

Solar Absorbing Surfaces of Anodized Dendritic Tungsten

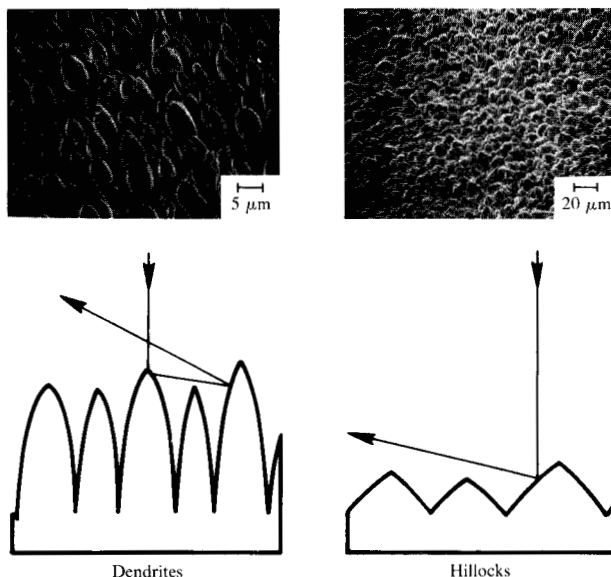
Abstract: Anodization of textured tungsten is shown to have merit either in creating a solar absorber of extremely high absorptance when applied to a large dendritic surface, or in enhancing the solar absorptance-to-emittance ratio when applied to smaller hillock topographies. The angular dependence of the absorption is reduced by the anodization coating, which consists of a thin conformal coating of WO_3 . The surface is stable up to temperatures of 520 K in air.

Introduction

The use of solar radiation to supply low-grade thermal energy is the subject of increasing research and development. The cost and efficiency of a solar-thermal conversion system are determined by several factors, includ-

ing the cost and efficiency of the absorbing surface. The important parameters of the absorber are solar absorptance, emittance, and mean lifetime at the operating temperature. In a solar-thermal system, net efficiency depends on the operating temperature as well as the spectral behavior of the absorbing material. Ideal spectral behavior would be exhibited by complete absorption over the solar spectrum ($\lambda = 0.3\text{--}2.0\ \mu\text{m}$) and no absorption for $\lambda > 2.0\ \mu\text{m}$ [1] at the operating temperature of the surface. Such a surface would have a low thermal emittance because of the reciprocity between reflectance and emittance at the wavelengths near the peak of its black body distribution curve. Those surfaces showing promise are electrodeposited films of black chrome [2-4] and black nickel [3], interference multilayers [5], and composite-layer structures [3, 6, 7]. Surfaces prepared by deposition of tungsten dendrites [8] are found to have high solar absorptance and good thermal stability, qualities that make this material attractive for high-temperature systems in which high sunlight concentration is used. These structures depend for their solar absorptance on multiple reflections of the incident radiation. Therefore, the solar absorptance is limited by the spectral reflectivity of elemental tungsten, which is not highly wavelength selective. The reflectance of smooth tungsten in the region of the solar peak is about 0.50 and increases to about 0.9 at the long wavelength tail of the solar spectrum. For thick ($250\ \mu\text{m}$) dendritic layers where the incident radiation

Figure 1 Scanning electron micrographs of typical tungsten black dendritic and hillock surfaces. Also shown are ray tracing paths for normal incidence irradiation and subsequent reflections.



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undergoes many reflections before re-emission, the solar absorptance can be as high as 0.96 for normal incidence radiation. For thin ($2.50\ \mu\text{m}$) layers, the absorptance is only 0.76 because of the smaller number of reflections before re-emission. In either case, the absorptance falls off noticeably when the light is not incident normal to the surface because there are fewer reflections of the incident radiation before re-emission.

We have significantly increased the solar absorptance of dendritic tungsten films by applying, by means of electrochemical anodization, a conformal anti-reflective coating. The self-limiting nature of the anodization produces a uniform film of transparent WO_3 [9] over the irregular dendritic surface. Interference between the rays reflected from the top and from the bottom of the deposited layer results in a nonreflecting spectral band whose minimum depends in a very controlled way on the oxide thickness. Multiple reflections between the dendritic faces serve to increase the bandwidth of the nonreflecting region over that observed from a single reflecting surface.

