THEORETICAL EVALUATION OF SELECTIVE RADIATION-ABSORBING SURFACE

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Abstract

An algol computer program is described, by means of which the spectral reflectivity for any angle of incidence may be calculated for a surface consisting of up to two thin absorbing films on a bulk substrate. The values of optical constants, n and k, for the materials used and also the thickness of the films, are the only data required. Calculated reflectivities have been shown to be consistent with experimental results.

Historical Background

There is now a vast amount of literature available on the subject of direct utilisation of the sun's energy. Daniels (1964) describes the well-established principles whereby the sun's rays can be used to heat water, cook food, operate refrigerators or air conditioners, generate electricity or distill salt water to produce drinking water. Numerous devices have been shown to work satisfactorily, but with few exceptions, interest has remained lukewarm. It was almost always cheaper or more convenient to use some other source of energy, usually derived from oil.

There are signs now that this situation may be changing. The trend of increasing costs of oil, and hence of electricity, is not likely to be reversed. Consequently, there has been a great revival of interest in solar energy schemes, not of course as a replacement of conventional energy sources but as a useful supplement. The conference of the International Solar Energy Society, held in Paris in 1973, attracted some 300 papers, of which nearly 100 dealt with the use of solar radiation as an energy resource. The conclusions of a Solar Energy Panel, appointed by the U.S. government, was that a staggering 20% of the annual power expenditure of the U.S.A. could be saved by making greater use of solar energy for heating and cooling buildings (W.R. Cherry and F.H. Morse 1973).

For a tropical country such as this, there is a great deal that can be done even now using present knowledge. Each house in Tanzania has about 750 watts (approximately the power of one electric cooker plate) falling on each square metre area of its roof at midday. If used for the distillation of sea water in a simple solar still, for example, this represents the production of about one half litre of pure drinking water per hour. The problems, then, are not technical, but simply those of popularisation.

The efficiency of solar devices can be greatly increased by the application of basic physical principles. In whatever device the energy is to be used, the solar radiation must first be absorbed by some material surface, the optical properties of which are a crucial factor in determining the proportion of incident energy which is absorbed, and the proportion which is reflected and therefore lost. In this paper the principles for the production of a surface having maximum nett absorption of energy are outlined, and a computer method demonstrated for the calculation of absorption for specific surfaces.

Introdution

For many years, inventors of solar devices have employed absorbing surfaces which were painted or coated with black materials because these are more effective in absorbing radiant energy. However, even the perfect-black-body surface of Theoretical Physics has the disadvantage in this case that when its temperature is raised, it also becomes a very good radiator of energy. What is required for maximum nett gain of energy is a surface which is a good absorber of radiation, but a poor emitter. This is impossible to achieve at any single wavelength, but for use in solar devices, one may make use of the fact that the peak intensity in the sun's spectrum occurs at a wavelength of about 0.5 micron, whereas the peak of the radiated energy from a hot object, even at temperature of 600°C is about 4.0 micron. This difference in peak wavelength, shown in figure 1A and 1B, leads to the concept of the **selective surface**, which has the spectral reflectivity shown in figure 1C. Such a surface appears black for sunlight and is consequently a good absorber, but white for longer wavelengths and is hence a poor radiator of its own energy. Such a surface, placed in sunlight, becomes much hotter than even a perfect-black-body surface.

Selective surfaces can be manufactured by superimposing thin layers, or firms, of suitable materials having the required optical properties. A copper surface, for example, can be made selectively absorbing oy careful oxidation. The thin film of oxide increases the absorption at short wave-

lengths but has very little effect at longer wavelengths (Close 1962). Electro-deposited layers of nickel, if sufficiently thin, can also produce the same effect (Silo and Mladinik 1969). Alternatively, if cost is not an important factor, virtually any required shape of spectral reflectivity can be generated by vacuum deposition of alternate layers of metal and insulator (Meinel 1972). The ideal surface, however, would remain highly selective for different angles of incidence, would be cheap to produce in large areas and would be stable over extended periods at high temperatures.

From the great variety of materials and layer thicknesses possible, promising combinations are chosen after theoretical calculations of the spectral reflectivity. These calculations as usually only possible numerically, and become so tedious that an electronic computer is essential. Let us consider briefly the established principles involved.

General Theory

It is a fundamental property of electromagnetic waves that on meeting the boundary between two media, a part of the energy of the wave is transmitted across the boundary (refracted) and part is reflected into the first medium. The relative proportions depend on the refractive indices of the two media, the angle of incidence and also on the orientation of the plane of vibration of the electric field of the wave with respect to the plane of incidence.

