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THIN FILMS

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CHAPTER 6

optical properties and applications of thin films

THE high performance of modern optical instruments depends upon the quality of components such as lenses, prisms and mirrors. These all have reflecting or partially reflecting surfaces, and their performance would be limited by the natural reflectivities of the materials of which they are made, were it not for the possibility of altering the reflectivity by the deposition of a thin transparent film. This technique allows, for instance, the control of losses due to reflection in lenses, and makes possible the construction of mirrors with unique properties. The method is even more useful in equipment designed to utilize infra-red radiation, since reflection losses are much greater in the infra-red than in the visible part of the spectrum. In this chapter we shall therefore interpret the term 'optical' to include infra-red radiation, and, moreover, to include the technique of influencing the emission and absorption by a body of heat radiation (which is at infra-red wavelengths).

Reflection at a surface: the electromagnetic theory

The simplest case to study is shown in fig. 6.1, where a thin film of a transparent medium of refractive index n_1 is shown on the surface of a glass substrate of refractive index n_2. The thin film could in principle be made of glass, but other materials, such as silicon monoxide, magnesium fluoride or zinc sulphide, are much easier to deposit as thin films and are commonly used for this purpose.

The figure illustrates the fact that reflections occur at both surfaces of the thin film, so that the total intensity of the reflected radiation must be found by adding up the intensities of all the partially reflected beams. Since there is the possibility of *interference* between these beams, as they are initially coherent and have travelled different distances, the summation of their intensities is not straightforward. Moreover, it is necessary to know the relative strengths of the rays, so first we must investigate the case of a single reflection at a surface.

Figure 6.2 shows the usual ray diagram for reflection of light at the surface separating media of refractive indices n_1 and n_2, where n_2 is assumed the greater. We know that the angles of incidence and reflection are equal, and that the transmitted ray is refracted at an angle ϕ_2 to the normal, given by Snell's law:

$$n_1 \sin \phi_1 = n_2 \sin \phi_2.$$

The question we must answer now is: what are the relative *intensities*
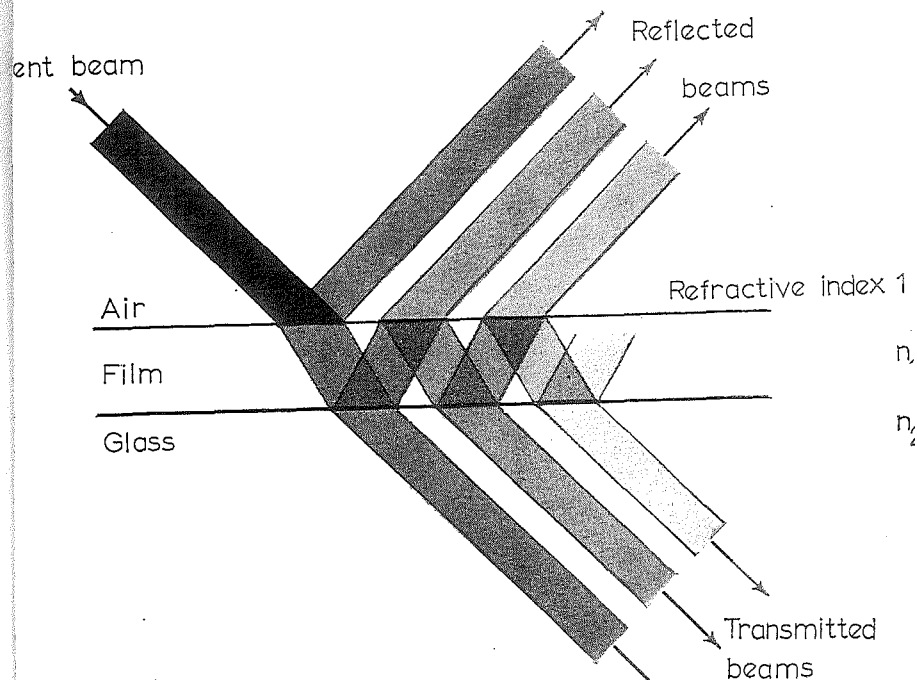
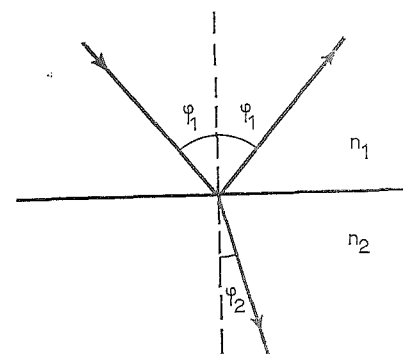Fig. 6.1. Multiple reflections in a thin film.

Fig. 6.2. Ray diagram for a single surface.

of the incident, refracted and reflected rays? These can be calculated using the theory of electromagnetic waves, of which light is but one example. An electromagnetic wave consists of a wave-like combination of electric and magnetic fields. Figure 6.3 is an attempt to indicate what we mean by this. At each point along a 'ray' of light there is an electric field and a magnetic field which are at right angles to each other

and to the ray itself. The strengths of both fields vary sinusoidally along the ray, and the whole distribution is moving along at 3×10^8 m s^{-1}. The wavelength ranges from 400 nm at the violet end of the visible spectrum, through 700 nm in the red, to several tens of micrometres in the far infra-red.