At the anti-reflection minimum the total reflectance can be reduced to as low as 2.5×10^{-4} in the case of thick dendritic films. For thin layers, the solar absorptance is increased from 0.76 to 0.90. Also, the added coating decreases the directionality dependence of the absorption to such a level that solar tracking may not be necessary for a practical system. The coatings were found to be thermally stable at operating temperatures up to 520 K in air. At higher operating temperatures, the bare dendritic films are more attractive because the coating on anodized surfaces degrades at these temperatures. In addition, requirements on the emittance of the surface are relaxed for bare films.

Experimental procedure

Dendritic surfaces are grown by a chemical vapor deposition (CVD) process that uses hydrogen reduction of tungsten hexafluoride for depositing tungsten on surfaces of electropolished tungsten wafers [8]. Layers with thicknesses from $25.0\text{--}250\ \mu\text{m}$ are labeled *black dendritic* surfaces. Deposits from $2.50\text{--}25.0\ \mu\text{m}$ thick are denoted *grey dendritic* or hillock surfaces. The distinctions are evident in Fig. 1, which shows a conceptual ray tracing sketch and an actual microphoto of each type of surface morphology. The black dendritic surfaces have facet-included angles of less than 90° . For normal incidence illumination, the radiation is forced to undergo two or more reflections before re-emerging. For the hillock surfaces, the facet angles are greater than 90° , and the fiber heights are short, resulting in two or fewer bounces before the radiation re-emerges.

Anodization of the tungsten surfaces was performed in $0.1\ \text{N}$ phosphoric acid. The thickness of the resulting tungsten oxide coating was determined by the limiting

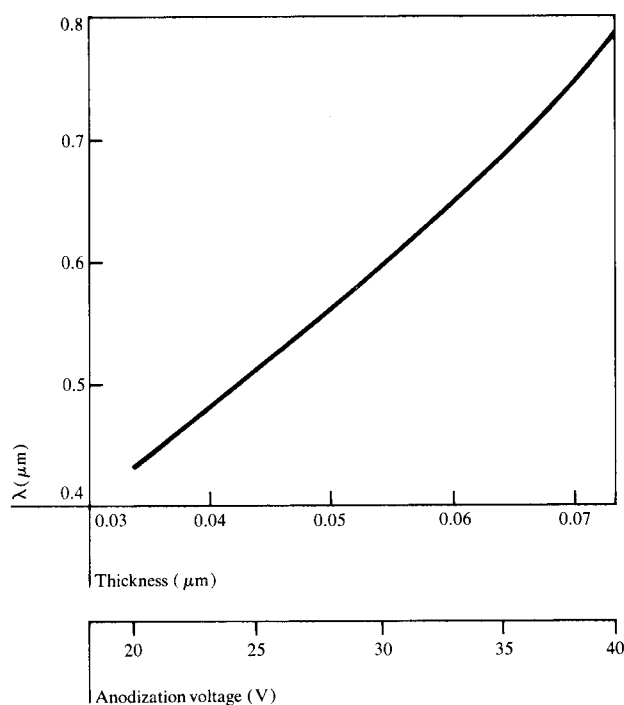


Figure 2 Wavelength of anti-reflection minimum as a function of anodizing voltage for WO_3 on tungsten. Coating thickness is also indicated.

Table 1 Refractive index values for the WO_3 oxide at various wavelengths.