Consider light falling at an angle of incidence ϕ_1 on the plane boundary between two transparent media 1 and 2, having refractive indices n_1 and n_2 respectively. It can be shown (Born and Wolf 1964) that the ratio of the reflected amplitude to the incident amplitude, for light having the plane of the electric vector parallel to the plane of incidence (called the (p) component) is

$$r_{12(p)} = \frac{n_1 \cos\phi_2 - n_2 \cos\phi_1}{n_1 \cos\phi_2 + n_2 \cos\phi_1}$$

where $r_{12(p)}$ represents light travelling from medium 1 to medium 2 and ϕ_2 is the angle of refraction in medium 2.

For light having the plane of the electric vector perpendicular to the plane of incidence (called the (s) component from the German word 'senkrecht' meaning perpendicular) the amplitude ratio is

$$r_{12(s)} = \frac{n_1 \cos\phi_1 - n_2 \cos\phi_2}{n_1 \cos\phi_1 + n_2 \cos\phi_2}$$

Plane polarised light in any orientation may be treated by considering its

components in the (p) and (s) directions. The reflected energy, proportional to the square of the amplitude, is shown in Figure 2 which is a plot of $[r_{12(p)}]^2$ and $[r_{12(s)}]^2$ against angle of incidence ϕ_1. Note that at the "Brewster Angle" the value of $r_{12(p)}$ is zero so that the reflected light is entirely plane polarised in the (s) direction.

The ratio of transmitted amplitude to incident amplitude, called the transmission coefficient, t ,also differs with the orientation of the plane of the electric vector with respect to the plane of incidence.

For the (p) component, $\quad t_{12(p)} \quad = \quad \dfrac{2n_1 \cos\phi_1}{n_1 \cos\phi_2 + n_2 \cos\phi_1}$

For the (s) component, $\quad t_{12(s)} \quad = \quad \dfrac{2n_1 \cos\phi_1}{n_1 \cos\phi_1 + n_2 \cos\phi_2}$

For the transmitted wave, travelling in a different medium and in a changed direction, the conservation of energy flow across the boundary requires that the transmitted energy is not given by the square of t_{12}, but by the quantity $t_{12} \cdot t_{21}$ (Born and Wolf 1964 Page 41). The law of conservation of energy therefore gives :—

$$1.0 \quad = \quad \left[r_{12} \right]^2 \quad + \quad t_{12} \cdot t_{21} \qquad \text{(i)}$$

$$\underset{\substack{\text{Incident} \\ \text{Energy}}}{} = \underset{\substack{\text{Reflected} \\ \text{Energy}}}{} + \underset{\substack{\text{Transmitted} \\ \text{Energy}}}{}$$

All the equations so far apply only for transparent materials, but may be modified for absorbing media simply by replacing the refractive index, n by the complex refractive index, N in which the imaginary part is related to the absorption of energy by the medium (Heavens 1965). To show this, consider light moving through a vacuum. The variation of intensity of the electric field, E with distance x and time t is given by

$$E = E_o \cos w \left(\frac{nx}{c} - t \right) \qquad \text{where n is the reflective index.}$$

When the light penetrates a smooth metal surface, for example, the free electrons of the metal gain energy from the oscillatng electric field whose intensity is thereby attenuated exponentially with distance. The field therefore becomes $E = E_o e^{-\frac{kwx}{c}} \cos w \left(\frac{nx}{e} - t \right)$

where k is defined as the "extinction coefficient". Writing this is the complex form gives $\quad E = E_o e^{-iw} \left(N \frac{x}{c} - t \right)$

where $N = n - ik$ and is called the complex refractive index".

When using the complex refractive index for non-normal incidence, the form of Snells Law is still valid. For absorbing media, this becomes

$$N_1 \sin\phi_1 \ = \ N_2 \sin\phi_2$$

so that the sines of the angles of refraction become complex quantities. The physical significance of this lies in the fact that the planes of equal phase and of equal amplitude no longer coincide. The planes of equal amplitude are always parallel to the surface while the planes of equal phase make some other angle with them, which varies with the angle of incidence.

Although the penetration depth of electromagnetic radiation into a metal surface is very small, usually 20 to 30 nm, when very thin layers of metal are formed on a substrate, the intensity of multiply-reflected beams may be sufficiently large as to modify appreciably the amplitude and phase of the reflected light. Consider Figure 3 which represents an absorbing film (medium 2) having a thickness of d_2, on an absorbing substrate (medium 3).

