reach a minimum temperature lying $\sim 50^\circ\text{C}$ below that of the ambient.¹⁸³ The cooling power at 20°C below ambient temperature can be $\sim 25 \text{ W/m}^2$ even with a realistic nonradiative heat input of $1 \text{ W/m}^2 \text{ K}$, which appears to give prospects for refrigeration by purely passive means.¹⁸³

The role of spectral IR selectivity for radiative cooling to low temperatures was first appreciated some twenty years ago.¹⁸⁴⁻¹⁹⁰ Since then several investigations have been presented which use smooth metal surfaces coated with

polyvinylchloride (PVC),¹⁹¹
polyvinylfluoride (PVF, Tedlar),¹⁹²⁻²⁰⁰
poly-4-methylpentene (TPX),¹⁹⁶
silicon monoxide,^{183,201} and
other materials.²⁰²

Similar studies have been reported for approximate blackbody radiators.^{177,203-206} Cooling to 40°C below the ambient temperature has been observed under particularly favorable climatic conditions,^{190,191,205} whereas temperature differences of $\sim 15^\circ\text{C}$ are more typical. No surface used so far has been optimized with regard to cooling performance.

The surface which shows the highest degree of IR selectivity is silicon monoxide evaporated onto smooth aluminum. The solid curve in Fig. 3 depicts a reflectance spectrum at normal incidence of a $1.0\text{-}\mu\text{m}$ thick film as reproduced from our own work.^{183,201} A strong lattice absorption, caused by Si-O stretching modes, combines at this wavelength with a destructive inter-

ference to produce a deep reflectance minimum within the atmospheric window range. The spectral selectivity depends critically on film thickness. The dashed curve in Fig. 3 refers to a computation based on the dielectric permeabilities of SiO (Refs. 207 and 208) and Al.¹⁵⁷⁻¹⁵⁹ It is seen to agree well with the measurement.

IV. Example 3: Transparent Heat Mirrors

Two types of transparent heat mirror are of interest. The first serves to transmit visible light and reflect IR radiation. A window with such a coating placed on its outer surface will then provide natural lighting in the day while the near IR solar radiation is reflected so that the potential need for energy consuming air conditioning is diminished.²⁰⁹ It follows from Fig. 1 that the optical properties which are required for efficient energy utilization are high transmittance over the eye's sensitivity range, at $0.3 < \lambda < 0.7 \mu\text{m}$, and high reflectance in the IR part of the solar spectrum, at $0.7 < \lambda < 3 \mu\text{m}$. The ideal spectral curves are indicated by the dotted lines in Fig. 4. Another energy-related application is for increasing the luminous efficacy of incandescent lamps by reflecting the emitted IR radiation in the glass bulb so that it goes back to the filament.²¹⁰ This application ideally demands the same optical properties as discussed above, except that it is desirable that the high reflectance extends out to $\sim 10\text{-}\mu\text{m}$ wavelength.

Transparent heat mirrors of the present type have been known for at least thirty years.²¹¹ Most of the investigations regard thin films of free electronlike metals whose low absorption is used to advantage. Either the single film is employed or its performance is improved by means to diminish the visual reflectance. The work has been reviewed several times.²¹²⁻²¹⁴ Experimental studies include

films of Au,^{209,211,215-223} Ag,^{209,217} Cu,²⁰⁹ Al,²⁰⁹ In,²²⁴ Rh,²²⁵ and Au-Cr alloys²²⁶;
antireflection-coated noble metal films such as Au/
ZnS²¹⁷⁻²¹⁹ and Ag/ZnS²¹⁷;

triple-layer coatings, with destructive interference in the visual range, of the types $\text{Bi}_2\text{O}_3/\text{Au}/\text{Bi}_2\text{O}_3$,^{215,216,227} $\text{SiO}/\text{Au}/\text{SiO}$,²¹⁶ $\text{ZnO}/\text{Au}/\text{ZnO}$,²²⁷ $\text{TiO}_2/\text{Ag}/\text{TiO}_2$,^{210,228,229} $\text{ZnS}/\text{Ag}/\text{ZnS}$,²³⁰⁻²³³ $\text{ZnO}/\text{Ag}/\text{ZnO}$,²²⁷ $\text{Bi}_2\text{O}_3/\text{Cu}/\text{Bi}_2\text{O}_3$,²²⁷ and $\text{ZnO}/\text{Cu}/\text{ZnO}$,²²⁷;
cermets of Au-SiO²³⁴ and Ag-SiO.²³⁴