λ (nm)	n
400	2.500
450	2.397
500	2.333
550	2.289
600	2.258
650	2.235
700	2.217
750	2.204
800	2.193
900	2.176

value of the anodization voltage chosen. Because oxide growth during anodization is a self-limiting process, the film thickness is uniform over each dendrite surface. Optical constants (including the refractive indices) for the deposited oxide were determined from ellipsometric measurements on smooth electropolished wafers anodized under the same conditions as the textured surfaces. A series of smooth wafers was anodized at various voltages in order to determine the anti-reflection minima plotted in Fig. 2. The film thickness, indicated in Fig. 2, was determined ellipsometrically, by using published values [10] for the optical constants of tungsten. Table 1 lists the in-

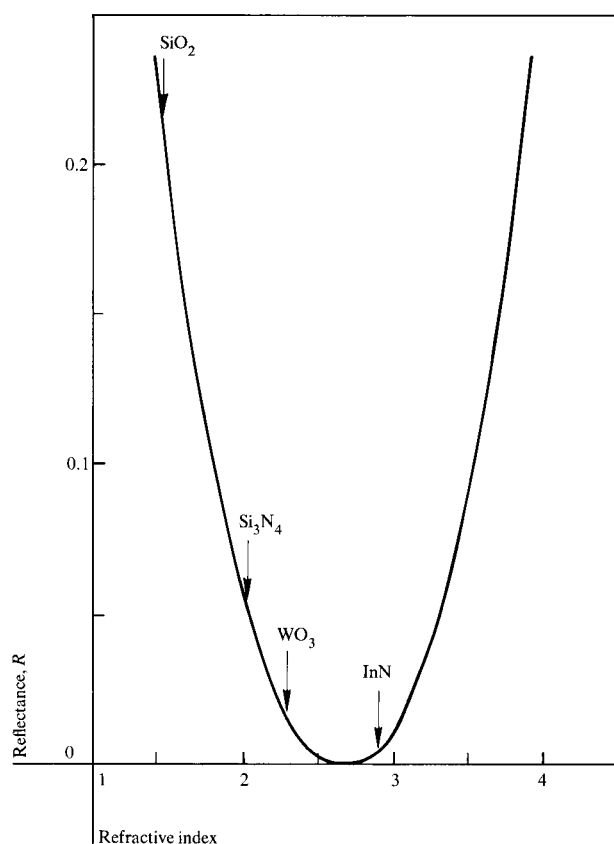


Figure 3 Calculated reflectance dependence on refractive index of coating materials on tungsten. Several coating materials are indicated at their respective index values. Curve is calculated for $\lambda = 550$ nm, adjusting the coating thickness to be the optimum value for minimum reflection.

dices of refraction n at various wavelengths. Figure 3 shows the calculated reflectances at 550 nm for anti-reflective coatings of different n on tungsten. The thicknesses of the various anti-reflective coatings at each n were chosen so as to minimize the reflectance at 550 nm. The WO_3 index value of 2.289 is fairly close to the ideal value of approximately 2.60. The suitability of the alternative coating materials SiO_2 , Si_3N_4 , and InN is also indicated on the curve.

The total reflectance R_T data were obtained with an integrating sphere similar to that described by Edwards et al. [11]. The sphere was about 23 cm in diameter, and was lined with a thick coating of MgO ; it had small ports for incident illumination, viewing, and detection. The illumination source was either a Xe or Zr arc lamp coupled with a 0.25-m-grating monochromator. Either a GaAs photocathode photomultiplier or a thermoelectrically cooled PbS cell was used for optical detection. The light was chopped at 400 Hz and the signal was amplified by a phase-sensitive detector. A long focal distance illumina-

tion geometry provided a sampling area of about 4×8 mm; the incident half angle was less than 2° . Measurements were made for angles of incidence up to 80° .

Sample wafers 2.5 cm in diameter were mounted on a rotatable holder at the center of the sphere. Suitable baffling was installed to prevent direct viewing of the sample by the detector. The reference surface was a diffuse reflector made of Eastman White Reflectance Coating [12] mounted on the reverse side of the holder. The decrease in reflectance of the reference coating [13] at wavelengths beyond $1.0 \mu\text{m}$ was included in the analysis of the reflectance data.

Results

The reflectance of smooth electropolished tungsten is shown in Fig. 4 (curve B). The data were taken at about 5° from normal incidence and agree with the reflectance obtained by using the published optical constants [10] for elemental tungsten. Curve A in Fig. 4 shows the decreased reflectance resulting from an anti-reflective coating of WO_3 , where the smooth tungsten surface was anodized to 33 V. The reflectance is selectively reduced to less than 0.04 at $\lambda = 630$ nm, and is significantly reduced over the visible portion of the spectrum. The coating is thin (about 60 nm), and thus it has little effect on the infrared reflectance ($\lambda > 2.0 \mu\text{m}$). The anti-reflective coating increases the solar absorptance of smooth tungsten without significantly increasing its emittance. However, the absorption band of smooth anodized tungsten is too narrow to be of importance as a solar absorber.