A beam of light in which the electric field is everywhere parallel to a given direction is said to be *plane polarized*. However, the light from an ordinary source is unpolarized, since it is emitted from a multitude of independent atomic sources, each radiating light that is polarized in a different plane. Such light can be polarized by passing it through a suitable material, such as the 'polaroid' frequently used in sunglasses.
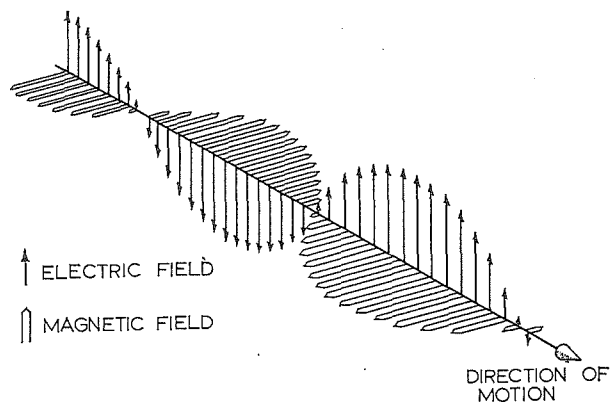

Fig. 6.3. Representation of an electromagnetic wave.

The intensity of a beam of light might be expected to depend upon the amplitude of the electric or magnetic fields; in fact, it is proportional to their product. Since the ratio of their amplitudes is always constant, the intensity is also proportional to the square of the electric field (multiplied by the refractive index), and use is made of this in calculating the reflected and transmitted intensities in the case illustrated in fig. 6.2. The details of this calculation are beyond the scope of this chapter, but we shall outline the method. It will be realized from the above discussion that the fact that the incident, reflected and transmitted waves in fig. 6.2 all have different intensities means that the amplitudes of these waves are also all different. But, at the interface between the two media, the field strengths on either side must obey the laws of electromagnetism. These show that the total electric or magnetic field in the first medium (the *sum* of the incident and reflected fields) is related to the corresponding field in the second medium by an expression which contains the permittivities or permeabilities of the two media. These last are, in fact, directly related to the refractive indices. By writing the equations which express these conditions, it is possible to relate the amplitudes of the three waves, and to deduce the reflection and transmission coefficients, i.e. the ratios of the amplitudes to the incident amplitude. It turns out that these ratios depend upon the angle (shown as α in fig. 6.4) between the electric field direction and the plane of incidence and also upon the angle of incidence, ϕ_1.
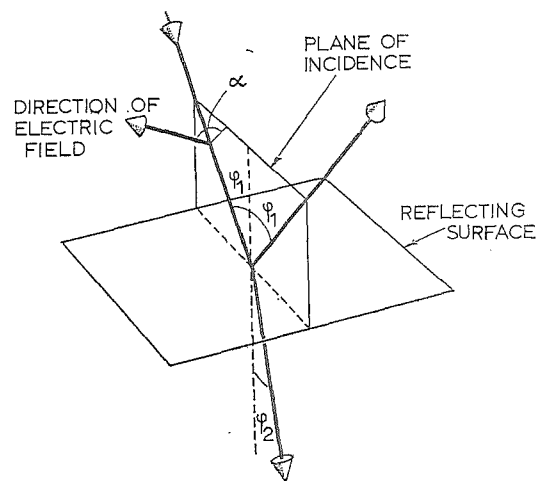

Fig. 6.4.

However, at normal incidence ($\phi_1 = \phi_2 = 0$) the distinction between different directions of the electric field disappear, and the expressions for the reflection coefficient r and the transmission coefficient t reduce to

$$r = \frac{n_1 - n_2}{n_1 + n_2}, \qquad (6.1\ a)$$

$$t = \frac{2n_1}{n_1 + n_2}. \qquad (6.1\ b)$$

The fact that r can be negative when $n_2 > n_1$ means only that the electric field in the reflected wave is *opposite in direction* to the incident electric field.

It is not possible to measure the amplitudes directly, but rather the energy carried by the beams (strictly, the energy crossing any plane in unit time) so that the ratio of the reflected and incident energies (reckoned in this way) is of interest. This is termed the *reflectance R*, and is simply equal to r^2 since the energy flow is the refractive index times the square of the amplitude of a wave. The *transmittance T* is similarly defined, but since the refractive indices differ in the two media, it is not just equal to t^2 but is given by

$$T = \frac{n_2}{n_1} t^2.$$

Using equations (6.1) the reflectance and transmittance of a single surface are easily obtained:

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2, \qquad (6.2\,a)$$

$$T = \frac{4n_1 n_2}{(n_1 + n_2)^2}. \qquad (6.2\,b)$$

At an air-glass interface, for which $n_1 = 1$ and $n_2 = 1\cdot 5$, the value of R is equal to $0\cdot 04$, i.e. 4 per cent of the incident light is reflected.

Note that, as you might expect, $R + T = 1$; this means that there is no loss of energy in the process of reflection. If the second medium is strongly absorbing, these equations are no longer accurate, but we shall not concern ourselves with this case.

Reflectance and transmittance of a thin film

In this section we shall describe how mathematical expressions may be constructed for the reflectance and transmittance of a thin film. Although the method is simple, the expressions are complicated, and the reader who wishes to overlook the mathematical details will nevertheless be able to understand the significance of the results.
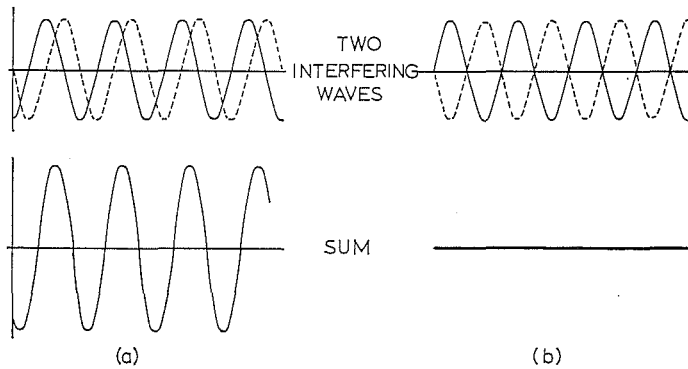
(a)   (b)

Fig. 6.5.