A transparent heat mirror which shows particularly large spectral selectivity is $\text{TiO}_2/\text{Ag}/\text{TiO}_2$, where each layer is 18 nm thick. Such coatings, sketched in the inset of Fig. 4, are being used in special lightbulbs.²¹⁰ The solid curves in Fig. 4 show measured transmittance and reflectance spectra as reproduced from a work by Fan and Bachner.²²⁸ These data approximate the ideal profiles rather well. The dashed curves represent computations based on the bulk dielectric permeabilities of Ag²³⁵⁻²³⁹ and TiO_2 (rutile).^{240,241} The overall agreement with the experimental results is fair.

The second type of transparent heat mirror is one which transmits solar radiation while heat emission is impeded. Such a coating deposited on a window hence diminishes its heat transfer coefficient and thereby the potential need for space heating.²⁴² Another related

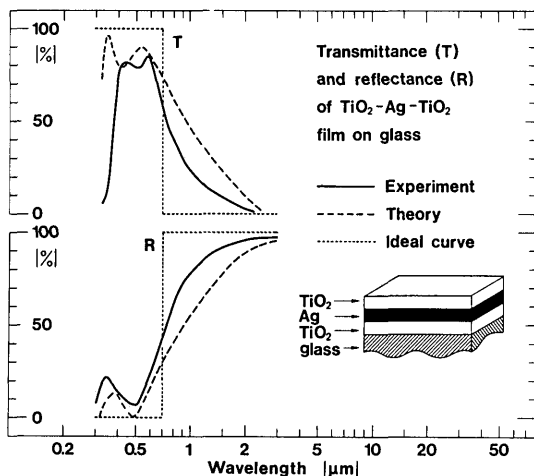


Fig. 4. Spectral transmittance and reflectance of a transparent heat mirror designed to transmit visual light and reflect IR radiation. Dotted curves show the ideal properties, solid curves reproduce measurements on a $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ stack on glass, and dashed curves represent computations for this configuration.

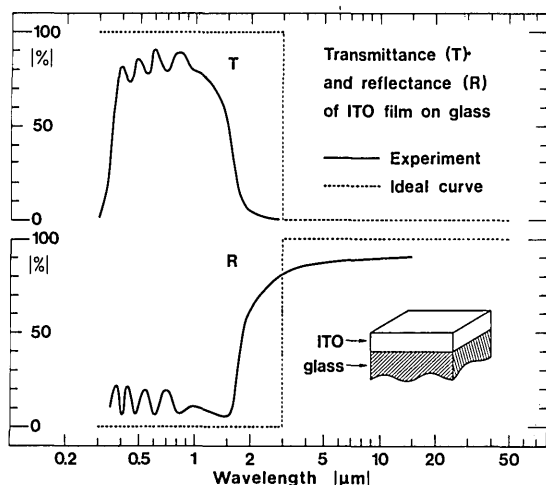


Fig. 5. Spectral transmittance and reflectance of a transparent heat mirror designed to transmit solar radiation and reflect heat radiation. Dotted curves show the ideal properties; solid curves reproduce measurements on an indium-tin-oxide film on glass.

application is on cover glasses for flat plate solar collectors.²⁴³ Figure 1 shows that the desired surfaces should be transmitting over the solar spectrum, at $0.3 < \lambda < 3 \mu\text{m}$, and reflecting for thermal radiation, at $3 < \lambda < 50 \mu\text{m}$. The ideal spectral profiles are shown by dotted lines in Fig. 5.