For deposits of grey ($\approx 25.0 \mu\text{m}$) dendritic tungsten, the reflectance (curve B, Fig. 5) is about 0.20 in the region of the solar peak. Figure 5 shows the enhancement of the absorption upon anodization (curve A) of such a hillock surface. Here the normal-incidence total reflectance has been reduced from 0.4 to 0.013 at $\lambda = 630$ nm. The 0.05 difference in reflectance at the long wavelength region is due to slight differences in surface topography for the two samples and is not attributed to the influence of the anti-reflective coating.

Black ($\approx 250 \mu\text{m}$) dendritic layers exhibit a normal incidence R_T of approximately 0.025 in the visible spectrum, which indicates an average of several bounces of the incident radiation before re-emergence. Figure 6 illustrates the reduction in reflectance for a typical black dendritic surface (curve B) upon anodization to 33 V (curve A). The sample illustrated has a minimum R_T of 0.0006. It is evident that an additional benefit of the anodization is the increase in the width of the anti-reflection curve due to multiple bounces. The total reflectance is less than 0.01 for wavelengths from $0.400 \mu\text{m}$ to greater than $1.000 \mu\text{m}$. The same black dendritic sample, after being stripped in NH_4OH and then re-anodized to 22 V, has a minimum R_T of 0.00025 at $\lambda = 0.475 \mu\text{m}$. The index of refraction n

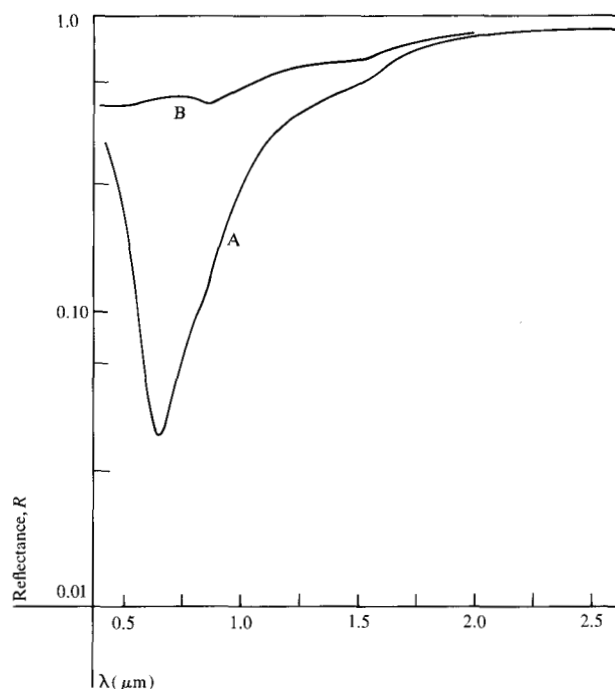


Figure 4 Normal-incidence reflectance of smooth electropolished tungsten. Curve A is after anodization to 33 V.