In fig. 6.1 we showed how a very narrow beam passes through a thin film on a transparent substrate. In practice, such a narrow beam cannot be used, and the various reflected and transmittted components overlap each other. The total energy in the transmittted beam cannot then be obtained simply by adding the energies directly because of the phenomenon of *interference*.

Two waves which overlap but are not exactly in phase, such as those shown in fig. 6.5 a, tend to partially cancel each other, because the total electric field strength at any point is the sum of two quantities which may differ in sign. This is the phenomenon we call *interference*. In fig. 6.5 b is shown a situation when the sum of the two waves is exactly zero everywhere!

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Thus to obtain the correct result when adding the amplitudes of the multiple reflections in a thin film we must take account of the relative phases of the components. The phases are controlled by the distances travelled by the various components, as illustrated in fig. 6.6. The transmitted ray T_2, for instance, has travelled further than the ray T_1 by
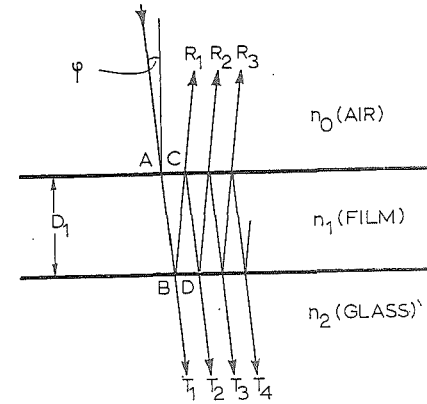
Fig. 6.6.

approximately the distance $(BC + CD)$; the same applies to any pair of adjacent rays. If this distance is not exactly equal to an integral number of wavelengths, then there will be some degree of cancellation in the transmitted beam. By adding up all the amplitudes, taking account of phase, it is found that the total reflectance and transmittance may be expressed straightforwardly in terms of the reflection and transmission coefficients r_1, r_2 and t_1, t_2, of the upper and lower interfaces[*]:

$$R = \frac{r_1{}^2 + r_2{}^2 + 2r_1 r_2 \cos \dfrac{2\pi(AB + BC)}{\lambda_1}}{1 + r_1{}^2 r_2{}^2 + 2r_1 r_2 \cos \dfrac{2\pi(AB + BC)}{\lambda_1}}, \qquad (6.3\,a)$$

$$T = \frac{t_1{}^2 t_2{}^2}{1 + r_1{}^2 r_2{}^2 + 2r_1 r_2 \cos \dfrac{2\pi(AB + BC)}{\lambda_1}}, \qquad (6.3\,b)$$

[*] R is the ratio of *intensities*, while the ratio r of reflected and incident *amplitudes* may be expressed most easily by using complex numbers, as is done in the theory of alternating currents in electricity. Thus

$$r = \frac{r_1 + r_2 \exp -2i\pi \dfrac{(AB + BC)}{\lambda_1}}{1 + r_1 r_2 \exp -2i\pi \dfrac{(AB + BC)}{\lambda_1}},$$

where $i = \sqrt{-1}$
R is now not just the square of r, but the square of its modulus. Thus R is just r multiplied by the complex conjugate of r.

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where λ_1 is the wavelength of the light in the film, which is smaller than that in air by the factor $1/n_1$. Note that the relation $r^2 + n_2 t^2/n_1 = 1$ allows us to write R in terms of r_1 and r_2 alone. At normal incidence ($\phi = 0$) these quantities can be expressed fairly compactly in terms of the refractive indices. Putting $n_0 = 1$ for air we find:

$$R = \frac{(n_2{}^2 + n_1{}^2)(1 + n_1{}^2) - 4n_2 n_1{}^2 + (n_2{}^2 - n_1{}^2)(n_1{}^2 - 1)\cos\dfrac{4\pi D_1}{\lambda_1}}{(n_2{}^2 + n_1{}^2)(1 + n_1{}^2) + 4n_2 n_1{}^2 + (n_2{}^2 - n_1{}^2)(n_1{}^2 - 1)\cos\dfrac{4\pi D_1}{\lambda_1}} \quad (6.4\,a)$$

$$T = \frac{8n_2 n_1{}^2}{(n_2{}^2 + n_1{}^2)(1 + n_1{}^2) + 4n_2 n_1{}^2 + (n_2{}^2 - n_1{}^2)(n_1{}^2 - 1)\cos\dfrac{4\pi D_1}{\lambda_1}} \quad (6.4\,b)$$

These are rather clumsy expressions, and it is easier to grasp their meaning if we plot R or T against the ratio thickness/wavelength, i.e. D_1/λ_1. This is done in fig. 6.7 for several values of the refractive index n_1 of the film, taking that of glass to be $1\cdot5$. Since R and T sum to unity, one graph suffices for both, with different scales for R and T as shown.
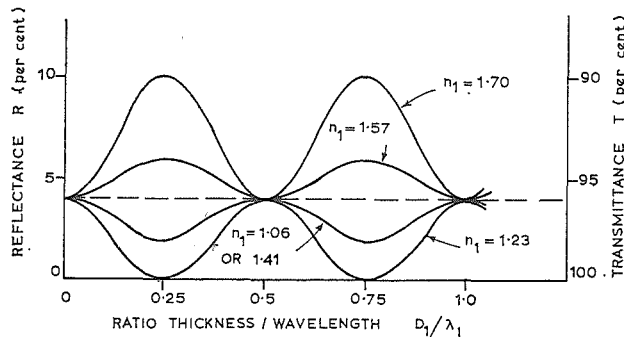
Fig. 6.7. Reflectance of a thin film coating on glass.

We see that, when D_1 is equal to one half wavelength or an integral multiple thereof, the reflectance and transmittance are unchanged from those of a plain glass surface. But a film with a thickness of a quarter wavelength or any *odd* multiple of a quarter wavelength produces a significant change in R and T. The most interesting result in the latter case occurs when $n_1 = 1\cdot23$, for then the reflectance is zero and the transmittance 100 per cent.