This kind of transparent heat mirror has been known as long as the one discussed earlier. Most experimental studies have been focused on semiconductors exhibiting three properties: (1) a sufficiently large band gap that transmittance is ensured down to $0.3\text{-}\mu\text{m}$ wavelength; (2) a limited number of excited levels within this gap; and (3) a free carrier concentration which is sufficiently large so as to give IR reflectance. These properties can be obtained in oxides of cadmium, indium, and tin. The required carrier densities can be achieved by adjusting the film preparation conditions so that a suitable nonstoichiometry is obtained or by a more or less controlled inclusion of dopants. Several reviews of this work are available.^{212-214,244,245} Experimental data have been reported with films of

CdO prepared by reactive sputtering²⁴⁶⁻²⁵⁴;

SnO₂ prepared by chemical vapor deposition (mainly by spray hydrolysis of tin chloride or by pyrolysis of tin-organometallic compounds),^{217,242,255-278} sputtering in reactive^{247,279-281} or nonreactive²⁸²⁻²⁸⁴ atmosphere, ion plating,²⁸⁵ flash evaporation of SnO₂ powder,²⁷⁴ and oxidation of Sn metal film^{260,286,287};

In₂O₃ prepared by chemical vapor deposition,^{256,266,276,288-290} sputtering in reactive^{247,291-293} or nonreactive^{283,294} atmosphere, evaporation in reactive atmosphere²⁹⁵⁻²⁹⁷ or in vacuum,²⁹⁸ ion plating,^{285,299,300} and oxidation of In metal film³⁰¹;

indium-tin-oxide (ITO) prepared by chemical vapor deposition,^{275,278,288,302-308} sputtering in reactive^{254,255,309-318} or nonreactive^{59,228,282,283,319-323} atmosphere and evaporation in reactive atmosphere^{297,324} or in vacuum²⁹⁸;

cadmium-tin-oxide (CTO) prepared by chemical vapor deposition^{325,326} and sputtering in reactive³²⁷⁻³³¹ or nonreactive³³²⁻³³⁴ atmosphere;

Cu₂S_{1+x} and Cu₃PSeS_x films made by evaporation.^{335,336}

Coatings of MgF₂ have been used to enhance the transmittance of ITO films.^{228,314} Another approach uses conducting micromeshes with a grid spacing of the order of a few microns.³³⁷⁻³⁴⁰ Solar radiation can then be transmitted while longer wavelength thermal radiation is reflected.

The solid curves in Fig. 5 depict measured transmittance and reflectance for a $0.46\text{-}\mu\text{m}$ thick ITO film deposited onto glass as reproduced from a work by Groth.²⁸⁸ These data are representative of ITO films with maximum carrier density. The transmittance is seen to be very high for $0.4 < \lambda < 1.5 \mu\text{m}$, while the reflectance is high for $\lambda > 3 \mu\text{m}$. The peaks stem from multiple interference. It is known³¹⁴ that the transmittance and reflectance data can be very accurately fitted to a free electron model, but surprisingly little work has been carried out to provide a more basic understanding of the optical properties of this material.

V. Example 4: Green Leaves

Green leaves convert solar radiation into energy which is useful for the living plant by photosynthetic reduction of carbon dioxide to hydrocarbons. From Fig. 1(d) it is inferred that the leaves must be absorbing at least within the wavelength range where photosynthesis is operative, at $0.3 < \lambda < 0.7 \mu\text{m}$. This absorption produces a heating of the leaves, which, in principle, can be serious since many physiological processes become critically affected already at temperatures of $40\text{--}50^\circ\text{C}$. Efficient cooling is therefore often a prerequisite for proper functioning of the leaves.