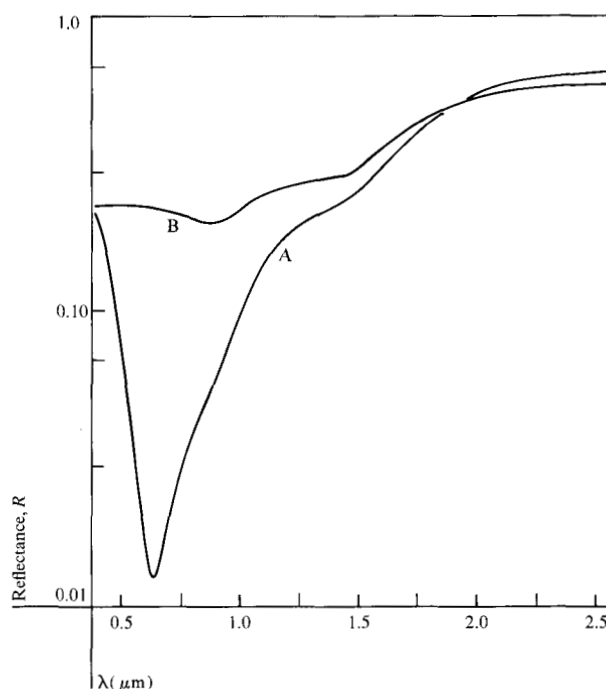
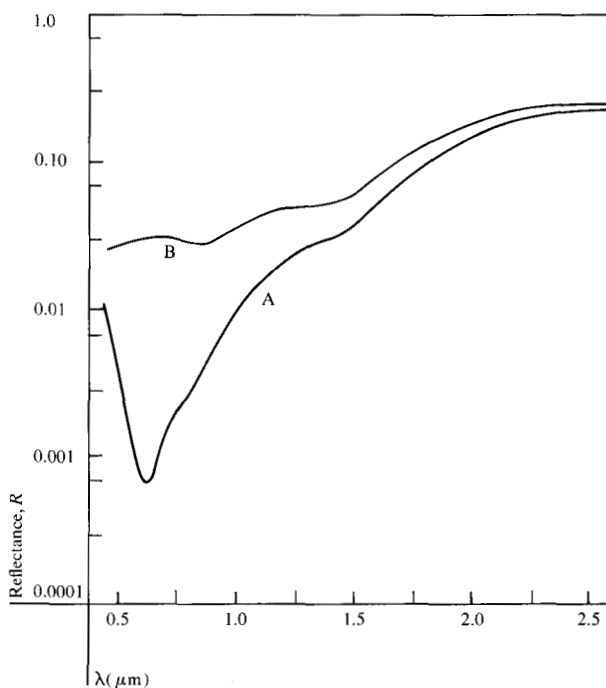


Figure 5 Normal-incidence total reflectance of hillock tungsten. Curve A is after anodization to 33 V.

match between the oxide and tungsten is closer to being ideal for destructive interference at the shorter wavelengths. This effect is shown in Fig. 7, where the same film has been anodized to three different voltages (22, 33, and 48 V) to produce anti-reflection minima at three widely separated wavelengths. The significant improvement as the coating is adjusted for shorter wavelength anti-reflection demonstrates the sensitivity of the reflectance to the refractive index match of substrate and oxide.

The figure of merit for solar absorbing surfaces is (α_s/ϵ_H) , where α_s is the average solar absorptance and ϵ_H is the hemispherical emittance at the temperature of operation. In Figs. 8(a-b), we show the solar absorptances for AM2 (solar spectral radiance at the earth's surface under normal, cloudy weather conditions) of both the thin (grey) and thick (black) tungsten deposits as a function of angle of incidence. For black dendritic surfaces, Fig. 8(a), the absorptance increases from 0.96 to 0.99 at normal incidence upon anodization and by an even greater factor for more glancing angles. The data demonstrate that a solar absorptance of greater than 0.90 is obtainable at angles of incidence from 0° to greater than 60°. For the thin deposits, Fig. 8(b), an even larger fractional improvement upon anodization is achieved as the absorptance is in-

Figure 6 Normal-incidence total reflectance of black dendritic tungsten. Curve A is after anodization to 33 V.