Light, assumed to have unit amplitude, falls on the surface at an angle of incidence ϕ_1. The reflected and transmitted amplitudes r_{12} and t_{12} are shown. Thereafter, the amplitudes of the various beams are indicated, noting that each time the light crosses the film, the extra optical distance travelled through medium 2 is $N_2 d_2 \cos\phi_2$, so that the phase change produced is given by the factor

$$e^{-i \left(\frac{2\pi}{\lambda} N_2 d_2 \cos\phi_2\right)} = e^{-i\delta_2} \quad \text{(say)}$$

The real part of this exponent represents the amplitude reduction due to the absorption in the medium, while the imaginary part gives the true phase change. The total reflected amplitude is obtained by summing, in both amplitude and phase, the infinite series of refleted beams. We may then attribute this to the effect of a ficticious surface going directly from medium 1 to medium 3, and equate the reflectd beam to an "effective" r_{13}.

Hence,

$$r_{13} = r_{12} + t_{12}t_{21}r_{23}e^{-2i\delta_2} + t_{12}t_{21}r_{21}r_{23}^2 e^{-4i\delta_2}$$

$$+ \ t_{12}t_{21}r_{21}^2 r_{23}^3 e^{-6i\delta_2} + \ . \ . \ . \ .$$

Apart from the first term r_{12}, the right-hand side of the above series is

a geometric progression having a first term, a equal to $t_{12}t_{21}r_{23}e^{-2i\delta_2}$ and a ratio, r equal to $r_{21}r_{23}\,e^{-2i\delta_2}$. The sum of such a series is given by the formula $\sum = \dfrac{a}{1-r}$

so that

$$r_{13} = r_{12} + \frac{t_{12}t_{21}r_{23}\,e^{-2i\delta_2}}{1 - r_{21}r_{23}e^{-2i\delta_2}} \qquad\qquad \text{(ii)}$$

We already have the result from equation (i) which originated from the conservation of energy, that $t_{12}t_{21} = 1.0 - r_{12}^2$ so when this is substituted into equation (ii) along with the relation $r_{21} = -r_{12}$ we obtain

$$r_{13} = \frac{r_{12} + r_{23}\,e^{-2i\delta_2}}{1 + r_{12}r_{23}e^{-2i\delta_2}}. \qquad\qquad \text{(iii)}$$

In a similar way, it may be shown that the "effective boundary" has a value of transmission coefficient, t_{13} given by

$$t_{13} = \frac{t_{12}t_{23}\,e^{-i\delta_2}}{1+r_{12}r_{23}e^{-2i\delta_2}} \qquad\qquad \text{(iv)}$$

For non-normal incidence, the different values of reflection and transmission coefficients at each real boundary for the (p) and (s) components ensures that the numerical values of both r_{13} and t_{13} are different for the (p) and (s) orientations. At normal incidence, the distinction between the (p) and (s) planes disappears so that the corresponding values of r_{13}, and also of t_{13}, become equal.

It may be seen from a comparison of figures 3 (a) and 3 (b) that the two boundaries 1-2 and 2-3 have been replaced by a single "effective boundary" 1-3. This process can be continued indefinitely to include the next boundary each time. This method has been employed by Vasicek for several **transparent** films superimposed (Vasicek 1950).

Essentially the same method can be employed for absorbing films **BUT** the simplifying assumptions made during the summation of the series **may not now be made.**

(a) It was assumed that $r_{12} = - r_{21}$

We have now $\quad r_{13} = \dfrac{r_{12} + r_{23}\, e^{-2i\delta_2}}{1 + r_{12} r_{23}\, e^{-2i\delta_2}} \quad$ from equation (iii)

and we deduce $\quad r_{31} = \dfrac{r_{32} + r_{21}\, e^{-2i\delta_2}}{1 + r_{32} r_{21}\, e^{-2i\delta_2}} \qquad\qquad$ (v)

Hence $\quad r_{31} \neq - r_{13}$

(b) The conservation of energy across the effective boundary 1-3 is not expected to apply because medium 2 is absorbing and some of the energy will be directly absorbed and converted into heat.

Hence $\quad t_{13} \cdot t_{31} \neq 1.0 - (r_{13})^2$

The multiple reflections can still be summed however, but without making the above assumptions. Using the same method of summing the multiple reflections leads to

$$r_{14} = r_{13} + \frac{t_{13} \cdot t_{31} r_{34}\, e^{-2i\delta_3}}{1 - r_{31} r_{34}\, e^{-2i\delta_3}} \qquad\qquad \text{(vi)}$$

and into this equation the various coefficients must be substituted directly.

The numerical values of r_{13}, r_{31}, t_{13} and t_{31} for both the (p) and (s) components must be calculated. Since so many complex quantities are involved, the enormous amount of computation is almost impossible without the use of an electronic computer.