Although it is necessary to use mathematics to derive the shape of the curves in fig. 6.7, there is a simple physical explanation of the maxima and minima which they display. When $n_1 < n_2$ and the film is one quarter wavelength in thickness, the path difference between any two adjacent reflected rays (see fig. 6.6) is exactly one half wavelength.

This means that they are exactly 180° out of phase with each other, and tend to cancel as do the two waves in fig. 6.5 b. Unlike the latter, the two reflected rays in fig. 6.2 are not of equal amplitude so that cancellation is not complete. However, it may be complete when we consider *all* the reflected rays (see fig. 6.1) and if their relative amplitudes are suitably adjusted by controlling the refractive index of the film.

A similar argument explains how the reflectance maxima of fig. 6.7 occur. In this case the path difference between an adjacent pair of rays in the reflected beam is equal to the wavelength*, so that they add directly to one another. Moreover, in this case, *all* the rays are in phase and hence they add to give the maximum possible reflectance.

The value of the mathematical expressions for R and T is that they enable us to find the value of n_1 for which zero reflectance occurs. By equating R to zero and putting $D = \lambda_1/4$ we find

$$(n_2{}^2 + n_1{}^2)(1 + n_1{}^2) - 4n_2 n_1{}^2 - (n_1{}^2 - 1)(n_2{}^2 - n_1{}^2) = 0,$$

from which the result appears with great simplicity:

$$n_1 = n_2{}^{1/2}. \quad (6.5)$$

The film thickness required to obtain zero reflectance may now be written in terms of the wavelength *in vacuo*, λ:

$$D = \lambda/4n_1.$$

Using a value $1\cdot5$ for n_2 gives the value $n_1 = 1\cdot23$ quoted earlier, while for zero reflectance at a wavelength of 500 nm (roughly the middle of the visible spectrum) a thickness D_1 of $101\cdot6$ nm is required.

It is worth while remarking that these values also give zero reflectance for a beam of light incident on the film from within the glass. Indeed, all values of R and T are unchanged in this situation—this would have been clear from equations (6.4) had we retained the refractive index of air in them.

The result, that the transmission coefficient can be increased to 100 per cent, is most important for it means that the 8 per cent loss of light intensity which usually occurs on transmission through a lens or a sheet of glass can be reduced to an insignificant level simply by coating both surfaces with a film of suitable refractive index and thickness.

Another important result which may be guessed from fig. 6.7 is that, by suitably coating a highly reflecting surface, its reflectivity may be improved—indeed, if a sufficient number of layers are superimposed, the reflecting substrate becomes superfluous. Thus a mirror may be made from a multilayer structure of transparent media—the whole being highly reflective because the thickness and refractive index of each layer is carefully chosen to achieve this.

Yet another possibility arises in the control of the absorption of a

* When $n_1 > n_2$, we have to take account of the phase change of π upon reflection at the lower surface of the film.

body by coating the surface—this is important in the field of temperature control of satellites and in obtaining electrical power from solar energy. These topics will now be dealt with in more detail.

Anti-reflection coatings

Anti-reflection coatings are used today on the surfaces of lenses, windows and prisms of almost all optical and infra-red optical equipment. The most familiar to the reader is probably the 'blooming' layer on a camera lens. A good lens may consist of four or more components, each with two surfaces at which slightly less than 8 per cent of the incident light is lost—the total loss is thus upwards of 28 per cent. The appearance of a bloomed lens is due to the fact that the coating can eliminate reflection completely at only one wavelength, so that the complementary colour is reflected. Since the thickness is chosen to optimize the performance in the middle of the visible spectrum where the colour is a yellowish green, the colour of the coating is in fact blue.

The first such coatings were formed chemically by H. D. Taylor, and reported in his book *The Adjustment and Testing of Telescope Objectives*, published in 1896. It was thought at first that their effect was simply to alter the ordinary reflectance of the surface (i.e. that given in equation 6.2 *a*), and the true nature of their action was discovered only in 1934. Nowadays vacuum evaporation is the favoured method for producing the most durable and efficient coatings. With sufficient attention to the conditions of deposition, it is now fairly easy to grow films of thickness 100 nm or so whose optical properties (i.e. refractive index and absorption) are identical with those of the bulk material. This greatly simplifies the search for a suitable material.

For crown glass, with a refractive index of 1·51, the film index would have to be 1·23 to give zero reflectance, but no material is available which is also durable. The best compromise is magnesium fluoride, MgF_2, with an index of 1·38, which on crown glass gives an overall reflectance of 1·33 per cent. This still gives a worthwhile improvement over the uncoated glass. Although this value is achieved only at one wavelength and at normal incidence, the reflectance does not rise above 2 per cent for any wavelength in the visible spectrum if the angle of incidence is no greater than 30°.

The thickness of the coating must be accurately controlled, but this is easy to achieve, simply by monitoring the reflectance of the surface while the film is being formed. A beam of light reflected from the surface is intercepted by a suitable photoelectric cell and the electrical output from the cell, displayed on a meter, is a direct measure of the reflectance. It is then easy to stop film growth when the reflectance reaches a predetermined level, and this may be done automatically. Many optical components may be coated simultaneously in this way.

Anti-reflection coatings for the infra-red

There are many uses for optical apparatus which works at infra-red wavelengths. Apart from purely scientific applications, the ability to form and record infra-red images of objects is of great interest, since it gives us night vision. Most of the heat energy radiated by solids is at infra-red wavelengths, so an infra-red image shows up variations in emitted intensity which result from variations in surface temperature; the effect of temperature on the emission of radiation will be explained more fully later in the chapter.