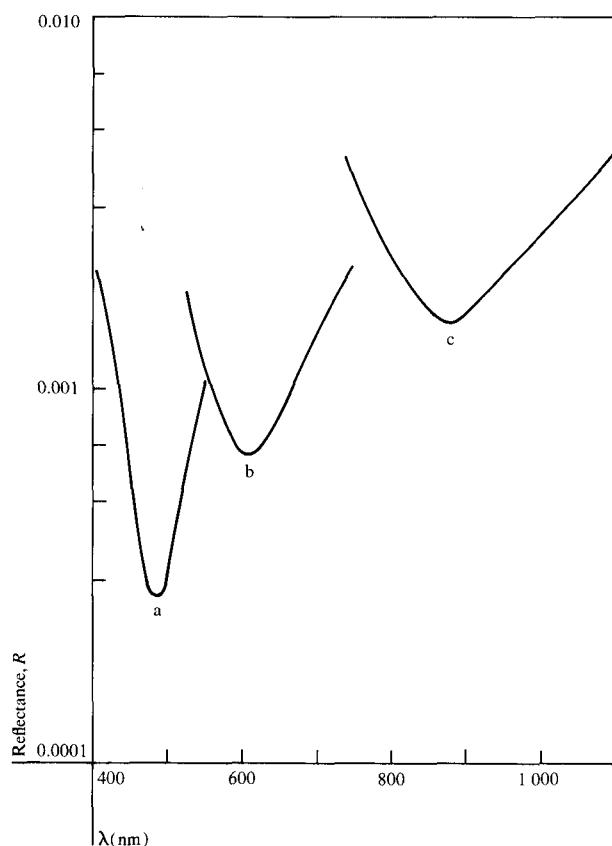


Figure 7 Normal-incidence total reflectance of black dendritic tungsten anodized to three different voltages: (a) 22, (b) 33, and (c) 48 V.

creased from 0.76 to 0.90. Here again, the dependence of the absorptance upon the angle of incidence is significantly improved following anodization.

The hemispherical emittance ϵ_H of these structures was determined by the thermal decay rate technique [14]. The samples were suspended by thin ($\approx 75 \mu\text{m}$) thermocouple wires from a holder mounted in a chamber evacuated to about $1.3 \times 10^{-1} \text{ Pa}$ (10^{-3} torr). The samples were heated radiantly to 523–573 K and the temperature decay rate was monitored when the heat source was blocked. The interior of the chamber was blackened to minimize stray reflections and to maximize the radiant cooling of the sample. The emittance is calculated from

$$\epsilon_H = \frac{C_p(\Delta T/\Delta t)}{A\sigma(T_0^4 - T_s^4)},$$

where T_s = sample temperature, C_p = heat capacitance, A = sample area, σ = Stefan-Boltzmann constant, and T_0 = chamber-well temperature.

Values for the emittance are very sensitive to the surface topography. For the hillock tungsten of the type shown in Fig. 1, the emittance was measured to be 0.18.

By contrast, the corresponding value for the black dendritic surface of Fig. 1 is 0.55. Slightly mechanically roughened tungsten surfaces have an emittance as low as 0.065 but the solar absorptance is only 0.78 for an anodized surface of this type. This available range of emittance values indicates that preparation conditions can be adjusted to produce a surface topography that maximizes (α_s/ϵ_H) for a particular value of α_s . Preliminary findings indicate that an (α_s/ϵ_H) of 5 for an α_s of 0.90 can be obtained from a hillock-type film anodized to 33 V.

The thermal stability of the anodization coating was tested by first radiantly heating the samples until a visual change was apparent in the surface color, and then by monitoring the change more carefully with the reflectance apparatus. The oxide shows good stability in air up to 473 K. At about 523 K, a slow shift in the anti-reflection minimum to longer wavelength occurs as the refractive index apparently increases. We have determined that this change in the optical properties of the oxide is associated with structural phase changes. Electron diffraction scattering measurements have demonstrated a shift from amorphous to crystalline structure upon prolonged heating at 523 K. The amorphous-to-crystalline phase transition shifts the absorption maximum to a slightly longer wavelength without significantly altering the spectral selectivity of the surface. At temperatures above 523 K, additional permanent changes occur in the optical properties of the oxide, resulting in a slow and irreversible reduction in the absorptance, which destroys the selective solar absorption properties of the surface. Three samples of anodized tungsten were life tested for 16 months in the laboratory environment. Samples were heated to 323, 473, and 548 K by radiant heating for eight or more hours per day. The two lower temperature samples remained amorphous and maintained their original properties, while the sample at 548 K went through an initial degradation change and then visually remained the same throughout the experiment.