Evaporation of water through the stomata is an important mechanism for cooling. However, the leaves also use spectral selectivity to advantage for maintaining a sufficiently low temperature with limited loss of water. This fact makes it interesting to regard green leaves as a naturally occurring counterpart to the previously discussed types of artificial selective surfaces.

Three spectral ranges need to be considered: (1) at $0.3 < \lambda < 0.7 \mu\text{m}$ the leaf absorptance should be significant; (2) at $0.7 < \lambda < 3 \mu\text{m}$ the absorptance should be low so that IR solar radiation does not provide unnecessary heating; and (3) at $3 < \lambda < 50 \mu\text{m}$ the emittance should be large so that thermal radiative coupling with the ambience, which normally has a temperature lower than that of the leaves, is facilitated. The thermal emittance is particularly important in the upward direction owing to the radiation cooling mechanism previously discussed in Sec. III. The ideal spectral profile is depicted by dotted lines in Fig. 6.

The solid curve in Fig. 6 reproduces a measurement of the spectral absorptance of a green leaf as taken from a work by Gates *et al.*³⁴¹ These data, which apply to *Populus deltoides* (Eastern cottonwood), are by no

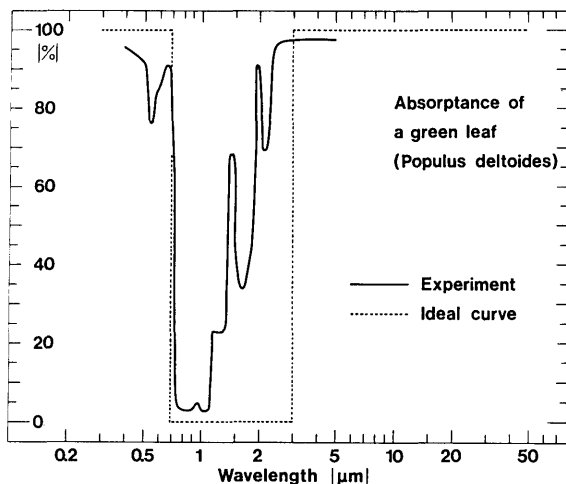


Fig. 6. Spectral absorbance of a green leaf. Dotted curve shows the ideal properties, and solid curve represents measurements on *Populus deltoides*.

means specific to this species, but quite similar spectral curves have been recorded for many other kinds of leaf.³⁴¹⁻³⁴³ The measured data agree rather well with the ideal curve, and in particular the drop in recorded absorbance is striking at 0.7- μm wavelength. In the short wavelength range, at $0.3 < \lambda < 0.7 \mu\text{m}$, the absorbance is largest at wavelengths which correspond with the peaks in photosynthetic efficiency [Fig. 1(d)]. This is a general phenomenon.⁶ In the intermediate wavelength interval, at $0.7 < \lambda < 3 \mu\text{m}$, the absorbance can reach a very low value, and the transmittance as well as the reflectance of leaves increase. These features were originally explained by Willstätter and Stoll³⁴⁴ as following from multiple reflections in boundaries between aqueous cells and air-filled intercellular spaces. Their model has been convincingly verified by ray tracing techniques.³⁴⁵⁻³⁴⁷ Pronounced absorption bands caused by water are seen at 1.4- and 1.9- μm wavelengths, similar to the case of the atmospheric absorbance spectrum [Fig. 1(c)]. For the longest wavelengths, at $3 < \lambda < 50 \mu\text{m}$, the high water content of the leaves makes them behave as efficient blackbody emitters. *Populus deltoides*, for example, shows a reflectance of < 0.1 in this range.³⁴⁸

Looking back at Figs. 2-6 it may be said that the green leaf is adapted to its specific requirements more ideally than the man-made selective solar absorber, low temperature radiative cooler, or transparent heat mirror. This fact is hardly surprising when one contemplates that surface coatings for efficient use of renewable energy sources have been vigorously developed only since the oil crisis in 1973, while natural selection has been at work in the green land plants for some 400,000,000 years.³⁴⁹

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