One slightly unexpected use of infra-red images is in medical diagnosis, for some conditions cause a local rise in the skin temperature which can be photographed using a film which is sensitive to infra-red rays.

All glasses begin to absorb strongly at wavelengths around 1 μm and cannot be used for infra-red work. The materials most commonly used for infra-red lenses, prisms and windows are purified germanium and silicon which are transparent at wavelengths above about 1·8 μm and 1·1 μm respectively. Although they absorb shorter wavelengths, they transmit in the infra-red region because of the presence of the *energy gap* in the electron energies which was discussed in Chapter 4. The energy of infra-red radiation is insufficient to excite electrons across the energy gap, and, since there are no other empty energy levels for the electrons, and few other ways of absorbing energy in the material, the radiation passes through with little loss of intensity.

The refractive indices of silicon and germanium are 3·5 and 4·1 respectively but they depend somewhat on temperature. Although one might sometimes wish for such high values in the visible spectrum, they have their disadvantages, as can be seen by putting these figures into equation (6.2 *a*). We find that a single germanium surface has a reflectance of 36·9 per cent. A component with two surfaces transmits only 40 per cent of the incident radiation at normal incidence, even though a negligible amount of absorption occurs. Five such components can transmit only 1 per cent, the rest being lost almost entirely by unwanted reflections! Clearly, there is a lot to be gained by the use of an antireflection coating, which should have a refractive index of 2·05 for use on germanium and 1·92 for silicon.

In the near infra-red (wavelengths between about 1 μm and 5 μm) silicon monoxide, SiO, has been found to make the most suitable coating for these materials. It has a refractive index of 1·95, but since it oxidizes rather readily to form SiO_2 and other intermediate compositions, the refractive index depends somewhat on the speed of deposition and on the partial pressure of oxygen in the vacuum chamber. By evaporating rapidly, a consistent index of 1·95 is readily achieved, and the resulting coating is very hard and durable. Using SiO, the transmittance of a parallel-sided plate of silicon can be increased to about 99 per cent at a selected wavelength. At other wavelengths the value

is considerably smaller; as an example, if the coating is correctly matched at $\lambda = 1.7\ \mu$m, then the transmittance falls to 80 per cent at about $1.2\ \mu$m and $2.5\ \mu$m—a useful improvement, though not as dramatic as that at $1.7\ \mu$m. The peak transmittance of a plate of germanium coated with SiO is slightly smaller than that of silicon owing to the poorer match of refractive indices.

Multilayer anti-reflection coatings

Although single-layer coatings produce a useful improvement in transmittance and are very easy to produce, they have some serious limitations. The lowest reflectance obtainable for a coating on crown
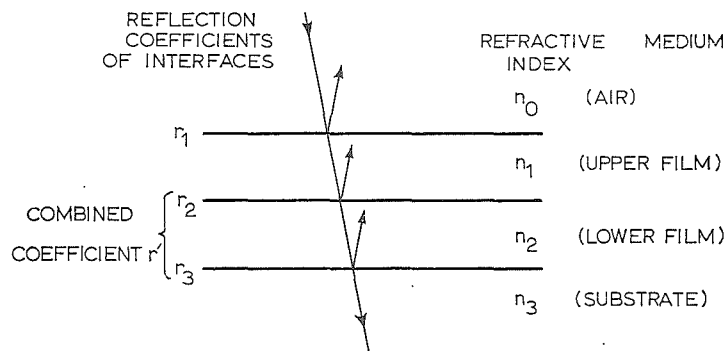
Fig. 6.8. A two-layer coating and its reflection coefficients.
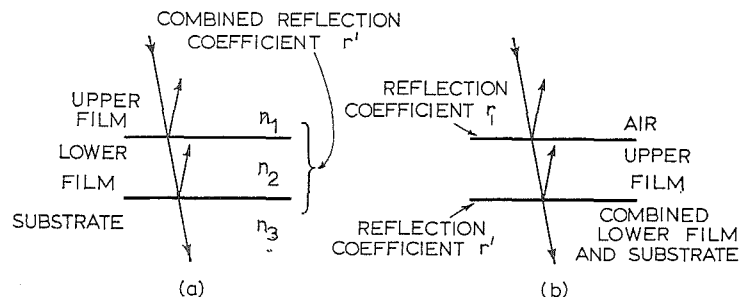
Fig. 6.9. Showing how the calculation of the reflectance of a two-layer coating is split into two separate calculations.

glass is 1·33 per cent and even in germanium the enormous improvement obtained with a coating is limited to a rather narrow band of wavelengths. By using coatings with two or more layers of different refractive indices both of these difficulties may to a large extent be overcome. A two-layer coating is shown in fig. 6.8. Its reflectance can be calculated using the equations given earlier, by splitting the problem into two parts as illustrated separately in figs. 6.9 a and 6.9 b.

Since account must be taken of the phase, the equation for r in the footnote (page 95) must be used, not the equation for R, which does not contain the phase relationships of the two waves.

In fig. 6.9 a the lower film and substrate are treated as a single layer on a substrate, the incident beam being not in air but in a medium of refractive index n_1. The reflection coefficient r' of this combination is calculated, then (fig. 6.9 b) this combination is treated as the 'substrate' for a calculation of the effect of the upper layer on the overall reflectance R.

The expression which is obtained for R is very clumsy, and since the only case of interest is when $R = 0$, we shall just quote the equations which give the condition for this.