Conclusions

A conformal, anti-reflective coating is shown to increase the solar absorptance and to significantly enhance the spectral selectivity of dendritic tungsten surfaces. Thin dendritic or hillock surfaces on which an anti-reflective surface was formed by anodization were found to exhibit a solar figure of merit (α_s/ϵ_H) of about 5. The conformal coating increases the average solar absorptance of the hillock surface from 0.76 to 0.90, and decreases the dependence of the absorptance on the angle of incidence. This results in an acceptance cone with a total included apex angle as large as 120° . One now is allowed considerable flexibility in optimizing absorptance and (α_s/ϵ_H) for various solar absorber applications below 523 K; this results from the range of surface topographies obtainable

from the vapor growth of tungsten, and from the ability to control thicknesses of anti-reflective coatings by means of anodization.

Thick or black tungsten films are not as well suited for some low-temperature solar collectors because of the high (0.55) emittance values. However, anodized surfaces of this type do exhibit very high solar absorptances (0.99), which makes surfaces of this type attractive in solar applications where high emittance can be tolerated. In addition, anodized black dendritic surfaces show a total reflectance as low as 2.5×10^{-4} at wavelengths in the visible spectrum. Such extremely high selective absorptance should be useful in laser beam attenuation.

The concept of using a multi-bounce textured surface in combination with a conformal, anti-reflective coating to achieve a broad spectral absorption may be extended to other material systems that would tolerate higher temperature operation.

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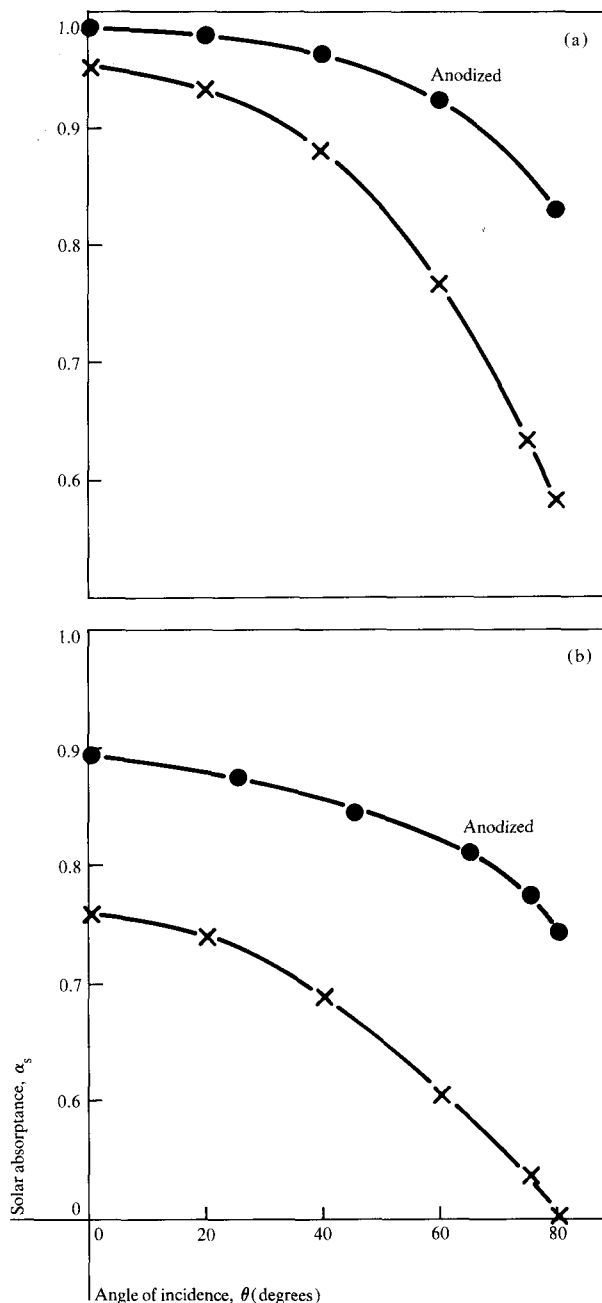


Figure 8 Directionality dependence of solar absorptance α_s for (a) black dendritic and (b) hillock surfaces both with (●) and without (x) anti-reflective coating. Angles of incidence are with respect to substrate plane.

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