The Program RFL 2 (Reflectivity of two films on a substrate)

The program is divided into convenient sections of which only the outline is given here. Full details can be found elsewhere (O'Shea 1974)

In the first section the cosines of the complex angles of refraction are calculated for each medium, for a given angle of incidence. (This is later varied in steps from zero to 90 degrees). Then the reflection and transmission coefficients for each individual boundary are computed and stored.

The individual boundary coefficients are then summed to the surface 1-4, according the equations (iii), (iv) and (vi). The final values of r_{14} for both the (p) and (s) components are given as single complex numbers in the form $r_{14} = a + ib$

The reflected energy is then obtained as $\quad R = |r_{14}|^2 = a^2 + b^2$

The values of energy reflectance, calculated for the (p) and (s) components are then averaged, since it may be assumed that direct sulight is randomly polarised.

Each data card must supply the appropriate values of n and k for each medium at the particular wavelength under consideration. The energy reflectance throughout the spectrum can then be investigated.

Caution must be exercised in choosing values of optical constants from published data. Values of n and k vary greatly with crystal structure, grain size, purity and smoothness of a surface. Also, these constants may be vastly different for the same material in bulk form or in the form of a thin film.

Specimen Calculation

The semiconducting material lead sulphide (PbS) exhibits an optical absorption edge and is one of several possible materials for the manufacture of selective surfaces. The properties of this material on a gold substrate were therefore investigated. The use of gold substrates is not prohibitively expensive because a layer of gold having thickness greater than the penetration depth of the electric field, say 40 nm, may be considered as "bulk" gold. The optical constants of gold, shown below in table 1, were used as data in program RFL 2 and the resulting variation of reflectivity with wavelength is shown in figure 4. It can be seen that the reflectivity remains highover most of the visible part of the spectrum.

The corresponding values of optical constants for lead sulphide, shown in table 2, were then used to investigate the effect of several layers of varying thickness on top of the gold. The results shown in figure 4 indicate that a layer of lead sulphide of thickness 15 nm produces the the greatest selectivity, i.e. low reflectance (high absorption) for short

wavelength sunlight, but high reflectance (low emissivity) for infra-red. This compound surface would therefore act as an efficient solar absorbing plate.

TABLE 1

OPTICAL CONSTANTS OF GOLD

Wavelength (n m)	n	k	
414	1.30	1.90	*
546	0.50	2.35	
620	0.30	2.90	
827	0.30	2.50	**
1240	0.32	8.00	
1550	0.75	9.00	
2066	1.00	11.50	

* Mayer, E. 1967, J. App. Phys. (US) 38 N9 pp. 3682-4
* * Motulevitch 1965, Sov. Phys. J.E.T.P. 20 pp. 560-72

TABLE 2
OPTICAL CONSTANTS OF LEAD SULPHIDE

Wavelength (n m)	n	k	
414	4.02	3.04	
546	4.40	1.70	
620	4.45	1.52	
827	4.50	0.91	***
1240	4.40	0.72	
1550	4.2	0.5	
2066	4.2	0.4	

* * * Wessel, R. 1967, Phys. Rev. (US) 153 N3 pp. 836-40

The selectivity may be improved by the addition of a further layer of transparent material to act as an antireflection coating. The required optical thickness of this coating for a wavelength λ is a multiple of $\frac{\lambda}{4}$. Magnesium fluoride, having a refractive index of 1.38, is a traditional material used for this purpose. Table 3 below shows the required actual thickness of an MgF_2 layer for various wavelengths.

TABLE 3

Actual Thickness of MgF_2 Antireflection Coatings

Wavelengths λ (n m)	Coating Thickness $t = \dfrac{\lambda}{4 \times 1.38}$ (n m)
414	70
442	80
500	90.5
600	109

The effect on reflectivity of the addition of a layer of magnesium fluoride. 80 nm thick to the surface consisting of 15 nm of lead sulphide on gold is shown in figure 5. As required, the short-wavelength reflectivity is considerably reduced, while the long-wavelength value is only slightly affected.

The variation of reflectivity with angle of incidence is shown in figure 6 for the single wavelength of 546 nm. As can be seen, the value is reasonably constant for angles below 50 degrees.

Conclusions

The program RFL 2 has been developed and satisfactorily predicts the spectral reflectivity of a double-layer coating on a metal surface. A large variety of materials can now be investigated, along with the effects of layer thicknesses, angle of incidence variations and also changes of optical constants brought about by high temperatures or aging. The aim is, of course, to suggest optium compound surfaces for further experimental study and ultimately commercial production.

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