If we put $\delta_1 = 2\pi D_1 n_1/\lambda$, and $\delta_2 = 2\pi D_2 n_2/\lambda$, the values for these quantities which give zero reflectance are given by a pair of equations as follows:

$$\left.\begin{aligned}
\tan^2 \delta_1 &= \frac{n_1{}^2(n_3 - n_0)(n_2{}^2 - n_0 n_3)}{(n_1{}^2 n_3 - n_2{}^2 n_0)(n_0 n_3 - n_1{}^2)}, \\[2mm]
\tan^2 \delta_2 &= \frac{n_2{}^2(n_3 - n_0)(n_0 n_3 - n_1{}^2)}{(n_1{}^2 n_3 - n_2{}^2 n_0)(n_2{}^2 - n_0 n_3)},
\end{aligned}\right\}
\tag{6.6}$$

where n_0, being the refractive index of air, is equal to unity.

It can be seen that many possible combinations of n_1 and n_2 can be used, all giving zero reflectance if δ_1 and δ_2 are chosen according to equations (6.6). There is a limitation on the range of values of n_1 and n_2, however, since $\tan^2 \delta_1$ and $\tan^2 \delta_2$ must both necessarily be positive. On the other hand, the square root of $\tan^2 \delta$ can be either positive or negative, so there are two possible values of δ_1 and δ_2 between 0 and π, one being less than $\pi/2$, the other greater than $\pi/2$. If, then, δ_1 and δ_2 are made equal, and we remember that they are inversely proportional to the wavelength, the two values of δ can be obtained (for any given n_1 and n_2) at two different wavelengths. By suitable choice of the values of n_1, n_2 and δ the two wavelengths at which zero reflectance is obtained can be placed so as to maintain low reflectance over quite a wide wavelength range. It is also true (but not so easy to demonstrate) that zero reflectance can be obtained at two wavelengths in certain cases when δ_1 and δ_2 are not equal.

Multilayer coatings for glass

Let us now consider some practical cases beginning with coatings for crown glass, for which $n = 1.5$.

If δ_1 and δ_2 are made equal to $\pi/2$ and π respectively, then the thicknesses of the layers are one quarter of a wavelength and one half a wavelength. Using refractive indices $n_1 = 1.38$ and $n_2 = 1.85$ it is then possible to obtain the theoretical results shown in fig. 6.10, curve

(a). These refractive indices, it will be remembered, are those of MgF_2 and SiO respectively, and a double layer coating with these materials would be quite satisfactory. Comparison with the curve (b) for a single-layer coating shows that the second layer gives an improvement, though a better result still can be obtained by adding a third layer (curve (c)). Since this adds only minor complications to the manufacturing process, three layers are therefore preferred where a single layer is not good enough. The best results with three layers are obtained when the middle film is one half wavelength thick, and the other two are each one quarter wavelength in thickness. Using the materials MgF_2 ($n_1 = 1\cdot38$), ZrO_2 ($n_2 = 2\cdot1$) and CeF_3 ($n_3 = 1\cdot65$), it is possible to obtain in practice (rather than just theoretically!) a reflectance of less than 0·3 per cent over the range $\lambda = 430$ nm to 790 nm—better than in the (different) case shown in fig. 6.10.

Multilayer coatings for germanium and silicon

Turning again to infra-red materials, we can relax the high standards required at optical wavelengths, for it is an achievement to reduce the reflectance to a few per cent over some narrow band of wavelengths. The
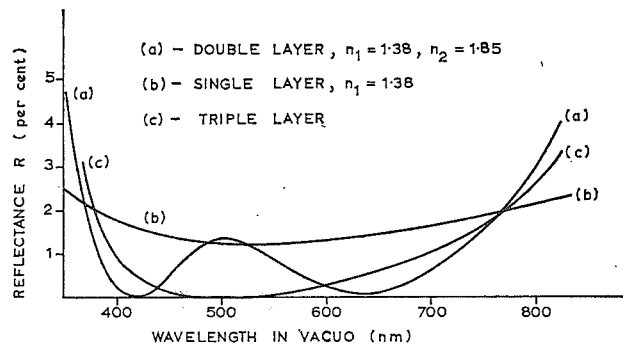
Fig. 6.10. Theoretical plots of reflectance R against wave-length.

best that can be achieved with Ge is a transmittance higher than 90 per cent from about 2·1 μm to about 6·5 μm wavelength. This is obtained with a three layer coating of MgF_2, CeO_2 and Si. Unfortunately nearly all such coatings absorb significant amounts of water from the atmosphere, which gives marked absorption of infra-red radiation at wavelengths close to 3 μm. The water can be removed by heating, but the absorption reappears within a few minutes at room temperature. Theoretically, it is possible to do even better than is possible with three layers, by using, say, twenty layers of graded refractive index, increasing gradually from unity at the topmost layer to nearly that of the substrate in the bottom layer. In practice this is not so easy, partly, as we have

seen, because of the limitations of available materials, and partly because the thicker the coating, the more likely it is to peel off due to the inbuilt stresses which are unavoidable when any film is made (see Chapter 2).

Dielectric mirrors

The equations given above for the reflectance of a thin film show that there is a possibility of making highly reflecting surfaces as well as surfaces with high transmittance. Moreover, high reflectance can be obtained near one wavelength only, so that at other wavelengths the 'mirror' will transmit quite efficiently.

Such properties are useful for a number of applications, the most prominent modern case being in gas lasers. Here, two mirrors are required to reflect light back and forth many hundreds of times through the gas which forms the active part of the system (see fig. 6.11). Each
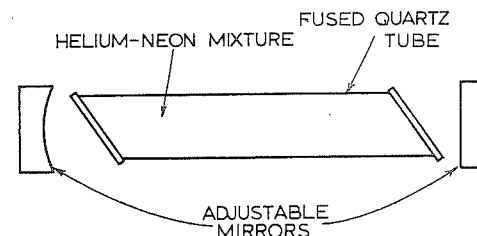
Fig. 6.11. The elements of a helium-neon laser.

time the light beam traverses the gas (a mixture of helium and neon in the laser shown) it is strengthened, i.e. amplified, by atomic processes. Amplification is possible only if there is little loss of energy at each reflection, so that mirrors of very high reflectivity are required. However, one mirror must be partially transparent in order that the light may get out of the system.

Since most lasers will operate at more than one wavelength, while only one is normally required, it is advantageous if the mirrors are efficient reflectors at only one wavelength. This can be reliably achieved by using a suitable multilayer combination of thin transparent films.

For this application, a thickness of a quarter of a wavelength is commonly chosen for each film, alternate films having high and low refractive indices.

The resulting structure is often called a 'dielectric mirror', since all its components are dielectric rather than metallic materials. It has the further advantage over a metallic mirror that the light which is not reflected is not entirely absorbed, but is transmitted through the mirror.

Since it is in any case necessary to have slight transmittance in order that the light beam may be used outside the laser, this is no loss.

The arrangement used in a laser of two mirrors separated by a fixed distance is derived from a scientific instrument known as an *interferometer*.

This is a device which uses the interference of light waves and enables the wavelength of the light to be accurately measured by comparison with the separation of the mirrors. Using such interferometers it was rapidly discovered that the wavelength of the light emitted from certain atoms was of such a well defined wavelength that it could be measured more accurately than the standard international metre allowed. The standard metre was at the time a bar of platinum kept in Paris and scribed with marks separated by 1 m, and the width of these scribed lines was much greater than the error involved in determining the wavelength! Thus it came about that in 1954 an international committee adopted the wavelength of emission from a particular element as a standard of length to replace the platinum bar. The accuracy of both this and the measure of wavelength depend upon the maintenance of high reflectivity and negligible absorption by the mirrors, so that it is vital to maintain careful control of the deposition conditions during their manufacture.

The control of absorptance and emittance by surface coatings

The absorption and emission of radiation by surfaces are important in many departments of science and technology, but the expanding field of space technology has brought the subject a new prominence. The internal temperature of satellites and rockets when in space is controlled by their surface properties, for there is no means, other than through radiation, of acquiring or disposing of heat energy. The principle of temperature control by regulating incoming and outgoing radiation has long been used by the gardener, whose greenhouse regularly maintains a temperature higher than its surroundings in summer. The explanation of this lies in the difference between the radiation from the sun, which is a very hot body, and from the plants, which are relatively cool. It is a general rule that, special surface treatments apart, the radiation emitted from a body occurs mostly around a wavelength which increases as the temperature of the surface falls. The glass walls of a greenhouse readily transmit the very short wavelength infra-red radiation from the sun, while the radiation from the plants inside has wavelengths much greater than 1 μm, the point at which glass begins to absorb strongly. This radiation cannot therefore escape, and the greenhouse must inevitably become hotter until the resulting increase in heat loss (by conduction and convection as well as radiation) re-establishes the balance.

The dependence of the predominant wavelength of radiation on the temperature of the radiating surface can be shown theoretically by applying the concepts of quantum mechanics to the case of a body with an ideal emitting and absorbing surface. Such a solid, termed a *black body*, absorbs all radiation falling upon it; if the body is in equilibrium, the emitted radiant energy must exactly balance the absorbed energy, otherwise the body would be heated or cooled.

The radiation from a black body is distributed over a relatively narrow range of wavelengths as shown in fig. 6.12 *a*, where the power emitted by unit area per unit wavelength interval is plotted against the
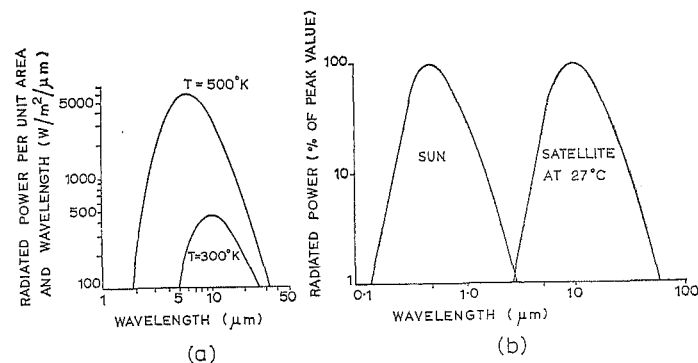
Fig. 6.12. The spectral distribution of thermal radiation.

wavelength. The general shape of this curve is independent of temperature, but the wavelength at which the maximum emission occurs is found to increase with a decrease in temperature. Simultaneously the height of the maximum decreases, since the total energy emitted must decrease with falling temperature. The total amount of energy radiated by unit area varies with temperature according to a very simple law: it is proportional to the fourth power of the absolute temperature.

The temperature of a satellite is determined by a balance between the radiation absorbed from the sun and that emitted from its own surfaces, which should be held at about 20°–70°C. Neither the sun nor the satellite is a perfect black body but the wavelength dependence of the emitted radiation in both cases is closely similar to that from a black body at the same temperature. This dependence is shown in fig. 6.12 *b*, where for easier comparison the peaks have been made the same height—they are, of course, enormously different in absolute magnitude. The important feature is that all but about 3 per cent of the Sun's radiation falls between the wavelengths 0·3 μm and 3 μm, while the corresponding figures for a surface at 27°C are 4·8 μm and 60 μm. But for this difference in spectral distribution it would not be possible to control the temperature simply by adjusting absorption and emission

from the surface, for at any given wavelength the two properties cannot be independently varied.

This is easily understood if we consider a body at a constant temperature which is absorbing a fraction a_λ of the radiant energy incident upon it, at a wavelength λ. If it emits a fraction e_λ of the radiation it would emit at the same wavelength if it were a perfect black body, then we can write an equation which simply states that in equilibrium the incoming energy equals the outgoing energy:

$$a_\lambda \times \text{incident energy} = e_\lambda \times \text{emission of black body.} \qquad (6.7)$$

As remarked above, the energy emitted by a black body exactly balances the incoming radiation. But the latter is the same for the imperfect radiator as for a black body at the same temperature. Therefore the two terms cancel in equation (6.7), leaving the result

$$a_\lambda = e_\lambda.$$

Note that there is a fraction $(1 - a_\lambda)$ of the incident energy which is not absorbed. As you might expect, this is just reflected, and does not need to be accounted for in equation (6.7) since it appears on both sides of the equation and hence cancels.

Solar absorptance and thermal emittance

As we mentioned earlier, temperature control is only possible because both e_λ and a_λ depend upon wavelength, and may differ considerably from one another if measured at widely different wavelengths. Of course, absorption and emission occur at more than one wavelength, and what is of interest is not a_λ or e_λ as such, but a sort of average value for each of these, to cover the wavelength ranges given in fig. 6.12. Thus we define the *solar absorptance a* as that fraction of the incident energy from the Sun (i.e. having the wavelength distribution of fig. 6.12 *b*) which is absorbed. Similarly we define the *thermal emittance e* as the fraction of the *total* black-body radiation which is emitted at the temperature of the surface concerned. Since a and e are averages over different wavelengths, they can differ widely. The actual temperature T reached by a body can then be determined by using an equation similar to equation (6.7), and substituting for the black body emission the expression σT^4, where σ is Stefan's constant.

If the absorbing surface area of the body is S_a and the emitting area is S_e the equation becomes:

$$a S_a E_0 = e S_e \sigma T^4,$$

where E_0 = incident energy, giving

$$T^4 = (E_0 S_a / \sigma S_e)(a/e).$$

The ratio S_a/S_e is frequently determined by mechanical and geometrical limitations, and cannot be very different from unity unless the body is held in a specific orientation with respect to the sun, so that the ratio a/e is of utmost importance for the control of temperature. We shall now discuss ways of using thin films to do this.

Satellite temperature control by thin films

Although the ratio a/e controls the mean temperature, the absolute values of a and e are important as they determine the rate of heating or cooling when, for instance, a satellite goes into or out of the Earth's shadow. For most purposes we require as small a variation in temperature as possible, so that both a and e would be low, for preference. For some applications a high ratio a/e is required, for instance on the surface of a 'solar cell', which is a device which converts solar energy into electrical power. So it is important to know how to obtain high and low values of both solar absorptance and thermal emittance.

Now $1 - a$ is equal to the solar reflectance, and $1 - e$ is correspondingly the thermal reflectance. So to obtain low values of a and e a highly reflecting surface such as a metal is required. The most satisfactory metal in all respects is aluminium: it is cheap, easily deposited on any surface by vacuum evaporation, is highly reflecting and does not tarnish in air. The solar absorptance of an evaporated film of aluminium is close to 0·08, but the thermal emittance at 27°C is even smaller, being very nearly 0·01. Thus aluminium has quite naturally a high ratio a/e, and is not suitable alone as a coating for bodies which must be held at fairly low temperatures.

Lower values of a/e may be obtained simply by overcoating the aluminium with a material which has a high emissivity (i.e. low reflectance) in the far infra-red but which does not absorb significantly at shorter infra-red wavelengths. The oxides of silicon and aluminium, SiO_2 and Al_2O_3, are very suitable for this purpose, and they may be readily applied by vacuum evaporation. The control of reflectance is not achieved in this case by interference of the light waves, but simply by absorption of the incoming rays. This means that the thermal absorptance (and likewise the thermal emittance) increase steadily with the thickness of the deposited layer. On the other side of the coin, the *solar* absorptance changes but little. It is thus possible to obtain any ratio of a/e, from the highest obtainable with pure Al down to less than 0·2, simply by controlling the thickness of the SiO_2 or Al_2O_3 overcoating. For instance, a thickness of 1 μm of SiO_2 produces values of a and e of about 0·11 and 0·22 respectively, while about 4 μm of SiO_2 is needed to raise the emittance to about 0·7.

'Dark mirror' coatings

For some applications, a high solar absorptance is required, combined with low thermal emittance. Coatings with these properties were first made for use in infra-red equipment in which it was desired to

absorb all stray visible light while reflecting the infra-red radiation. More recently they have been of use in 'solar cells' and other converters of solar radiation into electrical or heat energy, where re-emission of absorbed energy must be kept to a minimum. These coatings work by using optical interference in the films to enhance absorption in the optical region, and are commonly called 'dark mirror' coatings.

Germanium is a useful material for this purpose, since it absorbs strongly all visible wavelengths while having good infra-red transmission. It may be used on top of a thick coat of aluminium which efficiently reflects the infra-red components of the incident radiation (fig. 6.13).
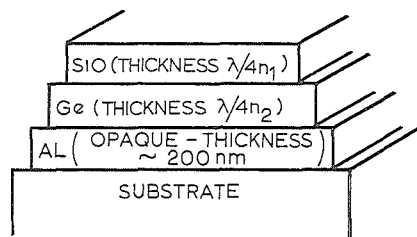
Fig. 6.13. Example of a 'dark mirror' coating.

An anti-reflection layer of SiO on top of the germanium further improves the performance. This is made a quarter wavelength thick at a wavelength in the visible region, so that it is much less than a quarter wavelength thick to all infra-red radiation which is therefore readily transmitted. The overall performance of the coating is a 2 per cent thermal emittance and a 70 per cent solar absorptance—the latter is highest in the visible region, being as high as 98 per cent at wavelengths below about 0·8 μm. The wavelength above which the reflectance rises rapidly can be adjusted to some extent by altering the film thicknesses, but its value is limited by the natural properties of Ge.

Coatings of this and other kinds have proved of immense value in the exploration of space and the use of earth satellites. In spite of earlier pessimistic predictions that they would rapidly be worn away by the impact of micrometeoric dust, they have an extremely long life and will doubtless continue in use for many years yet.